660. *Reactions of Nitrosyl Chloride. Part II.*

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The reaction between nitrosyl chloride and certain elements and their chlorides has been extended and the new *compound* $PdCl_2,2NOCl$ prepared. Nitrosyl chloride is formed in reactions between certain chlorides and dinitrogen tetroxide, and the latter from some nitrates and nitrosyl chloride; these reactions have been reinvestigated.

In an earlier publication (*J.*, 1948, 1952) the action of nitrosyl chloride on several metals and their compounds was described, and the present paper gives an account of further work with nitrosyl chloride and dinitrogen tetroxide.

Boyé and Rogers (*Phil. Mag.*, 1840, **17**, 397), by evaporating platinum with aqua regia, prepared a yellow deliquescent powder which they considered to be a compound of platinic chloride and nitric oxide. It contained 9·87% of water, not evolved at 100°. Weber (*Ann. Phys. Chem.*, 1867, **131**, 441), by mixing a solution of platinic chloride and fuming nitric acid, obtained a yellow precipitate which, after drying, gave a browish-yellow deliquescent solid corresponding to $PtCl_4,2NOCl,H_2O$. The platinum compound was prepared by Jörgensen (*Kgl. Danske Vid. Selsk. Skrift.*, 1867, [v], 6, 451) as orange-yellow octahedra and rhombododecahedra by evaporating chloroplatinic acid with fuming nitric acid or passing aqua regia vapour into chloroplatinic acid solution. Its composition corresponded to PtO_2NCl_3 (= $PtCl_4,2NOCl$ when modern atomic weights are used). Sudborough (*J.*, 1891, **59**, 655) and Asmussen (*Z. anorg. Chem.*, 1939, **243**, 127) obtained low yields of $PtCl_4,2NOCl$ by heating nitrosyl chloride with platinum in a sealed tube at 100°. The last observation was confirmed by us, but the reaction was very slow and incomplete at 100° and it was difficult to separate the deliquescent compound from unchanged metal. The reaction between platinous chloride and nitrosyl chloride proceeded quantitatively: $PtCl_2 + 4NOCl = PtCl_4,2NOCl + 2NO$. With platinic chloride the formation of $PtCl_4,2NOCl$ was rapid. The last two methods are suggested for the preparation.

Geuther (*Jena Z.*, 1873, **7**, 375; *J. pr. Chem.*, 1874, **7**, 354) found that dinitrogen tetroxide gave " a solid substance " with cooled boron trichloride. When the mixture, after being kept for 2 days, was distilled, volatile yellow crystals condensed in the receiver. He formulated the compound as $BCl_3,NOCl$, although in this $Cl/B = 4$ whilst the analysis gave $Cl/B = 3{\cdot}53$. The reaction was considered to be:

$$16BCl_3 + 6N_2O_4 = 12(BCl_3,NOCl) + 2B_2O_3 + 3O_2$$

It was not found possible to prepare pure $BCl_3,NOCl$ by this method, the distillate being probably a mixture of $BCl_3,NOCl$ and an ill-defined compound of boron trichloride and dinitrogen tetroxide. A similar result was obtained in the case of the tin compound, $3SnCl_4,4NOCl$ (see below).

The usual method of distilling excess of nitrosyl chloride from the solution gave only B_2O_3 as a decomposition product. The compound was obtained from weighed quantities of boron trichloride and nitrosyl chloride (*ca.* 4 : 5), by storage until crystals separated, and filtration through sintered glass in a sealed tube. Well-defined readily fusible crystals separated. Analyses corresponded well with $BCl_3,NOCl$ or $[NO]BCl_4$.

The compound melts to two liquid layers (at 26—27°), one of which disappears on heating the material to 65°; and on heating a solution homogeneous at room temperature (excess of nitrosyl chloride) two layers separate but on further heating one layer disappears. This behaviour corresponds with the phase diagram described by Roozeboom (" Die heterogenen Gleichgewichte," 1918, **2**, 175). On the melting-point curve the maximum, corresponding to compound formation, is not reached, since a completely closed curve (probably similar to that of the nicotine–water system) cuts the apex, and the compound does not melt without decomposition.

The corresponding fluorine compound, prepared by Wilke-Dörfurt and Balz (*Z. anorg. Chem.*, 1926, **159**, 197) by the reaction $2HBF_4 + N_2O_3 \rightleftharpoons H_2O + 2[NO]BF_4$, is stable, can be sublimed, and forms a monohydrate. Balz and Mailänder (*ibid.*, 1934, **217**, 161) prepared it from nitrosyl fluoride and boron trifluoride. There is no record of its melting to two layers on heating.

Jones and Matthews (*Proc. Camb. Phil. Soc.*, 1910, **15**, 529) examined the reducing action of hydrogen on nitrosyl chloride in presence of palladium at room temperatures; the metal was attacked with the formation of palladium dichloride, nitric oxide, and nitrogen. Puche (*Ann. Chim.*, 1938, **9**, 243) stated that palladium forms a deep-red solution with aqua regia, probably owing to the formation of $PdCl_4,2NOCl$. Manchot and Waldmüller (*Ber.*, 1926, **59**, 2363) found that nitric oxide containing a small quantity of alcohol vapour as catalyst, reacted rapidly with palladium dichloride. The brownish-black solid product rapidly evolved nitric oxide in air but immediate analysis gave the composition $PdCl_2,2NO$. This compound has been wrongly reported as " palladous dinitroxyl chloride, $PdCl_2,2NO_2$ " (Mellor, " Treatise, etc.," 1936, **15**, 628; *Abs.*, 1926, *A*, 1219).

It was found that nitrosyl chloride and palladium dichloride formed bright-red $PdCl_2,2NOCl$, stable in dry air but immediately reacting with water to evolve nitric oxide. Palladous nitrate gave the same *compound*, the reaction being incomplete at room temperature but quantitative at 100°: $Pd(NO_3)_2 + 4NOCl = PdCl_2,2NOCl + N_2O_4$. The compound when heated in dry nitrogen at 200° gave a residue of palladium dichloride. Dinitrogen tetroxide did not react with palladium dichloride. $PdCl_2,2NOCl$ could not be prepared from palladium and nitrosyl chloride owing to the formation of nitric oxide in the preliminary chlorination of the metal. From analyses it appeared that $PdCl_2,2NO$ and $PdCl_2,2NOCl$ are both formed, reaction (1) being followed by (2) and (3):

$$Pd + 2NOCl = PdCl_2 + 2NO \quad (1)$$

$$PdCl_2 + 2NO \rightleftharpoons PdCl_2,2NO \quad (2)$$

$$PdCl_2 + 2NOCl \rightleftharpoons PdCl_2,2NOCl \quad (3)$$

$PdCl_2$,2NO was also prepared from nitric oxide and palladium dichloride and, like the product from palladium and nitrosyl chloride, it became black on the addition of water.

Sudborough's (*loc. cit.*) observation that nitrosyl chloride reacted slowly with gold strip forming $AuCl_3$,NOCl was confirmed, and it was found that the rate of reaction depended on the state of division of the metal. A better method of preparation was from gold trichloride and nitrosyl chloride, this reaction going quickly to completion. When the substance was heated, nitrosyl chloride was evolved and the gold trichloride then decomposed into the metal and chlorine.

From mercury and nitrosyl chloride Sudborough obtained only mercuric chloride, although Gall and Mengdehl (*Ber.*, 1927, **60**, 86) and Asmussen obtained $HgCl_2$,NOCl from mercuric or mercurous chloride. It was found that the products of reaction varied with temperature. Mercurous chloride and nitric oxide were the sole products from mercury and nitrosyl chloride at $-40°$. At 20° mercurous chloride reacted to form mercuric chloride and nitric oxide (detected by Manchot's solution). The final product was $HgCl_2$,NOCl, easily decomposed into mercuric chloride and nitrosyl chloride in a vacuum :

$$\mathrm{Hg} \xrightarrow{\text{NOCl at } -40°} \mathrm{Hg_2Cl_2} \xrightarrow{\text{NOCl at } -20°} \mathrm{HgCl_2} \overset{\text{NOCl}}{\rightleftharpoons} \mathrm{HgCl_2,NOCl}$$

Dinitrogen tetroxide reacts with certain chlorides with the formation of nitrosyl chloride, but nitrosyl chloride reacts with thallium and palladium nitrates with the formation of the tetroxide. According to Perrot (*Compt. rend.*, 1935, **201**, 275) nitrosyl chloride reacts with silver nitrate to form silver chloride and dinitrogen tetroxide, but no experimental details are given. It was found that quantitative reaction occurs easily at room temperature : $AgNO_3 + NOCl = AgCl + N_2O_4$.

Lead nitrate reacted similarly, $Pb(NO_3)_2 + 2NOCl = PbCl_2 + 2N_2O_4$, but barium nitrate did not react, even when heated at 100° for a week. There was no reaction between dry sodium or potassium nitrate and nitrosyl chloride.

The reaction between dinitrogen tetroxide and boron trichloride was reinvestigated and the formation of some nitrosyl chloride was suggested by the blood-red colour produced in the first few minutes.

The literature on the reactions between dinitrogen tetroxide and stannic chloride is conflicting. Mellor ("Treatise, etc.," 1927, **7**, 445) and Gmelin-Kraut ("Handbuch der anorg. Chemie," 1911, **4**, 323) state that Weber prepared $SnCl_4,N_2O_3$ from stannic chloride and dinitrogen trioxide, whereas Weber (*Ann. Phys. Chem.*, 1863, **118**, 471) prepared the gas by heating lead nitrate and emphasised that the compound contained N_2O_3 and not NO_2 : "die Verbindung Salpetrigesäure, nicht Untersalpetersäure, enthält." On sublimation he obtained a poorly-defined product which he considered to contain some $SnCl_4$,2NOCl. Hampe (*Annalen*, 1863, **126**, 43) on passing the gas from lead nitrate, and from starch and nitric acid, into stannic chloride obtained a yellow product the sublimate from which on gentle heating corresponded with $3SnCl_2 + 2NO_2Cl$ (= $3SnCl_4$,4NOCl when modern atomic weights are used). A titanium compound $3TiCl_4$,4NOCl was also prepared. Thomas (*Ann. Chim. Phys.*, 1898, **13**, 145) found that direct combination gave $SnCl_4,NO_2$; in the presence of chloroform yellow $3SnCl_4,SnOCl_2,N_2O_5$ was obtained, on heating which $3SnCl_4$,4NOCl was formed. Reihlen and Hake (*Annalen*, 1927, **452**, 47) regarded the yellow compound from stannic chloride and dinitrogen tetroxide as $2SnCl_4,3N_2O_4$ and found that no definite product could be obtained from stannic chloride and dinitrogen trioxide.

Repetition of this work with dinitrogen tetroxide gave a *compound* $SnCl_4,2{\cdot}5NO_2$ in three separate experiments. Contrary to Reihlen and Hake's statement, this does not fume in air, and it seems probable that their product contained adhering dinitrogen tetroxide. The ratio Cl/Sn = 4 showed that no decomposition to $SnCl_4$,2NOCl occurred at this stage ; after sublimation some decomposition to $SnCl_4$,2NOCl was found to occur, as Weber suggested, but no definite compound could be isolated.

With titanium tetrachloride it was found, in agreement with Reihlen and Hake, that titanium tetranitrate was formed but the product always contained a small quantity of chloride, probably present as $TiCl_4$,2NOCl, which would agree with the feeble evolution of nitric oxide on the addition of water. Nitrosyl chloride was recognised as a product of the reaction and a specimen was isolated by fractional distillation (m. p. $-70°$). Analyses of the solid were inconsistent and did not warrant the definite formula $Ti(NO_3)_4$.

Frankland (*J.*, 1901, **79**, 1356) could detect no reaction between sodium or potassium chloride and nitrogen peroxide. Whittaker, Lundstrom, and Merz (*Ind. Eng. Chem.*, 1931, **23**, 1410) showed that the reaction $KCl_{(s)} + 2NO_{2(g)} = KNO_{3(s)} + NOCl_{(g)}$ occurs to the extent of 1·7% without moisture but, in the presence of 2·4% of moisture, the nitrogen content of the residue corresponded to 93·75% conversion into nitrate. Reed and Clark (*Ind. Eng. Chem.*, 1937, **29**, 333) found no chlorine and only a trace of hydrogen chloride to be formed in the reaction in presence of water.

In our experiments nitrogen peroxide free from nitric acid reacted with potassium or sodium chloride to a slight extent at 100° in a sealed tube. The reaction between potassium chloride and gaseous nitrogen peroxide in the presence of water was as described by Whittaker *et al.* The melting point and vapour pressure of nitrosyl chloride prepared in this way agreed with those of the product from nitrososulphuric acid and sodium chloride (*J. Physical Chem.*, 1949, **53**, 500).

These reactions between nitrates and nitrosyl chloride, in which dinitrogen tetroxide is formed, and the formation of nitrosyl chloride from chlorides and dinitrogen tetroxide support a nitrosyl-nitrate formula for the latter, which was given in the previous paper (cf. Addison and Thompson, *Nature*, 1948, **162**, 369). This formula has long been recognised and, although Mellor (" Treatise," **8**, 547) incorrectly gives the name " nitrosyl nitrite " to the compound so formulated, this cannot disguise the fact that it is obviously nitrosyl nitrate.

The colour of solid nitrosyl chloride has been described as blood-red (van Heteren, *Z. anorg. Chem.*, 1900, **22**, 277; Whittaker *et al.*, *loc. cit.*) and as lemon-yellow (Francesconi and Bresciani, *Atti R. Accad. Lincei*, 1903, [5], **12**, 75). It was found that nitrosyl chloride, which had been distilled in a vacuum, solidified to blood-red feathery crystals when cooled in ether–solid carbon dioxide, but that these became lemon-yellow when cooled in liquid air. The melting point of nitrosyl chloride was $-61·5° \pm 0·2°$ (determined with a calibrated low-temperature thermometer), this value being in agreement with those found by Trautz and Gerwig (−61·5°; *Z. anorg. Chem.*, 1924, **134**, 409) and Whittaker *et al.* ($-61·5° \pm 0·2$; *loc. cit.*).

EXPERIMENTAL.

Methods used for reactions and analysis were given in the previous paper.

Reaction with Platinum.—Nitrosyl chloride was heated at 100° in a sealed tube with 1 g. of platinum strip. A brown powder gradually formed and the supernatant liquid became black. The reaction was very slow and after several days some platinum was unchanged; formation of the compound was retarded by a black film on the surface of the metal. On opening the tube there was a considerable pressure of nitric oxide; the yellowish-brown powder was deliquescent and reacted with water evolving nitric oxide and forming a yellow solution. The platinum was determined by precipitation as ammonium chloroplatinate and ignition to metal (Found: Pt, 41·0, 41·6. Calc. for $PtCl_4,2NOCl$: Pt, 41·7%). Since chlorine in a solution of platinic chloride cannot be determined by precipitation with silver nitrate owing to the formation of a stable complex, the method described by Drew, Tress, and Wyatt (*J.*, 1934, 1787) was used (Found: Cl, 45·1, 45·3%; Cl/Pt = 6·0. Calc. for $PtCl_4,2NOCl$; Cl, 45·46%; Cl/Pt = 6·0).

Action of Nitrosyl Chloride on Platinum Dichloride.—1 G. of platinum dichloride reacted with nitrosyl chloride only when heated in a water-bath; the solid became yellowish-brown and the supernatant liquid black. After removal of excess of nitrosyl chloride the addition compound was obtained (Found: Pt, 41·3, 41·5; Cl, 44·8, 45·2; N, 5·6%; Pt : Cl : N = 1 : 5·98 : 1·88. Calc. for $PtCl_4,2NOCl$: N, 5·9%; Pt : Cl : N = 1 : 6 : 2).

Reaction between Platinic Chloride and Nitrosyl Chloride.—Platinic chloride, prepared by heating hexachloroplatinic acid in chlorine (Kharasch and Ashford, *J. Amer. Chem. Soc.*, 1936, **58**, 1733), was a very hygroscopic reddish-brown powder, becoming bright yellow after a few minutes in air (Found: Pt, 58·3. Calc. for $PtCl_4$: Pt, 57·9%). At 100° in a sealed tube reaction occurred between platinic chloride and nitrosyl chloride. After the excess of nitrosyl chloride had been boiled off the solid appeared to be identical with that obtained from platinum (Found: Pt, 41·2. Calc. for $PtCl_4,2NOCl$: Pt, 41·7%).

Preparation of Boron Trichloride.—The trichloride was prepared by the action of dry chlorine on heated boron. It was found better to pass the chlorine *through* rather than *over* the amorphous boron, so that excess was avoided. Glass wool reacts appreciably with chlorine at red heat and could not be used for packing. Preliminary drying of the boron considerably increased the yields. Boron trichloride was easily separated from any silicon tetrachloride by fractional distillation; if slightly yellow (owing to dissolved chlorine), a small quantity of mercury was added to it before sealing. All specimens distilled completely at room temperature.

Reaction between Boron Trichloride and Nitrosyl Chloride.—Two methods were tried but only the second was successful.

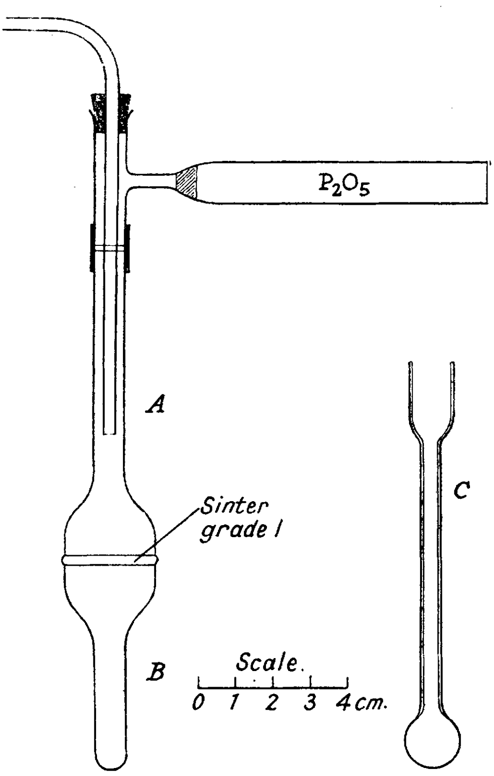
(a) *Boron trichloride and excess of nitrosyl chloride.* With all the previous chlorides the nitrosyl chloride compounds could be obtained by allowing liquid nitrosyl chloride to remain in contact with the chloride and evaporation of the excess.

Excess of nitrosyl chloride was distilled on boron trichloride cooled in solid carbon dioxide. A yellow solid separated which on sealing and shaking dissolved completely, forming a clear red solution. The following observations were made on heating the solution slowly in a water-bath.

Sharply at 45° the liquid became cloudy and a lower layer separated; as the temperature rose this layer decreased, and it disappeared at 60°. At a higher temperature the liquid boiled. On cooling, small oily drops separated and collected at the bottom of the tube, forming a clear red layer; as the tube cooled to room temperature the layer became less distinct and the whole finally became homogeneous.

The tube was opened and excess of nitrosyl chloride removed by evaporation in dry nitrogen. A white solid obtained was boric oxide (Found : B, 30·37, 30·65. Calc. for B_2O_3 : B, 31·03%).

(b) *Weighed quantities of nitrosyl chloride and boron trichloride.* It was found that crystals separated from approx. equimolecular quantities of nitrosyl chloride and boron trichloride. The filter tube (see figure) was used to isolate the compound in a pure state. To prevent hydrolysis the end of the tube was protected with a phosphoric oxide tube as shown. Air was displaced by dry nitrogen, and 1·84 g. of nitrosyl chloride were passed into the tube cooled in solid carbon dioxide, followed by 2·92 g. of boron trichloride (*i.e.*, 112·5% of nitrosyl chloride required for 1 : 1 compound). By lifting the delivery tube the tube could be sealed without exposure to air. Most of the reaction occurred in the lower half of the filter, and a yellow solid separated. On warming to 30° two liquid layers formed. By cooling *B* again in solid carbon dioxide the remainder passed through the sinter into *B*. In ice-water the upper layer quickly deposited small yellow crystals, and the lower layer formed a red jelly. After the apparatus had been kept in a vertical position overnight long needle-shaped crystals (the largest, 3 cm.) separated; the mother-liquor was light brown. By inverting the tube and cooling the tip *A* at −20° the mother-liquor passed through the sinter and was sealed off. The crystals so freed from excess of nitrosyl chloride changed from red to lemon-yellow.



(c) *Action of heat in a sealed tube.* Crystals of the compound, heated in a sealed tube, melted at 26—27° forming two liquid layers; the upper was clear reddish-brown, the lower orange but opaque. When warmed and shaken, the lower layer changed sharply from orange to clear red; on further heating it disappeared completely at 65°.

Nitrosyl chloride was soluble in excess of boron trichloride ($NOCl/BCl_3 = 2/5$) to form a light-brown solution but on gentle heating two layers did not separate.

In a sealed tube the crystals were well defined and the space above was colourless (small dissociation pressure). When the crystals melted the tube was filled with straw-coloured nitrosyl chloride vapour. On cooling, crystals were deposited on the upper part of the tube, showing a considerable dissociation pressure at the m. p. : $BCl_3 + NOCl \rightleftharpoons BCl_3,NOCl$.

(d) *Analytical method.* The compound evolved white fumes in air and it could not be weighed in a weighing bottle. With water nitric oxide was evolved and a white solid separated which dissolved readily on warming or stirring :

$$BCl_3,NOCl + 4H_2O = H_3BO_3 + HNO_2 + 4HCl$$
$$3HNO_2 = 2NO + HNO_3 + H_2O$$

Boron was determined by preliminary neutralisation of hydrochloric acid (using methyl-red), addition of excess of mannitol, and titration to a phenolphthalein end-point. The method was checked with a known mixture of pure boric and hydrochloric acid and gave good results. Cresol-red had no advantage over phenolphthalein, methyl-red however masked a bromothymol-blue end-point.

The analysis tube (see figure), was weighed empty, cooled in solid carbon dioxide, a small amount of the solid introduced and the tube drawn out thin at *C*. The sealed bulb, after weighing, was cooled in solid carbon dioxide and the tip broken under 20 ml. of water. The liquid was diluted to 30 ml. and gently warmed to decompose any nitrous acid and eliminate traces of carbon dioxide. To keep the volume 30—35 ml. the hydrochloric acid was almost neutralised with N-NaOH using methyl-red, and the neutralisation completed with N/10-NaOH to the first appearance of a yellow colour. 6 G. of mannitol were dissolved (the red colour of the indicator returning) and 2 drops of phenolphthalein added. The volume of N/10-NaOH necessary to produce a distinct pink colour was noted and this corresponded to the boric acid present. In no case did the addition of a further quantity of mannitol discharge the pink colour of the phenolphthalein.

Chlorine can be determined by chloride precipitation in presence of boric acid and it was shown by a control experiment that mannitol was without effect.

For the nitrogen determination the bulb was broken under sodium hydroxide solution, and the nitrite reduced to ammonia as in previous cases (Found : B, 5·6, 6·0, 6·2; Cl, 77·45, 77·49, 78·0; N, 7·75. $BCl_3,NOCl$ requires B, 5·92; Cl, 77·64; N, 7·67%).

Reaction between Boron Trichloride and Dinitrogen Tetroxide.—6 G. of dinitrogen tetroxide were distilled on to 16 g. of boron trichloride at −20°; a yellow solid separated immediately; there was a definite blood-red reaction zone (probably nitrosyl chloride). On removal of the mixture from the cooling-bath a vigorous reaction occurred, much heat was evolved, and the mixture was cooled again to prevent loss of boron trichloride. Combination occurred with a " cracking " noise.

By warming the mixture in a water-bath a yellow sublimate formed in the receiver, and large amounts of nitrogen peroxide were evolved. The residue was boric oxide. At room temperature the sublimate was semi-liquid and was analysed only with difficulty (Found : B, 6·45, 6·2; Cl, 74·5, 73·6; N, 6·52%; B : Cl : N = 1 : 3·6 : 0·8).

Reaction between Palladium Compounds and Nitrosyl Chloride.—Trial analyses were necessary to ensure that Cl : Pd could be accurately determined. Two methods were used, (*a*) the palladium salt was reduced with hydrazine (Gutbier and Falco, *Z. anal. Chem.*, 1910, **49**, 289) and (*b*) the palladium was precipitated with dimethylglyoxime and weighed as such or ignited to the metal. The former method was preferable.

The chlorine in a solution of palladium dichloride cannot be determined by the addition of silver nitrate owing to the formation of a stable chestnut-coloured complex, $PdCl_2(OHAg)_2$ (Bellucci and Cesaris, *Gazzetta*, 1908, **38**, II, 602).

A weighed amount of the palladium salt (0·05—0·1 g.) was dissolved in 200 ml. of water, and the solution heated to 70°. On adding a warm solution of hydrazine sulphate a fine yellow precipitate formed, but when the mixture was made alkaline with dilute sodium hydroxide solution nitrogen was evolved and the palladium was precipitated as a sponge. After being boiled and digested for 1 hour the mixture was filtered and the paper and metal were ignited separately. The filtrate was acidified with dilute nitric acid, and chloride determined gravimetrically as silver chloride.

Reaction between Nitric Oxide and Palladium Dichloride.—1 G. of dry palladium dichloride was placed in a combustion boat in a narrow glass tube, and a slow stream of nitric oxide passed over it for 2 hours. The maroon dichloride gradually became dark brown; it was removed from the boat and quickly powdered, and the treatment with nitric oxide repeated for another hour. Excess of nitric oxide was removed by warming to 40°. The substance was analysed immediately after preparation; when the compound was stored in air nitric oxide was evolved, rapidly in a vacuum-desiccator. In contact with water nitric oxide was evolved and a black residue separated (Found : Pd, 46·2; Cl, 30·6. Calc. for $PdCl_2,2NO$: Pd, 44·9, Cl, 29·85%).

Reaction between Palladium Dichloride and Nitrosyl Chloride.—Excess of nitrosyl chloride was sealed with 1 g. of palladium dichloride, and the tube heated at 100° for 5 hours. The compound was insoluble in liquid nitrosyl chloride. Evaporation of the excess of nitrosyl chloride gave a bright red residue, stable in dry air or in a sealed tube but deliquescing in moist air to form a dark red liquid, which on further exposure solidified to a reddish-brown solid (probably the dihydrate). Nitric oxide was evolved on the addition of water, and the solid dissolved forming a red solution. In no case was a black residue obtained [Found : Prepn. (1) : Pd, 34·2, 34·7; Cl, 46·3; N, 8·8. Prepn. (2) : Pd, 35·01; Cl, 46·6, 46·8; Pd : Cl : N = 1 : 4·05 : 1·94. $PdCl_2,2NOCl$ requires Pd, 34·59; Cl, 45·95; N, 9·08%; Pd : Cl : N = 1 : 4 : 2).

Reaction between Palladous Nitrate and Nitrosyl Chloride.—At 100°, in a sealed tube, nitrosyl chloride reacted with palladous nitrate forming a pale orange-red layer. After opening of the tube, the nitrosyl chloride was allowed to boil off and a quantity of dinitrogen tetroxide was removed by gentle warming. The residue appeared to be identical with that obtained from palladium dichloride (Found : Pd, 34·7, 35·3; Cl, 45·6, 45·7; N, 9·4%; Pd : Cl : N = 1 : 3·93 : 2·05).

Reaction between Nitrosyl Chloride and Palladium.—Reaction between nitrosyl chloride and palladium strip commenced at room temperature, and a brown powder collected. The supernatant liquid was black. There was a considerable pressure of nitric oxide in the tube. After evaporation of the excess of nitrosyl chloride a brown deliquescent powder remained, which had similar properties to the product of reaction of palladium dichloride and nitric oxide. On gentle heating to 100° some nitrosyl chloride was evolved. The brown solid, when heated in a stream of dry nitrogen for 3 hours to 200°, left a maroon residue of palladium dichloride (Found : Pd, 59·3. Calc. for $PdCl_2$: Pd, 60·04%). The analyses of several preparations of the brown solid were inconsistent, suggesting that it was a mixture [Prepn. (1) : Pd, 36·3. Prepn. (2) : Pd, 41·3. Prepn. (3) : Pd, 37·5, 37·3%].

Reaction between Gold and Nitrosyl Chloride.—Very thin gold strip was not attacked by nitrosyl chloride at room temperature and only very slowly at 100°. After a week at 140° only a small quantity of orange-coloured powder formed, the liquid becoming black. The extent of the reaction between nitrosyl chloride and gold depended to some extent on the state of division of the metal, finely divided gold being attacked at room temperature.

On gentle warming the solid evolved nitrosyl chloride and became reddish-brown. Gold was determined as metal by precipitation with sulphur dioxide, and was so removed from the solution before the chlorine determination (Found : Au, 54·7, 54·6; Cl, 37·9, 38·0%; Cl : Au = 3·86. Calc. for $AuCl_3,NOCl$: Au, 54·3; Cl, 38·5% : Cl : Au = 4·0).

Reaction between Gold Trichloride and Nitrosyl Chloride.—Gold trichloride was prepared by heating liquid chlorine with finely divided gold in a sealed tube at 100° for one week (Found : Au, 64·5. Calc. for $AuCl_3$: Au, 64·9%). The deep-red gold trichloride rapidly absorbed nitrosyl chloride, becoming orange. It was set aside for one day in a sealed tube at room temperature (Found : Au, 54·8; Cl, 38·2%; Cl : Au = 3·9).

Reaction between Mercury and Nitrosyl Chloride.—Nitrosyl chloride did not react with mercury at −30°, but on warming to −20° violent reaction occurred and nitric oxide was evolved. This continued even when the reaction vessel was cooled to −40°. A dark grey solid, which rapidly became white in air, remained after evaporation of the nitrosyl chloride. This was mercurous chloride, and no mercuric chloride could be detected. On heating with nitrosyl chloride, further reaction occurred. The yellow addition compound was decomposed in a vacuum-desiccator over concentrated sulphuric acid and left mercuric chloride (Found : Hg, 72·2, 73·6. Calc. for $HgCl_2$: Hg, 73·85%).

Reaction between Silver Nitrate and Nitrosyl Chloride.—Excess of nitrosyl chloride with dried silver nitrate at room temperature reacted vigorously with the evolution of heat; the tube was heated in a water-bath for 2 days to ensure complete reaction. After opening, the tube was placed in ice-water and the liquid remaining was shown to be N_2O_4 (Found : 0·3140 g. of $AgNO_3$ gave 0·2649 g. of AgCl. Calc. for the reaction $AgNO_3 + NOCl = AgCl + NO{\cdot}NO_3$ (*i.e.*, N_2O_4) : AgCl = 0·2648 g.).

Reaction between Lead Nitrate and Nitrosyl Chloride.—Nitrosyl chloride was heated with dry lead nitrate on a water-bath for 2 days, the nitrosyl chloride was allowed to boil off, and a small quantity of N_2O_4 remained : $Pb(NO_3)_2 + 2NOCl = PbCl_2 + 2N_2O_4$ (Found : Pb, 73·8. Calc. for $PbCl_2$: Pb, 74·5%).

Preparation of Dinitrogen Tetroxide.—Dinitrogen tetroxide was prepared by Ramsay's method (*J.*, 1890, **57**, 590). Silicone grease, which is resistant to the gas, was used on all ground joints.

Reaction between Dinitrogen Tetroxide and Stannic Chloride.—At room temperature dinitrogen tetroxide reacted vigorously with stannic chloride, heat was evolved, and a yellow solid separated. Some decomposition occurred and analysis gave inconsistent results. Dry dinitrogen tetroxide was condensed on to stannic chloride at −20° and the temperature allowed to rise slowly to −10°. A canary-yellow solid separated. Excess of dinitrogen tetroxide was very difficult to remove, and the pasty *product* gave variable analyses. At 40° and 20 mm. pressure (¼ hour) no decomposition of the product was apparent, the excess of N_2O_4 was removed, and consistent analyses were obtained [Found : Prepn. (1) : Sn, 32·17; Cl, 37·7. Prepn. (2) : Sn, 31·9; Cl, 37·5; N, 9·6. Prepn. (3) : Sn, 32·2; Cl, 37·7, 37·8; N, 9·9%; Sn : Cl : N = 1 : 3·93 : 2·5. $SnCl_4,2{\cdot}5NO_2$ requires Sn, 31·2; Cl, 37·3; N, 9·2%]. The yellow deliquescent solid with a small amount of water dissolved completely to a green solution. A solution in sodium hydroxide solution gave nitrite and nitrate reactions.

Sublimation of the compound. On heating the solid in a stream of dry nitrogen, part formed a yellow sublimate, and white stannic oxide remained. Analysis of the sublimate gave no definite proportions.

Reaction between Dinitrogen Tetroxide and Titanium Tetrachloride.—Excess of dinitrogen tetroxide was condensed on to titanium tetrachloride at −80°. In a sealed tube a vigorous reaction occurred at room temperature, the liquid becoming ruby-red. When kept overnight the yellow solid formed redissolved and two liquid layers formed. The lower layer was red and viscous, the upper dark brown and mobile. After 2 hours' heating on a water-bath the tube was cooled to room temperature, whereupon the lower layer solidified. The tube was cooled in solid carbon dioxide, and a side arm and trap were sealed on. The trap was cooled in solid carbon dioxide, and the cooling jacket round the tube was replaced by ice-water. In this way unchanged dinitrogen tetroxide could be retained. After ½ hour 2—3 ml. of nitrosyl chloride had collected. The dinitrogen tetroxide and nitrosyl chloride which remained were boiled off at 30° and the yellow powder analysed [Found : Prepn. (1) : Ti, 27·5, 27·6; Cl, 2·88, 2·01; N, 15·5, 14·08%. After 2 days (sealed tube), Ti, 28·56; N, 13·65. Prepn. (2) : Ti, 19·06, 19·5; Cl, 1·5, 1·4; N, 18·49%. Calc. for $Ti(NO_3)_4$: Ti, 16·25; N, 18·92%].

Reactions between Sodium and Potassium Chloride and Liquid Dinitrogen Tetroxide.—Dinitrogen tetroxide was heated with (*a*) potassium chloride and (*b*) sodium chloride at 100° for 3 days in a sealed tube. After reaction the excess of tetroxide was boiled off and the residue heated to 120° for 1 hour [Found : N, 5·0 (from KCl); N, 2·6% (from NaCl)].

Reactions between Moist Sodium and Potassium Chloride and Gaseous Dinitrogen Tetroxide.—The dried alkali chloride was contained in a column at the top of which a ground joint led to a receiver cooled to −20°. Nitrogen peroxide was passed through dry cupric oxide (to remove any trace of nitric acid) before entering the base of the column. In the presence of 2% of water a definite reaction zone formed, which moved slowly up the column, the temperature of this part of the column being about 10° higher than the upper part.

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