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I.—*The Photochemical Decomposition of Nitrous Oxide and Nitric Oxide.*

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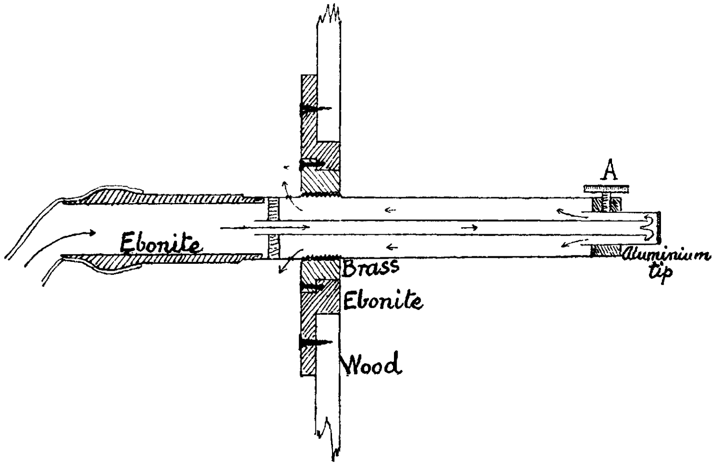
THE modes of decomposition of nitrous oxide by heat (Hinshelwood and Burk, *Proc. Roy. Soc.*, 1924, *A*, **106**, 284; Briner, Meiner, and Rothen, *Helv. Chim. Acta*, 1926, **9**, 409), by α-rays (Wourtzel, *Le Radium*, 1919, **11**, 332), and by the silent electric discharge (Joshi, *Trans. Faraday Soc.*, 1927, **23**, 227) have already been determined, and its photochemistry is of importance. Previous work on the subject has been done by Berthelot and Gaudechon (*Compt. rend.*, 1910, **150**, 1517) and by Regener and Warburg (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1904, 1228), who found that nitrogen peroxide was produced. It was considered advisable to extend their work, with a view to observe the quantum efficiency and to determine the mechanism of the decomposition.

Nitric oxide also has been studied, although less exhaustively, by other workers. Briner and Boubnoff (*J. Chim. physique*, 1913, **11**, 597) investigated its decomposition under the combined influence of pressure and heat, and found that two actions took place, the major yielding nitrous oxide and oxygen, and the minor nitrogen and oxygen. Berthelot (*Compt. rend.*, 1876, **82**, 1360; 1910, **150**, 1517) ascertained that in the silent electric discharge nitrous oxide was produced, and on exposure to a mercury-vapour lamp, nitrogen and oxygen. A fuller study was undertaken in the hope that the results would be of use in the interpretation of the decomposition of nitrous oxide. These results, however, are not so complete as in the case of nitrous oxide, and their interpretation is more difficult.

EXPERIMENTAL.

The Activating Wave-length.—Preliminary experiments showed that nitrous oxide is decomposed by light of wave-length less than 2000 Å., which is strongly absorbed (compare Leifson, *Astrophys. J.*, 1926, **63**, 73). A new quartz mercury-vapour lamp produced considerable decomposition in 2 hours, nitrogen peroxide being formed. That this was due to the line 1849 Å. of the mercury arc and not to the Cario–Franck mechanism, involving the activation of mercury atoms which were accidentally present, was shown both by reducing the risk of contamination with mercury to a minimum, whereupon no corresponding decrease took place in the extent of decomposition, and by interposing in the path of the light a gelatin screen which absorbed all light below 2000 Å., and thereby stopped the decomposition. It was found, however, that after 20—30 hours' use the mercury-vapour lamp aged, and decomposition could no longer be produced by it. A condensed aluminium spark, whose light is particularly rich in lines at 1860, 1930, and 1990 Å., was therefore substituted for it.

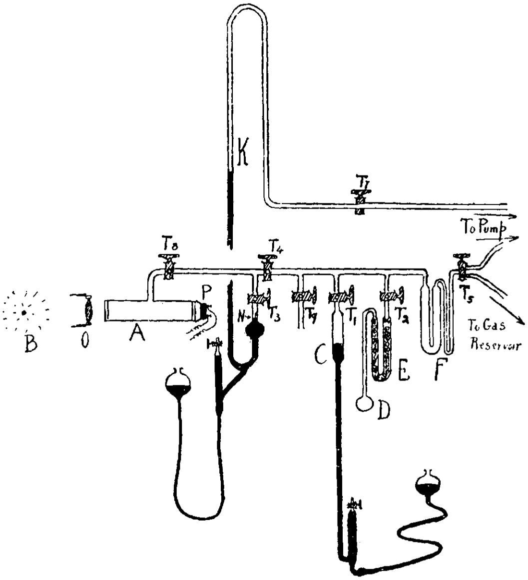
FIG. 1.



Apparatus.—The electrical circuit used was as follows. Alternating current at 100 volts, 15 amps., and 50 cycles was led from a rotary converter into a transformer and stepped up to 10,000 volts. It was then taken through high-frequency choke-coils (to protect the transformer from the high-frequency discharge) to the spark-gap, in parallel with which was a battery of condensers of total capacity 0·05 microfarad. The spark-gap was 1 cm. wide. Considerable difficulty was found in constructing efficiently cooled electrodes. These were finally made of 1-inch brass tube, being tipped with an aluminium cap turned out of ½-inch rod, each being cooled by a blast of air blown through an inner brass tube and returning through the annular space between this and the outer tube. A section of one of these electrodes is shown in Fig. 1, the arrows indicating the current of air. All connexions in the condenser–spark-gap circuit were made of heavy copper strip, to minimise the energy loss due to heating, which would otherwise have been considerable. The circuit was regulated both by means of a low-frequency choke-coil, with a variable magnetic gap, in the primary alternating circuit, and by rheostats on the direct-current circuit which fed the rotary converter.

Two reaction vessels of different types were used. Vessel A was of quartz, test-tube shaped and ground into a glass socket, and was about 3 cm. in diameter and 17 cm. in length. It was laid horizontally above the spark, 7·3 cm. from the electrodes, and was cooled by a draught of air. In spite of this, the temperature rose to about 40°, and all experiments with this vessel were carried out at that temperature. Such a vessel, having a comparatively large area exposed to the light, was suitable for experiments in which a considerable rate of decomposition was desired. Its shape, however, rendered it impossible to make any measurements of the light absorbed when using it, or to regulate the temperature accurately. Reaction vessel B consisted of a glass tube, 3 cm. in diameter and 15 cm. in length, with fluorite windows cemented to each end, and was cooled in a trough of water (see A, Fig. 2). The light was concentrated by a fluorite lens, O, and sent through the vessel in a

Fig. 2.



beam which was as nearly as possible parallel. A large-surface thermopile, P, was placed close to the second window.

As the analyses were based largely on pressure changes, it was necessary to use a pressure gauge in which nitrogen peroxide (formed in the reaction) did not come into contact with mercury. An all-glass gauge of the type described by Jackson (J., 1911, **99**, 1066) was at first employed, but as its accuracy was limited to about 1 mm. pressure, it was discarded in favour of the mercury manometer K (Fig. 2), in which the taps T_8 and T_3 maintained between the mercury surface and the reaction vessel an effective buffer of the gas being studied. By using a small microscope to set the mercury surface to the inserted glass pointer, N, and reading the height of the other column by a cathetometer, an accuracy of 0·1 mm. could be attained.

Analysis of the Products.—The method of procedure may be followed by reference to Fig. 2. It differed only in detail for the two gases studied. In both cases the purified gas was introduced through T_5 into the apparatus, until approximately the required pressure was present, the bulb D being kept evacuated. Fine adjustments of pressure could be made by altering the level of the mercury in C. All taps were closed, and the reaction vessel was exposed to the light for the required period. T_8 and T_3 were then opened, and the change of pressure resultant upon the exposure was measured, a correction being applied for the dead space between T_8 and the mercury surface. Next, liquid air was placed round the double U-tube F, and the permanent gases were pumped off through T_5 by means of a Langmuir mercury diffusion pump backed by a Töpler pump. The gases so removed were collected. When nitrous oxide was being studied, these consisted of nitrogen and oxygen. They were measured together, and subsequently measured again after treatment with pyrogallol. In the case of nitric oxide, nitrogen and a small proportion of the undecomposed nitric oxide were removed in the first few minutes' pumping, and, after treatment with ferrous sulphate to remove the nitric oxide, the nitrogen was measured. The remainder of the nitric oxide was then pumped off, the rate of evaporation being 20—30 c.c. per hour. The gases retained by the liquid air consisted of nitrous oxide (in large excess, when this was the substance studied), nitrogen peroxide, and nitrogen trioxide. When the all-glass gauge was used, the pressure of the residual gases was measured, but this could not be done when the mercury manometer was employed. Nitrogen peroxide was next removed by distilling the mixture through tubes of solid caustic soda E, D being immersed in liquid air. In a number of the experiments, any nitrogen trioxide present was first converted into peroxide by the addition of air, and the nitrous oxide which remained was then estimated from its pressure. When the amount of nitrous oxide was small, however, no air was admitted, and after passage through the caustic soda tubes the residual gas was pumped off and measured, nitric oxide produced from the decomposition of the trioxide being removed by ferrous sulphate.

It is sometimes stated (*e.g.*, Partington, " Text-book of Inorganic Chemistry," 1921, p. 588) that, although nitrogen trioxide is dissociated at room temperature into nitric oxide and nitrogen peroxide almost completely, the mixed gases are entirely absorbed by solid caustic soda, forming nitrite only, and thus acting as the trioxide. Nitric oxide was always found in the gas finally pumped off, however, indicating either that it is not completely absorbed in the presence of an equivalent of nitrogen peroxide, or that the mixture condensed in the liquid-air trap contains more than an equivalent of nitric oxide.

The nitrous oxide used in these experiments was obtained from cylinders, and was purified by passage over solid caustic soda and phosphorus pentoxide, and by fractionation from a liquid-air trap. The nitric oxide was prepared by the Lunge " nitrometer " reaction, and was pumped off from liquid air into the vessel in which it was stored.

Results with Nitrous Oxide.

The results of many analyses show that, under the conditions employed (*i.e.*, at 21·7—607 mm. pressure, at temperatures of 0—40°, and with times of exposure of 2—66·5 mins.), the final products consist almost entirely of nitrogen, nitrogen peroxide, and unchanged nitrous oxide. There is always, however, a little oxygen in the gas pumped off. Table I gives the results of two typical experiments at 15°, and serves to show the order of accuracy attained.

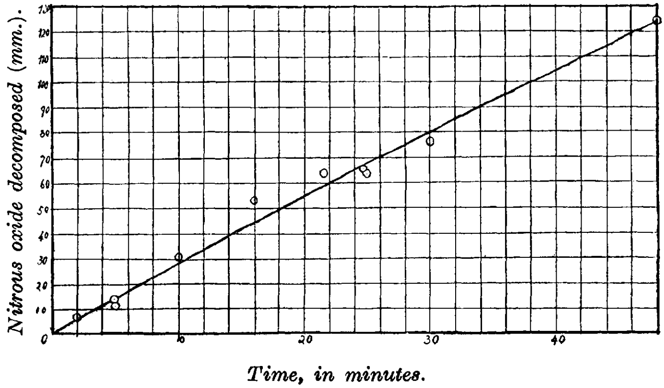
TABLE I.

	Expt. 13(a).		Expt. 13(b).	
	1.	2.	1.	2.
Initial pressure (mm.)	115·0		115·4	
Time of exposure (mins.)	10		49·5	
Increase of pressure (1) (mm.)	3·0	3·0	7·0	10·6
Increase of pressure (2) (mm.)	1·4	1·5	5·56	5·3
N_2O decomposed (mm.)	5·9	(5·9)	21·8	(21·8)
Vol. permanent gas removed (c.c.)	0·54		1·91	
Vol. absorbed in pyrogallol (c.c.)	0·01		0·04	
Corresponding pressure of N_2	4·3	4·4	15·6	15·9
Corresponding pressure of O_2	0·1		0·3	

Col. 1 gives the actual experimental figures. Col. 2 gives the pressures which would have been observed had all the nitrous oxide which disappeared decomposed according to the equation $4N_2O = 2NO_2 + 3N_2$. Two values are given for the increase of pressure due to decomposition. The first was measured immediately after the exposure. The second was obtained after condensation of the gases in the liquid-air trap, evaporation, and keeping for some time. The difference is due to the fact that during a short exposure the nitrogen peroxide is not present as such, but as an equivalent mixture of nitric oxide and oxygen. The combination of these two gases is slow at the extremely low partial pressures prevailing, and, according to Norrish (J., 1927, 761), nitrogen peroxide tends to decompose into nitric oxide and oxygen in ultra-violet light.

Fig. 3 shows the result of an experiment at 400 mm. pressure in which the time of exposure was varied. The curve is almost straight, there being no falling off in the rate of decomposition that cannot be accounted for by the lessened partial pressure of nitrous oxide present. There is no induction period. Similar experiments with vessel B showed a greater decrease of velocity with time, due to the screening effect of traces of nitrogen peroxide, formed by the slow combination of nitric oxide and oxygen, which took effect in the longer light-path in this vessel. In an experiment in which the combination of nitric oxide and oxygen was prevented by drying the apparatus and gas with special care, a high value was again obtained.

FIG. 3.



The results of experiments at 100 mm. and 600 mm. pressure in vessel A, and at 100 mm. pressure and 0° and 15° in vessel B, are in Table II. They are similar to that described above.

The results of experiments in which the pressure was varied and the time of exposure kept constant are in Table III. The values are plotted as circles in Fig. 4.

TABLE II.

Expt. 6. Vessel A. Initial pressure, 100 mm. Temp., 40°.

Time (mins.)	5	5	10	10	13	15	20	25	25·75	26	40
N_2O * (mm.)	9·6	8·6	15·1	13·3	18·5	26·6	21·0	35·1	31·3	27·5	41·6
N_2 (mm.) ...	13·5	13·9	11·6	—	14·3	21·6	—	32·1	28·1	—	39·2
NO_2 (mm.)	5·7	5·3	7·6	—	9·2	10·7	—	18·3	17·2	—	23·7
O_2 (mm.) ...	1·6	2·0	0·1	—	?	1·8	—	1·5	?	—	1·2

* The figures for N_2O denote the amount decomposed.

Expt. 7. Vessel A. Initial pressure, 600 mm. Temp., 40°.

Time (mins.) ...	5	10	12	13·5	20	25	27
N_2O (mm.)......	18·1	29·6	32·4	40·3	59·8	61·9	76
N_2 (mm.)	14·1	23·3	29·2	30·8	50·2	59·2	55·8
NO_2 (mm.)......	8·2	12·8	14·5	19·1	28·9	29·2	27·7
O_2 (mm.)	0·6	1·34	2·5	0·5	2·3	3·1	4·77

Expt. 8. Vessel B. Initial pressure, 100 mm. Temp., 15°.

Time (mins.) ...	7·3	8	10	12·5	12·7	18·25	21	34	66·5
N_2O (mm.)......	4·3	3·8	5·1	6·4	6·3	8·2	8·6	12·1	16·4
N_2 (mm.)	3·2	2·8	4·4	4·8	4·6	6·15	6·3	9·1	12·3
O_2 (mm.)	?	0·0	0·1	0·0	0·1	?	0·1	0·0	0·2

Expt. 9. Vessel B. Initial pressure, 100 mm. Temp., 0°.

Time (mins.)	9	19	27·8
N_2O (mm.)...........................	4·0	6·14	8·0
N_2 (mm.)	2·9	4·5	5·2
O_2 (mm.).............................	0·1	0·1	0·2

FIG. 4.

Nitrous oxide.

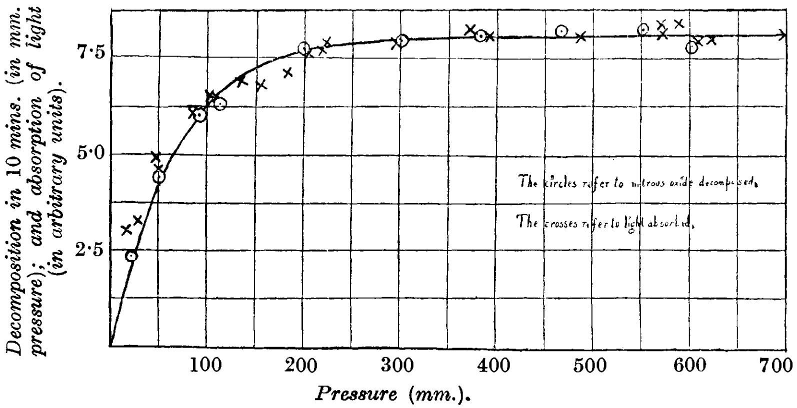


TABLE III.

Expt. 13. Vessel B. Decomposition in 10 minutes at 15°.

Initial press. (mm.)	21·3	49·7	91·1	115·0	200·8
N_2O decomposed (mm.) ...	2·3	4·4	6·0	6·3	7·75
Initial press. (mm.)	301·3	383·3	466·9	553·0	607·0
N_2O decomposed (mm.) ...	7·96	8·08	8·18	8·28	7·81

It was ascertained that the quantity of nitrogen peroxide formed in 10 minutes was negligible, and the values therefore give the true initial rate of decomposition.

The crosses in Fig. 4 show the absorption of light by nitrous oxide. This was measured by means of the thermopile, which received the light after it had passed through the vessel. The ordinates represent the difference between the deflexion of a Moll galvanometer when the light was allowed to pass through the evacuated vessel on to the thermopile, and that observed when the vessel was filled with a quantity of nitrous oxide. The abscissæ represent the pressure of nitrous oxide, as before. The observed deflexions were multiplied by a constant factor so chosen that one of the points (486 mm.) fell on the curve representing the rate of decomposition. It will be seen that the other points also fall on this curve, showing that the rate of decomposition, in the initial stages at least, is proportional to the amount of light absorbed.

That this absorption of light is represented quantitatively by Beer's law, *i.e.*,

$$\text{light absorbed} = \text{incident light} \times (1 - e^{-acd}) \quad . \quad . \quad . \quad (1)$$

(where a is the absorption coefficient, c the concentration, and d the length of the reaction vessel), is shown by the continuous line in Fig. 4, which is obtained by solving this equation for $c = 200$ mm. and $c = 600$ mm., two values of c being necessary in the absence of a direct measurement of the effective incident light.

The amount of light absorbed, as above measured, has been related to the decomposition occurring in unit time, thus giving the value of the quantum efficiency of the decomposition. First, the energy falling on 1 sq. cm. at 1 m. from a standard lamp in a certain position was determined by measuring the rate of rise of temperature on illumination of a metal disc which formed one junction of a thermocouple (compare Denning, *Phil. Mag.*, 1905, **10**, 270), and from this, the energy required to fall on the thermopile in order to give unit deflexion of the galvanometer was easily obtained. The value $2{\cdot}31 \times 10^{-4}$ cal. per sec. per cm. deflexion was found as a mean of about 12 determinations in each series, the maximum difference between any two experiments in either being 4%. This was multiplied by the deflexion caused by the presence in the apparatus of a given pressure of gas, so that the energy absorbed by that gas in 1 sec., and hence in 10 minutes, was obtained. This and the corresponding amount of decomposition were substituted in the formula

$$\gamma = (28470/\lambda) \times (\text{mols. decomposed/cals. absorbed}),$$

where γ is the quantum efficiency and λ the wave-length of active light in microns. Actually, the light used was not monochromatic; but it was confined principally to the three lines at 1860 Å., 1930 Å., and 1990 Å. to which Pflüger (*Ann. Physik*, 1904, **13**, 890) assigns the relative intensities 173, 58, and 50, respectively. On the assumption, therefore, that the absorption is constant throughout this range, and that the activity of each line is proportional to its intensity, the effect would be equal to that of one line at 1900 Å. ($0{\cdot}19\mu$) with the same total intensity, and this value was substituted for λ in the above equation. When a correction of 5% for the reflexion and scattering of light by the fluorite plates had been applied, the value of γ was found to be $3{\cdot}9 \pm 0{\cdot}2$ mols. decomposed per quantum absorbed.

Temperature Coefficient.—It is of great importance, in studying the mechanism of any reaction, to find the temperature coefficient of the process; but, in the case of photochemical reactions, it is useless merely to state the value of such a coefficient, without indicating what factor is altering, for it may be due to a change either in the quantum efficiency or in the absorption coefficient. As already pointed out, the rate of decomposition is proportional to the light absorbed at any temperature, and therefore

$$\text{rate} = KI(1 - e^{-acd}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where I is the intensity of the incident light and K is a constant. The value of this constant will depend on the quantum efficiency of the process, and it is necessary to find whether it is this or the value of a which changes with temperature.

If it can be assumed that a is independent of temperature, then it is merely necessary to compare the rates of reaction at the same concentration and different temperatures in order to obtain the temperature coefficient. If, however, a alters with temperature, the observed " temperature coefficient " will vary according to the pressure of gas under observation, for the rate of reaction is proportional to a at very low concentrations, and is independent of a when the pressure is sufficiently high to ensure that all the incident light is absorbed at the lowest temperature at which measurements are made. If K is constant, however, the variation of a with temperature can be found by comparing the pressures at which equal rates of reaction take place, for in this case the rates are equal when the product ac is the same in the experiments under comparison. Expt. 9 has therefore been compared with Expt. 8 (Table II) to give a value for the temperature coefficient on the assumption that a is constant, and with Expt. 13 (Table III) to give a value on the assumption that K is constant. These values are 1·24 and 1·49 respectively for a 10° rise.

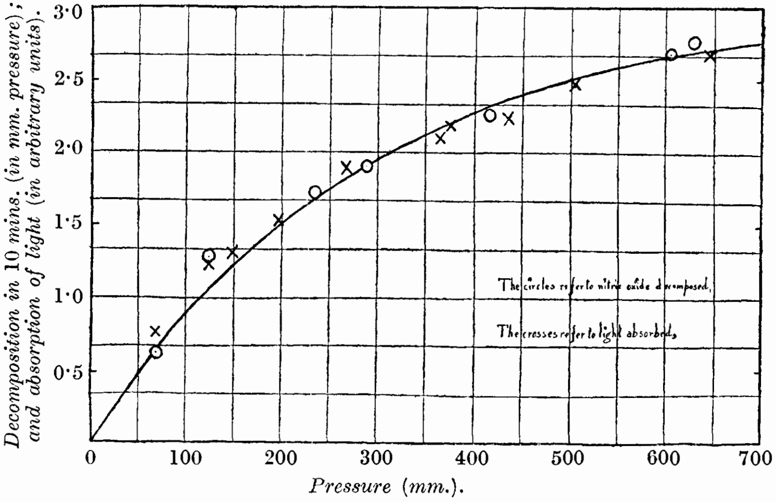
It has been possible to show more particularly the variation of the two constants by correlating experiments in vessel A with experiments in vessel B, a process which, however, involved certain approximations. The constants used in drawing the curve in Fig. 4, referring to vessel B at 15°, were : $KI = 8{\cdot}1$, $a = 1{\cdot}04 \times 10^{-3}$. Four experimental points giving the amount of reaction in 10 minutes in vessel A at 40° at different pressures were plotted, and equation (2) was solved with these values. The constants of this equation were : $KI = 29{\cdot}5$, $a = 2{\cdot}47 \times 10^{-3}$, the latter depending on a calculation of the effective value of d, as the average of all possible rays of light from the source through the vessel. The ratio of the values of a in the two series, reduced for a 10° rise, is 1·44. This approaches as near as could be expected to the value of 1·49 found between 0° and 15° on the assumption that K was constant. The ratio of the values of K depends on the ratio of the incident light. The latter was calculated approximately, allowance being made for the light reflected and absorbed by the quartz vessel. The ratio of the values of K worked out at $0{\cdot}95 \pm 0{\cdot}1$ for a 10° rise. The quantum efficiency, therefore, does not alter appreciably with temperature, which only affects the amount of light absorbed.

Results with Nitric Oxide.

This gas was less fully studied than nitrous oxide, which was the main object of research. Analyses showed that the reaction took place in two ways, one yielding nitrogen and oxygen, and the other nitrous oxide. The volume of nitrous oxide was only 10% of that of the nitrogen formed. In the majority of the experiments the nitrous oxide was present in too small a quantity to be estimated accurately, but there did not appear to be any considerable change in the proportion under the conditions studied, which were similar to those already described. The main experiments were directed towards determining the quantum efficiency, the rate of reaction and absorption of light at various pressures being also measured. The circles in Fig. 5 show the decomposition in 10 minutes (in mm. pressure) and the crosses show the light absorbed, reduced to the same scale. As in Fig. 4, the line is drawn as a solution of equation (2). The constants of this equation were : $KI = 3{\cdot}02$, $a = 2{\cdot}3 \times 10^{-4}$, so that the rate of reaction was lower than with nitrous oxide. The same wave-lengths of light were absorbed by nitric and by nitrous oxide, as was shown by the fact that both curves tended to the same maximum when light units (instead of mm. decomposition) were plotted as ordinates (compare also Leifson, *loc. cit.*). When this was again taken as 1900 Å., the quantum efficiency worked out at 1·45 mols. per quantum. That figure, however, is double the real value, for, in the major reaction at least, every atom of oxygen produced united with a molecule of nitric oxide, and thus two molecules of the latter substance disappeared for every one which actually decomposed. The real efficiency is therefore about 0·75.

FIG. 5.

Nitric oxide.



The Mechanism of the Changes.

We have seen that nitrous oxide decomposes in light according to the equation

$$4N_2O = 2NO + O_2 + 3N_2 \quad . \quad . \quad . \quad . \quad (3)$$

the proportions of the products remaining constant over a considerable range of conditions, and a very small proportion of oxygen being always found over and above that necessary to satisfy the equation. The quantum efficiency is 3·9, a figure which does not alter appreciably between 0° and 40°. The absorption of light, however, has a temperature coefficient of 1·47.

It has also been shown that nitric oxide decomposes in two ways, according to the equations

$$2NO = N_2 + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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

The proportion of the two reactions taking place was found to be about 90% of (4) and 10% of (5), a ratio which did not alter appreciably with the conditions of experiment, though comparatively small changes may have escaped observation. The quantum efficiency is about 0·75, and the absorption coefficient is less than that of nitrous oxide.

There are three general mechanisms by which nitrous oxide might decompose according to equation (3) : (*a*) One of the substances on the right-hand side might be an intermediate product in the formation of the others; (*b*) two concurrent reactions might take place; or (*c*) an intermediate product might be formed, which does not appear in the final products. Hypothesis (*a*) is disproved by the constancy of the products, and also by the fact that the known rates of decomposition of nitric oxide and of union of nitrogen and oxygen are far too slow to account for any measurable amount of such secondary reaction taking place. Mechanism (*b*), expressed as the equations

$$\left.\begin{aligned} N_2O + N_2O' &= 2N_2 + O_2 \\ N_2O + N_2O' &= 2NO + N_2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

(where N_2O' represents an activated molecule) is possible. The different courses of reaction could be explained by a difference in the activation of the molecule, either of two electrons being capable of elevation to a higher Bohr state, or by a different orientation at the moment of collision. In that event, however, the almost exact equivalence of nitric oxide and oxygen produced could only be fortuitous, and one would expect only 2 molecules to be decomposed per quantum instead of nearly 4, as found. The fact that the quantum efficiency did not alter with temperature or pressure is strong evidence that every activated molecule reacts, involving the decomposition of 3 other molecules. The length of an " indefinite " chain mechanism would be altered by an increase in the average energy of the system or in collision frequency. There remains the third mechanism, (*c*). The formation of nitrogen peroxide as an intermediary may be ruled out. Norrish (*loc. cit.*) found that the efficiency at 3650 Å. was not more than 0·03 molecule per quantum. To obtain the observed results, this would have to rise to a very high value (say, 20) at 1900 Å., and the very unlikely event of a four-fold collision would have to be assumed.

The following series of equations, however, satisfies all the necessary conditions :

$$\left.\begin{aligned} &(a) \quad N_2O + h\nu = N_2O' \\ &(b) \quad N_2O' + N_2O = O_2 + N_2 + 2N \\ &(c) \quad 2(N + N_2O = NO + N_2) \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (7)$$

The only one of these open to question is (*b*). Such a reaction between normal molecules would be endothermic to the extent of about 120,000 cals. per mol. The energy associated with a quantum of wave-length 1900 Å. is, however, 150,000 cals. per mol. The equation is, therefore, quite plausible thermally. The reaction may be pictured as follows. An active molecule comes into collision with a normal one, and a large amount of energy becomes available for redistribution. The first result is that two nitrogen atoms are ejected, and simultaneously the less energetic break-up of the complex N_2O_2 into nitrogen and oxygen occurs. The liberated nitrogen atoms will eventually come into collision with nitrous oxide molecules, and reaction (*c*) takes place. It is probable that a few of the nitrogen atoms combine with each other, for the observed rate of photochemical decomposition of nitric oxide is scarcely sufficient to account for even the small excess of oxygen found by analysis.

It is instructive to compare the photochemical decomposition of nitrous oxide with the other known decompositions. Both in the decomposition by α-rays (Wourtzel, *loc. cit.*) and in that by the silent electric discharge (Joshi, *loc. cit.*), reactions summarised by the equation $4N_2O = 2NO_2 + 3N_2$ take place. It is attractive to assume that in both these cases the mechanism outlined above operates. In the thermal reaction at comparatively low temperatures (Hinshelwood and Burk, *loc. cit.*) nitrogen and oxygen are the chief products. At higher temperatures, however, nitric oxide is produced in increasing quantities till a maximum is reached (Briner, Meiner, and Rothen, *loc. cit.*), when the rate of formation of this substance is balanced by its decomposition. As much as 25% of nitric oxide was found in the products. It is possible that in this case the higher temperature provides the energy necessary for reaction 7 (*b*) to take place also.

The mechanism of the decomposition of nitric oxide is much less clear. The quantum efficiency is low, and its variation with temperature is not known. If, as is probable, it increases with temperature, the maximum to which it tends is doubtful. On lines similar to those given above, a possible mechanism would appear to be the simultaneous reactions $NO + NO' = N_2 + O_2$ and $NO + NO' = N_2O + O$, followed by $NO + O = NO_2$. It should be noticed, however, that nitric oxide seems to be peculiarly liable to multimolecular reactions (compare Hinshelwood and Green, J., 1926, 730), pointing to some stability in the complex formed by the collision of two molecules. Should such a complex be struck by an active molecule, the reaction $(2NO) + NO' = N_2O + NO_2$ would take place, while the bimolecular reaction might give only nitrogen and oxygen. Briner and Boubnoff (*loc. cit.*) studied the thermal decomposition at high pressures. The reaction was of the third or fourth order, and nitrous oxide was mainly produced, some nitrogen being found. At high temperatures and ordinary pressures, Briner, Meiner, and Rothen (*loc. cit.*) found no nitrous oxide in the products of decomposition. A survey of the behaviour of nitric oxide under different modes of decomposition given by Briner and Boubnoff seems to show that the proportion of nitrogen generally increases with temperature. This might be due to the increase of energy of collision, or to the shortened life-period of the complex (2NO). The question requires further investigation.

Summary.

The decomposition of nitrous and nitric oxides in light of wave-length 1860—1990 Å. has been studied.

Nitrous oxide decomposes according to the general equation $4N_2O = 2NO + O_2 + 3N_2$, the proportions of the products being constant over a considerable range of conditions. The quantum efficiency is 3·9 ± 0·2, and does not vary appreciably with temperature between 0° and 40°, nor with pressures up to about 1 atmosphere. The absorption coefficient increases 1·47 ± 0·05 times for a 10° rise of temperature. A mechanism has been suggested for the decomposition which may be applicable to decompositions by other agencies.

Nitric oxide decomposes in two ways, according to the equations $2NO = N_2 + O_2$ and $3NO = N_2O + NO_2$, the first reaction constituting about 90% of the whole. The quantum efficiency is 0·73 ± 0·05. Two possible mechanisms are suggested. There is insufficient evidence, however, to warrant a decision.

Beer's absorption law holds strictly for both gases. Nitrous oxide, however, absorbs light several times more strongly than nitric oxide.

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