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Studies on the Discharge Reaction in Liquid Air. I

On the Discharge Reaction Products*

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Synopsis

Applying high tension from an induction coil or from a transformer, discharge reactions in liquid air were studied. The reaction products were examined by vapor pressure method, that is, by comparing the vapour pressure curves of the products with those of the known compounds. The results varied with the kinds of high tension sources and were very different from those of other authors; especially, the yield of ozone varied markedly with the current intensity and type of discharge. By raising the temperature after discharge, reactions and products were investigated. NO_2 or $(\text{NO}_2)_2$, nitrogen trioxide and N_2O_5 were ascertained. An explosion due to decomposition of ozone often occurred at about -100°C . The green coloured solid product was supposed to be a mixture of $(\text{NO}_2)_2$ and nitrogen trioxide. A higher oxide of nitrogen such as NO_3 was not obtained in the reaction.

I. Introduction

Discharge reactions in atmospheric air under various conditions have hitherto been studied extensively, but those in liquid air have scarcely been reported. During the discharge, reactions between ions or active substances take place and some ordinary thermal reactions rapidly follow them. In a discharge reaction in liquid air, however, the reactions which would proceed after the discharge at ordinary temperature is stopped or retarded by the cooling effect of liquid air.

D. Helbig⁽¹⁾ and E. Müller⁽²⁾ studied the reaction product from the ratio of nitrogen to oxygen in it by chemical analysis at room temperature after evaporating the condensed sample. It is clear, however, that their method cannot be used when the product is composed of various kinds of compounds. Besides, in such a system, some kinds of the products may be unstable and may dissociate or associate and some of them may react upon one another. Thus, the process of the discharge reaction cannot be clarified by such a method. In the present research, the authors investigated the condensed resultants of the reaction and pursued their changes with the rise of temperature by measuring vapour pressure.

* The 699th report of the Research Institute for Iron, Steel and Other Metals.

(1) D. Helbig, *Zeit. Elektrochemie*, **16** (1910), 205.

(2) E. Müller, *Chem. Ztg.*, **35** (1911), 634; *Zeit. anorg. Chem.*, **76** (1912), 324; *ibid*, **86** (1914), 230.

II. Method and apparatus

The main part of the experimental apparatus is shown in Fig. 1. Dry air was condensed in the reaction tube *A* cooled by liquid nitrogen. A high voltage from a transformer or an induction coil was applied between the electrodes of platinum wire immersed in liquid air, the gap being about 0.5 mm. The capacity of the transformer used was 300 Watt and usually, the voltage of about 10 KV

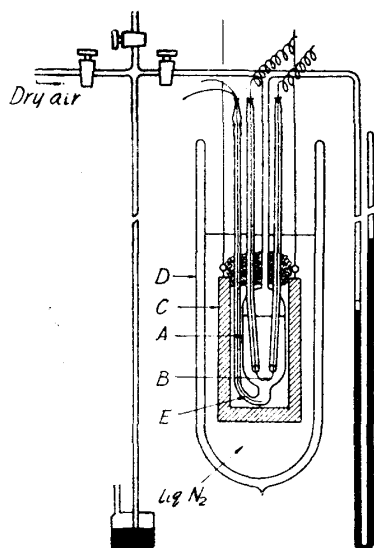


Fig. 1

was applied to the electrodes, and the induction coil was of the capacity of $10\text{ V} \times 6\text{ A}$ in the primary. The discharge was maintained for about two hours, and then residual liquid air was pumped out. This operation had to be carried out very carefully, because any residue of liquid air was undesirable in the measurement of the vapour pressure of the product obtained. By lowering the Dewar vessel *D*, the temperature of reaction tube *A* was raised slowly, as the heat capacity of the copper cylinder *C* (its weight was 1.1 kg.) was sufficiently large. The vapour pressure of the product was measured in the temperature range between -195°C and room temperature by usual mercury manometer *M*, the mercury surface being covered by butyl phtalate to protect mercury from the attack of NO_2 and ozone. Temperature was measured with a copper-constantan thermocouple *E*. The accuracy of the measurements of vapour pressure and temperature was not so high as in an ordinary vapour pressure determination, because the volume of the bulb for the sample was rather large, being used as the reaction vessel. We could, however, examine the products by comparing the vapour pressure curve of the products with those of the known nitrogen oxides and ozone. Furthermore, from the trend of the pressure versus temperature curve, we could see some chemical reactions taking place in the course of rising temperature.

III. Experimental results of discharge reaction

During the discharge in liquid air, the liquid was kept boiling and the discharge reaction proceeded in the gaseous phase between the electrodes surrounded by liquid air. The nature of discharge and results of the reaction were different in two cases, in one a transformer and in the other an induction coil were used as the source of high tension.

A. Discharge with a transformer

Discharge reactions were tried by applying various potentials between the electrodes. After the discharge took place for a while, a green amorphous solid, resembling freshly precipitated chromium hydroxide, was obtained.

The vapour pressure was measured by the procedure mentioned above. One of the results is shown in Fig. 2. The existence of ozone was confirmed from the small pressure increase at the temperature between -180°C and -160°C , its amount increasing with lowering voltage. The decrease of pressure at about -85°C is suggestive of a secondary reaction taking place, which will be reported in next paper. The last increase of the curve *I* at about -70°C is very similar to the curve *B*. The curves *A* and *B* were obtained by R. H. Purcell and G. H. Cheeseman⁽³⁾, who measured the vapour pressure of the liquid after condensing the gaseous mixture of NO_2 and NO . In each case the concentration of NO_2 was 8.9 or 85.6 mol per cent. The condensed system in these cases were supposed to consist of nitrogen trioxide and others. Comparing curve *I* with *B*, it will be seen that the product of the above reaction is mainly NO_2 accompanied with a small amount of NO . It may be probable, therefore, that NO and NO_2 are the resultants of the discharge reaction in an early stage. They cannot exist in original state but some of them may combine into other nitrogen oxides, for instance, nitrogen trioxide. As the colour of solid nitrogen trioxide is blue and that of solid $(\text{NO}_2)_2$ is pale yellow or white, the green coloured precipitate may mainly be $(\text{NO}_2)_2$ mixed with a small amount of nitrogen oxide.

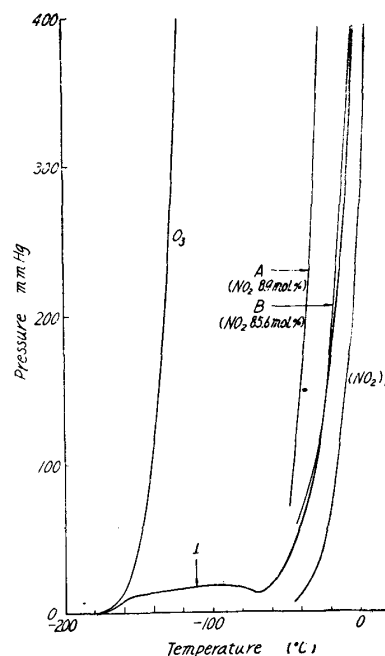


Fig. 2

B. Discharge with an induction coil

In an extreme case, two types of discharge occurred according to the current intensity. Of course, these two were mixed in an ordinary case of a long run. The characteristics in the two cases are tabulated below*.

Primary current	1A	5A
type of discharge	spark	arc
colour of discharge	strong, bluish white	weak, violet pink
boiling of liquid air	moderate	vigorous
colour of residual liquid	violet due to ozone	colourless
colour of solid product	gray	green

In the case, with a transformer, a spark-type discharge appeared at the beginning, but soon it was displaced by an arc-type one, so the experiment of a spark-type discharge could not be made. The characteristics and the solid

(3) R.H. Purcell and G.H. Cheeseman, Jour. Chem. Soc. (1932), 826.

* The emission spectra and current wave forms under various conditions will be reported in the succeeding paper.

products of the arc-type discharge with an induction coil were similar to those with a transformer. The measurement of pressure-temperature curve by the procedures already mentioned showed that a large amount of $(\text{NO}_2)_2$ and a small amount of ozone and nitrogen trioxide were produced.

The colour of the product obtained by a spark-type discharge was, at first sight, dark gray, but when the product was filtered, it also appeared somewhat greenish on the filter paper. Gray colour was due to the dust of platinum spattered from electrodes during the discharge. From the colour of the solid products and from the pressure-temperature curves it seemed that an arc-type discharge was preferable to a spark-type one for producing nitrogen trioxide, while the inverse was the case for producing ozone. The difference in nature between two types of discharge will be discussed in the subsequent papers.

In the course of measurement of vapour pressure of the product obtained by a spark-type discharge, an explosive increase of pressure was often observed at about -100°C . An example is shown in Fig. 3. The vapour pressure of the

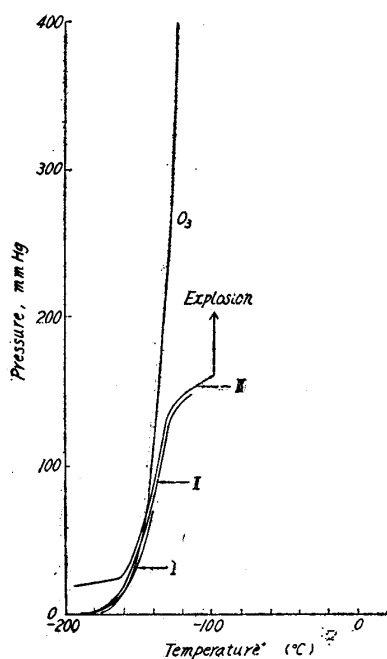


Fig. 3

product was measured after getting rid of residual liquid air at -195°C . The temperature was first raised to -138°C (curve *I*), then was lowered again to -195°C , and the vapour pressure was measured up to -118°C (curve *II*), from which the sample was again cooled to -195°C , and the pressure was measured again (curve *III*). The difference between curves *I* and *II* is very small, but curve *III* is very different from them; it is about 10 mmHg at the lowest temperature and shows an abrupt, almost explosive, pressure rise at -100°C . The existence of ozone in the products may be confirmed from the similarity of the pressure curve *I* or *II* to the vapour pressure curve of ozone. The marked difference of curve *III* from curve *I* or *II* shows the behaviour of ozone thus produced. The inflexions of curves *II* and *III* near -130° may be due to

the evaporation of liquid ozone and the increase of pressure in curve *III* at the beginning may be attributed to the partial decomposition of ozone into oxygen in the temperature range between the highest points of curves *I* and *II*, $-138\sim-118^\circ\text{C}$. The abrupt rise of pressure at -100°C must be due to the sudden decomposition of ozone.

The explosive decomposition of ozone did not always take place. In Fig. 4 the pressure increase is shown almost along the vapour pressure curve of ozone (curve *I*) and the deviation begins near -140°C , above which the pressure increases gradually with the rise of temperature showing no explosive change. Again the gaseous sample was cooled from room temperature to -195°C and

the pressure was measured. The result is shown by curve *II*, from which it can be seen that ozone was decomposed during the first rise in temperature. Curve *III* was obtained by measuring vapour pressure of the residue after non-condensable gases had been pumped out at the temperature of liquid nitrogen. The curve runs quite similar to the vapour pressure curve of N_2O_5 and, accordingly, it can be concluded that the residual condensed system is N_2O_5 and that the inflexions near *c* in curves *I* and *II* are attributed to the vapour of N_2O_5 .

When the vapour upon the condensed system was pumped out at -140°C instead of at -195°C as in the case of curve *III* and the vapour pressure was measured, curve *IV* in Fig. 4 was obtained. It is quite similar to curve *B* of Purcell and Cheeseman—the vapour pressure curve of nitrogen trioxide system. The difference between curves *III* and *IV* rises from the action of ozone. In the case of *III*, ozone is not pumped out and if it does not decompose explosively and keeps existing as vapour, it will react with $(NO_2)_2$ or nitrogen trioxide to form N_2O_5 in the temperature range up to -80°C . When the production of ozone is very small as in the case of arc-type discharge or when it is pumped out as in the case of curve *IV*, the existence of nitrogen trioxide system can always be seen from the vapour pressure curve.

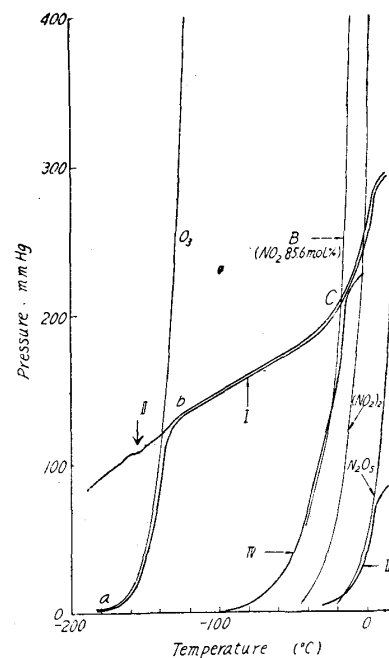


Fig. 4

IV. Discussion

1. The primary product

The excited or ionized atoms and molecules are generated by discharge and then they form stable primary products, followed by some thermal secondary reactions when its rate is very large. Therefore, the very primary reaction in the discharge cannot be determined even by the present method, though the secondary reactions of moderate rates could be traced. A spectroscopic method should be used for this purpose. J. W. Westhaver and A. K. Brewer⁽⁴⁾ and O. H. Wansbrough-Jones⁽⁵⁾ supposed that NO_2 was formed primarily, but E. J. B. Willey⁽⁶⁾ proposed NO as a primary product. In the present experiment, though ozone could be detected as a primary product from its vapour pressure, the existence of NO could not be ascertained. As NO easily reacts with oxygen or ozone at low temperature forming NO_2 , it may be supposed that ozone and NO are the primary products of the discharge reaction. Nitrogen trioxide

(4) J. W. Westhaver and A. K. Brewer, *Jour. Phy. Chem.*, **34** (1930), 554.

(5) O. H. Wansbrough-Jones, *Proc. Roy. Soc.*, **A 127** (1930), 511.

(6) E. J. B. Willey, *Proc. Roy. Soc.*, **A 159** (1937), 247.

seems to be produced by the discharge reaction in liquid air, but the present experiments show that it is formed in the later reaction between NO and $(\text{NO}_2)_2$.

2. On the higher oxide of nitrogen: NO_3

E. Warburg and G. Leithäuser⁽⁷⁾, H. J. Schumacher and G. Sprenger and others⁽⁸⁾ reported that some absorption bands appeared in their experiments on reactions between ozone and NO_2 or between ozone and N_2O_5 , which were attributed to NO_3 . Since then, NO_3 has been adopted to explain the mechanism of reactions in which various oxides of nitrogen take part, but it has not yet been separated, accordingly, it may be hypothetical. R. Schwarz and H. Achenbuch⁽⁹⁾ reported that NO_3 was obtained at the wall of a reaction vessel cooled by liquid air when the mixture of oxygen and a large amount of NO_2 was subjected to an electric discharge, but A. Klemenc and W. Neuman⁽¹⁰⁾ stated that no higher oxide such as NO_3 was obtained by a glow discharge through NO_2 - O_2 mixture under the similar experimental conditions. E. Müller⁽²⁾ first asserted that the green product obtained by the discharge reaction in liquid air was NO_3 , while D. Helbig stated that it was nitrogen trioxide. E. Müller concluded later that his view mentioned above had been incorrect and that the product was the mixture of nitrogen trioxide, $(\text{NO}_2)_2$ and NO.

Such disagreements may have occurred from the following reasons: they determined the compound by estimating the ratio of oxygen to nitrogen, supposing the reaction product to be a pure substance. The ratio, however, might be overestimated because it was difficult to exclude oxygen or ozone perfectly from the products. Indeed, ozone can hardly be pumped out, as its vapour pressure at the temperature of liquid nitrogen is very small (about 0.015 mmHg). Such undesirable circumstances could be avoided by the vapour pressure method in the present experiment. From the present results it can safely be affirmed that no new nitrogen oxide such as NO_3 can be found in the discharge products in liquid air and that the green coloured product must be a mixture of $(\text{NO}_2)_2$ and a small amount of nitrogen trioxide.

From the present investigation, it was concluded that during and after the discharge in liquid air the following processes would take place:

- 1) ozone and NO were produced by discharge,
- 2) NO reacted with oxygen and ozone into NO_2 ,
- 3) NO_2 associated to $(\text{NO}_2)_2$,
- 4) ozone decomposed gradually or explosively into oxygen,

(7) E. Warburg and G. Leithäuser, *Ann. Phys.*, **23** (1907), 209.

(8) H. J. Schumacher and G. Sprenger, *Zeit. Phys. Chem.*, **136** (1928), 77; *Zeit. Phys. Chem.*, **B 2** (1929), 267; *Zeit. angew. Chem.*, **42** (1929), 697.
G. Sprenger, *Zeit. Elektrochem.*, **37** (1931), 674.

H. J. Schumacher, *Zeit. anorg. all. Chem.*, **233** (1937), 47.

E. J. Jones and O. R. Wulf, *Jour. Chem. Phys.*, **5** (1937), 873.

T. M. Lowry and J. T. Lemox, *Nature*, **135** (1935), 433.

(9) R. Schwarz and H. Achenbach, *Ber.*, **68** (1935), 343.

(10) A. Klemenc and W. Neumann, *Zeit. anorg. allge. Chem.*, **232** (1937), 216.

- 5) NO and NO₂ combined into nitrogen trioxide,
- 6) ozone reacted with nitrogen trioxide to form N₂O₅.
- 7) the amount of ozone and the kinds of oxides of nitrogen formed varied with the type of discharge.

These conclusions will be completed by the researches to follow.

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