CXXI.—*The Oxidation of Atmospheric Nitrogen in Presence of Ozone.*

By THOMAS MARTIN LOWRY.

SOME five years ago the writer had the opportunity of making a spectroscopic examination of the bleaching gases produced by passing air (*a*) through an ozoniser, (*b*) through a series of spark-gaps, (*c*) through both ozoniser and spark-gaps, either in parallel or in series, in accordance with a process devised by Leetham in 1903. The experiments showed that the superior bleaching properties of the Leetham gas might be attributed in part to an increased yield of nitrogen peroxide, which appeared to be produced as a result of the oxidation by ozone of an unstable, oxidisable variety of nitrogen manufactured in the spark-gaps.

Electrical Arrangements.—In normal working, air from a Root's blower was sent at the rate of about 70 cubic feet per minute through an Andreoli ozoniser, containing thirteen aluminium sheets or grids, 30″ × 30″ in area, separated by sheets of micanite; it then passed into a rectangular box containing six pairs of iron studs, separated to a distance of 3/32″, three of which were employed as spark-gaps. The spark-gaps and ozoniser were all in series, the whole system taking an alternating current of 0·1 ampere at 9000 volts. Arrangements were available whereby the ozoniser and spark-gaps could act on the air, either consecutively or in parallel; it was also possible to employ two ozonisers or to increase the number of spark-gaps to seventeen.

Spectroscopic Arrangements.—As the gases to be examined were very dilute, it was necessary to use an exceptionally long column in order to observe the absorption-spectrum of the gas. The experiments were therefore made with a wooden trunk, 64 feet in length and 3″ × 3″ in internal section, the volume of the trunk being thus about 4 cubic feet. The gas from the ozoniser or spark-box was led into the trunk at one end through a distribution-box and lead piping, the total volume of which was probably less than that of the trunk. The trunk was provided with glass windows at each end; at the near end, a condensing lens of 3¼″ focal length was illuminated by means of a Nernst lamp with filament vertical; at the far end, the light was concentrated by an achromatic lens of 11″ focal length on the slit of a spectroscope. On account of the great distance between the two lenses the effective illumination was confined to that emanating from a small portion of the centre of the filament, about 1/100″ in diameter, and the image on the slit was always circular.

The spectroscope was provided with a single glass prism; the collimator lens was of 13″ focus, and the camera lens of 22″ focus. An exposure of six minutes with Wratten and Wainwright's "Panchromatic" plates was found to be sufficient when two minutes were allowed for development in total darkness.

Standard Spectra of Nitrogen Peroxide.—Standard mixtures of nitrogen peroxide and air were made by passing nitric oxide (prepared from mercury and nitric acid and tested by absorbing a sample with ferrous sulphate solution) at a known rate through a capillary tube into the centre of an air-jet. The flow of oxide was determined by the displacement of the gas by means of mercury from a large cylinder-funnel of 1 litre capacity; the mercury was passed in at a regular rate through a small funnel drawn out into a capillary tube; from the total volume of mercury used and the time occupied by the experiment, the average rate of flow was calculated. The flow of air was regulated by means of blow-off taps, and was measured by means of a standard meter. The consistency of the results obtained showed that this method of working was sufficiently accurate. The standard mixtures prepared in this way were passed into the 64-foot trunk, and their absorption spectra were observed and photographed again and again until it was easy to judge the concentration of the gas by mere inspection, even without referring to the negatives which formed the permanent record of the experiments.

Visibility of Nitrogen Peroxide.—No absorption could be detected by the eye or in the photographs when using a 64-foot column of air charged with 1/16,000 and 1/12,000 parts by volume of nitrogen peroxide. The absorption spectrum began to be visible in a 64-foot column at a concentration of about 1/8000 NO_2; when using a 15-foot column * it could just be seen at 1/3500 concentration. The visibility of the spectrum was therefore roughly proportional only to the square-root of the length of the column of gas, when all the other experimental conditions remained unchanged.†

At higher concentrations the absorption became very marked; at a concentration of 1/3500 the spectrum showed, throughout the greater part of its length, the ripples or flutings characteristic of nitrogen peroxide; at 1/1700 about half the spectrum was blocked out; and at 1/1200 about two-thirds had disappeared, the remainder showing very strong bands or flutings.

Action of the Ozoniser and of the Spark Discharges on Air.

On passing into the 64-foot trunk air which had been submitted to the action of the ozoniser or of three spark-gaps, no trace of nitrogen peroxide could be detected, either by the eye or in photographs of the absorption spectra; but the Leetham gas, which had been submitted to both forms of spark discharge by passing through the ozoniser and then through three spark-gaps, gave a well-marked spectrum, agreeing closely with that of nitrogen peroxide at a concentration of about 1/4000 NO_2. This remarkable development of the spectrum of nitrogen peroxide is in accord with the fact (to which Cramp and Hoyle have called attention, *Proc. Inst. El. Eng.*, 1909, **42**, 328) that the yield of this gas from an arc-discharge can be increased considerably by ozonising the air-supply.

Comparison of the Three Varieties of "Combined" Gas.—Contrary to what was expected, an absorption spectrum of almost equal intensity was produced when the direction of the air-current was reversed, so that the gas passed through the spark-gaps and then through the ozoniser. Under these conditions the ozoniser was converted into an efficient generator of nitrogen peroxide. This

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* A glass slide was inserted so that the gas only entered the first portion of the trunk and then escaped into the atmosphere.

† An even more marked diminution of visibility by dilution is seen on comparing the present observations with those of Robertson and Napper (Trans., 1907, **91**, 761), who were able to detect a concentration of 1/2000 NO_2 in a tube 40 cm. in length.

novel function of the ozoniser is the more remarkable because ready-made nitrogen peroxide was completely bleached by passing slowly through the machine, probably because it was oxidised to nitric anhydride or nitric acid (compare Helbig, *Atti R. Accad. Lincei*, 1903, [v], **12**, 211); the spectrum could be restored completely by passing the gas through a hot tube, an operation that had no effect whatever on the spectrum of the gas prepared by the Leetham process.

The problem of discovering the nature of the mechanism whereby these increased yields of nitrogen peroxide were produced was much simplified when it was found that an absorption spectrum of only slightly less intensity could be produced by running the two air-currents in parallel and mixing the gases from the two machines before observing their absorption spectra. It was then evident that the increased production of peroxide was not an electrical phenomenon, but was due to a purely chemical interaction between the ozone and some oxidisable form of nitrogen manufactured in the spark-gaps.

Action of Seventeen Spark-gaps on Air.—As the high-tension discharge without a solid dielectric is used to manufacture nitrogen peroxide on a large scale in commercial practice, experiments were made to detect this gas in air which had been submitted more strongly to this form of discharge. For this purpose the whole of the power available was used to energise a series of seventeen spark-gaps. The product, when passed quickly through the trunk, showed a very weak spectrum of nitrogen peroxide, the concentration being perhaps 1/7000; a stronger spectrum, corresponding with a concentration of about 1/3000 NO_2, was observed when the same gas was passed through the trunk at the rate of only half a cubic foot per minute, in order to allow ample time for the gas to mature. No such increase of intensity was observed in the gases prepared with the help of ozone. The increase in the case of the gas from the seventeen spark-gaps may be taken to indicate that the production of nitrogen peroxide by this form of discharge is not a direct or instantaneous process, but that the peroxide is formed gradually during a period slightly longer than the time (about seven seconds) required to drive the gas at full speed through the trunk.

The Slow Oxidation of Nitric Oxide.—As it is well known that nitric oxide is oxidised only slowly by oxygen (Raschig, *Zeitsch. angew. Chem.*, 1905, **18**, 1281), but very quickly by ozone (Strutt, *Proc. Roy. Soc.*, 1911, *A*, **85**, 533), it was conceivable that the main action of the ozone in the Leetham process was to accelerate the oxidation of nitric oxide. If this had been the explanation of the phenomena, however, spectra of equal intensity should have been produced by merely allowing a longer time for the gas from the three spark-gaps to mature before observing its absorption spectrum, whilst the seventeen spark-gaps should, under similar conditions, have given a yield of nitrogen peroxide five or six times greater than that produced by three spark-gaps with the help of ozone; actually, however, the seventeen spark-gaps gave a yield only about 30 per cent. greater, or about the same yield as that which might have been expected from four spark-gaps with the help of ozone. The inefficiency of the later spark-gaps in producing oxides of nitrogen might be attributed in part to the higher temperature of the air supplied to them, or even to some destruction of nitrogen peroxide already formed in the earlier spark-gaps; but no explanation of this kind would be adequate to account for some thirteen additional spark-gaps doing nothing whatever to increase the yield of nitrogen peroxide beyond that already available, with the help of ozone, from the first four.

An Oxidisable Variety of Nitrogen.

In view of the facts described above, the idea that the ozone acted merely as a rapid oxidiser of nitric oxide was abandoned, and the view was adopted that the oxidisable substance was a modification of nitrogen itself. This opinion was expressed as follows: "It seems to be clearly demonstrated by the experiments of Carius and Berthelot that ordinary nitrogen is not oxidised by ozone, but the present observations show that, when air has been sparked, the nitrogen, probably because it has become 'atomised' ($N_2 \longrightarrow 2N$), 'electrified,' or 'ionised' (that is, conducting), is readily oxidised by ozone. The ordinary 'combined' arrangement generates 'ionised nitrogen' in air that is already ozonised; the reversed arrangement leads 'ionised nitrogen' into an apparatus which produces ozone; and finally, in the parallel arrangement 'ionised nitrogen' and ozone are produced separately and merely mixed together. The ozoniser is able to decompose oxygen and convert it into ozone, but the discharge is not sufficiently powerful to break up many of the more stable nitrogen molecules, and the product is therefore mainly ozone. The spark discharge, on the other hand, probably decomposes both the oxygen and the nitrogen molecules; but owing to the relatively small amount of ozone that is formed (and the relative inertness of the ozone at high dilutions), only a part of the 'ionised' or 'atomised' nitrogen becomes oxidised, and most of it merely reverts to molecular nitrogen. The more quickly the 'ionised' nitrogen can be brought into contact with ozone the smaller will be the proportion that thus reverts, and the greater will be the yield of nitrogen peroxide; in this way it is easy to account, not only for the production of nitrogen peroxide by the three modifications of the Leetham process, but also for the relative quantities produced in the three cases."

At the time when these observations were made, the conclusion that nitrogen could be rendered active by a spark-discharge was so far novel that it did not appear to be desirable to put it forward on the basis of a single series of experiments. The recent experiments of Strutt (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219; 1911, *A*, **86**, 56; 1912, *A*, **86**, 105), however, have established so definitely the existence of a chemically active variety of nitrogen, that no hesitation need now be felt in assuming that a similar substance may be produced by the electrical discharge under conditions differing somewhat widely from those used in the experiments of Strutt. The behaviour of the two products is, however, not the same. I am indebted to Prof. Strutt for the information that when chemically active nitrogen and ozonised oxygen are mixed together at a low pressure and then cooled with liquid air, no trace of oxides of nitrogen can be detected in the product. Whether this difference of behaviour is due to some difference in the nature of the oxidisable substance produced by sparking air under ordinary pressures, or whether it is due merely to the different experimental conditions, is a matter that cannot be decided by means of the data at present available. But the observations now described serve at least to suggest the possibility that an active variety of nitrogen may be produced by the electric discharge in air under ordinary pressures, and that the formation of such a substance and its oxidation by ozone may play an important part in technical processes for the fixation of nitrogen. It is in order to call attention to this possibility, rather than with the idea of giving any dogmatic explanation of the experiments, that the present paper has been written.

The view that nitrogen is broken up by the spark-discharge and converted into an unstable oxidisable modification, affords a simple and adequate explanation of the remarkable effects produced by combining the "spark" and the "silent" discharges in the way suggested by Mr. Leetham. It only remains to suggest some allied phenomena to which the hypothesis of oxidisable nitrogen may be applied. Foremost amongst these is the production of nitrogen peroxide by the spark discharge without the addition of ozone. The simultaneous production of oxides of nitrogen and of ozone by the discharge is so familiar (see, for instance, Cramp and Hoyle, *Proc. Inst. El. Eng.*, 1909, **42**, 312; Strutt, *Proc.*

Roy. Soc., 1911, *A*, **85**, 536) that no objection can well be taken to the idea that *the spark-discharge may give rise both to active nitrogen and to ozone*, the proportions varying very widely with the experimental conditions. In the experiments now described there must have been a marked deficiency of ozone in the gas from the spark-gaps, since added ozone was capable of producing a very large increase in the yield of nitrogen peroxide; but under other conditions ozone is the predominant product. There can be no doubt that by a happy combination of conditions, oxidisable nitrogen and ozone might be produced by the spark-discharge in just the right proportions to give a maximum yield of nitrogen peroxide with no excess of either active constituent.

The slow maturing of the gas from the spark-gap may also be explained on the same hypothesis, as due, not necessarily to the slow oxidation of nitric oxide by air, but (on an equally reasonable view) to the slow oxidation of active nitrogen by ozone at extreme dilutions.

Finally, it is not unreasonable to ask whether the production of oxides of nitrogen by the electric discharge in all its various forms must not be attributed to the interaction of active nitrogen and active oxygen, either in the form of ozone or of atomic oxygen. If so, the production and oxidation of active nitrogen must already be ranked amongst the foremost of the technical operations of the present day.

The author is indebted to Mr. Henry Simon, of Manchester, for permission to publish an account of the experiments now described, to Mr. Cramp for much helpful criticism, and to Prof. Strutt for permission to refer to his unpublished experiments on the admixture of ozone and chemically active nitrogen. To each of these the author wishes to accord his heartiest thanks.

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