396. *The Action of Nitrosyl Chloride on Some Metals and Their Compounds.*

By J. R. PARTINGTON and A. L. WHYNES.

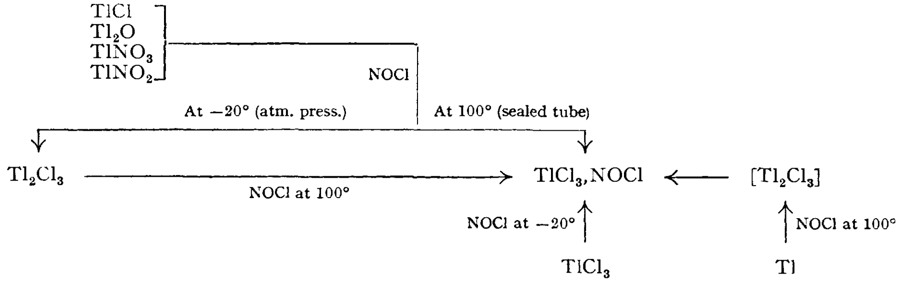
The action of nitrosyl chloride on several metals and their chlorides has been reinvestigated and much of the earlier work confirmed. The reaction has been extended to thallium, and a new method for the preparation of Tl_2Cl_3 described. Two new *compounds*, $InCl_3,NOCl$ and $GaCl_3,NOCl$, have been prepared in several ways.

WEBER (*Ann. Phys. Chem.*, 1863, **118**, 471) found that stannic chloride and titanium tetrachloride absorb " the very carefully dried vapour set free from concentrated aqua regia on warming," and that ferric chloride and aluminium chloride melt when heated in a gentle stream of the vapour. His descriptions of the reactions are concise and accurate, and he recognised that the product was a compound of the metal chloride and nitrosyl chloride.

Geuther (*J. pr. Chem.*, 1874, **8**, 354) prepared $BCl_3,NOCl$ by the action of dinitrogen tetroxide on boron trichloride and sublimation of the product. Sudborough (*J.*, 1891, **59**, 655) obtained the following compounds: $ZnCl_2,NOCl$, $TlCl,TlCl_3,2NOCl$, $FeCl_3,NOCl$, $SnCl_4,2NOCl$, $(SbCl_5)_2,5NOCl$, $BiCl_3,NOCl$, $AuCl_3,NOCl$, and $PtCl_4,2NOCl$. Although lead, mercury, aluminium, manganese, nickel, and arsenic formed the corresponding metallic chlorides, no stable addition products were observed. Cuttica, Tarchi, and Alinari (*Gazzetta*, 1923, **53**, 189) prepared $CuCl,NOCl$, and $TlCl_2,3NOCl$ by the action of nitrosyl chloride in a sealed tube on cuprous oxide and thallous oxide. The compound $TlCl_2,3NOCl$ has been wrongly reported in the literature as " thallous nitrosyl chloride," $2TlCl,3NOCl$ (Mellor, " Treatise, etc.," 1928, **8**, 617), and as $TlCl_2,NOCl$ (*Chem. Zentr.*, 1923, III, 357). Gall and Mengdehl (*Ber.*, 1927, **60**, 86) and Rheinbold and Wasserfuhr (*ibid.*, p. 732) prepared $AlCl_3,NOCl$ from aluminium chloride, whilst Sudborough obtained only aluminium chloride from aluminium and nitrosyl chloride. Asmussen (*Z. anorg. Chem.*, 1939, **243**, 127) measured the magnetic susceptibilities of some of the addition compounds and analysed most of them, including $AlCl_3,NOCl$ and $TlCl,TlCl_3,2NOCl$.

Thallium sesquichloride, $3TlCl,TlCl_3$ or Tl_2Cl_3, was first prepared by Crookes and Church (*Chem. News*, 1863, **8**, 1) by evaporation of a solution of thallous chloride with aqua regia until the evolution of chlorine ceased, but analyses by Werther (*J. pr. Chem.*, 1864, **91**, 385) gave the ratio Tl : Cl varying from 2 : 3 to nearly 1 : 3. Thomas (*Compt. rend.*, 1906, **142**, 840) stated that excess of liquid chlorine converts thallous chloride completely into Tl_2Cl_3, but he later (*Ann. Chim. Phys.*, 1907, **11**, 204) found that very dry liquid chlorine does not attack thallous chloride, and was unable to specify conditions for the exclusive formation of Tl_2Cl_3. Gogorishvili and Kul'gini (*J. Gen. Chem. Russia*, 1938, **8**, 302) prepared Tl_2Cl_3 by passing a current of chlorine into a solution containing a mixture of thallous sulphate and thallous nitrate with 30% hydrogen peroxide at room temperature.

The discrepant results with the aluminium and thallium compounds were thought worthy of reinvestigation. It was found that aluminium metal and aluminium trichloride gave the same product, $AlCl_3,NOCl$, with nitrosyl chloride. The products with thallous compounds and nitrosyl chloride varied with temperature. Thallium sesquichloride was obtained in theoretical yield by the action of nitrosyl chloride on thallous chloride at −20° and atmospheric pressure, and this reaction gives a convenient method of preparation: $2TlCl + NOCl = Tl_2Cl_3 + NO$. With thallous oxide the reaction is $Tl_2O + 3NOCl = Tl_2Cl_3 + 2NO + NO_2$. (Dinitrogen tetroxide has no action on thallium sesquichloride.) Thallous nitrate and nitrite were first converted into chloride, which then reacted as above with excess of nitrosyl chloride: $TlNO_3 + NOCl = TlCl + NO{\cdot}NO_3$ (*i.e.*, N_2O_4), and $2TlNO_2 + 3NOCl = Tl_2Cl_3 + 2N_2O_3 + NO$. The product obtained from thallium and nitrosyl chloride at 100° was $TlCl_3,NOCl$, chlorination taking place in stages; some Tl_2Cl_3 was isolated in the reaction. Thallous oxide and nitrosyl chloride at 100° gave $TlCl_3,NOCl$, which was also formed from thallous chloride, nitrate, nitrite, or the sesquichloride, and nitrosyl chloride in a sealed tube at 100°. Thallous bromide and thallous iodide and nitrosyl chloride formed $TlCl_3,NOCl$ with liberation of bromine and iodine. At −20° nitrosyl chloride reacted directly with anhydrous thallic chloride forming $TlCl_3,NOCl$. Reactions between thallous compounds and NOCl are summarised below.



Indium metal, indium monochloride, dichloride, and trichloride all gave a new *compound* $InCl_3,NOCl$. The chlorine of nitrosyl chloride replaces bromine in indium mono- or tri-bromide to give the trichloride, a molecule of nitrosyl chloride then being added to give the same compound. Indium dichloride or trichloride is most suitable for the preparation of $InCl_3,NOCl$.

Gallium reacts vigorously with nitrosyl chloride to form the new *compound* $GaCl_3$,NOCl, which is also obtained from gallium trichloride.

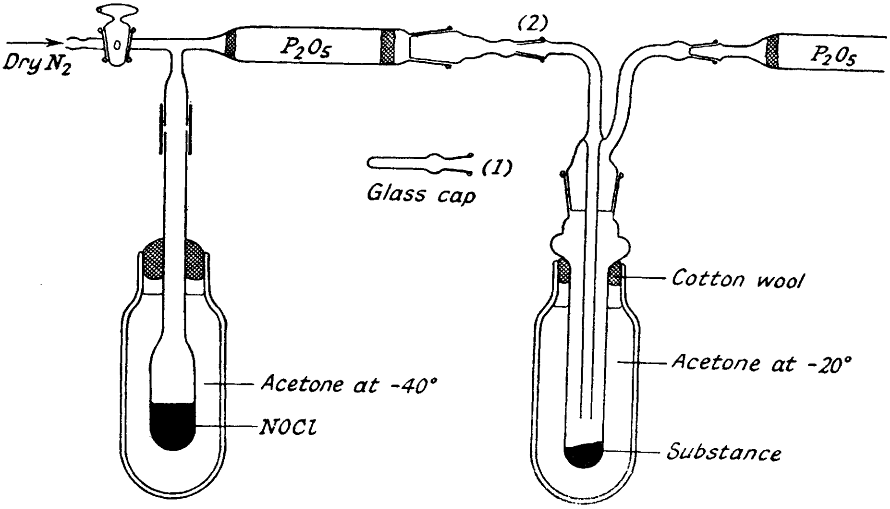
EXPERIMENTAL.

Preparation of Nitrosyl Chloride.—Nitrosyl chloride was obtained by warming nitrososulphuric acid and sodium chloride below 100° (Tilden, *J.*, 1874, **27**, 630). An all-glass apparatus was used, the gas being thoroughly dried with phosphoric oxide, condensed at −20°, and fractionally distilled in a slow current of nitrogen. The receivers were " Pyrex " tubes 14 cm. long, of 55 ml. capacity, and having 20-cm. necks. A small portion evaporated completely before the ice round the trap had melted, which was not the case if any nitrogen dioxide was present. Nitric oxide forms an almost black solution with nitrosyl chloride, and this accounts for the colour change in some reactions.

Two methods were used for reaction of nitrosyl chloride with metals and metallic salts : (*a*) the nitrosyl chloride was kept in contact with the substance at a low temperature (*e.g.*, −20°) for some hours ; (*b*) nitrosyl chloride was sealed with the substance, then heated to 100°. These methods are described in detail.

(*a*) The tube of nitrosyl chloride was cooled to −40° in a narrow-mouthed Dewar flask, and the tip broken, a piece of pressure tubing fitted, and the phial connected to the apparatus. Rubber is only slowly attacked by nitrosyl chloride. Dry nitrogen was passed through for some time, the Dewar flask removed, and the required amount of nitrosyl chloride allowed to distil, dried through 20 cm. of phosphoric oxide, and condensed in a trap on the substance, the exit tube being protected by 20 cm. of phosphoric oxide. By varying the amount of solid carbon dioxide added, any temperature between 10° and −70° could be obtained. Excess of nitrosyl chloride was distilled off by putting a small glass cap (1) (see Fig. 1) on the ground glass joint (2), removing the cooling bath from the trap, and allowing it to warm to room temperature. (*b*) The vapour pressure of nitrosyl chloride is considerable at 100°. Ordinary " Pyrex " tube, 1½ cm. diameter with 1-mm. walls, bursts at this temperature. The sealed tubes used were 1—1·5 cm. diameter with 3-mm. walls.

FIG. 1.



After reaction, the tube was cooled in solid carbon dioxide, whereupon the nitrosyl chloride solidified, but there was a considerable pressure of nitric oxide. The tip of the tube was heated with an oxygen flame, and a small hole 2 mm. in diameter blown in the glass. This was enlarged, the tube connected to the receiver, and the excess of nitrosyl chloride distilled off by removing the carbon dioxide jacket. The solid was quickly brought from the tube into a desiccator over concentrated sulphuric acid for about 5 minutes.

Methods of Analysis.—The compounds were very deliquescent; they were weighed in tightly stoppered bottles or in very thin glass bulbs which were broken by vigorous shaking with water in a stoppered bottle. The solution was always strongly acid.

Chlorine determination. Silver chloride was precipitated after acidification with nitric acid and weighed. A special method is described under the particular metal (*e.g.*, thallium).

Nitrogen determination. The nitrogen was determined by dissolving the substance in 5% sodium hydroxide solution, adding 10 ml. of 20% sodium hydroxide and 3 g. of very fine Devarda's alloy, and after 1 hour distilling the ammonia into standard hydrochloric acid, the excess being titrated with 0·1N-sodium hydroxide and methyl-red.

Formulæ of compounds previously described were confirmed by the following results. (S, Sudborough ; C, Cuttica *et al.* ; A, Asmussen ; G.M., Gall and Mengdehl ; W, Weber ; R.W., Rheinbold and Wasserfuhr ; *locc. cit.*)

Starting material.	Product.	Reference.	Found, %.			Required, %.		
			Cu.	Cl.	N.	Cu.	Cl.	N.
Cu	CuCl,NOCl	S.	39·19	43·45	8·01	38·64	43·14	8·5
Cu_2O	CuCl,NOCl	C.	38·02	42·82	—	—	—	—
CuCl	CuCl,NOCl	C., A., G.M.	38·16	43·62	—	—	—	—
			Zn.	Cl.	N.	Zn.	Cl.	N.
Zn	$ZnCl_2$,NOCl	S., A.	32·03	53·3	6·1	32·4	52·74	6·9
			Hg.	Cl.	N.	Hg.	Cl.	N.
$HgCl_2$	$HgCl_2$,NOCl	G.M., A.	60·14	31·16	4·40	59·5	31·58	4·15
HgCl	$HgCl_2$,NOCl	G.M.		Cl/Hg = 2·96	—		Cl/Hg = 3·0	
			Ti.			Ti.		
$TiCl_4$	$TiCl_4$,2NOCl	W., R.W.	15·2	65·64	—	14·93	66·33	—
			Sn.			Sn.		
Sn	$SnCl_4$,2NOCl	S.	29·71	53·49	—	30·37	54·35	7·16
$SnCl_2$	$SnCl_4$,2NOCl	—	29·82	53·91	6·51	—	—	—
$SnCl_4$	$SnCl_4$,2NOCl	W., R.W., A.	29·92	53·85	7·08	—	—	—
			Mn.			Mn.		
$MnCl_2$	$MnCl_2$,NOCl	G.M., A.	28·71	54·95	7·51	28·73	55·62	7·31
			Fe.			Fe.		
Fe	$FeCl_3$,NOCl	S.	24·18	62·50	—	24·53	62·30	6·15
$FeCl_3$	$FeCl_3$,NOCl	W., G.M.	24·29	62·60	6·3	—	—	—
$FeCl_2$	$FeCl_3$,NOCl	G.M.	24·7	62·07	6·4	—	—	—

The Reaction with Aluminium.—Nitrosyl chloride was condensed on very fine aluminium powder; at −40° there was no reaction but at −20° reaction occurred with incandescence. 0·5 G. of very fine aluminium wire was cooled to −60° and excess of nitrosyl chloride added; a very vigorous reaction took place on warming to about −20°, nitric oxide being evolved. Vigorous reaction occurred with strips of aluminium foil at −40° but could be controlled by further cooling. After standing in contact with nitrosyl chloride for 14 hours a red syrupy liquid was obtained; when warmed to 30° to remove excess of nitrosyl chloride, this gave a yellow solid which evolved nitric oxide with water and appeared to be identical with that obtained from aluminium chloride. The aluminium was precipitated as hydroxide and ignited to oxide (Found: Al, 14·21, 14·34; Cl, 71·01; N, 6·7. Calc. for $AlCl_3$,NOCl: Al, 13·62; Cl, 71·30; N, 7·04%).

The Reaction with Aluminium Chloride.—Nitrosyl chloride was condensed at −20° on 1·0 g. of iron-free, resublimed aluminium chloride and allowed to stand at this temperature for six hours; excess was removed from the viscous red syrup as above (Found: Al, 13·92; Cl, 71·83; N, 7·05%). The lemon-yellow compound evolved nitrosyl chloride on standing for 3—4 minutes in air, leaving a white residue of aluminium chloride. With a small amount of water, nitric oxide was evolved, and the aluminium chloride formed rapidly dissolved when a further drop of water was added. A small quantity of $AlCl_3$,NOCl was sublimed at atmospheric pressure in a current of dry nitrogen. In a sealed tube it melted with decomposition at 109—112°.

Action of Nitrosyl Chloride on Gallium.—Nitrosyl chloride was condensed on 0·4 g. of gallium at −50°; no reaction occurred but at −30° nitric oxide was evolved and the metal dissolved to a black solution. The reaction continued for some time even when the tube was placed in solid carbon dioxide. At room temperature considerable heat was evolved. On heating on a water-bath the liquid separated into two layers, the lower plum-coloured, the upper black (gallium chloride melts at 77°). On shaking, the two layers mixed and did not separate on cooling or on standing for several weeks. At room temperature a viscous red liquid was obtained which tenaciously retained nitrosyl chloride. The tube was warmed at 60°, whereupon excess of nitrosyl chloride was readily evolved, giving a yellow crystalline *solid* which was immediately sealed for analysis. It was extremely deliquescent, forming a colourless liquid in a matter of seconds. The gallium was estimated by sulphite hydrolysis (Dennis and Bridgman, *J. Amer. Chem. Soc.*, 1918, **40**, 1531), the gallium hydroxide being obtained in a granular, easily filtrable form (Found: Ga, 29·77, 29·63; Cl, 58·2. $GaCl_3$,NOCl requires Ga, 28·84; Cl, 58·75%).

Reaction with Gallium Trichloride.—Gallium trichloride was prepared by passing dry, air-free hydrogen chloride over the metal (1 g.) in the boat (Fig. 2), and the temperature was slowly raised to 200°. The exit end of the tube was protected with phosphoric oxide. After 3 hours (40 bubbles/min.) all the gallium had reacted. The apparatus was swept out with nitrogen, and the gallium trichloride melted and run into the side-arm *A*, which was cooled in solid carbon dioxide, and nitrosyl chloride passed in. The tube was then sealed off along *ab*. The trichloride was very soluble in nitrosyl chloride, forming a red solution (Found: Ga, 29·0, 30·28; Cl, 58·1. $GaCl_3$,NOCl requires Ga, 28·84; Cl, 58·75%).

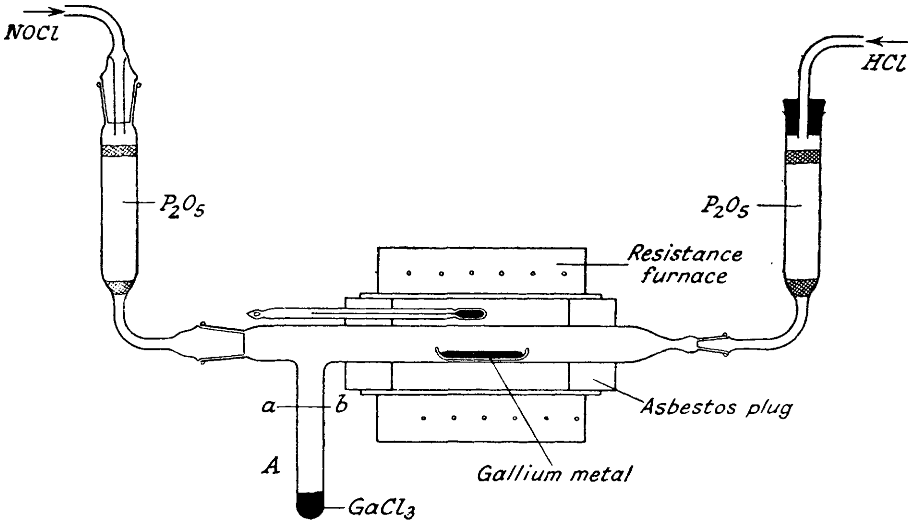
Action of Nitrosyl Chloride on Indium.—At room temperature in a sealed tube there was a slight reaction between 1·2 g. of fine indium shavings and nitrosyl chloride. A yellow outside layer formed which prevented further action. The tube was heated at 100° for 5 days, a further portion then being attacked, but a large amount of indium was unchanged. The solution in water gave characteristic In^{3+} reactions.

Indium dichloride was prepared by passing dry, air-free hydrogen chloride over molten indium; the metal changed to a reddish-brown colour, then clear yellow, and volatilised completely, a white powder being deposited on the cold parts of the tube. At room temperature vigorous reaction occurred between indium dichloride and nitrosyl chloride, the solid turning yellow, then orange. After 4 days' standing, a yellow deliquescent solid was obtained which dissolved readily in a small amount of water, evolving nitric oxide. It was stable in dry air with no tendency to evolve nitrosyl chloride; when gently heated, it evolved nitrosyl chloride and the white residue dissolved completely in water, no grey indium being deposited. On stronger heating the residue sublimed forming white plates in the upper part of the tube (Found: In, 51·45. Calc. for $InCl_3$: In, 51·87%). The sublimate was sealed with nitrosyl chloride and on heating dissolved completely to a red solution; on cooling, yellow flakes separated, giving the same yellow solid as previously. Indium was determined by a modification of the method of Moser and Siegmann (*Monatsh.*, 1930, **55**, 14).

A weighed amount of the *compound* (*ca.* 0·2 g.) was decomposed with 150 ml. of water, 3 drops of methyl-orange added, dilute ammonia (1 : 10) run in dropwise from a burette until the indicator turned yellow, and the solution heated to boiling; then 1 ml. excess of ammonia was added, the liquid being stirred all the time. The flocculent precipitate of indium hydroxide, on being gently warmed and stirred, became granular and compact. It was filtered off, and washed with a small quantity of hot water until free from chloride (the sesquioxide is volatile in the presence of chlorides), and the filter-paper and residue carefully dried and ignited below 700°. After acidification with nitric acid, chlorine was determined in the filtrate in the usual way [Found : (*a*) In, 39·31; Cl, 49·06; Cl/In = 4·03. (*b*) In, 39·62; Cl, 49·04; Cl/In = 4·0. (*c*) Cl, 48·28. (*d*) N, 4·0. $InCl_3$,NOCl requires In, 40·02; Cl, 49·51; N, 4·8%].

Indium monochloride. A weighed quantity of the dichloride (1·0 g.) was introduced into a thick "Pyrex" tube, a slight excess (10%) of indium shavings added, and the tube sealed, shaken, and warmed with a small burner. The contents rapidly formed a dark red, almost black, liquid which was kept in the molten state for several minutes. On cooling, it solidified to a light red solid. The mixture was gently heated in a porcelain boat in a stream of dry nitrogen; orange-red monochloride sublimed, leaving a grey bead of excess indium. Indium monochloride reacted with nitrosyl chloride in a sealed tube at room temperature, turning yellow, and the supernatant liquid became black immediately. When the compound was heated in a water-bath, the nitrosyl chloride became cherry-red but became black again on cooling and shaking : $InCl + 3NOCl = InCl_3,NOCl + 2NO$ (Found : Cl, 48·97%).

FIG. 2.



Indium trichloride was prepared by passing a current of dry, air-free chlorine over the heated dichloride at 370°. The trichloride sublimed as pearly white plates in the colder parts of the tube. It dissolved completely in water, with no trace of indium due to hydrolysis of unchanged indium dichloride. 1·5 G. of indium trichloride rapidly absorbed nitrosyl chloride, turning yellow immediately. The addition compound was fairly soluble in liquid nitrosyl chloride but not to the same extent as the aluminium, gallium, or thallium compound. On gentle heating, nitrosyl chloride was evolved and indium trichloride could be obtained as previously (Found : In, 39·26, 39·29; Cl, 49·25%; Cl/In = 4·05).

Indium tribromide. Indium tribromide was prepared by heating indium in a current of bromine and nitrogen. Bromination took place through the monobromide (dark red) and dibromide (colourless). The product depended to some extent on the temperature; at 200° the dibromide was obtained after 4½ hours' passage of bromine. At 370° indium tribromide sublimed as pearly white hexagonal plates (the largest 0·7 cm.) which were sublimed twice in dry nitrogen; yield 90—95% (Found : In, 32·21; Br, 67·81. Calc. for $InBr_3$: In, 32·35; Br, 67·65%). Reaction occurred between indium tribromide and nitrosyl chloride at room temperature, the solid turned yellow, the supernatant liquid black. On being heated in a water-bath it partly dissolved, crystallising on cooling. After removal of excess of nitrosyl chloride a reddish-brown solid remained which, when gently warmed by the hand, evolved bromine. The yellow solid remaining contained no bromine (Found : Cl/In = 4·07).

Indium monobromide, prepared by warming the tribromide with indium shavings, was sublimed in nitrogen as for the monochloride. The carmine indium monobromide was not deliquescent; on addition of water there was no immediate reaction, but it turned grey, due to the separation of indium, after 15 minutes, forming a solution of the tribromide. With nitrosyl chloride the solid turned yellow, and after 2 days' heating on a water-bath the yellow $InCl_3$,NOCl was obtained. There was no trace of bromide in the residue.

Preparation of Thallium Compounds.—The thallium compounds used were prepared from thallous sulphate; all precautions were taken to ensure pure products.

The Action of Nitrosyl Chloride on Thallous Chloride.—Excess of nitrosyl chloride was condensed on to 1 g. of thallous chloride at −30°. No reaction occurred after one hour, but at −20°, reaction took place, nitric oxide was evolved, and the substance turned yellow. It was left for 14 hours at −20°. The yellow solid appeared to be homogeneous under a microscope. It was not deliquescent and was insoluble in cold water. It dissolved in hot water to form a colourless solution which on cooling deposited glittering hexagonal plates, which could be recrystallised from water with three drops of concentrated nitric acid without hydrolysis. Since Tl^{3+} interferes with chlorine estimation as silver chloride, it was removed before the addition of silver nitrate.

A weighed amount of the compound (*ca.* 0·2 g.) was washed into 300 ml. of water and a few drops of dilute nitric acid and heated to boiling. The solution was cooled to room temperature, and the Tl^{3+} removed by precipitation with potassium hydroxide solution. The residue was washed with hot water, and the filtrate acidified with dilute nitric acid and precipitated with silver nitrate.

Determination of thallium. Precipitation as thallous chromate was used. About 0·2 g. of the substance was dissolved in 100 ml. of water, 10 ml. of sulphurous acid added, and the whole stirred and allowed to stand for a day to reduce Tl^{3+} to Tl^{+}. Excess of sulphur dioxide was boiled off, the solution cooled, neutralised with ammonia, heated to 80°, and 2 g. of potassium chromate added (10% soln.) with constant stirring. After standing at room temperature for 2 days, the precipitate was collected in a Gooch crucible, washed with 1% potassium chromate solution, then with 50% alcohol, and dried at 120° to constant weight [Found (in product straight from reaction): Cl, 19·2, 20·98; (in recrystallised product): Cl, 21·73, 21·99; Tl, 78·71, 79·07; Cl/Tl = 1·49. Calc. for $3TlCl,TlCl_3$, *i.e.*, Tl_2Cl_3: Cl, 20·67; Tl, 79·33; Cl/Tl = 1·5]. Thus the product before and after recrystallisation was Tl_2Cl_3.

Action of Nitrosyl Chloride on Thallium.—Metallic thallium was unattacked by nitrosyl chloride at room temperature, but when heated to 100° for 5 days it formed a yellow solid. The nitrosyl chloride became black when viewed through 0·75 cm. On cooling in solid carbon dioxide, yellow crystals separated from the solution. The solid was very deliquescent but did not evolve nitrosyl chloride at room temperature; it dissolved completely even in a small amount of water, evolving nitric oxide. Thallium was determined after reduction, and chloride after removal of Tl^{3+} (Found: Tl, 53·89, 53·8; Cl, 37·24, 37·04; Cl/Tl = 3·9; N, 3·36. $TlCl_3,NOCl$ requires Tl, 54·29; Cl, 37·73; N, 3·72%). The yellow *solid* was qualitatively examined for Tl^{+}. The solution was made alkaline with 3% potassium hydroxide solution, and the bulky brown precipitate of hydrated Tl_2O_3 filtered off and washed with hot water. Potassium chromate did not give a precipitate in the filtrate (*i.e.*, no Tl^{+} present). In a similar reaction with Tl_2Cl_3 the presence of Tl^{+} as well as Tl^{3+} could readily be detected.

The Incomplete Reaction of Thallium with Nitrosyl Chloride.—The two reagents were heated together at 100° for 1 day. The top part of the solid consisted of the yellow addition compound; at the bottom of the tube a yellow solid remained (with unchanged thallium) which was insoluble in cold water, but soluble in hot water, forming yellow hexagonal plates on cooling (Found: Tl, 79·69. Calc. for Tl_2Cl_3: Tl, 79·33%).

Reaction between Tl_2Cl_3 *and Nitrosyl Chloride.*—On heating Tl_2Cl_3 with nitrosyl chloride for 6 hours it dissolved completely, forming a red solution. On removal from the tube and shaking, the liquid turned black: $Tl_2Cl_3 + 5NOCl = 2(TlCl_3,NOCl) + 3NO$. After removal of the excess of nitrosyl chloride the addition compound was obtained which gave no Tl^{+} reaction.

Reaction between Nitrosyl Chloride and Thallous Chloride at 100°.—1·2 G. of thallous chloride and 5 ml. of nitrosyl chloride, heated for 3 days at 100°, formed a black solution. On cooling, the solid separated slowly and there was some tendency to supersaturation. The yellow *compound* contained no Tl^{+} (Found: Tl, 54·71; Cl, 37·83%; Cl/Tl = 3·98).

Reaction between Nitrosyl Chloride and Thallous Oxide.—Thallous hydroxide was prepared by double decomposition of thallous sulphate and carbonate-free barium hydroxide. The crystals were partly dehydrated in a desiccator over phosphoric oxide, then heated to 120° in a steady current of dry nitrogen.

At −20° nitrosyl chloride reacted very slowly with thallous oxide, but at −10° nitric oxide was evolved and the solid turned yellow. The temperature was kept at −10° to −20° for 48 hours, and excess of nitrosyl chloride distilled off, leaving a yellow solid which could be recrystallised from dilute nitric acid in characteristic crystals of Tl_2Cl_3.

Nitrosyl chloride was heated with 1 g. of thallous oxide at 100° for 10 hours. The solid product reacted with water, evolving nitric oxide and precipitating Tl_2Cl_3. It was quickly broken up, more nitrosyl chloride added, and the tube resealed and heated for 3 days. The yellow solid then obtained dissolved completely even in a small amount of water (Found: Tl, 54·99%).

Action of Nitrosyl Chloride on Thallous Nitrate.—Nitrosyl chloride was condensed on to 1 g. of the nitrate at −20°, and after 20 hours excess of nitrosyl chloride was evaporated off at about 5°. The solid obtained was orange; about 0·5 ml. of brown-red liquid remained, which smelt of nitrogen dioxide; this was boiled off into sodium hydroxide solution which gave good nitrite and nitrate reactions. After 5 hours in an evacuated desiccator over phosphoric oxide the orange solid turned yellow and could be recrystallised as Tl_2Cl_3: $TlNO_3 + NOCl = TlCl + N_2O_4$.

Action of Nitrosyl Chloride on Thallous Nitrate.—When these reagents were heated to 100° the liquid turned black, and the solid dissolved completely, separating out as very small hexagonal crystals on cooling (Found: Tl, 53·84%). From the black excess of nitrosyl chloride green "dinitrogen trioxide" could be distilled.

Action of Nitrosyl Chloride on Thallous Nitrite.—The nitrite was prepared by double decomposition of the sulphate with barium nitrite. Evaporation of the solution at 80° gave a light orange solid. The concentrated solution was pale yellow, the dilute colourless.

At −20° thallous nitrite rapidly absorbed nitrosyl chloride; the orange solid turned yellow, and recrystallisation gave Tl_2Cl_3.

1 G. of thallous nitrite was heated with nitrosyl chloride on a water-bath for 3 days. After excess of the latter had been boiled off, about ¼ ml. of dinitrogen tetroxide remained. The yellow addition *compound* dissolved completely in water (Found: Tl, 53·89%).

Reaction between Nitrosyl Chloride and Thallous Bromide.—The bromide was sealed with the chloride and heated on a water-bath for 4 days. It dissolved completely and hexagonal crystals separated on cooling (Found: Tl, 54·49; Cl, 36·7%; Cl/Tl = 3·88).

Reaction between Nitrosyl Chloride and Thallous Iodide.—When 1 g. of the iodide was heated with nitrosyl chloride, it remained yellow and the liquid became black; on further heating, a black solution was formed, from which small hexagonal crystals separated after cooling. A black solid remained which reacted with water liberating iodine; this was extracted three times with carbon tetrachloride The aqueous solution was made alkaline with sodium hydroxide, warmed, and filtered, and the filtrate gave no reaction for Tl^+.

Action of Nitrosyl Chloride on Thallic Chloride.—Crystalline hydrated thallic chloride placed over phosphoric oxide at 20 mm. pressure for 1 week dissolved in the water of crystallisation, and then solidified to a white powder. Chloride was estimated after removal of Tl^{3+} by sodium hydroxide (Found: Cl, 33·95. Calc. for $TlCl_3$: Cl, 34·26%). Nitrosyl chloride was condensed on anhydrous thallic chloride at −20°. The solid rapidly absorbed the first few drops and became yellow, but it dissolved on shaking with more liquid, forming a red solution, which deposited small hexagonal crystals on cooling. The solid appeared to be identical with that obtained from thallium metal (Found: Cl, 37·55%).

Conclusions.—(1) The following compounds have been confirmed: $CuCl,NOCl$, $ZnCl_2,NOCl$, $HgCl_2,NOCl$, $TiCl_4,2NOCl$, $SnCl_4,2NOCl$, $MnCl_2,NOCl$, $FeCl_3,NOCl$.

(2) The action of nitrosyl chloride on Ga and $GaCl_3$ gave the new compound $GaCl_3,NOCl$.

(3) Indium or its chlorides or bromides gave a new compound, $InCl_3,NOCl$.

(4) Compounds described by Sudborough ($TlCl,TlCl_3,2NOCl$) and Cuttica *et al.* ($TlCl_2,3NOCl$) are really $TlCl_3,NOCl$.

(5) Contrary to Sudborough's results, it was found that aluminium and aluminium chloride both form $AlCl_3,NOCl$ with nitrosyl chloride.

The authors thank Professor R. P. Linstead, C.B.E., F.R.S., of the Chemical Research Laboratory, Teddington, for the loan of gallium metal, and Imperial Chemical Industries Ltd. for a gift of nitrosyl chloride. One of them (A. L. W.) is indebted to East Suffolk Education Committee for a maintenance grant.

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON).

[*Received, December 22nd,* 1947.]