

19. *On Active Nitrogen. Part X. A Supposedly Oxidisable Variety of Nitrogen.*

By ERIC JOHN BAXTER WILLEY and STANLEY GEORGE FOORD.

It has been thoroughly established by a number of workers (e.g., Strutt, *Proc. Roy. Soc.*, 1911, **86**, A, 56; König, *Z. Elektrochem.*, 1915, **21**, 267) that the ordinary "active nitrogen" is not oxidised either by oxygen or by ozone; much interest therefore attaches to the claim of Lowry (J., 1912, **101**, 1152; *Trans. Faraday Soc.*, 1913, **9**, 189) to have produced a variety which reacts with the latter substance to give nitrogen peroxide. During a study of processes for the preparation of nitrous gases for flour bleaching (Cramp and Leetham, *The Electrician*, 1906, p. 769), he passed air at 70 cu. ft./min. through an ozoniser, a box containing four 3/32" spark gaps, and thence to a wooden trunk which was fitted for photographic measurement of the absorption spectrum of the nitrogen peroxide; the plates obtained were compared with standards, and hence the peroxide was estimated. Lowry found, in agreement with Cramp and Leetham, that preozonising the air supply nearly doubled the yield of nitrogen peroxide as compared with that obtained when the sparks were used alone.

An almost equally marked increase occurred when the sparked gas was treated with ozone or passed through an ozoniser; this was considered remarkable since ready-made nitrogen peroxide was destroyed under the same conditions although it could be regenerated by passing the bleached gas through a hot tube; this was attributed to the conversion of nitrogen peroxide to pentoxide in the ozoniser, followed by a reverse decomposition of the pentoxide when heated. Much the same increased yield was observed when the sparked, but not ozonised, air was mixed with another current of air which had been separately ozonised; this suggested that the effects were chemical in origin rather than electrical. These results were attributed to the formation in the spark of an unstable modification of nitrogen, which was unaffected by oxygen but reacted with ozone.

An alternative explanation, mentioned by Lowry, is that the phenomena may be due to the great difference in the rates of oxidation of nitric oxide by ozone and by oxygen, the former process being very rapid and the latter very slow; were this so, higher concentrations of peroxide should be obtained by circulating the gas more slowly, while at the same time the effect of ozonising, or adding ozonised air, should be much diminished. Both of these phenomena were actually observed, but Lowry rejects the "time-

factor" theory on the ground that under these conditions an increase in the number of spark gaps from 4 to 17 raised the peroxide concentration in the emergent air by only about one-third instead of 4—5-fold.

The experiments now to be described show that the foregoing results can all be attributed to the great difference in the rates of oxidation of nitric oxide by oxygen and ozone, and a theoretical treatment of the subject is given which leads to an identical conclusion.

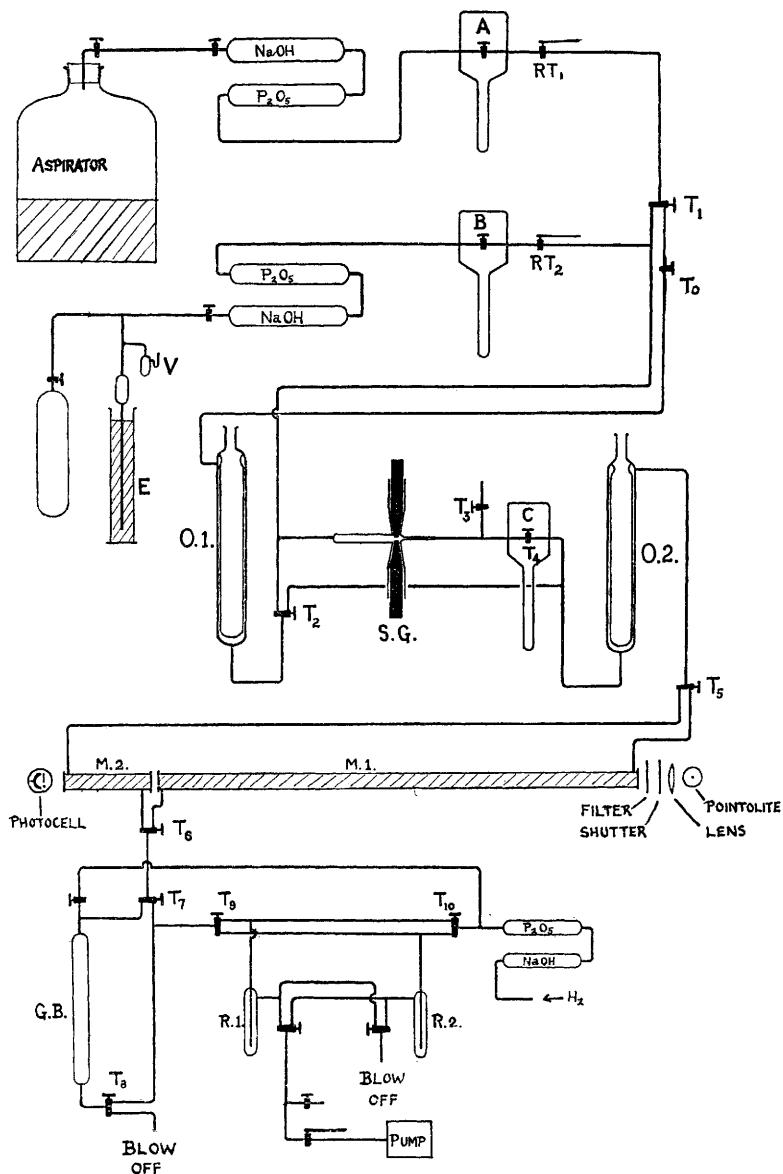
EXPERIMENTAL.

1. *Apparatus.*—The main apparatus is shown in Fig. 1, and consists of (a) two independent gas-supply systems, (b) an arrangement of two ozonisers and one spark gap, (c) a device for the photometric determination of nitrogen peroxide by a photocell, and (d) a gas burette and condensing traps for a similar analysis by chemical means, this last also being available for the estimation of ozone.

(a) The constant-head aspirator is used for mixtures of gases which are not available compressed in cylinders, and the flow is regulated by the fine-adjustment tap RT_1 , and measured by the venturimeter *A*. The other supply line is used where the gas can be taken from a cylinder, and has incorporated in it a constant-head blow-off *E* and safety valve *V*; measurement and regulation of flow are obtained by the venturimeter *B* and control tap RT_2 respectively, while a tap T_0 isolates this line from the rest of the apparatus when desired. By means of the two-way taps T_1 and T_2 , any desired gas can be (i) ozonised, (ii) sparked, (iii) ozonised and sparked, (iv) sparked and ozonised, or (v) sparked and treated with another ozonised gas, whereas the taps T_3 and T_4 , together with their associated venturimeter *C*, enable only a part of the gas which has passed through the spark to be fed to the second ozoniser *O.2*, the rest being blown off to atmosphere if desired.

(b) The ozonisers *O.1* and *O.2* are of the ordinary Siemens type, 60×4 cm. with an annular space of 2 mm. The spark passes between "Armco" iron studs which are screwed into a heavy brass rod bored out and fitted for water-cooling as illustrated (Fig. 2); the diameter of the spark gap is *ca.* 2 mm. The shape of the electrodes is such that they fit fairly closely into the side arms of the spark gap tube, and they are sealed in with a thin gasket of asbestos paper backed by picein wax; the auxiliary electrode in the water-cooling line prevents any trouble arising from electrolysis of the water due to electrical leakage through the glass spiral connecting the two electrodes. The ozonisers and spark are supplied with their appropriate electrical power from

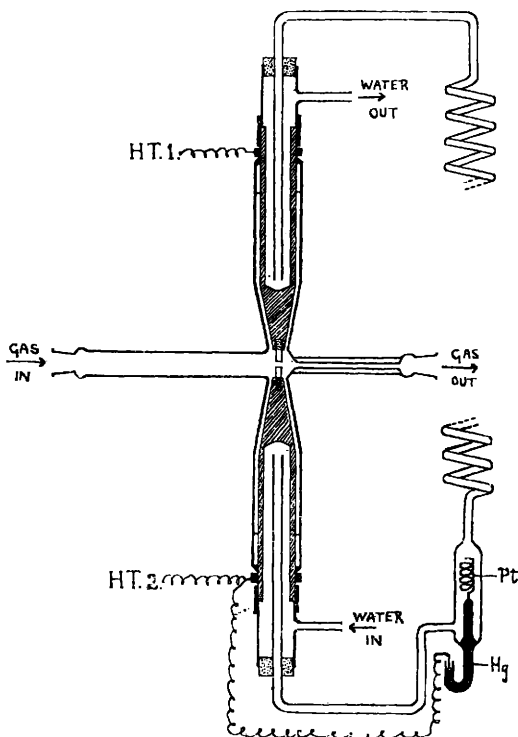
FIG. 1.



three transformers worked off 50-cycle A.C. and entirely independently controlled; approximate values of volts and amperes upon the discharges are: ozonisers, 4000 volts, 1.5 milliamps.; spark, 500 volts, 100 milliamps.

(c) After leaving the second ozoniser, the gas passes to T_5 and T_6 via either of the plane-ended and optically aligned photometer tubes $M.1$ and $M.2$, whose dimensions are: $M.1$, 175×2.5 cm.; $M.2$, 26×2.5 cm. The nitrogen peroxide is determined photometrically with a potassium photocell according to a technique already described (Willey and Foord, *Proc. Roy. Soc.*, 1932, in the press).

FIG. 2.



(d) The gases which leave the photometer tubes can be diverted by T_7 through either of two condensing traps $R.1$ and $R.2$, which are cooled by liquid air, or through the gas burette $G.B.$, whose capacity is 496 c.c. Nitrogen peroxide condensed in $R.1$ or $R.2$ is blown out, at the end of an experiment, by a stream of hydrogen admitted *via* T_{10} and its amount estimated by means of potassium iodide, as usual; with two traps in parallel, it is possible to run the apparatus undisturbed while making continuous chemical analyses of the reaction products. Ozone is determined similarly by allowing the gas burette to fill with the gas under examination,

an amount equal to three or more times the volume of the burette being passed to ensure a proper sampling, after which the flow is diverted to the condensing-traps line and the gas in *G.B.* blown out through potassium iodide solution according to the usual technique. In both cases the iodide was in 5% solution, and the titrations were carried out with *N/50*-sodium thiosulphate, but without the starch indicator, since it was found that by using a spiral bubbler of capacity 45 c.c. (compare Willey and Foord, *loc. cit.*), the stirring of the solution being done by the current of hydrogen, the change in colour could be detected by eye.

2. *Calibration of Apparatus.*—(a) Venturimeters were calibrated by means of the constant-head aspirator before being incorporated in circuit; in all cases a linear relation was found to hold between head of liquid in the meter and flow speed of gas. Meters *A* and *B* were filled with concentrated sulphuric acid, and *C* with medicinal paraffin (“Nujol”).

(b) Ozonisers were also calibrated on both air and oxygen over a wide range of flow speeds and currents supplied to the transformer. It was found that slow streaming and high currents gave the highest concentrations of ozone, and oxides of nitrogen could never be detected.

Results.

(1) In the first series of experiments pure nitrogen, as used for the preparation of “active nitrogen,” was sparked and mixed with air, oxygen, ozonised air, or ozonised oxygen. The time (Δt) elapsing between sparking and treatment with diluent ranged from 0.25 sec. to 60 secs. with concentrations of ozone up to 2% in the diluent. About twenty such runs were made, but in no case could the slightest formation of nitrogen peroxide be detected; 1 part in 10,000 parts could have been measured with ease.

(2) A second series of six experiments was made in which nitrogen-oxygen mixtures containing 96, 92, 91, 93, 90, and 80% of nitrogen were sparked and mixed with equal amounts of ozonised oxygen; Δt varied from 0.25 sec. to 6 secs. In no case was the amount of nitrogen peroxide altered by switching off the ozoniser so that oxygen only was employed as diluent.

(3) An equal number of similar experiments was made in which the nitrogen-oxygen mixture was ozonised before sparking; no change in peroxide yields could be found.

(4) Two further attempts were made to repeat Lowry's results, air being sparked at pressures of 560 and 180 mm. and (i) mixed with ozonised oxygen ($O_3 = 0.3\%$), (ii) preozonised; the concentrations of peroxide were unaffected by either treatment.

In all experiments of series (2), (3), and (4), the concentration of

ozone was never permitted to exceed that of the nitric oxide, calculated from the final yield of peroxide; the importance of this will appear later.

(5) A number of experiments was made in which air was pre-ozonised and then blown through the spark, the amount of ozone produced in the ozoniser being increased in successive small amounts beyond the concentration of peroxide obtained with the spark alone. Whenever the molecular ratio $O_3 : NO$ exceeded unity, the yield of peroxide diminished approximately in proportion to the excess of ozone, as shown by results of a typical experiment :

O_3 , %	0.00	0.04	0.06	0.09	0.16	0.17	0.19	0.21	0.23
NO_2 , %	0.16	0.16	0.16	0.16	0.16	0.13	0.10	0.04	0.02

(6) The apparatus was then modified by inserting a small absorption tube immediately below the spark in the gas stream, the volume between the spark and the entrance to this extra tube being only 1.5 c.c.; the ozone inlet was fitted opposite to that of the main gas so that with a flow speed of 16 litres/hour the sparked gases could be treated with the reagent within 0.3 sec. This extra absorption tube was fitted for measurement of peroxide by a photocell as already indicated and was calibrated against the first one by filling the apparatus with nitrogen peroxide diluted with nitrogen and observing the corresponding photoelectric currents as the apparatus was gradually evacuated. Of the two absorption tubes, that nearer the spark will be termed tube 1, that further away, tube 2.

The following experiments were then made: (a) Air at 16 l./hour was sparked, and the peroxide measured in both tubes; that in tube 1 was 0.02%, in tube 2, 0.07%, but when the air was pre-ozonised, both contained 0.07%. (b) Air at 8 l./hour was sparked and mixed with an equal feed of ozonised air; the concentration in both tubes was 0.04% and remained throughout at this figure in tube 2, but fell to 0.02% in tube 1 when the ozoniser was switched off.

Other experiments following the same procedure gave similar results unless the flow speeds were too much reduced, in which case the concentrations in tubes 1 and 2 became equal.

In the course of these experiments we have confirmed the observation of Warburg and Leithauser (*Ann. Physik*, 1907, **23**, 209), that addition of more than traces of peroxide to oxygen inhibits the production of ozone therein. This does not appear to be due to the cyclic reaction $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$, $N_2O_5 + O_3 \rightarrow N_2O_6 + O_2$, $N_2O_6 \rightarrow 2NO_2 + O_2$, etc., since nitrogen pentoxide is known to be fairly stable in the presence of ozone. From the present experiment it would seem that ozone is actually formed in

the usual way, but is destroyed by the cyclic reaction $2\text{NO}_2 + \text{O}_3 \longrightarrow \text{N}_2\text{O}_5 + \text{O}_2$, $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \text{O}$, the second step representing an electrical decomposition of pentoxide.

Discussion.

We may first consider some well-established facts relative to the synthesis of nitrogen peroxide by the spark in nitrogen-oxygen mixtures: (a) The primary product of the spark is nitric oxide (compare *inter alia*, Haber and König, *Z. Elektrochem.*, 1907, **13**) 725; *ibid.*, 1908, **14**, 689). (b) Although the termolecular oxidation of nitric oxide by oxygen is very slow (*e.g.*, Bodenstein, *ibid.*, 1918, **24**, 183), the bimolecular reaction with ozone is practically instantaneous (Helbig, *ibid.*, 1906, **12**, 550; Foerster and Koch, *Z. angew. Chem.*, 1908, **21**, 2161, 2209; Wulf, Daniels, and Karrer, *J. Amer. Chem. Soc.*, 1922, **44**, 2398). (c) The amount of nitric oxide produced in unit time depends upon the amperage in the discharge, and provided that the spark be long enough to allow of adequate contact of the gases with the discharge, the rise in voltage which accompanies an increase in discharge length has no particular effect; *i.e.*, the synthesis follows a law of electrochemical equivalence (for the latest work upon this subject, see papers by Brewer and collaborators, *J. Physical Chem.*, 1929, *et seq.*).

When these considerations are applied to Lowry's results, the latter may be explained without postulation of an oxidisable active species of nitrogen or of a nitrogen oxide which reacts with ozone but not with oxygen.

Bodenstein has shown (*loc. cit.*) that the rate of oxidation of nitric oxide by oxygen may be expressed by the equation

$$-d[\text{NO}]/dt = k_p[\text{NO}]^2[\text{O}_2] \quad . \quad . \quad . \quad (1)$$

in which $k_p = 6.87 \times 10^{-5}$ at 16° , the unit of pressure being mm. of bromonaphthalene; to express this in mm. of mercury we multiply by the square of the ratio of the densities, *i.e.*, by $(13.59/1.49)^2 = 82$, whence $k_p = 5.7 \times 10^{-3}$. Since but small amounts of oxygen are removed in the oxidation of nitric oxide in the quantities encountered by Lowry, we may write the integrated form of equation (1) as

$$k_p \cdot 150 \cdot t = 1/(a - x) - 1/a \quad . \quad . \quad . \quad (2)$$

where 150 = partial pressure of oxygen in air, a = initial concentration of nitric oxide, and x = concentration of peroxide at t sec., all expressed in mm. of Hg.

In his first experiments, Lowry used air flowing at 70 cu. ft./min., and since his observation trunk was 64 ft. \times 9 sq. ins. cross section, it follows (assuming, in the absence of further data, that the volume

of the spark box was small compared with that of the trunk) that the time elapsing between the air being sparked and leaving the trunk will be 3.4 secs. Substituting this value for t in equation (2), we find that in order that x shall be equal to $0.9a$, *i.e.*, that the nitric oxide shall be 90% oxidised before leaving the apparatus, its initial concentration, a , must be 3.1 mm. (*i.e.*, 1 : 245), whereas in the experiments without ozone where the highest concentrations of peroxide were obtained, the mean value of x in the trunk was *ca.* 1 : 7000, *i.e.*, 0.1 mm.; hence we see that it was quite impossible for more than a small fraction of the nitric oxide to become oxidised in *ca.* 3 secs. under these conditions.

Trustworthy data upon the velocity of the reaction between nitric oxide and ozone are lacking, but as all workers are agreed that it is very high, we may conclude that the increased yields of peroxide obtained by Cramp and Leatham, and by Lowry, when they ozonised the very rapid streams of air employed in their experiments, may be ascribed to the occurrence of the rapid reaction $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$, in preference to the slower change $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$. If this be so, it follows that when a lower air speed is employed to allow more time for the sparked air to mature before its peroxide content is measured, little or no effect should be produced by ozonising, as was observed by Lowry. Where a flow of $\frac{1}{2}$ cu. ft./min. was used, the time between the air's being sparked and its leaving the apparatus would be 480 secs., whence we may calculate that 90% oxidation would be attained, at this flow speed, in air containing initially 0.02 mm. of nitric oxide; since 0.24 mm. of peroxide was actually measured, we see that oxidation would here be practically complete in the absence of ozone.

The experiments in series (6), in which Lowry's results are confirmed when the ozone is added before the sparked gas matures, or when ozonising is carried out with air at high flow speeds, provide experimental support for the views expressed above.

We would emphasise that this explanation was considered qualitatively by Lowry, but rejected in favour of the "active gas" theory on the grounds that, as already indicated, an increase in the number of spark gaps produced no rise in the concentration of peroxide. Since no mention is made of any other alteration in the electrical arrangements, we assume that the same power was supplied in the cases when, in view of the electrochemical equivalence effect mentioned earlier, no change in peroxide yield should have been found, other than a small increase due to the larger amount of air coming into contact with the larger number of sparks.

The bearing of our own experiments upon this subject is now

considered. Series (1) shows that no form of active nitrogen can be produced in a spark which can react with ozone 0.25 sec. after its formation, and in view of the large amount of work done recently upon active nitrogen and the nitrogen spectrum, we think that the evidence is all against the existence of such a substance.

In Series (2), (3), and (4), equally negative evidence is presented for a nitrogen oxide which can react with ozone but not oxygen, and in series (5) the results provide definite disproof of such a view. Remembering that nitric oxide and ozone may react to give either nitrogen peroxide or pentoxide, we see that when a gas containing nitric oxide is treated with ozone, then so long as the $O_3 : NO$ ratio does not exceed unity, the final yield of peroxide will be equal to that obtained if oxygen were used instead; if, however, an excess of ozone is present, some will produce peroxide and the rest will carry the oxidation to the pentoxide stage. Now, were any other ozone-reactive substance present, this simple stoichiometric ratio would be upset, a possibility which is definitely negated by our results.

Summary.

A search has been made for a modification of nitrogen, or an unstable nitrogen oxide, which can react with ozone to give nitrogen peroxide, and whose existence had been postulated by Lowry from earlier results obtained by him. No evidence for such a substance has been obtained, but much against, and it is furthermore shown that Lowry's results may be interpreted on the basis of known reactions of the nitrogen oxides and ozone.

We desire to express our thanks to Professor F. G. Donnan, F.R.S., for his interest in these investigations, and to the University of London for a scholarship which has enabled one of us (S. G. F.) to participate therein; in the experimental work we have been much helped by Mr. W. A. Bayliss, to whom our acknowledgments are also due.

THE SIR WILLIAM RAMSAY LABORATORIES OF INORGANIC AND
PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE,
LONDON, W.C. 1.

[Received, November 3rd, 1931.]
