X.—*Action of Heat on Nitrosyl Chloride.*

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It is well known that nitric peroxide, N_2O_4 , begins to dissociate at temperatures just above the boiling point of the liquid. When the gas is heated, dissociation into nitrogen dioxide is far advanced, according to Playfair and Wanklyn at a temperature of 97.5° , and is complete, according to Deville and Troost, at 140° (*Compt. rend.*, **64**, 237). Richardson has studied the action of heat upon this compound at higher temperatures, and has found that at 620° nitrogen dioxide is completely dissociated into nitric oxide and oxygen (*Trans.*, 1887, **51**, 397).

We determined to examine the action of heat in like manner upon nitrosyl chloride, the only known oxychloride of nitrogen, as it seemed probable that it would dissociate into nitric oxide and chlorine more readily than nitrogen dioxide splits into nitric oxide and oxygen.

To elucidate this point, we undertook several series of experiments, of which this paper contains a brief account.

Preparation of Nitrosyl Chloride.

As a means of preparing the chloride, we invariably used nitrosyl sulphate (chamber crystals) and sodium chloride. The sulphate we obtained by passing the red gas evolved from copper and nitric acid or white arsenic and nitric acid into sulphuric acid. The red fumes were first passed through a Liebig condenser with a Woulff's bottle attached, so as to condense any nitric acid which might pass over, and all traces of moisture were removed by interposing a calcium chloride tube. The purified gas was then passed into the sulphuric acid. That these precautions were necessary was proved by the fact that our first sulphate—prepared by merely passing the nitrous fumes into sulphuric acid without previous drying—contained a small amount of nitric acid, and the chloride prepared from it always contained traces of nitrogen peroxide and hydrochloric acid, the former of which was readily detected by its absorption spectrum.

When the nitrous fumes had been passed into the sulphuric acid for some eight or nine hours, small crystals of nitrosyl sulphate appeared; the reaction was then stopped, as the sulphate in a semi-liquid form was much more convenient. The sodium chloride used was merely common salt thoroughly dried. The two salts were mixed together in a Wurtz's flask, and the nitrosyl chloride, which was evolved on gently warming, was passed through a calcium chloride tube.

That the gas thus evolved was practically pure nitrosyl chloride, was proved by estimating the amount of chlorine in a given weight of the gas.

Vapour Density at Ordinary Temperatures.

The vapour density of nitrosyl chloride at ordinary temperatures had been previously determined by Tilden (*Journ. Chem. Soc.*, 1874, 27, 632). From his results, it was clearly established that the molecule of the gas at ordinary temperatures is represented by the formula NOCl, and not by any multiple of this.

Density found.	Calculated for NOCl.
33.25	32.67

Our investigations consisted of determinations of the vapour density at temperatures ranging from 15° to 985°. Where possible, the density was obtained by weighing the gas, and checked by esti-

inating the chlorine; but, in some cases, we had to rely merely on the amount of chlorine found in order to calculate the density.

In order to fill the bulbs with the gas, we used one of the two following methods:—

(1.) Condensing the gas by placing the bulb in a freezing mixture, till several cubic centimetres of the liquid were formed, and then allowing it to boil off (b. p. -8°). In this case, we found it very requisite to have the bulb perfectly dry, and to have the outlet tube as far removed from the freezing mixture as possible, as the moisture which condensed around the cold tube readily decomposed the chloride as it passed into the air, and the nitrous and hydrochloric acids thus formed would readily find their way back into the bulb.

(2.) By passing the gas through a bulb open at both ends till all the air was expelled. We usually let the gas pass through for from 30 to 45 minutes.

Sulphuric Acid Bath.

Our first set of experiments was made at temperatures between 15° and 165° . The method used was that of condensing the gas in the tube. The kind of tube we found most convenient, both for fitting in the bath and also for obtaining the liquid free from moisture, is that represented in the figure.

The bulb had two openings, the larger one, which was wide enough to allow an ordinary piece of glass tubing to pass down, was ground, and had a glass stopper to fit, whilst the smaller one consisted of a long narrow capillary. The gas was passed in through the wide

neck by means of a piece of glass tubing which reached to the bottom of the bulb. When a quantity of liquid was condensed, the neck was stoppered, and a cap placed over the end of the capillary. The bulb was cleaned, and the cap removed. It was then put into the sulphuric acid bath, which was large enough to cover the bulb up to the stopper. The temperature was slowly raised, and the bath kept at the required temperature for 10 minutes. The cap was then replaced, the bulb removed, cleaned, and inverted in distilled water; the cap was removed, and the water allowed to enter. The solution thus obtained was mixed with excess of ammonia, and evaporated on the water-bath to dryness in order to get rid of all nitrite; the residue was then dissolved, and the solution titrated with decinormal solution of silver nitrate. From the amount of chlorine found, the vapour density was readily determined.

Three determinations made in this way at 15° gave a mean result of 32.5. The density according to theory is 32.67.

Experiments conducted in the same way at 65° , 115° , and 165° gave results which showed that no dissociation had taken place. In all cases, the density came out above 32.

Bath of Methyl Salicylate Vapour.

We next proceeded to heat the gas in a bath of methyl salicylate vapour, the temperature of which was 222° . In this set of experiments, the gas was allowed to pass through the bulb for about 45 minutes. The bulbs used were merely large boiling tubes of about 150 cubic centimetres capacity drawn out at both ends into fine long capillaries. When the gas had passed through for the allotted time, one end was sealed off; the bulb was then lowered into the bath, and the open end allowed to project through the cork; this open end was fitted with a smaller bulb containing nitrosyl chloride, in order to prevent diffusion during the experiment. The salicylate was then boiled, and after the bulb had been in the vapour for about 10 minutes, the open end was sealed off. The bulb was then removed, allowed to cool, and weighed; and from this weight the density was calculated. The end of the capillary tube was afterwards broken off under water, the chloride dissolved, and the chlorine estimated as before; this served as a check on the density determined by weighing. Three experiments were conducted at this temperature; the resulting density was 32.3, thus indicating that no dissociation had taken place.

Bath of Sulphur Vapour.

Our next experiments were conducted in a bath of sulphur vapour. The vessel in which the sulphur was boiled was not of very large

dimensions, and consequently the vapour became superheated. It was, therefore, necessary to determine the temperature by means of an air thermometer. This was readily done by taking a dry bulb of approximately the same size as the one used for the nitrosyl chloride, and fusing off when it had been in the vapour for 10 minutes. When cool, it was opened under water, and the volume of residual air determined; from this and the total capacity of the bulb the temperature was easily calculated. Three temperatures determined in one day only varied by 7° ; the numbers found were $690\cdot6^{\circ}$, $692\cdot3^{\circ}$, and $697\cdot8^{\circ}$.

Four determinations of the density were conducted in the sulphur vapour. In the first two, we liquefied the gas in the bulb, and allowed all excess to boil away after the neck had been drawn out into a long capillary. At first, we experienced great difficulty in keeping the bulbs free from moisture whilst the gas was passing in; we eventually got over this difficulty by fixing a long T-tube on to the neck of the bulb, and leading the gas through a capillary which passed down the T-tube, and reached to the bottom of the bulb, where it was condensed. In the last two experiments conducted at this temperature, we merely passed the gas through the bulbs for about 30 minutes. The four results agreed fairly well, ranging from $32\cdot3$ to $33\cdot1$, and thus they indicate that no dissociation had taken place.

Air-bath.

We next made two determinations of the density in an air-bath, which was heated by means of four large Bunsen burners. The temperature was determined both before and after each experiment by means of air thermometers. The bulbs were filled with the chloride by passing the gas through, and the two following results were obtained:—

Temperature.....	796°	V. d. ... ,	$31\cdot36$
Temperature.....	816°	V. d.	$31\cdot00$

These numbers indicate a percentage decomposition of about 13.

Combustion Furnace.

Our last experiments were conducted in a combustion furnace. We first used a method similar to that adopted by V. Meyer and Züblin in their investigations on chlorine, oxygen, &c., at high temperatures (*Berichte*, **12**, 1430). The tube used was an ordinary piece of combustion tubing, the same length as the furnace; to one end was fixed a tap, whilst the other was drawn off into a capillary.

A determination of the temperature was made both before and after each experiment.

The tube was first dried by aspirating dry air through it for half an hour whilst the tube was red hot. The tap was then turned off and the tube allowed to remain at the temperature of the furnace for 10 minutes; the residual air was then measured by driving it into a Schiff's nitrometer, filled with strong caustic potash solution. A stream of carbon dioxide, dried by passing through two sulphuric acid tubes, was used for driving the air over.

The carbon dioxide, in its turn, was displaced by the nitrosyl chloride, which was allowed to pass through the tube for about half an hour. A flask was attached to the capillary at the end of the tube in order to prevent diffusion. That a certain amount of dissociation did take place was proved by the fact that the gas which passed out of the flask turned red on meeting the air, thus showing the presence of a certain amount of nitric oxide. When we considered that all the carbon dioxide had been displaced, the tap was again turned off and the tube allowed to remain for 10 minutes. The nitrosyl chloride was then driven out by means of a stream of carbon dioxide into a Varrentrap's bulb, containing either distilled water or ammonia. When all had been absorbed, the solution was treated as in the former experiments, and the chlorine estimated. Another determination of the temperature was then made by aspirating dry air through the tube, allowing it to expand, and measuring the residue in the nitrometer. We found that the temperatures were generally very concordant, rarely differing by more than 10° , and often coming within 1 or 2 degrees of each other. Three determinations of the vapour density were made in this way with the furnace at its full heat. The results obtained were 29.73, 29.1, and 29.1. In all these cases we found that the nitrosyl chloride acted on the glass tube forming chlorides of the alkalis. These were volatilised by the great heat, and deposited in the capillary. As the gas was kept passing through the tube for some time, the amount of these chlorides was quite appreciable.

We, therefore, made several determinations in the combustion furnace, the gas having previously been liquefied in the tube. This we accomplished by taking a piece of combustion tubing nearly the same length as the furnace, rounding off one end, and drawing the other out slightly. Three or four cubic centimetres of the chloride were then condensed in the tube, and whilst it was still in the freezing mixture the open end of the tube was drawn out into a very fine capillary; the excess of nitrosyl chloride was allowed to boil away, then the tube was warmed by placing it on the bricks over the furnace. A small bulb was fixed on to the capillary to serve as a

reservoir, and thus prevent diffusion. When warm, the tube was pushed straight into the hot furnace, the bed of which was lined with asbestos paper in order to keep the tube from sticking, and also to facilitate the pulling in and out of the tube. The tube was left in the furnace for about a quarter of an hour; the capillary was then sealed off and the tube pulled out. When cool, the end was broken off under water, and from the solution thus obtained the density was calculated by estimating the chlorine in the usual way. The temperature was determined both before and after each experiment by means of air thermometers. These consisted of tubes approximately of the same length as that used for the nitrosyl chloride. They were first thoroughly dried, then pushed into the hot furnace, left for 10 minutes, sealed off, pulled out of the furnace, and, when cool, opened under water.

An experiment conducted in this way, with the burners only partly on, gave a mean temperature of 784° , and a density of 31.77. Another experiment at 928° gave a result of 29.0.

Two more experiments gave the following:—

Mean temperature....	968°	V. d.	27.3
*Mean temperature....	985°	V. d.	27.0

This indicates a dissociation of practically 50 per cent. of the nitrosyl chloride molecules at a temperature not much below 1000° .

As we were not able to obtain higher temperatures with the apparatus at our command, and using glass tubes, we concluded our experiments at this stage.

The table (p. 80) gives a *résumé* of the results of our experiments.

From these results, it is evident that nitrosyl chloride behaves in a very different manner from nitrogen dioxide when subjected to high temperatures. Thus, at 620° , a temperature at which nitrogen dioxide is completely dissociated, nitrosyl chloride shows not the least trace of dissociation; and near 1000° , only about 50 per cent. of the molecules are dissociated. This fact would seem to point to a difference in the constitution of the molecules of the chloride and the oxide of nitrosyl, as nitrogen dioxide may be called.

Nitrosyl chloride, in its reactions with water, behaves as the chloride of nitrous acid, and inasmuch as nitrous acid not only forms nitroso-compounds, but by acting on the group —CH_2 produces oximes, —C:N·OH , nitrous acid would appear to have the formula

* The following are a few of the results with the air tubes; they show that the estimations of temperature were fairly concordant, and may be relied upon:—

(1.) 925.2°	(1.) 967°
(2.) 930.0°	(2.) 969°

Vapour Density of Nitrosyl Chloride between 15° and 985°.

Method adopted for obtaining bulb full of gas.	Bath.	Temperature.	V. d. (H=1).	Per cent. amount of dissociation.
Passing gas for 45 mins...	Air	15°	32·57	0
Liquefying	Sulphuric acid	15	32·50	0
"	"	65	33·04	0
"	"	115	32·50	0
"	"	165	32·18	0
Passing gas	Methyl salicylate ...	222	32·30	0
"	Sulphur vapour	693	32·90	0
"	"	693	32·31	0
Liquefying	"	693	33·24	0
"	"	693	33·12	0
"	Combustion furnace	784	31·77	8·09
Passing gas	Air-bath	796	31·36	11·86
"	"	815	31·00	15·17
Liquefying	Combustion furnace	928	29·00	33·51
Passing gas	"	964	29·73 ?	
"	"	965	29·10 ?	
"	"	965	29·10 ?	
Liquefying	"	968	27·30	49·21
"	"	985	27·00	51·97

V. d. calculated for NOCl 32·65.

V. d. calculated for complete dissociation 21·78.

O:N·OH, and the chloride therefore O:N·Cl. Now, NOCl is incapable of directly combining with oxygen, and the compound NO₂Cl seems to have no existence (Williams, Trans., 1886, 49). Hence, we must suppose that that part of the valency of nitrogen which in NO is concerned with linking on another atom of oxygen to form NO₂ or N₂O₄ (according to temperature) is already occupied by chlorine in NOCl.

Since nitric oxide, NO, and nitrosyl chloride, NOCl, show no tendency to polymerise, the union which is established between NO₂ and NO₂ at temperatures below 140° is probably owing to the oxygen. We have been accustomed to regard nitric peroxide as nitroso-nitric anhydride, representing it by the formula O:N·O·N $\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$, but since the molecules of NO₂, concerned in the process of combination, are all alike, an unsymmetrical formula seems improbable.

The formula O:N·O·O·N:O seems to satisfy the requirements of the case, as it would account for the formation of nitric, as well as of nitrous, acid by the action of water,

CURVE SHOWING VAPOUR DENSITY OF NITROSYL CHLORIDE
BETWEEN 600° AND 1000° C.

and this leads to the formula $O\cdot N\cdot O-$ for the dioxide. This may, perhaps, account for the instability of this oxide at high temperatures by representing it as due to the unsaturated condition of the oxygen, while the more stable chloride may owe its greater permanence at high temperatures to the fact that the chlorine is not in the same degree unsaturated.

In conclusion, we have to thank Dr. Tilden for suggesting the work and supervising most of the experiments.

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