

**244.** *Exchange of Chlorine-36 of Some Group III Chlorides with Nitrosyl and Phosphoryl Chlorides.*

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Complete and rapid exchange of radiochlorine has been observed between aluminium, gallium, indium, and thallium(III) chloride and liquid nitrosyl chloride as solvent, in agreement with the conception of the 1:1 addition compounds formed in these systems as nitrosonium compounds. Transfer of radioactivity in similar systems with phosphoryl chloride as solvent was very slow, except in the presence of added inactive chloride ion. The nature of the species in solution, and possible structures for the addition compounds, *i.e.*,  $\text{POCl}_3, \text{MCl}_3$ , are discussed.

Two explanations have been offered for the solvent-solute interaction which takes place when metal chlorides are dissolved in non-aqueous solvents such as phosphoryl chloride and nitrosyl chloride. According to the first, the solvent behaves as a chloride-ion donor, and the products comprise the cation characteristic of the solvent, *i.e.*,  $\text{POCl}_2^+$ ,  $\text{NO}^+$ , and complex chlorometallate ions. The second is based on Lewis acid-base interaction involving unshared electrons of the oxygen atom of the solvent, the metal chloride behaving as a Lewis acid; ionization of the acid-base adduct may then occur, producing species such as  $[\text{MCl}_2(\text{POCl}_3)_n]^+[\text{MCl}_4]^-$ .

The solvent-system approach<sup>1</sup> has proved valuable in correlating the results of conductance measurements, conductimetric titrations, and spectrophotometric data, but recent structure determinations indicate that in two phosphoryl chloride addition compounds, namely,  $\text{POCl}_3, \text{SbCl}_5$ <sup>2</sup> and  $2\text{POCl}_3, \text{TiCl}_4$ ,<sup>3</sup> bonding occurs by way of the phosphoryl-oxygen atom in the solid state. Infrared<sup>4</sup> and Raman spectra<sup>5</sup> of various phosphoryl chloride adducts have been interpreted as supporting this conclusion, while the

<sup>1</sup> Gutmann, *J. Phys. Chem.*, 1959, **63**, 378; *Osterr. Chem.-Ztg.*, 1961, **62**, 326.

<sup>2</sup> Lindqvist and Brändén, *Acta Cryst.*, 1959, **12**, 642.

<sup>3</sup> Brändén and Lindqvist, *Acta Chem. Scand.*, 1960, **14**, 726.

<sup>4</sup> Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.

<sup>5</sup> Gerding, Koningsstein, and van der Warm, *Spectrochim. Acta*, 1960, **16**, 881.

similar behaviour of solutions of anhydrous iron(III) chloride in phosphoryl chloride and in triethyl phosphate<sup>6</sup> is significant evidence in favour of the oxygen-donor theory.

In several cases, rapid exchange of radiochlorine between chloride ion and inorganic chlorides considered to be ionizing solvents has been demonstrated.<sup>7-9</sup> Although this is in agreement with the postulate of self-ionization in these media, it cannot prove that such ionization in fact occurs. In organic solvents, the exchange between chloride ion and phosphoryl chloride is of the first order in both species, indicating that a mechanism involving self-ionization of phosphoryl chloride may not be important.<sup>8</sup>

The behaviour of nitrosyl chloride is superficially similar to that of phosphoryl chloride. However, the higher dielectric constant and "long" N-Cl bond indicate a greater possibility for chloride-ion transfer in this solvent. Spectroscopic studies show that the nitrosonium ion (NO<sup>+</sup>) is present in certain nitrosyl chloride addition compounds,<sup>10</sup> whereas the presence of the analogous ion POCl<sub>2</sub><sup>+</sup> has not been unequivocally demonstrated.

Both phosphoryl chloride and nitrosyl chloride form addition compounds with Group IIIA trichlorides and it was of interest to examine the radiochlorine exchange between these compounds and an excess of the oxychlorides.

#### EXPERIMENTAL

Nitrosyl and phosphoryl chloride were purified as described previously.

*Aluminium Chloride.*—The compound, labelled with <sup>36</sup>Cl, was prepared<sup>11</sup> by heating silver chloride containing <sup>36</sup>Cl with 30-mesh aluminium in a vacuum and was purified by vacuum-sublimation.

*Gallium Trichloride.*—The radioactive compound was prepared similarly, from metallic gallium and silver chloride (Found: Cl, 60.2. Calc. for GaCl<sub>3</sub>: Cl, 60.4%).

*Indium Trichloride.*—The inactive material was prepared by passing chlorine over heated indium and was purified by vacuum-sublimation. The labelled compound resulted when nitrosyl chloride of high specific activity was added to indium chloride. After several hours at -20°, the yellow adduct, NOCl,InCl<sub>3</sub>, was isolated. This was heated at 140° for 4 hr., leaving pure indium trichloride (Found: In, 51.6; Cl, 48.0. Calc. for InCl<sub>3</sub>: In, 51.9; Cl, 48.1%).

*Thallium(III) Chloride.*—A stream of chlorine was passed into a suspension of thallium(I) chloride in water until a clear solution was obtained. Dissolved chlorine was removed by heating the solution on a steam-bath and the residue was taken to dryness *in vacuo* at room temperature. The remaining white solid was heated to constant weight (P<sub>2</sub>O<sub>5</sub> at 46° *in vacuo*). No decomposition to thallium(I) occurred in these circumstances. In a sealed tube, the compound became yellow at 145° and melted at 148—153°. Cooling gave a pale yellow solid containing both thallium(I) and thallium(III) (Found: Tl, 65.1; Cl, 34.2. Calc. for TlCl<sub>3</sub>: Tl, 65.7; Cl, 34.4%). Labelled thallium(III) chloride was obtained by adding H<sup>36</sup>Cl (0.1 ml.) (1 μc) to a solution of thallium(III) chloride (3 g.) in the minimum amount of distilled water. Treatment as above gave the anhydrous material.

*Exchange Runs.*—The apparatus and general techniques were those described previously for exchange reactions with nitrosyl chloride<sup>7</sup> and phosphoryl chloride.<sup>8</sup> Solutions of the metal chloride were prepared with minimum contact with the atmosphere. After various times, samples of the solvent were removed under a vacuum and hydrolysed in dilute sodium hydroxide solution, and the chloride ion was precipitated as mercury(I) chloride. Samples for radioassay were matted to infinite thickness. A standard was prepared for each exchange run on the basis of complete exchange between the radioactive metal chloride and the solvent.

#### RESULTS AND DISCUSSION

*Reactions in Nitrosyl Chloride.*—1:1 Addition compounds between nitrosyl chloride and the Group IIIA metal chlorides may be obtained by direct combination of the

<sup>6</sup> Meek and Drago, *J. Amer. Chem. Soc.*, 1961, **83**, 4322.

<sup>7</sup> Lewis and Wilkins, *J.*, 1955, 56.

<sup>8</sup> Lewis and Sowerby, *J.*, 1957, **33**.

<sup>9</sup> Masters, Potter, Asher, and Norris, *J. Amer. Chem. Soc.*, 1956, **78**, 4252.

<sup>10</sup> Gerding and Houtgraaf, *Rec. Trav. chim.*, 1953, **72**, 21; Waddington and Klanberg, *Z. anorg. Chem.*, 1960, **304**, 185.

<sup>11</sup> Wallace and Willard, *J. Amer. Chem. Soc.*, 1950, **72**, 5275.

components or, in some instances, by treating the free metal with nitrosyl chloride.<sup>12</sup> Aluminium, gallium, and thallium trichloride are readily soluble in liquid nitrosyl chloride, but the indium compound is only sparingly so. Burg and Campbell<sup>13</sup> have shown that aluminium chloride behaves as a strong uni-univalent electrolyte in liquid nitrosyl chloride. The results of radiochlorine exchange summarized in the Table show complete exchange in all cases within the time of separation of the first solvent fraction.

Exchange of radiochlorine between nitrosyl chloride and the Group IIIA trichlorides at  $-10^{\circ}$ .

Solute	Concn. (mole l. <sup>-1</sup> )	Time of contact (min.)	Activity of NOCl (counts/min.)	Value for 100% exchange (counts/min.)
AlCl <sub>3</sub> .....	0.313	4	260	250
		9	259	
		31	256	
GaCl <sub>3</sub> .....	0.169	4	127	128
		8	132	
		34	127	
InCl <sub>3</sub> .....	0.062	10	129	136
		27	135	
TlCl <sub>3</sub> .....	0.124	4	104	107
		10	104	
		35	103	

The rapid randomization of radiochlorine, in conjunction with the conductance data, indicates that the most likely structure for the Group IIIA addition compounds is one involving the nitrosonium ion and a tetrachlorometallate ion, *e.g.*,  $\text{NO}^+\text{AlCl}_4^-$ . We previously reported rapid chlorine exchange with other soluble metal chlorides [iron(III) and antimony(V)] and discussed possible structures for the addition compounds.<sup>14</sup> Tin(IV) chloride and nitrosyl chloride give a very stable, insoluble compound,  $2\text{NOCl}\cdot\text{SnCl}_4$ , which does not exchange chlorine with an excess of nitrosyl chloride; in this case, other evidence is available supporting the nitrosonium ion formulation.<sup>15</sup>

*Solutions in Phosphoryl Chloride.*—In contrast to the rapid radiochlorine exchange mentioned above, the homogeneous exchange between labelled aluminium, gallium, and thallium(III) chloride and phosphoryl chloride at  $18^{\circ}$  is very slow (at concentrations similar to those shown in the Table for nitrosyl chloride, counts of 0—4 per minute were observed for 3—160-minutes' contact). Even after thallium(III) chloride had been in contact with an excess of phosphoryl chloride for 14 days, the solvent activity was 3 counts/min., compared with 230 counts/min. on the basis of complete exchange.

A similar situation arises in the aluminium chloride-carbonyl chloride system. Although no information is available on the homogeneous exchange between chloride ion and liquid carbonyl chloride (owing to the insolubility of all the ionic chlorides tested), exchange between labelled aluminium chloride and liquid carbonyl chloride is very slow.<sup>16</sup> A 1:1 addition compound between the components was formulated as  $(\text{COCl})(\text{AlCl}_4)$ , but Huston *et al.* showed that the carbonyl chloride in the solvate was only slightly more active than the solvent, and thus, that the chlorine atoms in the addition compound were not equivalent, as is implied by the formula above.

Chlorine-exchange experiments show that no transfer of radioactivity occurs between phosphoryl chloride and an excess of boron trichloride, but complete exchange (within one minute at  $0^{\circ}$ ) in the presence of an excess of phosphoryl chloride.<sup>17</sup> The mechanism postulated depends upon self-ionization of the solvent and formation of an intermediate,

<sup>12</sup> Partington and Whynes, *J.*, 1948, 1952.

<sup>13</sup> Burg and Campbell, *J. Amer. Chem. Soc.*, 1948, **70**, 1964.

<sup>14</sup> Lewis and Sowerby, *J.*, 1957, 1617.

<sup>15</sup> Lewis and Sowerby, *J.*, 1956, 150.

<sup>16</sup> Huston, *J. Inorg. Nuclear Chem.*, 1956, **2**, 128; Huston and Lang, *ibid.*, 1957, **4**, 30.

<sup>17</sup> Herber, *J. Amer. Chem. Soc.*, 1960, **82**, 792.

$[\text{Cl}_4\text{BO}=\text{PCl}_3]^-$ , from chloride ion and the 1:1 addition compound. The infrared spectrum of the solid 1:1 adduct has been interpreted as indicating the presence of  $\text{BCl}_4^-$  ion,<sup>18</sup> but this has recently been questioned and the alternative structure involving bond formation through the oxygen atom of phosphoryl chloride has been suggested.<sup>19</sup> This is in agreement with the interpretation of the infrared spectra of other addition compounds of phosphoryl chloride.<sup>4</sup>

Few data are available on the properties of solutions of the Group III chlorides in phosphoryl chloride. Conductance measurements for the aluminium<sup>20</sup> and the thallium(III) chloride system<sup>21</sup> indicate behaviour as very weak and fairly strong electrolytes, respectively. Greenwood and Wade<sup>22</sup> have reported that the molten addition compound of gallium trichloride behaves as  $[\text{POCl}_2]^+[\text{GaCl}_4]^-$ , but is mainly in the form of ion-pairs.

The absence of radiochlorine exchange between solute and solvent apparently precludes formulæ similar to those postulated for nitrosyl chloride, *i.e.*, of the type  $\text{POCl}_2^+\text{MCl}_4^-$ . The equivalence of the chlorine atoms in the tetrahedral chloro-anions would lead to rapid exchange, if self-ionization of the solvent occurred. A tacit assumption here is that the  $\text{AlCl}_4^-$  ion is labile towards exchange with (solvated) chloride ion itself. An alternative formulation, based on a donor bond between the phosphoryl-oxygen atom and the metal, would agree with the absence of exchange. As phosphoryl chloride contains two donor sites, a third structure can be written for the addition compounds in question. The complex may be formulated as involving a bond between a chlorine atom and the metal  $\text{OPCl}_2-\text{Cl}\cdot\cdot\text{MCl}_3$ . This also would be in agreement with the exchange results, if fission of the phosphorus-chlorine bond did not then occur.

Addition of a soluble ionic chloride to solutions of aluminium trichloride in phosphoryl chloride will presumably form  $\text{AlCl}_4^-$  ions in solution,  $\text{AlCl}_3$  being a stronger chloride-ion acceptor than phosphoryl chloride. Several exchange reactions were, therefore, carried out in which a slight excess of inactive tetraethylammonium chloride was added beyond that required to convert all the labelled aluminium chloride into the anion. For example, tetraethylammonium chloride was added to 0.165M-aluminium chloride so that the molar  $\text{Et}_4\text{NCl}:\text{AlCl}_3$  ratio was 2:1. In these circumstances, complete exchange occurred within 5 minutes, the minimum time required to separate a fraction of phosphoryl chloride for radioassay. When the molar ratio was less than unity, exchange was not complete, *e.g.*, 49% exchange occurred when a ratio of 0.52:1 was used. This exchange was complete within the time of separation but no further exchange occurred during longer periods. A similar type of exchange was observed for the thallium(III) chloride-tetraethylammonium chloride-phosphoryl chloride systems.

These observations imply that (1) the ion  $\text{AlCl}_4^-$  undergoes chlorine exchange with phosphoryl chloride, (2) the ion  $\text{AlCl}_4^-$  is not formed in absence of an ionic chloride, and (3) exchange does not take place between the  $\text{AlCl}_4^-$  ion and aluminium chloride bonded to phosphoryl chloride.

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<sup>18</sup> Gerrard, Mooney, and Willis, *J.*, 1961, 4255.

<sup>19</sup> Wartenberg, Proc. 7th Internat. Conference on Co-ordination Chem., 1962, Stockholm, preprints, p. 214.

<sup>20</sup> Gutmann and Himml, *Z. phys. Chem. (Frankfurt)*, 1955, 4, 157; Gutmann and Baaz, *Monatsh.*, 1959, 90, 729.

<sup>21</sup> Lewis and Sowerby, *Chem. Soc. Special Publ. No. 10*, 1957, 123.

<sup>22</sup> Greenwood and Wade, *J.*, 1957, 1516.