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Photochemical Studies. XXVII. The Effect of Radiation on Mixtures of Nitrogen Dioxide and Nitrous Oxide and its Relationship to the Photochemical Decomposition of Nitrous Oxide

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Oxygen atoms were produced in NO_2-N_2O mixtures by the photochemical decomposition of NO_2 alone. No reaction of these atoms with N_2O could be detected. Results of calculations give a minimum activation energy of 14,000 cal. for the reaction $O+N_2O=2$ NO and a probable maximum activation energy of 24,000 cal. The activation energy of the reaction $O+NO_2 = NO+O_2$ is estimated to be 4000 cal. It is concluded that *two primary processes* are necessary to explain the direct photochemical decomposition of N_2O, $N_2O+h\nu=N_2+O$ and $N_2O+h\nu = NO+N$. The latter reaction must be followed by $N+N_2O=NO+N_2$ to explain previously determined quantum yields. The energy of activation of this reaction is probably less than 10,000 cal.

IN a previous article[1] the number of molecules formed upon irradiation of nitrous oxide per absorbed quantum, and which were uncondensed by liquid air, was determined. It was found that the over-all reaction could be represented empirically by the equation

$$4N_2O = 2.8N_2 + 2.5NO + 0.7O_2, \qquad (1)$$
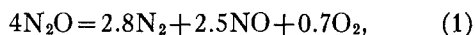
which agrees roughly with results previously obtained by Macdonald.[2] It had also been established definitely that nitric oxide is one of the products by Wulf and Melvin[3] who showed that the bands of this substance appear in absorption when nitrous oxide is irradiated. Since nitrogen dioxide appears after condensation with liquid-air oxygen, also, must be formed as shown by Macdonald.[2]

The value of the quantum yield for nitrous oxide decomposition will depend upon the mechanism assumed for the primary process and for the secondary reactions. Molecular oxygen can only be formed if at least part of the primary process is

$$N_2O+h\nu = N_2+O. \qquad (2)$$
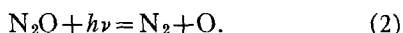
Since nitric oxide is formed, if (2) is the sole primary process a secondary reaction

$$O+N_2O = 2NO \qquad (3)$$

must occur. An accompanying reaction

$$O+O(+M) = O_2(+M) \qquad (4)$$
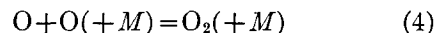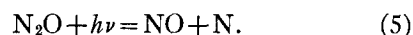
must occur either on the walls or as the result of termolecular collisions to explain the known production of O_2.

It was suggested[1] that an alternative explanation could be based on two primary processes, namely (2) and (5)

$$N_2O+h\nu = NO+N. \qquad (5)$$

The fate of the nitrogen atoms might be either

$$N+N_2O = NO+N_2 \qquad (6)$$

or $\qquad N+N(+M) = N_2(+M) \qquad (7)$
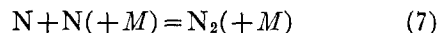
or both. It should be re-emphasized that (5) cannot be the sole primary process unless a reaction between nitrogen atoms and NO is used to explain the appearance of O_2. The latter is improbable in view of the small amount of reaction which was allowed to occur and the fact that the extent of the reaction did not affect in any marked manner the value of the yield.

The present experiments were undertaken with a view to obtaining evidence for or against reaction (3), thus permitting a decision to be made as to whether primary process (2) alone or both primary processes occur. It is true that Musgrave and Hinshelwood[4] have postulated reaction (3) to explain the appearance of NO

[1] W. A. Noyes, Jr., J. Chem. Phys. **5**, 807 (1937).
[2] J. Y. Macdonald, J. Chem. Soc. 1 (1928).
[3] O. R. Wulf and E. H. Melvin, Phys. Rev. **39**, 180 (19); L. Henry, A.-M., Compt. rendus **200**, 656 (1935).
[4] Musgrave and C. N. Hinshelwood, Proc. Roy. Soc. (London) **A135**, 23 (1932).

during the thermal decomposition of nitrous oxide, but their experiments were carried out at about 1000°K so that this reaction might have an energy of activation too high to permit it to be of importance at room temperature.

A convenient source of oxygen atoms is found in the primary dissociation of nitrogen dioxide by ultraviolet light, since this substance absorbs in a region where nitrous oxide is transparent. Henri[5] reports that nitrogen dioxide possesses two regions of predissociation, one near 3700A and the other below 2450A leading to the production of ^3P and ^1D oxygen atoms, respectively. The photochemical decomposition of nitrogen dioxide has been investigated by Norrish[6] and by Dickinson and Baxter.[7] Approximately two molecules of nitrogen dioxide decompose per quantum absorbed, a fact which may be explained by the reactions

$$NO_2 + h\nu = NO + O, \qquad (8)$$

$$O + NO_2 = NO + O_2. \qquad (9)$$
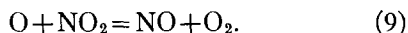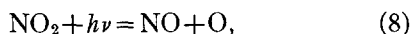
EXPERIMENTAL METHOD

Nitrogen dioxide was obtained from pure, dry lead nitrate and purified by fractional distillation with liquid air through anhydrous magnesium perchlorate. The middle fraction was vaporized into a series of small tubes with capillary ends, which were sealed off. The nitrous oxide was a commercial product and was purified by bubbling slowly through saturated potassium hydroxide. It was fractionally distilled several times through anhydrous magnesium perchlorate with liquid air and the final middle fraction was collected in a bulb provided with a stopcock.

In order to observe possible separate effects due to ^3P and ^1D oxygen atoms two light sources and reaction vessels were used. The normal ^3P atoms were produced from nitrogen dioxide by using a Pyrex tube 100 cm long with plane Pyrex windows sealed on and as a light source a General Electric type H3 mercury lamp. The Pyrex windows did not transmit radiation below 3000A. A fused silica vessel 20 cm long with sealed on plane windows was used for the ^1D

[5] V. Henri, Nature **125**, 202 (1930).
[6] R. G. W. Norrish, J. Chem. Soc. 761 (1927); 1158, 1604, 1611 (1929).
[7] R. G. Dickinson and W. P. Baxter, J. Am. Chem. Soc. **50**, 744 (1928).

atoms. This was illuminated with a cadmium spark operated at 2 kva, 25,000 volts. Radiation between 2150 and 2350A was isolated by filters. Two cm of 0.05 m acetic acid containing 1 percent acetone absorbed from 2350 to 2900A and below 2150A. Five centimeters of chlorine gas at atmospheric pressure absorbed from 2800 to 4300A, above which the nitrogen dioxide is not dissociated.[6, 7] The acetic acid-acetone solution was renewed every three hours. The reaction cells were attached as shown in Fig. 1.
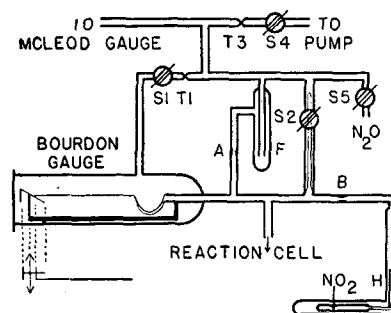

FIG. 1.

Pressures were measured with a glass Bourdon gauge which operated a lever carrying a small mirror. Images of a graduated scale placed at a distance of fifteen feet were read with a telescope. Readings were reproducible to 0.3 cm on the scale. Temperature variation over a period of time decreased this to perhaps 0.5 cm. Three gauges, designated A, B and C, were used during the course of the work. Calibrations showed that a 1 cm scale reading was equivalent to 0.00460, 0.00719 and 0.00201 cm of mercury, respectively, for the three gauges.

In Fig. 1, S indicates stopcocks lubricated with low pressure grease, T indicates mercury cut-offs and A and B constrictions for sealing off. Projecting through $S2$ is a capillary tube sealed at the upper end whose use will be apparent.

To explain the procedure used to obtain the results it is necessary to refer to reactions (3), (8) and (9) as well as the sum of (8) and (9)

$$2NO_2 = 2NO + O_2 \qquad (4')$$
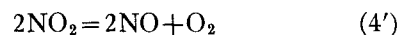
and the sum of (3) and (8)

$$NO_2 + N_2O = 3NO. \qquad (5')$$

After illumination there will be a pressure increase $\Delta P_4 + \Delta P_5$ due to reactions (4') and (5').

It is known that the termolecular reaction $2NO + O_2 = 2NO_2$ goes to completion at liquid-air temperatures. This was verified in our experiments. Hence the increase in pressure after illumination is $\Delta P_4 + \Delta P_5$ and the residual pressure after freezing down a number of times is ΔP_5.

Bourdon gauge readings are called $R1$, $R2$, etc. Some of these were made merely to check constancy of conditions and do not appear in later calculations. No readings were taken until the temperature difference between the gauge and reaction vessel was approximately 0.2–0.3° which seemed to be the value most easy to maintain.

The entire system was pumped and baked out until the pressure was less than 10^{-5} mm and the reading $R1$ made. $S4$ and $T3$ were closed and N_2O introduced through $S5$ to a pressure of 10–20 cm and the pressure read on $T3$ after which $S5$ was closed. The N_2O was then frozen out by placing liquid air on F and the system pumped through $S4$. $T3$ and $S4$ were closed, the N_2O evaporated at $-80°C$ and the pressure was read on $T3$. The reading $R2$ was made, $S1$ was closed and the apparatus sealed off at A and the reading $R3$ made.

NO_2 was introduced by breaking the capillary end of a tube with the magnetic hammer, H, and $R4$ made. Side tubes attached to the reaction vessel and gauge jacket were simultaneously cooled with liquid air (to avoid breaking the gauge) and $R5$ taken. The liquid air was removed and one hour allowed for diffusion, after which $S1$

was closed and $R6$ made. The $N_2O - NO_2$ mixture was next illuminated for a period of four to nine hours, after which $R7$ was made.

After illumination the gases were continually distilled between two wide side tubes attached to the reaction vessel. At about two hour intervals the liquid air was removed and the gases evaporated. This was continued until readings $R8$ (with liquid air) and $R9$ (without liquid air) became constant. $S2$ was then turned, breaking the capillary, and $S1$ and $T1$ opened to equalize the pressure. $R10$ was made and in every case agreed with $R1$, $R2$ and $R5$ within experimental error. In experiments with ^1D atoms, the system was sealed off at B before $R6$ was made.

For experiments at higher temperatures, the reaction vessel was covered first with wire gauze, then asbestos and wrapped with resistance wire. The vessel was heated between readings $R6$ and $R7$.

RESULTS

The necessary pressures, $P(NO_2)$, ΔP_f (final pressure increase while frozen down), ΔP_4, ΔP_5 are obtained from gauge readings as follows: (a) $P(NO_2) = R4 - R3$; (b) $\Delta P_4 + \Delta P_5 = R7 - R6$; (c) $\Delta P_5 = R9 - R6$; (d) $\Delta P_f = R8 - R5$. During distillation of the gases by liquid air after illumination, the pressure decreased steadily for two hours and then remained constant for three to five hours. This reading is called ΔP^0. Thereafter the pressure decreased again and finally reached ΔP_f. Since the volume of the fused silica cell was much less than that of the Pyrex cell, the

TABLE I. *Summary of experimental results. (Pressures are in centimeters of Hg).*

Exp.	$P(N_2O)$	$P(NO_2)$	$\Delta P_4 + \Delta P_5$	ΔP^0	ΔP_f	ΔP_5	Temp. (during illum.)	Time of illum. hr.	Gauge
1A	0	0.5	0.198	0	0	0.002	26°C	4	A
1B	0	0.5	0.078	0	-0.002	0	26	2	A
2(1)	10.0	0.384	0.175	0.021	0.021	0.030	25	6	A
3A	11.2	0.293	0.146	0.044	0	0.002	26	9	A
3B	11.2	0.293	0.137	0.039	0	0	26	8	A
4	12.4	0.186	0.089	0.021	-0.002	0	180±15	5	A
5	18.5	0.216	0.090	0.040	-0.0036	-0.0036	265±16	6.5	B
6A	12.6	0.371	0.226	—	0	0.004	25	8	B
6B(2)	12.6	0.371	0.176	—	0.036	0.032	215±15	8	B
7A(2)	15.7	0	0.043	—	0.012	0.043	205±15	5.5	C
7B	15.7	0	0	—	0	0	215±15	4.5	C
8A(3)	13.0	0.3±0.05	0.107	—	0	0.036	25	8	C
8B	13.0	0.3±0.05	0.056		-0.002	0.002	24	9	C
8C	13.0	0.3±0.05	>0.140		-0.002	-0.002	225±15	9	C
9A	16.8	0.191	0.076		-0.002	0.002	25	8.5	C
9B	16.8	0.191	0.068		-0.001	0.003	240±15	6.5	C

time to bring $\Delta P_4 + \Delta P_5$ to ΔP_f was only three to five hours in the experiments with ^1D atoms. The relative rapidity of the reverse reaction $2NO + O_2 = 2NO_2$ prevented the observation of a ΔP^0 here. In the experiments with ^3P atoms, ΔP^0 may possibly indicate a solid complex, resulting from a system containing N$_2$O, NO$_2$, NO and O$_2$ which has an appreciable vapor pressure at liquid-air temperatures.

The results are recorded in Table I. Experiments $1A$–5 were made with ^3P atoms and $6A$–$9B$ with ^1D atoms.

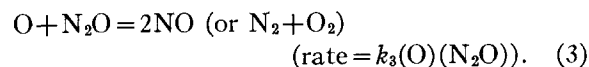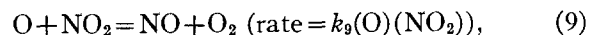(1) In this run no distillations were made. The ΔP_f obtained was probably ΔP^0.

(2) Although the reaction cell was flamed before the N$_2$O was introduced, the pressure increase was probably due to gas coming off the walls. The facts that in $7A$ there is no difference between $\Delta P_4 + \Delta P_5$ and ΔP_5 and that the photochemical decomposition of N$_2$O leads to NO and O$_2$ verify this belief.

(3) ΔP_5 may be due to that fact that some mercury was present. This was avoided in subsequent runs by protecting the reaction system with a dry-ice-ether mixture during evacuation.

At the nitrogen dioxide pressures used, less then four percent of this substance was present as N$_2$O$_4$ at room temperature and less than one percent at the higher temperatures.

DISCUSSION

Following the primary process (8), there are two competing reactions for oxygen atoms

$$O + NO_2 = NO + O_2 \ (\text{rate} = k_9(O)(NO_2)), \quad (9)$$

$$O + N_2O = 2NO \ (\text{or } N_2 + O_2)$$
$$(\text{rate} = k_3(O)(N_2O)). \quad (3)$$

Within experimental error all of the oxygen atoms reacted with NO$_2$. Although this does not exclude the possibility of reaction (3), k_9 must be very much greater than k_3. It is possible, from the experimental data, to fix a lower limit to the activation energy of (3). From the previous results[1] on the photochemical decomposition of nitrous oxide (assuming reactions (2), (3) and (4)) it is possible to calculate an approximate upper limit to the activation energy of (3).

Assumption of a steady state gives

$$d(NO_2)/d(N_2O)$$
$$= (2k_9(NO_2) + k_3(N_2O))/k_3(N_2O) \quad (10)$$
$$= (K(NO_2)/(N_2O) + 1).$$

This is of the form $dy/dx - Ky/x = 1$.

Integration gives

$$(NO_2)(N_2O)^{-K} - (N_2O)^{1-K}/(1-K) = \text{const.} \quad (11)$$

In run 5, which will give the highest value of the lower limit, $P(N_2O)$ (initial) is 18.5 cm and $P(NO_2)$ (initial) is 0.216 cm. ΔP_4 is assumed to be 0.0036 cm. The final $P(N_2O)$ is $18.5 - \Delta P_4 = 18.496$ cm, the final $P(NO_2) = 0.216 - 2\Delta P_5 - \Delta P_4 = 0.040$. $(\Delta P_4 + \Delta P_5 = 0.090$ cm, $T = 265°C.)$

Therefore

$$(0.216)(18.5)^{-K} - (0.040)(18.496)^{-K}$$
$$= \frac{(18.5)^{1-K} - (18.496)^{1-K}}{(1-K)}, \quad (12)$$

which reduces to

$$0.216 - 0.040 \times (1.000195)^K$$
$$= (18.5 - 18.4964 \times (1.000195)^K)/(1-K). \quad (13)$$

Remembering that $(1+A)^K \cong 1 + KA$ if A is small, one finds

$$K \cong 2.2 \times 10^4 \quad \text{and} \quad k_9/k_3 \cong 1.1 \times 10^4. \quad (14)[8]$$

Now $k = fk^0 \exp(-E/RT)$ for a bimolecular reaction where f is a steric factor and $k^0 = \sigma^2(8\pi RT(1/M_1 + 1/M_2))^{\frac{1}{2}}$ (σ is the mean of the molecular diameters and the M's are molecular weights). Certainly the mean molecular diameters and masses are almost the same and therefore $k_3^0 \cong k_9^0$. The steric factors should be about 0.01 and there is no reason for believing that they are different for the two reactions.

Spealman and Rodebush[9] estimate that $k_9 = 10^{-5} k_9^0$ at 40°C. From their results we calculate the energy of activation of (9) to be 4300 cal. and hence that of (3) to be 14,000 cal.

[8] Schumacher (J. Am. Chem. Soc. **52**, 2377 (1930)) illuminated mixtures of nitrogen dioxide and hydrogen and assumed from his results that there were two competing reactions (a) $O + H_2 = OH + H$; (b) $O + NO_2 = NO + O_2$. In order to account for the fact that all of the oxygen atoms seemed to react with the nitrogen dioxide, he states that (a) must be at least 10^4 times as fast as (b). It is interesting to compare this result with our value of k_9/k_3.

[9] M. L. Spealman, and W. H. Rodebush, J. Am. Chem. Soc. **57**, 1474 (1935).

We may now calculate the maximum energy of activation of (3) from the previous results[1] using reactions (2), (3), (4) and (15)

$$O + walls = \tfrac{1}{2}O_2 \quad (rate = k_{15}(O)/2(N_2O)). \quad (15)$$
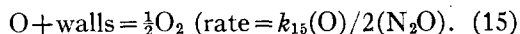
Assuming a steady state and integrating we obtain

$$(O_2) = k_4(O)^2(N_2O)t + k_{15}(O)t/2(N_2O), \quad (16)$$

$$(NO) = 2k_3(O)(N_2O)t. \quad (17)$$

Assuming the usual formula for k_3, we obtain from (16) and (17)

$$4(O_2)(N_2O)/(NO)^2$$
$$= (k_4 \exp (2E_3/RT))/t(f_3)^2(k_3{}^0)^2$$
$$+ (k_{15} \exp (E_3/RT))/f_3 k_3{}^0 (NO)(N_2O). \quad (18)$$

It is possible to evaluate $k_{15}/k_3{}^0$ by Smoluchowsky's equation $Z = 3\pi X^2/4L^2$ where Z is the number of collisions suffered by the oxygen atoms with the nitrous oxide molecules before they reach the wall, X is the mean displacement of the atoms in reaching the wall and L is the mean free path of the oxygen atoms.

With a nitrous oxide pressure of 10 cm at 25°C[1] and assuming diameters of 1.6A and 4.6A for oxygen atoms and nitrous oxide molecules respectively, 10^{-4} cm is found for L. X is approximately 1.25 cm. Hence $Z = 4 \times 10^8$. Therefore

$$k_{15}/k_3{}^0 = (N_2O)^2/4 \times 10^8. \quad (19)$$

Reaction (4) must certainly be a very efficient process requiring little or no activation energy. It will be shown below that (4) is of no importance even if the steric factor were as large as unity; hence $f_4 \exp (-E_6/RT)$ will be assumed to be 0.1. Therefore

$$k_4{}^0/k_3{}^{02} = 1.25 \times 10^{-12}. \quad (20)$$

Introducing (19) and (20) into (18) it is found that

$$4(O_2)(N_2O)/(NO)^2 = (\exp (2E_3/RT))/8$$
$$\times 10^9 t + (\exp (E_3/RT))/4 \times 10^6. \quad (21)$$

The ratio of oxygen to nitric oxide is 0.28[1] and with a time of 3600 sec. and a final pressure of NO of 3.8×10^{-4} cm, one obtains

$$1 = (\exp (2E_3/RT))/8.4 \times 10^{17}$$
$$+ (\exp (E_3/RT))/4.5 \times 10^6. \quad (22)$$

The first term on the right (arising from triple collisions) obviously can be neglected. Thus $E_3 = 9200$ cal.

A comparison of the energy of 14,000 cal. for (3) calculated from the data in this article with the 9200 cal. obtained from the previous data[1] indicates that practically all of the oxygen atoms produced by photochemical decomposition of nitrous oxide will form oxygen molecules by collisions with the walls.

Since nitric oxide is known to be formed,[1-3] primary process (2) must be accompanied by (5), which will be followed by (6) and (23)

$$N + walls = \tfrac{1}{2}N_2, \quad (23)$$
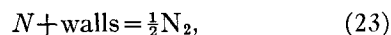
since the homogeneous termolecular combination of nitrogen atoms may be neglected for the same reasons as (4).

Since the number of molecules of N_2 and NO together formed per quantum absorbed is 1.9₅,[1] (6) must occur if (3) is excluded. For the speed of (6) to be comparable with that of (23) it can be shown by the above methods that E_6 must be less than 10,000 cal.

From the results of Musgrave and Hinshelwood,[4] the activation energy of (3) must be less than 24,000 cal. if this reaction is to compete successfully with (15). The 10,000 cal. difference between this figure and the minimum found in the present article might well explain why reaction (3) takes place to a small extent at 1000°K.