XXI.—*Observations on the Influence of the Silent Discharge on Atmospheric Air.*

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Nearly forty years ago, the late Professor Andrews observed that when air is exposed to the action of the silent discharge of electricity it contracts to a certain extent, that if it be then left in contact with oil of vitriol for a few hours it undergoes further contraction, and that if the residue be afterwards again submitted to the discharge its volume may be yet further diminished. He accounted for these phenomena by supposing that one or more of the higher oxides of nitrogen had been formed from the air. At the same time, Andrews called attention to the fact that it is impossible to generate ozone in oxygen which contains small quantities of nitrogen if the mixture has recently been exposed to the action of disruptive discharge. This he also attributed to the "presence of a trace of hyponitric acid gas produced by the electrical sparks" (*Trans. Roy. Soc.*, 1860, p. 127).

Berthelot (*Compt. rend.*, 1881, **92**, 82), and Hautefeuille and Chappuis (*Compt. rend.*, 1881, **92**, 80 and 134) have also recognised oxides of nitrogen among the products of the action of the silent discharge on atmospheric air, and most of Andrews' successors in this field of work have taken pains to employ very carefully purified oxygen for their experiments. Our knowledge, however, of the phenomena described by Andrews still stands almost at the stage at which he left it; and, therefore, as the subject is both interesting from the scientific point

* The oil of vitriol is not mentioned in Andrews' description of his experiment, but it was present in the manometers he used.

of view, and of some importance to those who seek to apply ozone medically, and for other technical purposes, we have recently spent some time in an attempt to follow up this part of Andrews' beautiful researches.

We are conscious that the work described in this paper by no means exhausts our subject, but we venture to present the results already obtained to the Society at this stage, since we hope they may be found interesting and useful to other workers, and because the difficult character of the experiments still before us may make our future progress rather slow.

I. *A Method of Detecting Nitric Peroxide in the Presence of Ozone.*

The oxide of nitrogen produced by the action of the silent discharge on air always exists in the presence of excess of oxygen or ozone; therefore, as there is no reason to suspect that nitrous oxide is formed by the discharge, nitric peroxide is the only oxide of nitrogen which is at all likely to be met with; in order to detect and estimate this in the presence of ozone, we draw the gas to be tested through a very dilute solution of soda, and then determine the nitrite formed by means of Riegler's reagent (Abstr., 1897, ii, 464). As the action of the latter seems to depend in the first instance on the forming of α-diazo-naphthylenesulphonic acid, by the interaction of nitrous acid with 1 : 4-naphthylaminesulphonic acid, and on its subsequent conversion into a red dye, its usefulness, as might be expected, is not affected by the presence of ozone, and we believe it to be very suitable for the purpose to which we have applied it.

II. *Influence of the Silent Discharge on Moist Air.*

Experiment I.—An ozone generator provided with a manometer (Trans., 1893, **63**, p. 943, Fig. 3) was filled with atmospheric air saturated with water at 0°, from which the ammonia and carbon dioxide had previously been removed; the contents of the apparatus were then submitted to the discharge at 0°, as described in previous accounts of similar experiments on oxygen (*loc. cit.*, p. 938). The difference of potential employed corresponded to 44·4 C. G. S. units (electrostatic), and great care was taken not to raise the temperature of the gas by employing too rapid a succession of discharges. As soon as the discharge was applied to the air, it condensed rapidly and to a remarkable extent, presently the rate at which it contracted became slower, and then, suddenly, it commenced to re-expand; the latter change ceased whenever the discharge was discontinued, but occurred again as often as the sparking was recommenced. When a large part of the ozone formed during the first stage had evidently been

destroyed, but while a little still remained, a hole was pierced in the bottom of the ozone generator, another at the end, *Z* (*loc. cit.*), of the manometer, and its contents were drawn through cold water, which was afterwards examined for nitrites in the manner described above. Unmistakable indications of the presence of nitric peroxide were obtained.

Owing to the suddenness with which the secondary action of the discharge set in, we are unable to state exactly the maximum amount of ozone formed. We satisfied ourselves, however, from the measurements taken, that not less than 91 per cent. of the oxygen present had been converted into ozone; we believe this proportion has never been exceeded except in one of our own experiments.*

Having now obtained a general idea of the mode of action of the silent discharge on air, we arranged our subsequent experiments largely for the purpose of gaining answers to the following questions.

a. What is the highest yield of ozone that can be obtained from air under the most favourable conditions?

b. At what stage is nitric peroxide first formed, and what is its subsequent history?

c. What influence has the presence of moisture on the various phenomena under investigation?

In all the experiments described in this paper, we employed the ozone generator formerly used by one of us for examining the influence of the silent discharge on moist, and on carefully dried oxygen. The present work on air is therefore strictly comparable with the former work on oxygen (Trans., 1897, **71**, p. 471). A small tail was added to the bottom of the ozone generator (*loc. cit.*, Fig. 3), in order that we might attach an absorption tube to it by a paraffin joint when it was necessary to withdraw its contents in order to test for nitric peroxide.

III. *The Maximum Yield of Ozone produced by the Action of the Silent Discharge on Air at* 0°.

From the results of a number of experiments, we found that, in order to produce the largest proportion of ozone from air, it is necessary that moist air should be employed, also that great care be taken not to apply the discharges in too rapid succession, and that frequent intervals be allowed for cooling towards the end of the operation.

It is rather difficult to hit the point at which the condensation of

* Brodie (*Trans. Roy. Soc.*, 1874, **164**, p. 101) submitted carbon dioxide to the action of the silent discharge and found that as much as 85 per cent. of the oxygen liberated might consist of ozone. Only a few c.c. of ozone were obtained, however, from a considerable volume of carbon dioxide in Brodie's experiment.

the air attains its maximum, because immediately this point is reached the contents of the ozoniser re-expand rapidly. Ozonised air, moreover, appears to be far more sensitive to rise of temperature, such as may be caused by the use of a too rapid succession of discharges, than is the case with ozonised oxygen. The effect of this sensitiveness is well illustrated by the results of our three earliest experiments.

Experiment I.—This was the preliminary experiment described above. The discharges were delivered at a moderate rate with frequent intervals for cooling, air saturated with water at 0° being used.

91 per cent. of the oxygen present was converted into ozone.

Experiment II.—Air saturated with water at 0° was used, the succession of discharges was more rapid, but the intervals for cooling were the same as in the previous experiment.

Only 82·1 per cent. of the oxygen was converted into ozone.

Experiment III.—The dynamo did not work well during this experiment, and consequently the succession of discharges was *very* slow; moist air was used, and the intervals for cooling were the same as in the other two experiments.

98 per cent. of the oxygen present was converted into ozone.

If the last of these results be compared with what has previously been done, it will be seen that not only does the proportion of the oxygen which was ozonised far exceed anything previously obtained, but also that the charge of ozone carried by the gas is exceedingly high, much higher, for example, than was obtained by one of us, by means of the same ozone generator, and under the most favourable conditions from moist oxygen, namely, 13·6 per cent. (Trans., 1897, 71, p. 475).

IV. *Experiments to ascertain the Influence of Moisture on the Formation of Ozone from Air.*

It has been shown by one of us, in a previous paper, that well-dried oxygen yields little or no ozone when it is subjected to the action of the silent discharge (Trans., 1897, 71, p. 479); a single experiment such as was then performed occupied many months, and during its progress the ozone generator was not available for other work. To avoid such cause of delay on this occasion, we dried our air in a more simple manner, partly because it seemed almost a foregone conclusion that very highly-dried air would, like oxygen, be practically unaffected by the discharge, and partly because the progress of the research as a whole was more important at the time than the making of a single experiment to minutely investigate one particular point.

Before we made the experiments with dried air, the ozone generator was dried by heating it, when exhausted, with the little furnace previously described (*loc. cit.*, 478); it was then filled with dried air

re-exhausted and re-filled. The air was dried by passing it slowly over a column of purified phosphoric anhydride (Trans., 1893, **63**, p. 475) which had previously been freed from carbon dioxide.

It should be mentioned that the air used in VI was more nearly dry than that used in IV and V, as it was purposely passed at a slower rate over the drying material.

A.—Results obtained with wet oxygen.

Experiment I.	91	per cent.	of the oxygen	present was ozonised.
Experiment II.	82·1	,,	,,	,,
Experiment III.	98	,,	,,	,,

B.—Results with dried oxygen.

Experiment IV.	66·7	per cent.	of the ozygen	present was ozonised.
Experiment V.	67·0	,,	,,	,,
Experiment VI.	60·0	,,	,,	,,

Similar results were obtained in the course of two other experiments with moist and dried air; in these, the air was rapidly ozonised for the purpose of examining its composition at later stages, and consequently the maximum proportion of oxygen ozonised was smaller than before, but the results tell the same tale.

A.—Dried air	63·5	per cent.	of the oxygen was ozonised.
B.—Moist air	80·0	,,	,,

V. *Experiments to Trace the Formation of Nitric Peroxide from Air by means of the Silent Discharge.*

We have seen from Experiment I that air which has been highly charged with ozone, and subsequently partly reduced by the continued action of the silent discharge, contains nitric peroxide. In order to trace the formation of the latter substance at various stages of an experiment and, if possible, to learn in what manner its appearance is connected with the destruction of the ozone which follows the continued application of the discharge, we made the following experiments.

Experiment VII.—The ozone generator was filled with dried air, and its contents submitted to the action of the silent discharge until the rate at which the gas contracted and the proportion of oxygen ozonised, 63·5 per cent., indicated that the point of maximum contraction was nearly reached; the contents of the ozone generator were then drawn off and examined for nitric peroxide.

No nitric peroxide was found.

Experiment VIII.—This was a repetition of the previous experiment, except that the action of the discharge was not carried quite so far, only 61·8 per cent. of the oxygen being ozonised. In this case, also,

no nitric peroxide could be detected, although so small a quantity as 0·000001 gram of nitrous anhydride can be recognised by Riegler's reagent in 100 c.c. of water.

Experiment IX.—The ozone generator having been recharged with dried air, its contents were submitted to the silent discharge until a portion of the ozone first formed, 67 per cent., was again destroyed. The residue was then tested for nitric peroxide.

No less than 0·041 c.c. was found.*

The observed increase of the volume of the gas in this experiment corresponded to a reduction of the percentage of oxygen ozonised from the maximum 67 to 54 per cent.; the actual proportion of ozone remaining was, however, somewhat less than 54 per cent., because some nitric peroxide had been simultaneously formed.

Similar experiments were next made upon moist air.

Experiment X.—Moist air was submitted to the discharge until 80 per cent. of its oxygen was ozonised; as the rate at which it contracted had then become slow, the discharge was stopped and the contents of the apparatus were tested as before.

No nitric peroxide was detected.

Experiment XI.—This experiment was a repetition of X, and gave a similar result.

Experiment XII.—Moist air was submitted to the discharge until some of the ozone first formed had been destroyed again, but the destruction of the ozone was not carried so far as in the corresponding experiment with dried air.

The residue was found to contain 0·020 c.c. of nitric peroxide, N_2O_4.*

The expansion at the second stage corresponded in this case to a reduction of the ozone from the maximum 82·1 to 72 per cent., but allowance must be made for the nitric peroxide simultaneously formed.

From these results, it is evident that nitric peroxide is not produced by the action of the silent discharge on air, either moist or when dried, at 0°, until a large proportion of the oxygen present has been converted into ozone; and this fact, together with the rapid destruction of ozone which accompanies the appearance of the nitric peroxide, suggests the idea that the latter may be formed at the expense of the

* These volumes are calculated on the assumption that the formula of nitric peroxide is N_2O_4. There is reason to believe, however, that, under the conditions of the experiment, this gas is partly dissociated.

It is of course possible that the presence of ozone with the moisture, and nitric peroxide, &c., may favour the formation of nitric acid when the mixed gases are drawn through a dilute alkaline solution, and thus lead one to underestimate the amount of nitric peroxide present. This, however, if true, would rather increase the significance of the results obtained in experiments IX and XII, and these alone are likely to have been affected by such a disturbing cause.

ozone, and not by the combining of nitrogen and ordinary oxygen. This view of the matter is supported by the result of Experiment III (p. 249), which shows that only a few tenths of a per cent. of oxygen were present in the gas at the moment when the formation of the nitric peroxide probably began, and is further upheld by the important fact that the formation of nitric peroxide from air under the influence of the silent discharge is distinctly retarded by the presence of water vapour and promoted by dryness. (Compare IX with X and XI. Compare also the results of I, II and III, in which 82 to 98 per cent. of oxygen was probably ozonised before sensible quantities of nitric peroxide were formed, with those of IV, V, VI, in which only 60—67 per cent. of oxygen was ozonised when its destruction, presumably due to nitric peroxide, set in.) For it has previously been shown by one of us (Trans., 1897, 71, *loc. cit.*) that the stability of ozone is increased by the presence of moisture, which might lead us to expect its power as an oxidising agent to be lower in the presence of water than when dry. Ordinary oxygen, on the other hand, is well known to oxidise best in many cases in the presence of water.

But whatever may be the truth in regard to this matter, it is at any rate very interesting to meet with a fresh case of chemical change which is retarded by the presence of water vapour (see also Trans., 1897, 71, *loc. cit.*).

In connection with the above, it must be remembered that although the presence of a large proportion of ozone is necessary for the formation of nitric peroxide from air by the influence of the silent discharge at 0°, yet a rapid destruction of ozone sets in simultaneously, or almost simultaneously, with the formation of nitric peroxide. The latter change is accompanied by the destruction of a great part of the nitric peroxide first formed.

The following examples will make this clear.

A. In Experiment IX, some dry air was ozonised, then a part of the ozone was destroyed; the residual contents of the ozoniser were found to contain 0·041 c.c. of nitric peroxide.

B. Some moist air was similarly treated (Experiment XII); it yielded 0·020 c.c. of peroxide, N_2O_4.*

C. Some dry air was ozonised and then re-sparked until the final volume showed that all but a trace of the ozone was destroyed; it afterwards yielded only 0·007 c.c. of peroxide, N_2O_4.

D. Another specimen of dry air was similarly treated; it yielded 0·006 c.c. of peroxide, N_2O_4.

E. Some moist air was ozonised and then submitted to the continued

* The difference in the hygrometric state of the air may possibly account for the difference between the results of A and B, since the presence of moisture retards the formation of nitric peroxide.

action of the discharge until only a trace of ozone remained; it was found to contain only 0·008 c.c. of peroxide, N_2O_4. These last three results do not, it is true, agree very closely, but the difference between the proportions of nitric peroxide present in A and B, when most of the ozone still remained undestroyed, and that found in C, D, and E, after the ozone was destroyed, are sufficiently marked.

On the other hand, ozone and nitric oxide do not thus destroy each other at 0°, except under the influence of the silent discharge, if moist. For example, on one occasion, 8·405 c.c. of moist gas containing 0·824 c.c. of ozone and 0·020 of nitric peroxide, or an equivalent volume of the products of its dissociation, were preserved for more than half an hour without any sensible change of volume taking place, and other similar observations have been made. We have reason to suspect, however, that above 0°, or if dry, these gases interact far more readily. Experiments on this subject are being carried out.

Finally, our experience entirely confirms the statement made by Andrews, that oxygen cannot be converted into ozone if a trace of nitric peroxide be present. In one experiment made to test this point, 8·74 c.c. (at 760 mm. and 0°) of dried air was ozonised, and the product, 8·35 c.c., was then submitted to the continued action of the discharge until it ceased to expand; its volume was then 8·72 c.c. After this it was submitted to the silent discharge for 75 minutes, but it remained quite unaffected, and at the end its volume was still 8·72 c.c.

Summary.

1. Oxygen, diluted by nitrogen, yields a higher proportion of ozone when submitted to the influence of the silent discharge, under given conditions, than pure oxygen; the proportion of oxygen ozonised may be as high as 98 per cent. of the oxygen submitted to the discharge. This fact deserves the notice of those who are interested in the technical applications of ozone.

2. If the process of ozonising air be not pressed too far, no peroxide of nitrogen will make its appearance.

3. The presence of water vapour is very favourable to the production of a high yield of ozone, and retards the appearance of nitric peroxide.

4. At a certain stage in the process of ozonising the oxygen of the air, which depends on the amount of vapour present, and probably also on the temperature of the gas, nitric peroxide is formed. Its appearance is immediately, or almost immediately, followed by a rapid disappearance of the ozone, and this in its turn results in the destruction of most of the nitric peroxide.

5. That, as stated by Andrews, the presence of a trace of nitric per

oxide renders it impossible to convert oxygen into ozone by means of the silent discharge.

6. That nitric peroxide and ozone when moist do not mutually destroy one another at 0°, or do so at a very slow rate, unless they are under the influence of the silent discharge.

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February, 1898.