CCCCXVIII.—*The Decomposition of Nitrous Oxide by Cathode Rays.*

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IT has already been shown (Gedye and Allibone, *Proc. Roy. Soc.*, 1931, *A*, **130**, 346) that it is possible to make accurate determinations of the amount of energy (expressed in electron-volts) required per molecule reacting under the influence of cathode rays. From this can be calculated the number of molecules reacting per ion pair or the M/N ratio, if the necessary ionisation data are available. The only trustworthy data for ionisation by cathode rays are those for air (Eisl, *Ann. Physik*, 1929, **3**, 227), but on the assumption that the total ionisation relative to air is the same for cathode rays as for α-particles, a value of M/N was obtained for the decomposition of ammonia in good agreement with that obtained by Wourtzel (*Le Radium*, 1919, **11**, 289, 332) for α-particles. The applicability of the method has now been extended by examination of the decomposition of nitrous oxide.

This reaction has been extensively investigated under a variety of conditions. Wourtzel (*loc. cit.*), who studied it under the action of α-particles, calculated $M/N = 1{\cdot}74$ at ordinary temperatures, rising to 2·55 at 315°, but if these are corrected for the loss of energy due to deposition of Ra-*A* and Ra-*C* on the walls (Mund, *J. Physical Chem.*, 1926, **30**, 890) they become 2·7 and 4·0 respectively. Similarly, Macdonald (J., 1928, 1) obtained a quantum efficiency of 3·9 in ultra-violet light at ordinary temperatures. The reaction has also been investigated in the silent discharge by Joshi (*Trans. Faraday Soc.*, 1927, **23**, 227). In all three cases the observed reaction is represented by the equation $4N_2O = 2NO_2 + 3N_2$ or $4N_2O = 2NO + O_2 + 3N_2$, and is followed by the decomposition of the nitrogen peroxide. In the thermal reaction, on the other hand, except at comparatively high temperatures, the products are almost entirely oxygen and nitrogen (Hinshelwood and Burk, *Proc. Roy. Soc.*, 1924, *A*, **106**, 284; van Praagh and Topley, *Trans. Faraday Soc.*, 1931, **27**, 312), the homogeneous decomposition being unimolecular (Volmer and Kummerow, *Z. physikal. Chem.*, 1930, **9**, 141). At higher temperatures, however, considerable quantities of nitric oxide are obtained, and Briner, Meiner, and Rothen (*Helv. Chim. Acta*, 1926, **9**, 409) found that in silica vessels at 1300° as much as 25% of the nitrous oxide could be converted into nitric oxide. It thus appears that nitrous oxide is able to decompose in two ways, that which yields nitric oxide being favoured by a high energy of activation.

EXPERIMENTAL.

A beam of electrons from a Lenard discharge tube of the type described by Gedye and Allibone (*loc. cit.*) was passed through a thin aluminium window into the Pyrex-glass reaction vessel, which was 22 cm. long and 8·5 cm. in diameter. A flange at the top was ground flat and fitted to a window support. This consisted of a brass grid structure which was waxed to the vessel and provided with a water cooling tube. The window consisted of aluminium foil 0·020 mm. in thickness, fixed to the support by means of a cellulose paint which was protected from the destructive action of the rays by a metal shield. Before use, the vessel was thoroughly out-gassed by electron bombardment. Nitrous oxide from a cylinder was passed over solid potassium hydroxide and phosphoric anhydride, and twice distilled from liquid air before admission to the reaction vessel, mercury vapour being excluded. The chemical system was as described by Gedye and Allibone (*loc. cit.*). Nitrous oxide, which exerts a pressure of less than 0·001 mm. at the temperature of liquid air, and nitrogen peroxide were frozen out in liquid air after exposure, and the pressure of the residual gases, nitrogen, oxygen, and nitric oxide, was noted on a McLeod gauge. All exposures were carried out at 18°.

The results recorded below show that the reaction occurring during electron bombardment may be represented by the equation $4N_2O = 3N_2 + 2NO + O_2$. This was followed by the combination of nitric oxide and oxygen to form nitrogen peroxide. The reaction $2NO + O_2 = 2NO_2$ is largely homogeneous at ordinary temperatures in glass vessels, and, since it is termolecular, its rate falls off very rapidly with pressure (Bodenstein, *Z. physikal. Chem.*, 1922, **100**, 68). It has a negative temperature coefficient and proceeds much more rapidly at liquid-air than at ordinary temperatures. Hence when the partial pressure of the nitric oxide–oxygen mixture is low, the greater part will remain uncombined for a considerable time. Thus, when the yield is small, unless a long time elapses before measurements are taken, the volume of permanent gas calculated from the reading of the McLeod gauge should approach twice the volume of nitrogen formed directly, whilst for larger yields, especially if left at liquid-air temperature for some time, the permanent gas measured will be mainly nitrogen. Analyses of the gas collected by a Töpler pump showed in every case that it was pure nitrogen (see Table I, where all volumes are corrected to *N.T.P.* as also elsewhere).

It was further observed that the volume of nitrogen collected was always less than that of permanent gas, calculated from the McLeod gauge readings, as illustrated in Table II.

TABLE I.

		Vol. after absorption by		
Yields, c.c.	Initial vol., c.c.	KOH.	KOH and pyrogallol.	$FeSO_4$.
1·31 + 1·78	3·09	3·09	3·09	3·09
0·20 + 0·23	0·43		0·43	
0·19 + 0·265				
+0·19 + 0·655	1·30	1·30	1·29	

TABLE II.

Expt. No.	Yield, calc. from gauge reading, V_1, c.c.	Approx. time between end of exposure and measurement of V_1.	Vol. of N_2 measured directly, V_2, c.c.	V_2/V_1.
1	2·96	4 hours	2·40	0·81
2	2·09	4 ,,	1·78	0·85
3	1·56	4 ,,	1·31	0·84
4	1·01	1 hour	0·655	0·65
5	0·47	15 mins.	0·265	0·56
6	0·393	15 ,,	0·19	0·48
7	0·35	15 ,,	0·19	0·54

In Expt. 4, a small steady fall in the readings of the McLeod gauge was observed, indicating combination of nitric oxide and oxygen. On the other hand, in experiments in which the yield was of the same order of magnitude, as in Expts. 5, 6, and 7, the pressure of the permanent gases underwent no measurable decrease in $\frac{1}{2}$ hour. We may therefore conclude that in these experiments no appreciable combination had taken place before collection of the gases. The volumes of gas collected could be measured to ± 0·005 c.c., but an additional error was involved in the possible sticking of a small bubble of gas at the end of the capillary tube of the pump, which meant that, on this account, any individual reading might be as much as 0·02 c.c. low. The samples of gas in Expts. 5, 6, and 7 were, however, collected together, so that this error could occur once only in measurement of the total volume. Thus, although each individual reading of V_2 may be low by 0·025 c.c., the error in the total volume collected is no larger. The mean value of V_2/V_1 for Expts. 5, 6, and 7 is therefore 0·54 ± 0·03, if allowance is made for an error of ± 2% in the reading of the McLeod gauge.

In order to interpret these results, it was necessary to investigate the reaction between mercury and nitrogen peroxide, for, although such a reaction is known to occur, it appears never to have been satisfactorily investigated. Moore and Noyes (*J. Amer. Chem. Soc.*, 1924, **46**, 1367) state that reaction occurs "probably according to the equation $4Hg + 2NO_2 = 4HgO + N_2$," but record no analysis of products.

Nitrogen peroxide, prepared by heating lead nitrate, was passed into mercury. A white substance soluble in water was formed, and proved by the ordinary tests to be a mixture of mercurous and mercuric nitrates, the former predominating. Lead nitrate was also heated in a vacuum, and the gases evolved were passed through mercury during collection by a Töpler pump. Consistent results were obtained showing that the collected gas contained 60% of oxygen and 40% of nitrogen by volume. Since lead nitrate decomposes on heating according to the equation $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$, these results show that the nitrogen peroxide reacts with mercury, forming nitrates and liberating one-third of its nitrogen.

If nitrous oxide is decomposed by electron bombardment according to the equation $4N_2O = 3N_2 + 2NO + O_2$, the nitric oxide and oxygen will combine on compression and react with mercury. If no appreciable combination between them occurs *before* the non-condensable gases are pumped off, the volume of nitrogen collected should be equal to 5/9 of the total non-condensable gas. This is in agreement with the results of Expts. 5, 6, and 7, recorded above, and proves that the initial products are nitric oxide and oxygen, and that combination to form nitrogen peroxide is a secondary reaction.

The readings in Table III were taken with a peak voltage of 180 kv. to determine the number of electron-volts per molecule decomposed. Calorimetric experiments carried out as previously described (*loc. cit.*) showed that the mean energy per electron entering the reaction vessel at this voltage is 44·5 kv. It was shown that with this maximum voltage absorption of energy in the gas phase was complete for ammonia, and hence the same must be true for the denser gas, nitrous oxide. In Expts. 8—11, in which the yield is small, the readings of the McLeod gauge showed no drift with time, and the yield of nitrogen has been taken as half the total volume of non-condensable gas. In Expt. 4, in which appreciable combination had taken place, the nitrogen was determined by direct measurement after collection, a correction being applied for that produced by action of the peroxide on the mercury.

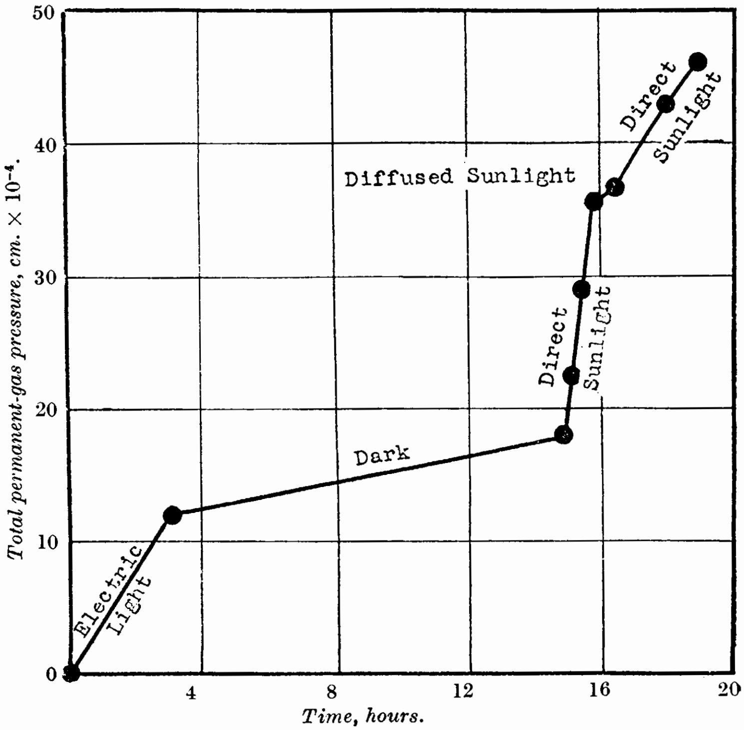
TABLE III.

Expt. No.	Initial press. (cm. Hg).	Time (mins.).	Current (micro-amps.).	Yield of N_2, c.c.	Molecules decomposed per electron.	Electron-volts per molecule.
4	66·0	10	1·01	0·595	$5{\cdot}22 \times 10^{-3}$	8·5
8	73·0	10	0·345	0·206	5·72 ,,	7·8
9	73·0	10	0·339	0·200	5·65 ,,	7·9
10	73·0	10	0·286	0·157	5·27 ,,	8·4
11	73·0	10	0·524	0·306	5·60 ,,	8·0
						Mean 8·1

Taking 1·02 as the total ionisation in nitrous oxide relative to air for α-particles (Bragg, *Phil. Mag.*, 1907, **13**, 333; Laby, *Proc.*

Roy. Soc., 1907, *A*, **79**, 206), and assuming that this value also holds for cathode rays, we obtain from Eisl's result of 32·2 electron-volts per ion pair in air, a value of 31·6 for nitrous oxide, giving $M/N = 3{\cdot}9$. The accuracy of the method was discussed in detail by Gedye and Allibone (*loc. cit.*). The most serious source of error is the variation of the electron power supplied by the Tesla coil, which could only be controlled to ± 5%. The probable error in the value of M/N given above is estimated to be not greater than ± 0·4. In preliminary results of this investigation (*Trans. Faraday Soc.*, 1931, **27**, 474), the volume of nitrogen collected in Expt. 4 had not been corrected as indicated above, and M/N was given as 4·0.

FIG. 1.



It was observed that if, after an exposure to electron bombardment, the reaction vessel was cooled in liquid air for some time, the permanent gases pumped off, and the liquid air removed, then a photochemical reaction occurred resulting in further liberation of permanent gas. The condensable gases were frozen out in the reaction vessel for each reading, and the permanent gases pumped off after measurement of the pressure. The effect observed is illustrated in Fig. 1. This is clearly due to the photochemical dissociation of nitrogen peroxide into nitric oxide and oxygen, as found by Norrish (J., 1927, 761).

Discussion.

The value of 3·9 calculated for the M/N ratio is somewhat higher than Wourtzel's corrected value of 2·7 at ordinary temperatures. The difference may be partly accounted for by the fact that reaction had to be carried well beyond the initial stages in order to be measurable under the conditions of his experiments. He remarks that his M/N ratios for this reaction are only of secondary interest owing to the complexity of the reaction. The difference is therefore not sufficient to indicate a true variation between the yields per ion pair produced by the two agents. The result is in very good agreement with Macdonald's value of 3·9 for the quantum efficiency in the photochemical decomposition, a fact which suggests that, after the primary process, the subsequent steps are the same in the two cases.

In the region in which photochemical reaction occurs, Leifson (*Astrophys. J.*, 1926, **63**, 73) found that nitrous oxide absorbs continuously, showing that dissociation of the molecule occurs immediately on absorption of the quantum, and it may, therefore, be concluded that a similar dissociation occurs on the recombination of ions. There are two possible methods for the dissociation of nitrous oxide, *viz.*,

$$N_2O = NO + N \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

and

$$N_2O = N_2 + O \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

The available data for the heat of formation of this gas are somewhat conflicting, but if we take the value of — 0·74 electron-volts ("International Critical Tables"), and 5·13 and 9·2 respectively for the heats of dissociation of oxygen and nitrogen, we obtain for the above reactions, absorptions of (i) 4·7 and (ii) 1·8 electron-volts. The critical increment for the homogeneous thermal reaction calculated from the temperature coefficient is 2·3 electron-volts, and hence, as pointed out by Ramsperger and Waddington (*Proc. Nat. Acad. Sci.*, 1931, **17**, 103), the primary process must in that case be (ii). The difference between the products of the thermal reaction, on the one hand, and the photochemical and ionic reactions, on the other, might then be accounted for if the primary process in the latter case were (i). In order to test this possibility, Dr. E. J. B. Willey (private communication) has kindly made experiments on the effect of active nitrogen, which contains nitrogen atoms, on nitrous oxide. No appreciable reaction occurs, the glow being actually more intense in the presence of nitrous oxide, on account of its photogenic effect. The dissociation

$$N_2O = N_2 + O' - 6{\cdot}0 \text{ volts} \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

where O′ is an atom in the metastable $^1S_0$ state (4·17 v.) (Frerichs, *Physical Rev.*, 1930, **36**, 398), agrees, within the limits of accuracy of the available data, with the beginning of the continuous absorption at 2000 Å (6·17 v.).

Possible subsequent steps which might account for the observed products and efficiency are

$$O' + N_2O = 2NO + 5{\cdot}6 \text{ volts} \quad . \quad . \quad . \quad \text{(iv)}$$

and the thermal dissociation of two further molecules of nitrous oxide by collision with the activated products of reaction (iv).

Finally, it may be noted that there is no evidence to support a cluster mechanism for this reaction as suggested by Lind (*J. Physical Chem.*, 1928, **32**, 573), since this would require the formation of an excited molecule of finite life, which would result in a fine structure for the absorption spectrum and a dependence of quantum efficiency on pressure, neither of which has been observed.

Summary.

(1) Nitrous oxide is decomposed by cathode rays according to the equation $4N_2O = 3N_2 + 2NO + O_2$. After exposure, if sufficient time is allowed, the nitric oxide and oxygen combine to form nitrogen peroxide.

(2) Each molecule decomposed requires 8·1 electron-volts, which, on the assumption of 31·6 electron-volts per ion pair, gives $M/N = 3{\cdot}9$.

(3) The photochemical and the ionic reaction are strictly similar, about four molecules reacting per excited or ionised molecule formed. Reasons are given for believing that the first step after absorption of the quantum or recombination of ions is dissociation of the molecule into $N_2 + O$, and the possible subsequent steps in the reaction are discussed.

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