XXV.—Reactions supposed to yield Nitroxyl or Nitryl Chloride.

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In all the larger text-books that I have examined, it is stated that nitryl chloride not only exists, but is readily prepared.

These statements are based on the researches of Odet and Vignon (*Compt. rend.*, **69**, 1142, and **70**, 96), Williamson (*Proc. Roy. Soc.*, **7**, 15), and Hasenbach (*J. pr. Chem.* [2], **4**, 1).

When these papers are examined, however, it is at once obvious that the definite and plausible statements of the text-books are based on very imperfect evidence. Odet and Vignon, in the papers cited, were working in the hope of elucidating the process introduced by Deville for the preparation of nitrogen pentoxide. The formation of the latter by the action of chlorine on silver nitrate, they explain by the equations—

$$\begin{array}{l} \operatorname{NO}_{2} \\ \operatorname{Ag} \end{array} \right\} O + \operatorname{Cl}_{2} = \operatorname{AgCl} + \operatorname{NO}_{2}\operatorname{Cl} + O \dots \dots (1), \\ \operatorname{NO}_{2} \\ \operatorname{Ag} \end{array} \right\} O + \operatorname{NO}_{2}\operatorname{Cl} = \frac{\operatorname{NO}_{2}}{\operatorname{NO}_{2}} \right\} O + \operatorname{AgCl} \dots \dots (2),$$

and in order to test the correctness of these equations, they resolved to bring nitroxyl chloride into contact with nitrate of silver.

It is therefore with some surprise that one learns that in order to prepare the nitroxyl chloride they have recourse to a reaction in which, if formed, it will on their own hypothesis be immediately decomposed, viz., the action of phosphorus oxychloride on excess of lead or silver nitrate. It is stated that the product boiled at 5°, and it is described as of a pale-yellow colour.

In their second investigation, in which they endeavoured to obtain the nitroxyl chloride formed as an intermediate product (according to their view) in Deville's process, they say that they were five hours in collecting 2 c.c. of liquid, which they assume to be nitroxyl chloride. It boiled in the hand, and was yellowish-brown in colour.

In neither paper is there any account of a quantitative examination, nor did they take any steps to identify the compound.

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Thus far Odet and Vignon. Turning to Williamson's paper (*loc. cit.*), we find that he poured sulphuryl chlorhydrin, $SO_2CI \cdot OH$, on dry fused nitre, and found that a gas smelling of aqua regia was evolved, giving hydrochloric and nitric acids when passed into cold water. This, he remarks, is doubtless nitryl chloride.

Hasenbach passed a mixture of chlorine (in excess) and nitric peroxide through a *strongly heated combustion-tube*. Since no temperature is stated, I think one is justified in supposing that the tube was red-hot. As to the product, he merely says that it was "possessed of the properties of NO₂Cl." After one rectification the liquid was considered pure and contained 44 per cent. of chlorine, the theoretical quantity for NO₂Cl being 43.5 per cent.

This coincidence I regard as purely accidental; for in the first place, the analysis of only one specimen is given, and secondly, in my own experiments, when working under like conditions, I have never obtained a liquid with even approximately a constant boiling point, or which could be considered pure after one redistillation.

The large proportion of chlorine is readily accounted for by the fact, as I shall show, that nitrosyl chloride, NOCl (54 per cent. Cl), is a principal product, and further, that chlorine dissolves to a large extent both in NOCl and in N_2O_4 .

It is also worthy of remark that in endeavouring to prepare NO_2Br by the direct union of NO_2 and Br, Hasenbach found only 34 per cent. Br in the product, as against 63 per cent. theory. NO_2I could not be prepared.

On the other hand, Armstrong in 1873 found that when acetic chloride acts on a nitrate, the *components* of nitryl chloride are formed, but not the substance itself. Peroxide of nitrogen and chlorine are evolved, while a certain quantity of acetic anhydride is produced simultaneously (*Chem. Soc. J.*, 1873, **26**, 683).

From *nitrites* on the contrary, nitrosyl chloride was readily obtained by similar treatment.

Quite recently, however, reactions of the same class have been reexamined by Lachowicz (*Ber.*, **17**, 1281; **18**, 2990). He does not seem to be aware of Armstrong's experiments, for he makes no mention of them, and states that from silver nitrate and an acid chloranhydride, the acid anhydride is obtained. By this reaction, he prepared acetic, benzoic, and phthalic anhydrides in theoretical quantity. The gaseous products are peroxide of nitrogen and oxygen. Here he differs both from Armstrong and myself, but in any case the reaction does not avail for the preparation of nitryl chloride. Lachowicz gives as the typical equation for this decomposition, $2AgNO_3 + 2X \cdot COCl = 2AgCl + [X \cdot CO \cdot]_2O + N_2O_4 + O$, where X is a hydrocarbon radicle.

Judging, therefore, by the light of previous research, it appears that the evidence for the existence of nitryl chloride is by no meams complete.

With the object of further investigating this question, and of preparing nitryl chloride for use as a reagent, I have made a number of experiments such as might be expected to yield the substance. I shall now proceed to describe these.

1. Action of Phosphorus Oxychloride on Lead Nitrate in Excess.

This reaction was discussed some time ago by Mills (*Phil. Mag.* [4], 40, 134). Oxychloride of phosphorus contained in a tap funnel was allowed to drop on to pure dry lead nitrate in a distilling flask, connected with a spiral condenser cooled by a freezing mixture of ice and salt, the flask being surrounded by warm water to promote reaction.

This process fails utterly as a source of nitryl chloride. No liquid product was obtained in any quantity, and throughout the experiment a gas having the smell and bleaching properties of chlorine escaped. The vapours in the flask had a reddish colour, resembling that of dilute nitrogen peroxide, and after the experiment had gone on for some hours, a few drops of a yellowish-red liquid were collected, but the quantity was far too small to be of any use.

2. Action of pure Nitric Acid on Phosphorus Oxychloride in Excess.

The same apparatus was used, the $POCl_3$ being now placed in the flask. The reaction seemed at first more promising than the last, as more liquid distillate was obtained. On examination, however, it was found that all distillates contained $POCl_3$, even though distilled at 20° to 30° , and it therefore seemed likely that the nitryl chloride, if formed in this way, combined with the excess of $POCl_3$.

3. Action of Nitric Acid on Phosphorus Oxychloride in Equivalent Proportions.

The materials were heated at 100° for about two hours in sealed tubes. The contents separated into two layers, the upper deep red and mobile, the lower yellow and viscid. The latter consisted doubtless of phosphoric acid. On opening the tubes, a very volatile vapour having the odour of aqua regia escaped, which did not condense at -19° . A portion of this vapour was collected over strong sulphuric acid, and after absorption of the hydrochloric acid gas by water, was found to be chlorine.

It is probable that through dehydration of the orthophosphoric

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acid, and consequent formation of hydrochloric acid, the aqua regia reaction took place, with production of chlorine and nitrosyl chloride. On account of this complication, the reaction was not further studied, but, after the experiments of Williamson with sulphuryl chlorhydrin had been repeated, it was decided to use sulphuryl dichloride and nitric acid, or potassium nitrate, in which case dehydration of the resulting acid was not probable. I should mention that the reaction between nitric acid and phosphorus oxychloride takes place, to all appearance completely, in the cold after long standing. In this respect, the action of phosphorus oxychloride is in marked contrast with that of sulphuryl dichloride.

4. Action of Sulphuric Chlorhydrin, SO₂(OH)Cl, on Potassium Nitrate in Equivalent Proportions.

When a small quantity of the dry fused nitrate is placed in a testtube and sulphuric chlorhydrin is added to it, the mixture becomes hot Subsequently, on applying heat, nitric peroxide and evolves chlorine. is given off in large quantity. No other substance save these two could be detected, even when considerable quantities of the materials were employed in equivalent proportions, and the evolved vapours passed through a condenser cooled to -18° . At first, chlorine alone escaped and no liquid condensed, but on the application of heat to the flask red vapours were formed, which on passing into the condenser gave a small quantity of a deep red liquid now perfectly familiar to me as a solution of chlorine in nitrogen peroxide. The issuing gas on being passed into hot water always gave chlorine. With cold water, of course hydrochloric acid is produced, due to the oxidation by the chlorine of the nitrous acid formed by the solution of the peroxide in water.

The "gas smelling of aqua regia" is therefore chlorine together with a little nitrogen peroxide, and it is noteworthy that the evolution of the chlorine *before* the peroxide was also observed by Armstrong when potassium nitrate is treated with acetic chloride.

Possibly the nitric peroxide first formed combines with unattacked chlorhydrin, forming a nitrosyl compound, in this way :---

(i.) $2SO_2(OH)Cl + 2KO \cdot NO_2 = 2SO_2(OH)(OK) + N_2O_4 + Cl_2$,

(ii.) $SO_2(OH)Cl + NO \cdot NO_3 = SO_2(O \cdot NO)Cl + HNO_3$,

while the chlorine escapes. When heated, such a compound might easily decompose in presence of excess of potassium nitrate, forming chlorine and nitric peroxide, the latter being now in excess:—

(iii.)
$$2SO_2(0 \cdot NO)Cl + 4NO_2 \cdot OK = 3N_2O_4 + Cl_2 + 2SO_2(OK)_2$$
.

5. Action of Sulphuryl Dichloride, SO₂Cl₂, on Potassium Nitrate.

This experiment was tried as a crucial test of this class of reaction Sulphuryl dichloride was prepared by heating the chlorhydrin in sealed tubes for some days at 180° , the liquid being then distilled on a water-bath. The product, which contained 98 per cent. SO_2Cl_2 , was sealed up in a tube with an equivalent quantity of potassium nitrate (upon which it could not be made to act in an open tube), and heated at 100° for some hours. A certain amount of red gas was formed, and on opening the tube chlorine was collected over hot water. This does not leave much room for doubt that the reaction is—

$$\mathrm{SO}_2\mathrm{Cl}_2 + 2\mathrm{KO}\cdot\mathrm{NO}_2 = \mathrm{N}_2\mathrm{O}_4 + \mathrm{Cl}_2 + \mathrm{SO}_2(\mathrm{OK})_2.$$

The reaction takes place with great difficulty, and is very incomplete.

Towards absolute nitric acid, sulphuryl dichloride exhibited still greater inertness.

From such experiments as I have described, I infer that generally when a nitrate is acted on by an acid chloride—conditions under which we might reasonably expect nitroxyl chloride to be formed—we do not obtain this substance, but, instead of it, its component parts, nitrogen peroxide and chlorine.

6. Action of Chlorine on Nitric Peroxide.

I now pass to the consideration of the method of direct union suggested by Hasenbach.

Three principal series of experiments were performed under this head: in the first, which I shall call series A, the chlorine and peroxide of nitrogen were passed through a *red-hot tube*, in the other two, the components were heated at a temperature not exceeding 150°. The difference between series B and C will be explained later.

A. In these experiments, the chlorine, generated from manganese dioxide (in lumps) and hydrochloric acid, washed with water, and dried by sulphuric acid, was bubbled through liquid peroxide of nitrogen, contained in a wide test-tube which could be warmed if necessary. The vapours were thoroughly mixed in a dry Woulff's bottle and then entered the combustion tube, which was packed with small pieces of clay pipe and heated to redness. Condensation was effected in a spiral condenser cooled by ice and salt, the receiver, a small Würtz flask, being also well cooled in a similar way. The uncondensed gas passed away by the delivery tube of the latter. A closed receiver of this kind was found to be absolutely necessary, as many experiments failed owing to the rapid action of the moisture of the air on the product.

Now, since NO₂ dissociates at a red heat into NO and oxygen, it was likely that NOCl would be a chief product. A portion of the escaping gas, on being tested, was found to contain a large proportion of oxygen, thus proving indirectly the presence of nitrosyl chloride. The product was a very volatile, mobile, crimson liquid, and in order to ascertain its composition a portion was distilled through a series of large thin glass bulbs, previously weighed. When about full, the bulbs were sealed, temperature and pressure being noted, and weighed again.



The contained vapour was now absorbed by water, a process accomplished by connecting the two extremities a and b of the bulb with burettes A and B, filled with water, the intervening tubing being also quite full. The point a was then broken off inside the tube, and the vapour was rapidly absorbed. When absorption was complete the point b was broken, and a little more water sucked over to wash out the tube a.

Burette A was now completely filled and inverted in a beaker of water, and the levels being adjusted, a mark was made at c where the water stood in the narrow tube. Burette B was now read, and from it water was run into the bulb (through b) till its level rose to the mark c, when B was again read. This gave the volume of unabsorbed gas, the greater part of which was now contained in the burette A. The contents of the bulb were then washed into a beaker for the determination of the chlorine. The volume of gas in A was read and the nitric oxide then absorbed by ferrous sulphate solution, after which the volume of

residual gas (nitrogen) was again read. From these readings, it was known how much nitrogen and, consequently, how much air had been unexpelled from the bulb during distillation; this volume was subtracted from the total capacity of the bulb, which was now measured by running in water from a burette.

The data thus obtained furnished material for the determination of the vapour-density and of the chlorine present in the gas. The following table contains the numbers. Of the bulbs, No. I is nearest the distilling flask, and contains therefore the least volatile portion of the vapours.

	I.	II.	111.	
$\begin{array}{c c} \mathbf{v}_b \dots \dots & 118 \cdot 6 \\ \mathbf{v}_a \dots \dots & 0 \cdot 85 \end{array}$		155·2 1·0	176 1 · 4	
Vv	117 .75	154 ·2	174.6	
$\mathbf{B}_v \dots \dots$ $\mathbf{B}_a \dots \dots$	18 • 1513 17 • 9341	4·5168 4·2374	23 ·8571 23 ·5376	
$\mathbf{W}_{v=a}$ \mathbf{W}_{a}	0 ·2172 0 ·1367	0·2794 0·17906	0·3195 0·20275	
$W_v \dots \dots$ AgCl	0 ·3539 0 ·3076	0 · 45846 0 · 4077	0·522 25 0·4794	
V.D	37 • 35	36 ·95	37 . 17	
Cl per cent	21 . 5	22.00	22.71	

SERIES A.—Bulbs sealed at 18.5° and 728.8 mm.

 $V_b = vol.$ of bulb; $V_a = vol.$ of unabsorbed air; $V_v = vol.$ vapour; $B_v = weight$ of bulb full of vapour; $B_a = weight$ of bulb full of air; $W_{v-a} = weight$ of vapour - weight of equal vol. of air;

 W_a = weight of equal vol. of air (calc.); W_v = weight of vapour.

In order to interpret these results, the following assumptions and calculations were made.

Hypothesis α .—If we assume that all the chlorine is combined as NOCl, the volume of the latter can be calculated from the percentage of chlorine, and hence the partial pressure on the admixed peroxide. Then by means of the formula and tables of Professor J. W. Gibbs (*Chem. News*, 1879, 298) the extent of the dissociation of the peroxide can be determined. From this, the percentage composition of the gas in the bulb is known, and the density of this mixture is then readily obtained by a very simple calculation.

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Hypothesis β .—The chlorine is supposed to be free, and the calculation made in the same way.

Hypothesis γ .—Nitroxyl chloride is supposed to be the chlorinated substance.

The calculated and observed numbers are contained in the following table, but the figures for the density of the gas in the first bulb obtained on hypotheses β and γ , were so wide of the mark that it was thought unnecessary to work out the results for bulbs II and III:---

	I.		11.		III.	
	Densities.	Diff.	Densities.	Diff.	Densities.	Diff.
Found Calc. α , β , γ	$ \begin{array}{r} 37 \cdot 35 \\ 37 \cdot 88 \\ 40 \cdot 92 \\ 41 \cdot 00 \\ \end{array} $	0.53 3.57 3.65	36·95 38·08	1 ·13 	37 ·17 37 ·92 — —	0.75

SERIES A.

There can be little doubt therefore that when chlorine and nitric peroxide are passed through a red-hot tube the product is a mixture of nitric peroxide with nitrosyl chloride, although no doubt some chlorine is present in both in solution.

B. In these experiments, the mixed gases, obtained as before, were led through a large U-tube filled with broken glass and heated in an air-bath to a temperature varying from 130° to 150° . This temperature was chosen as being about that at which nitric peroxide completely dissociates into $2NO_2$, and at which therefore one would naturally suppose that direct combination with chlorine would most readily take place.

The product of the experiment was a red volatile liquid similar to that obtained in series A, but since no oxygen could be detected in the escaping gas, we must conclude that dissociation of NO_2 into NO and O_2 had not taken place, and, by implication, that nitrosyl chloride was not formed in these experiments.

Vapour-density determinations were performed exactly as before, except that the distillation of the vapour through the bulbs was continued for a very considerable time, the object being to ascertain, by the action of the escaping vapour on glacial acetic acid, whether free chlorine were present.

I do not consider this series of determinations to be as accurate as vol. xLIX. $$\tt R$$

the next (C), as, owing to the purpose just alluded to, the distillation was pushed so far that a considerable quantity of liquid condensed in the first bulb, which was only removed with great difficulty.

The glacial acetic acid through which the issuing vapours were bubbled was contained in a small distilling flask. After the operation, the acid had a deep crimson colour, which, however, completely disappeared when dry air was led through the acid for a short time at a temperature of 100°. A portion of the acid was then diluted, and nitric acid and silver nitrate added, the precipitate (a very small one) being filtered off. The liquid was subsequently treated with excess of rotash, and after boiling for some time the solution was acidified with A considerable quantity of silver chloride remained unnitrie acid. dissolved.

It is therefore certain that a notable amount of chloracetic acid had been formed, even in ordinary daylight and at ordinary temperatures. from which fact we must draw the inference that free chlorine was almost certainly present in the vapours.

The following are the numbers for this series :---

	I.	II.	III.	
$\mathbf{v}_b \dots \dots \mathbf{v}_a$	117·8 0·0		175 ·0 (approx.)	
$V_v \dots \dots$ $B_v \dots \dots$ $B_u \dots \dots$	117·8 73·7767 73·5345	155 60 · 8276 60 · 5154	175 79.6245 79.2724	
\mathbf{W}_{v-a} \mathbf{W}_{a}		0·3122 0·184775	0·3521 0·20845	
\mathbf{W}_v	0.38263	0 • 496975	0.56055	
v .D	3 9 · 33	38 •82	38.80	
Cl per cent	5.66	5.2		

SERIES B.—Bulbs sealed at 24° and 761.7 mm.

During the manipulation of bulb III, it was broken, and consequently no chlorine determination could be made. Its volume was taken as being approximately 1 c.c. less than in series A, in order to obtain an approximate vapour-density, as it was thought that possibly this might be useful.

Calculations were made as in series A, the nitrosyl chloride hypothesis being now excluded.

SERIES B.

	I.		II.		
-	Densities.	Diff.	Densities.	Diff.	
Found Calc. hyp. β	$39 \cdot 33$ $41 \cdot 63$ $41 \cdot 70$	2.30 2.37	$38 \cdot 82 \\ 41 \cdot 64 \\ 41 \cdot 73$	$2 \cdot 82$ $2 \cdot 91$	

There is here a slight difference in favour of β , but considering how small it is and how widely both series of calculated numbers vary from the observed density, the figures cannot be taken as proving anything.

C. The liquid for use in this series was prepared in the same way as for the last, but the distillation was allowed to go on for a *short time* only, in order that the most volatile portions of the vapour should have influence. Hence the large amount of unexpelled air and high percentage of chlorine.

	I.	II.	III.	
$\overline{\begin{array}{c} \hline \mathbf{V}_b & \dots \\ \mathbf{V}_a & \dots \end{array}}$	117 ·9 0 ·55	154.7 4.5	144 18 ·85	
V _v	117.35	150.2	125.15	
$\mathbf{B}_v \dots \dots \mathbf{B}_a$	74 · 5864 74 · 3507	$ \begin{array}{r} 60 \cdot 4787 \\ 60 \cdot 1814 \end{array} $	65 · 5103 65 · 2689	
\mathbf{W}_{v-a} \mathbf{W}_{a}	0 · 2357 0 · 13926	$ \begin{array}{r} 0.2973 \\ 0.17824 \end{array} $	$ \begin{array}{r} 0.2414 \\ 0.14852 \end{array} $	
$\mathbf{W}_v \dots \dots$ $\frac{2}{5}$ AgCl \dots	0 ·37496 0 ·1527	0 · 47554 0 · 2206	0 · 38992 0 · 2219	
V .D	38.87	38.51	37.9	
Cl per cent	25.12	28.68	35.11	

SERIES C.—Bulbs sealed at 20.1° and 748.3 mm.

The numbers in this series are, I think, fairly trustworthy, as everything worked very smoothly throughout.

The following are the calculated results :---

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	Т.		11.		I II.	
	Densities.	Diff.	Densities.	Diff.	Densities.	Diff.
Found Calc. β , γ	38 · 87 40 · 40 40 · 88	$\frac{1.53}{2.01}$	$38.51 \\ 40.10 \\ 40.70$	$\frac{1\cdot 59}{2\cdot 19}$	$37 \cdot 90 \\ 39 \cdot 54 \\ 40 \cdot 50$	$\frac{1.64}{2.60}$

SERIES C.

Here there is a decided difference in favour of hypothesis β . The extreme variation in the differences is only 0.11, though it must be admitted that the differences themselves are rather large.

Now in the calculated values on hypothesis γ , the variation in the differences amounts to 0.59, and the whole series is from 0.48 to 0.96 farther from the truth than the other. These discrepancies are considerable, occurring as they do in a total difference never exceeding 2.6.

With regard to the uniform difference of 1.5 between the observed densities and the numbers obtained on hypothesis β , I think it is easily understood when we remember that Gibbs' formula is only approximate, and that a like variation, the same in direction and nearly the same in amount, was observed by Ramsay and Cundall in calculating the density of a similar mixture with the help of this formula.

From these experiments, I think we may reasonably conclude that direct combination of nitric peroxide and chlorine, like all the other methods, fails to yield nitryl chloride; the product hitherto regarded as such being merely a *solution* of chlorine in nitric peroxide, together with nitrosyl chloride, when the experiment is performed at a red heat.

In two samples of this product, prepared at 150° on different occasions, the chlorine was determined, and was found to be 8.6 and 9.2 per cent. respectively.

Now if a compound were formed, we should expect the amount of chlorine to vary in products formed at different rates and during different times. We must, therefore, I think, regard these numbers as expressing the *solubility* of chlorine in the peroxide at the temperature of the condenser, which varied probably from -20° to -15° .

Indeed, a solution containing 475 per cent. of chlorine was readily prepared by cooling the test-tube containing the peroxide during the passage of the chlorine, and though the solution was probably not saturated, nor was it so cold as in the spiral condenser, still the liquid after this treatment strongly resembled that which dripped from the delivery tube of the condenser.

I must mention, however, that when endeavouring to prepare a specimen of this solution a few days ago for exhibition to the Society, the peroxide, though it absorbed the chlorine with great vigour, underwent no appreciable change of colour, nor was any such change induced when a portion of the liquid was warmed slightly. The temperature of the experiment was -15° , and the peroxide was quite free from water, as was shown by its solidifying during the passage of the chlorine.

I am inclined to think that a trace of moisture is necessary for the development of the red colour, which is probably due to a small quantity of nitrosyl chloride :---

 $Cl_2 + H_2O = 2HCl + O$; $HCl + (NO)NO_3 = NOCl + HNO_3$.

In conclusion, I must render my hearty thanks to Dr. Tilden especially, and also to Dr. Nicol, for their ready and kindly help.