Salt-like Behaviour of Covalent Halides. Part IV.[1-3] † Electrolytic Conductance of Solutions of Thionyl Chloride, and its Reactions with Silver Salts and Lewis Acids in Acetone

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Thionyl chloride behaves as a weak electrolyte in acetone solution; values for its molar conductance are given. The mode of ionisation is envisaged as formation of chlorothionyl and thionyl cations. Metathetic exchanges of thionyl chloride with silver(I) nitrate and perchlorate produce thionyl dinitrate, $SO(NO_3)_2$, and chlorothionyl and thionyl perchlorates, $ClSO(ClO_4)$ and $SO(ClO_4)_2$, respectively, in acetone solutions. Its reactions with Lewis acids give series of chlorothionyl and thionyl salts of complex chloro-anions, $ClSO^+(MCl_{x+1}^-)$, $SO^{2+}(MCl_{x+1}^-)_2$, (M = Fe^{III}, P^{III}, P^V, OP^V, As^{III}, Sb^{III}, Sb^V, Ti^{IV}, and Sn^{IV}), and $(SO^{2+})_3(MCl_{x+3}^{3-})_2$ (M = Fe^{III}, P^{III}, OP^V, As^{III}, Sb^{III}, Sb^V, Ti^{IV}; x = 3—5), which have been identified by conductimetric evidence in acetone solutions.

THIONYL CHLORIDE, $SOCl_2$, has been shown to behave as an ionising solvent.[4] The mode of ionisation is believed to be as in equation (1). Acid–base reactions in this

$$SOCl_2 \rightleftharpoons ClSO^+ + Cl^- \rightleftharpoons SO^{2+} + 2Cl^- \quad (1)$$

solvent have also been reported.[5] The Lewis acids $SbCl_3$, $SbCl_5$, $FeCl_3$, $AlCl_3$, $SnCl_4$, *etc.* have been found to function as acids in thionyl chloride solution because of their tendency to form chlorometallate anions thereby increasing the relative concentration of the solvent cation, $ClSO^+$ [*cf.* equation (2)]. Mercury(II) chloride,

$$SbCl_5 + SOCl_2 \rightleftharpoons ClSO^+SbCl_6^- \rightleftharpoons ClSO^+ + SbCl_6^- \quad (2)$$

zinc(II) chloride, substituted ammonium chlorides, amines, and organic carbonyl compounds function as bases in this solvent. The solvent adducts with bases give rise to cationic adducts, *e.g.* $(R_3N,ClSO)^+$ and $(R_2CO,ClSO)^+$, and release chloride ions [equations (3) and (4)]. The complex chlorometallate anions, or the

$$Et_3N + SOCl_2 \rightleftharpoons Et_3N,SOCl_2 \rightleftharpoons (Et_3N,ClSO)^+ + Cl^- \quad (3)$$

$$Me_2CO + nSOCl_2 \rightleftharpoons Me_2CO,nSOCl_2 \rightleftharpoons (Me_2CO,nClSO)^{n+} + nCl^- \ (n = 1 \text{ or } 2) \quad (4)$$

organic bases, are considered responsible for stabilising the chlorothionyl cation, $ClSO^+$, but there is as yet no evidence, however, for stabilisation of thionyl ion, SO^{2+}.

The solvent-system approach has proved valuable in correlating results of conductance measurements, conductimetric titrations, and spectrophotometric data which are in accord with formation of complex anions *via* chloride-ion transfer from the solvent ionisation equilibrium to the solute [equations (1) and (2)].[4,5] However, *X*-ray,[6] i.r.,[7] and Raman[8] studies have led some authors[9,10] to suspect the validity of the ionisation of thionyl chloride [equation (1)]. It was therefore of interest to examine the electrolytic behaviour of thionyl chloride in suitable solvents, and, then, to study some of its salt-like reactions. The main object of the present investigation was to evaluate thionyl chloride as a source of thionyl ions.

RESULTS AND DISCUSSION

The behaviour of thionyl chloride in liquid sulphur dioxide has been studied previously.[11-13] It dissolves freely to give a conducting solution, and in this medium has been found to undergo acid–base reaction with calcium sulphite, salt-like exchanges with ammonium thiocyanate, silver(I) acetate, and potassium bromide leading to corresponding thionyl derivatives, and complexation with antimony(III) chloride to give the thionyl salt $(SO^{2+})_3(SbCl_6^{3-})_2$.[13]

In explaining these reactions Jander and his co-workers[12,14] assumed dissociation of the solvent sulphur dioxide as in equation (5), and ionisation of the solute

$$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-} \quad (5)$$

thionyl chloride as in equation (1). On the other hand, Johnson *et al.*[15] observed that when thionyl chloride (bromide) is dissolved in liquid sulphur dioxide tagged with the radioactive isotope ^{35}S, sulphur exchange is very slow, which would not be the case if the solvent

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† Refs. 1—3 are regarded as Parts I—III of this series.

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[15] R. E. Johnson, T. H. Norris, and J. L. Huston, *J. Amer. Chem. Soc.*, 1951, **73**, 3052.

and thionyl chloride both gave SO^{2+} ions. Sulphur exchange, however, becomes rapid in the presence of excess of halide ions. This could be explained by assuming formation of $ClSO^+$ ions by equilibration of the solvent cations, SO^{2+}, with halide ions [equation (6)].[11]

$$SO^{2+} \overset{Cl^-}{\rightleftharpoons} ClSO^+ \qquad (6)$$

Other workers[16,17] consider ^{35}S exchange between thionyl chloride and liquid sulphur dioxide to follow a molecular mechanism entailing base catalysis by halide ions. Later, Potter[10] found both triethylamine and acetone to catalyse sulphur exchange.

Bateman, *et al.*[18] discounted the ionisation theory of liquid sulphur dioxide [equation (5)] on the grounds that they were unable to isolate products of the type $(R_3N,SO)^{2+}SO_3^{2-}$ from mixtures of liquid SO_2 and Et_3N. Potter[10] drew similar conclusions in respect of thionyl chloride when he failed to obtain evidence for existence of either $(Et_3N,ClSO)^+$ or $(Me_2CO,ClSO)^+$ ionic species in SO_2–$SOCl_2$–Et_3N or SO_2–$SOCl_2$–Me_2CO mixtures respectively. This led him to disfavour Spandau and Brunneck's[5] solvent-system concept for reactions in thionyl chloride. However, Masters *et al.*,[19] while studying chlorine radio exchange reactions with $SOCl_2$ in liquid SO_2, considered equilibrium (7) to be operative in this medium.

$$SOCl_2 \rightleftharpoons ClSO^+ + Cl^- \qquad (7)$$

The utility of acetone as an ionising solvent for sulphur dichloride, SCl_2, has been demonstrated previously,[2,3] when otherwise unstable chlorosulphur cation, SCl^+, was found to be stabilised in acetone solution. Thionyl chloride has been found to dissolve readily in acetone to form conducting solutions. In the present work measurements on *freshly prepared* solutions showed that the conductance rose with addition of thionyl chloride. This is attributed to the increase in the number of available ions through ionisation of thionyl chloride. The conductance of a 1·02M- solution was $3{\cdot}62 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 25 °C (*cf.* $2 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ for the pure solvent). Solutions covering a range of concentration were examined. When molar conductance was plotted against the square root of the molar concentration, end points corresponding to the higher dilution fell nearly on a straight line which, on extrapolation to zero concentration, gave a value of $50\ \Omega^{-1}\ cm^2\ mol^{-1}$ for the molar conductance at infinite dilution. This is a significantly high value considering the nature of the type of electrolyte. Thus, the relatively high conductance of these solutions leads to the conclusion that, in acetone, thionyl chloride ionises with the probable occurrence of solvation of the resulting ions.

Ionisation of thionyl chloride in the presence of acetone has also been considered previously by Spandau and Brunneck.[5] They used acetone as solute in thionyl chloride solvent, wherein the former functions as a base. Solvation of acetone molecules by thionyl chloride was followed by release of chloride ions [equation (4)]. The cation $(Me_2CO,nClSO)^{n+}$ ($n = 1$ or 2) was found to survive through a complex set of reactions.[5] When the proportion of acetone is in relative excess, *i.e.* as the solvent with thionyl chloride as the solute, the mode of solvation probably changes. Thionyl chloride can function as a weak Lewis base, using the lone pair on the oxygen atom, and, also, more surprisingly, as a weak Lewis acid, using vacant *d* orbitals of sulphur. In a basic medium, *viz.* acetone solution, extensive solvation of thionyl chloride probably increases the electron density on the sulphur atom, which may help scission of the S–Cl bonds. Moreover, in the presence of excess of base the probability of any thionyl ion being stabilised through solvation is high, thereby shifting equilibrium (8) more to the right. This gives rise to the possibility

$$\begin{aligned} SOCl_2 + nMe_2CO &\rightleftharpoons nMe_2CO,SOCl_2 \rightleftharpoons \\ &(nMe_2CO,ClSO)^+ + Cl^- \overset{Me_2CO}{\rightleftharpoons} \\ &\qquad (nMe_2CO,SO)^{2+} + 2Cl^- \qquad (8) \end{aligned}$$

of formation of the thionyl cation (solvated) and chloride anions in the solution [*cf.* equation (4)].

This is supported by the fact that the two chlorine atoms of thionyl chloride are quantitatively precipitated by silver(I) ions from acetone solutions. Both silver(I) nitrate and perchlorate were found to precipitate solid silver(I) chloride, and to give thionyl dinitrate, $SO(NO_3)_2$, and thionyl perchlorate, $SO(ClO_4)_2$, respectively, which remain in solution.[20] The ionic nature of these reactions

$$SOCl_2 + AgNO_3 \longrightarrow ClSO(NO_3) + AgCl \qquad (9)$$

$$SOCl_2 + 2AgNO_3 \longrightarrow SO(NO_3)_2 + 2AgCl \qquad (10)$$

$$SOCl_2 + AgClO_4 \longrightarrow ClSO(ClO_4) + AgCl \qquad (11)$$

$$SOCl_2 + 2AgClO_4 \longrightarrow SO(ClO_4)_2 + 2AgCl \qquad (12)$$

was confirmed by conductimetric evidence. Titrations of acetone solutions of thionyl chloride with acetone solutions of either silver(I) nitrate or perchlorate resulted in steady variation of specific conductance and there were sharp breaks in the conductance curves (Figure 1) at appropriate molar ratios of 1 : 1 and 1 : 2, implying precipitation of the first and second chlorine atoms respectively. In the case of the perchlorate the intermediate chlorothionyl perchlorate, $ClSO(ClO_4)$, was detectable [Figure 1(*b*)]. Previously, Thorpe[21] found that powdered silver(I) nitrate reacted directly with thionyl chloride to give solid silver(I) chloride and a product of composition $ClSO(NO_3)$. The latter was probably chlorothionyl nitrate [see equation (9)]. This is clear evidence in support of ionic dissociation of thionyl chloride [equation (1)].

Conductimetric studies further showed that the thionyl

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[16] B. J. Masters and T. H. Norris, *J. Amer. Chem. Soc.*, 1955, **77**, 1346.

[17] R. H. Herber, T. H. Norris, and J. L. Huston, *J. Amer. Chem. Soc.*, 1954, **76**, 2051.

[18] L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1944, 243.

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perchlorates were relatively stronger electrolytes in acetone solution than thionyl chloride and nitrate. The small increase in conductance at the beginning of the titration of thionyl chloride with silver(I) nitrate in acetone medium [Figure 1(*a*)] is attributed to micellar conductivity of the sol $(AgCl)Cl^-ClSO^+$, in very dilute solution.[3,22] This is probably characteristic of electrolytically weak sulphur–nitrate systems, and has been observed previously[3] when a solution of sulphur dichloride in acetone was titrated conductimetrically with an acetone solution of silver(I) nitrate. This effect was not observed either in the presence of an initial excess of silver ions, or, in the presence of relatively stronger electrolytes, *viz.* the perchlorates.

As was observed earlier, sulphur dioxide functions as an acid in thionyl chloride.[4,5] Its behaviour may therefore be represented as in equation (13) [*cf.* equation (2)].

$$SOCl_2 + SO_2 \rightleftharpoons ClSO^+ + ClSO_2^- \qquad (13)$$

When SO_2 is present in relative excess chloride abstraction may proceed further [equation (14)]. This may

$$SOCl_2 + 2SO_2 \rightleftharpoons SO^{2+} + 2ClSO_2^- \qquad (14)$$

$$ClSO_2^- \rightleftharpoons SO_2 + Cl^- \qquad (15)$$

explain some of Jander's observations,[12] even if the ionisation mechanism of sulphur dioxide is not considered.[18] When, however, a new base, *viz.* Et_3N or Me_2CO, is added to the system SO_2–$SOCl_2$, the base, like the chloride ions, will naturally compete for the SO_2 molecules and become associated[18,23] with the latter (SO_2), which are present in large excess. Possible association of Et_3N or Me_2CO with SO_2 molecules may make them unavailable for further interaction with $SOCl_2$, precluding formation of either $(Et_3N,ClSO)^+$ or $(Me_2CO,ClSO)^+$ ion in the mixtures. This explains why Potter[10] failed to observe such ionic species in sulphur dioxide solutions. Moreover, his reaction conditions are not comparable to those in which Spandau and Brunneck[5] produced the salt $(Et_3N,ClSO)^+SbCl_6^-$, when a solution of triethylamine in pure thionyl chloride was used for reaction with antimony pentachloride.

The fact that pure thionyl chloride has a small but definite conductance ($3{\cdot}5 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$) points to ionisation as indicated earlier.[4] When Lewis acids or bases are added to thionyl chloride the conductance of the solution rises, indicating further ionisation. In thionyl chloride solutions of Lewis acids, the primary solvation step may be followed by ionisation of two types [equation 16(a), as postulated by Spandau and Brunneck[5] or 16(b) as advocated by Meek[9]].

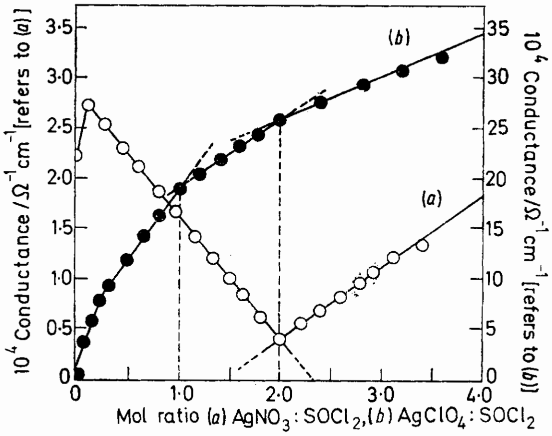

FIGURE 1 Conductimetric titration of thionyl chloride in acetone with (*a*) silver(I) nitrate and (*b*) silver(I) perchlorate

$$\begin{tikzcd}
 & (ClSO^+)_n(MCl_{x+n})^{n-} \text{ (a) (solvent-system model)} \\
nSOCl_2 + MCl_x \overset{K_1}{\rightleftharpoons} nSOCl_2,MCl_x \arrow[ur, shift left, "K_2'"] \arrow[ur, shift right, leftarrow] \arrow[dr, shift left, "K_2''"] \arrow[dr, shift right, leftarrow, "MCl_x"'] & & (16) \\
 & [(n+y)SOCl_2,MCl_{x-y}]^{y+}(MCl_{x+y})^{y-} \text{ (b) (solvent-co-ordination model)}
\end{tikzcd}$$

Conductimetric titration of acetone solutions of thionyl chloride with acetone solutions of various Lewis acids furnished interesting results. When thionyl chloride was titrated with iron(III) chloride, both freshly dissolved in acetone, steady variation of conductance took place initially, but the conductivity curve (Figure 2) showed two distinct breaks corresponding to the $SOCl_2 : FeCl_3$ molar ratios of 1 : 1 and 1 : 2, implying formation of the complex salts chlorothionyl tetrachloroferrate(III), $ClSO^+FeCl_4^-$, and thionyl bis[tetrachloroferrate(III)], $SO^{2+}(FeCl_4^-)_2$ (solvation not shown). The chlorothionyl salt exists as an intermediate to the thionyl salt. When the same titration was carried out in the reverse order, *i.e.* an acetone solution of iron(III) chloride was titrated with an acetone solution of thionyl chloride, the conductivity curve first showed a sharp break at an $SOCl_2 : FeCl_3$ molar ratio of 1 : 2, indicating rapid formation of the thionyl salt, and then with excess of thionyl

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[23] R. H. Herber and T. H. Norris, *J. Amer. Chem. Soc.*, 1954, **76**, 3849.

chloride another break occurred at a point corresponding to a molar ratio of 3 : 2, which represented formation of the complex $3SOCl_2,2FeCl_3$, which may also be formulated as trithionyl bis[hexachloroferrate(III)], $(SO^{2+})_3(FeCl_6^{3-})_2$. It appears that when the iron(III) chloride is initially present in excess, scission of the second S–Cl bond in $SOCl_2$ is rapid [see Figure 2(*b*)].

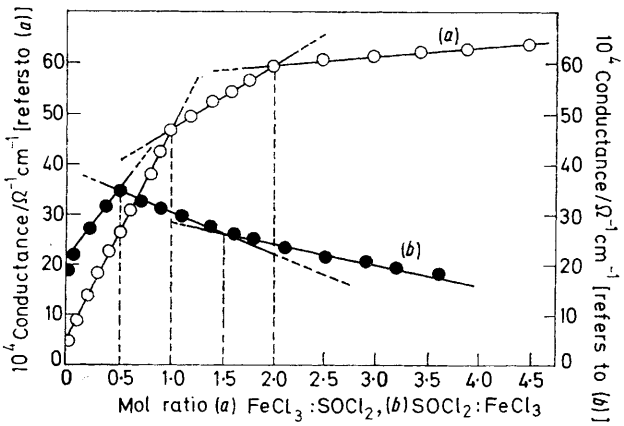

FIGURE 2 Conductimetric titration in acetone solution of (*a*) thionyl chloride with iron(III) chloride, (*b*) iron(III) chloride with thionyl chloride

When similar reactions of thionyl chloride were undertaken with phosphorus(III) chloride, PCl_3, chlorothionyl tetrachlorophosphate(III), $ClSO^+PCl_4^-$, and thionyl bis[tetrachlorophosphate(III)], $SO^{2+}(PCl_4^-)_2$, were formed in acetone solution. When phosphorus(III) chloride was initially present in excess, *i.e.* thionyl chloride was added to it slowly, the 1 : 2 complex salt was formed immediately (Figure 3). If the addition of thionyl chloride was continued, a more complex anion incorporated in the 3 : 2 complex salt, formulated as trithionyl bis[hexachlorophosphate(III)], $(SO^{2+})_3(PCl_6^{3-})_2$, resulted. Phosphorus(V) chloride, PCl_5, reacted with thionyl chloride to give chlorothionyl hexachlorophosphate(V), $ClSO^+PCl_6^-$, and thionyl bis[hexachlorophosphate(V)], $SO^{2+}(PCl_6^-)_2$, in acetone solution. By reversing the order of addition of the reactants conductimetric evidence showed formation of the 1 : 2 complex salt (Figure 4).

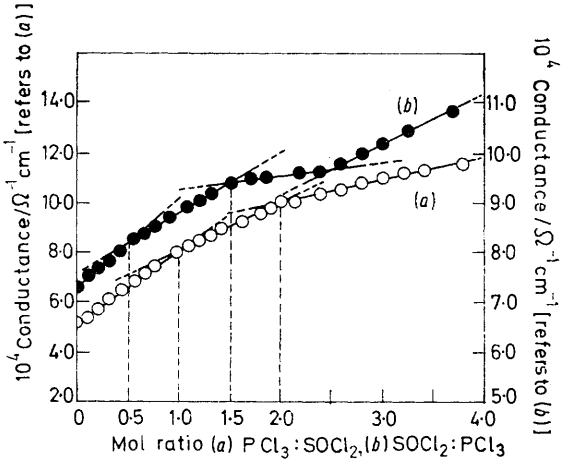

FIGURE 3 Conductimetric titration in acetone solution of (*a*) thionyl chloride with phosphorus(III) chloride, (*b*) phosphorus(III) chloride with thionyl chloride

The reaction of phosphoryl chloride with thionyl chloride in acetone solution led to formation, first, of the 1 : 1 complex salt chlorothionyl tetrachloro-oxophosphate(V), $ClSO^+OPCl_4^-$, and then the 1 : 2 complex salt, thionyl bis[tetrachloro-oxophosphate(V)], $SO^{2+}(OPCl_4^-)_2$. When an acetone solution of phosphoryl chloride was titrated with thionyl chloride, in excess of thionyl chloride, the titration curve showed a distinct break at $SOCl_2 : POCl_3$ molar ratio of 3 : 2. This observation leads one to believe formation of the 3 : 2 complex salt in solution which, as before, can be formulated as trithionyl bis[hexachloro-oxophosphate(V)], $(SO^{2+})_3(OPCl_6^{3-})_2$. Of the various chlorophosphate anions which have been postulated during the present set of reactions, PCl_4^- and PCl_6^- and PCl_6^{3-} are known species; the five-co-ordinate tetrachloro-oxophosphate $OPCl_4^-$ corresponds to PCl_6^-, having one oxygen atom replacing two chlorine atoms. The seven-co-ordinate hexachloro-oxophosphate $OPCl_6^{3-}$ has no exact parallel known, and is unusual. Its structure is not immediately understood. Further studies are in progress.

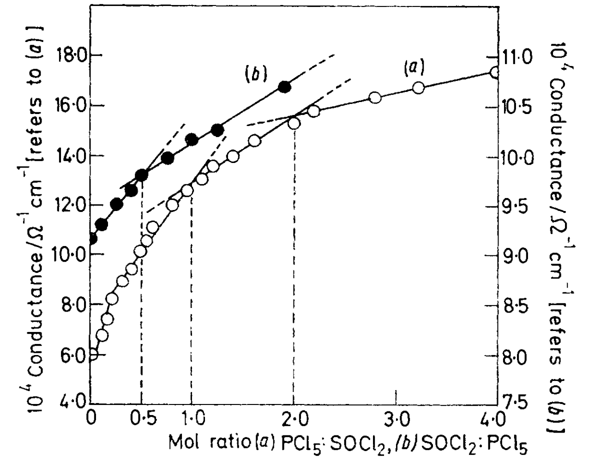

FIGURE 4 Conductimetric titration in acetone solution of (*a*) thionyl chloride with phosphorus(V) chloride, (*b*) phosphorus(V) chloride with thionyl chloride

It will be seen below that the two antimony chlorides undergo a similar pattern of reactions as the phosphorus chlorides with thionyl chloride in acetone solution, but, unfortunately, exact comparison with the two arsenic chlorides is not possible. Arsenic(III) chloride, $AsCl_3$, however, was found to react with thionyl chloride in acetone solution, giving two complex salts, chlorothionyl tetrachloroarsenate(III), $ClSO^+AsCl_4^-$, and thionyl bis[tetrachloroarsenate(III)], $SO^{2+}(AsCl_4^-)_2$. By varying the mode of mixing of the reactants, *i.e.* adding thionyl chloride to arsenic(III) chloride, conductimetric evidence suggested immediate formation of the 1 : 2 complex salt, and, in excess of thionyl chloride, formation of the 3 : 2 complex salt, formulated as trithionyl bis[hexachloroarsenate(III)], $(SO^{2+})_3(AsCl_6^{3-})_2$, in acetone solution.

Antimony(III) chloride, $SbCl_3$, on slow addition to thionyl chloride, both in acetone solution, resulted in formation, first, of the 1 : 1 complex salt, chlorothionyl tetrachloroantimonate(III), $ClSO^+SbCl_4^-$, and then the 1 : 2 complex salt, thionyl bis[tetrachloroantimonate(III)], $SO^{2+}(SbCl_4^-)_2$. On reversing the order of addition of the reactants, the conductimetric evidence showed ready formation of the 1 : 2 complex salt, and then, in excess of thionyl chloride, the 3 : 2 complex salt trithionyl bis[hexachloroantimonate(III)], $(SO^{2+})_3(SbCl_6^{3-})_2$. A similar salt to the latter was previously reported [13] as being formed in liquid sulphur dioxide solution. Antimony(V) chloride reacted with thionyl chloride in acetone medium to give chlorothionyl hexachloroantimonate(V), $ClSO^+SbCl_6^-$, and thionyl bis[hexachloroantimonate(V)], $SO^{2+}(SbCl_6^-)_2$. Reversing the mode of addition of the reactants, *i.e.* when thionyl chloride was added to antimony(V) chloride, immediate formation of the 3 : 2 complex, $3SOCl_2,2SbCl_5$, was indicated. This complex, by analogy with the above cases, may be formulated as trithionyl bis[octachloroantimonate(V)], $(SO^{2+})_3(SbCl_8^{3-})_2$. Salts containing $SbCl_4^-$, $SbCl_6^-$, and $SbCl_6^{3-}$ ions are known. Higher chloroantimonates, *viz.* $SbCl_7^{2-}$ and $SbCl_8^{3-}$, have been reported as salts of Mg^{II}, Fe^{III}, and Cr^{III}, but their structures appear to be less certain.[24,25]

Titanium and tin chlorides behaved similarly to the Group V chlorides. Titanium(IV) chloride, $TiCl_4$, reacted with thionyl chloride leading to formation of chlorothionyl pentachlorotitanate(IV), $ClSO^+TiCl_5^-$, and thionyl bis[pentachlorotitanate(IV)], $SO^{2+}(TiCl_5^-)_2$, in acetone solution. By reversing the order of addition, *i.e.* thionyl chloride to titanium(IV) chloride, conductimetric evidence showed formation, first, of the 1 : 2 complex salt and, then, on addition of excess of thionyl chloride, the 3 : 2 complex salt, formulated as trithionyl bis[heptachlorotitanate(IV)], $(SO^{2+})_3(TiCl_7^{3-})_2$. Tin(IV) chloride, $SnCl_4$, when added slowly to thionyl chloride, reacted as usual to give in acetone solution the 1 : 1 and the 1 : 2 complex salts, chlorothionyl pentachlorostannate(IV), $ClSO^+SnCl_5^-$, and thionyl bis[pentachlorostannate(IV)], $SO^{2+}(SnCl_5^-)_2$, respectively. By reversing the order of addition, *i.e.* thionyl chloride to tin(IV) chloride, both in acetone solutions, conductimetric evidence identified formation of the 1 : 2 complex salt. It is interesting to note formation of the ions $TiCl_5^-$, $TiCl_7^{3-}$, and $SnCl_5^-$, which are less common than those of $TiCl_6^{2-}$ and $SnCl_6^{2-}$.

It is therefore seen that in acetone solution thionyl chloride reacts with Lewis acids through chloride-ion transfer giving rise to complex chloro-anions and thionyl cations. The step-wise reactions are as in equations (17) and (18) (solvation not shown: M = Fe^{III}, P^{III}, P^V, As^{III}, Sb^{III}, Sb^V, Ti^{IV}, or Sn^{IV}; and $x = 3—5$).

$$SOCl_2 + MCl_x \rightleftharpoons ClSO^+(MCl_{x+1}^-) \qquad (17)$$

$$ClSO^+(MCl_{x+1}^-) + MCl_x \rightleftharpoons SO^{2+}(MCl_{x+1}^-)_2 \qquad (18)$$

In excess of thionyl chloride the reaction stoicheiometry in some cases is changed to $3SOCl_2 : 2MCl_x$, and the complex salt formed is formulated as $(SO^{2+})_3(MCl_{x+3}^{3-})_2$

$$3SOCl_2 + 2MCl_x \rightleftharpoons (SO^{2+})_3(MCl_{x+3}^{3-})_2 \qquad (19)$$

[equation (19), M = Fe^{III}, P^{III}, OP^V, As^{III}, Sb^{III}, Sb^V, or Ti^{IV}; $x = 3—5$]. On the other hand, the mode of reaction of Lewis acids with ' absolute ' thionyl chloride was found to follow the course as represented in equation (16a) (M = Fe^{III}, Al^{III}, Sb^{III}, Sb^V, or Sn^{IV}; $x = 3—5$; $n = 3—1$).[5] This representation is based on the mode of ionisation of $SOCl_2$ [equation (1)]. There is however a fundamental difference in the nature of the products formed in acetone compared with that in pure thionyl chloride. The product of the interaction, for example, of iron(III) chloride in ' absolute ' thionyl chloride solution was formulated as $(ClSO^+)_3FeCl_6^{3-}$ on conductimetric evidence, where iron attains its maximum chlorine co-ordination number of six. There is no evidence for the existence of the 1 : 1 complex salt $ClSO^+FeCl_4^-$ under these conditions, whereas in acetone the ion $FeCl_4^-$ is most commonly formed [*cf.* equations (17) and (18)]. This is probably due to the greater solvating power of acetone compared with that of thionyl chloride. Evidently, the relative order of basicity of the co-ordinating groups appears to be $SOCl_2 < Me_2CO < Cl^-$. Also, the apparent failure to form thionyl salts in pure thionyl chloride clearly indicates that the effect of the polarising power of the acceptor molecule is minor compared with that of solvation in bringing about ionisation of the S–Cl bonds in thionyl chloride.

In acetone solution reactions of thionyl chloride proceed in steps; ionisation of the two S–Cl bonds is rate determining. The steps may however merge if the polarisation energy is matched with the solvation energy by increasing the relative initial concentration of the Lewis acid [see curve (*b*) in Figures 2—4]. Maximum chlorine co-ordination for the central atom may be attained by making excess of thionyl chloride available for interaction with the Lewis acid, as is the case in pure thionyl chloride [*cf.* equations 16a and 19].

As observed earlier, conductimetric data on complexometric reactions in thionyl chloride can be explained by both the solvent-system [5] and solvent-co-ordination models.[9] In the present case the possibility for occurrence of any equilibrium of the type (22) is of little significance in the context of conductimetric results pertaining to MCl_x–$SOCl_2$ titrations in acetone, unless of

$$3SOCl_2 + FeCl_3 \rightleftharpoons 3SOCl_2,FeCl_3 \rightleftharpoons (ClSO^+)_3FeCl_6^{3-} \qquad (20)$$

(Solvent-system model)

$$12SOCl_2 + 4FeCl_3 \rightleftharpoons 4(3SOCl_2,FeCl_3) \rightleftharpoons (4SOCl_2,FeCl_2^+)_3FeCl_6^{3-} \qquad (21)$$

(Solvent-co-ordination model)

$$m(Me_2CO),FeCl_3 \rightleftharpoons (m + 1)Me_2CO,FeCl_2^+ + Cl^- \qquad (22)$$

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[24] R. F. Weinland and C. Feige, *Ber.*, 1903, **36**, 252.

[25] N. V. Sidgwick, ' Chemical Elements and their Compounds,' Clarendon Press, Oxford, 1950, vol. 1, p. 800.

course the added $SOCl_2$ can occupy co-ordinating positions over the central (metal) atom by displacing Me_2CO groups, which is unlikely as $SOCl_2$ is a weaker base than Me_2CO. It is possible that, although in the solid state oxochlorides may sometimes act co-ordinatively through their oxygen atoms towards Lewis acids, in solutions of suitable ionising solvents the chloride-transfer mechanism is operative. The prerequisite of all such reactions however is solvation of thionyl chloride by acetone molecules; this helps to generate and stabilise the chlorothionyl and thionyl cations [equation (8)]. The stability of the highly charged chloro-anions is probably attributable, in turn, to the large cation $(n\mathrm{Me_2CO,SO^{2+}})_n$.

TABLE 1

Conductance of thionyl chloride in freshly prepared acetone solutions at 25 °C

Concn./mol l^{-1}	0·0003	0·0005	0·0010	0·0020	0·0040	0·0080	0·0160	0·0638	0·2250	0·510	1·020
$10^4\kappa/\Omega^{-1}$ cm^{-1}	0·015	0·016	0·025	0·34	0·64	1·12	2·00	5·57	19·10	29·80	36·20
Λ/Ω^{-1} cm^2 mol^{-1}	49·60	32·00	25·00	16·70	15·90	13·80	12·50	8·25	7·48	5·85	3·56

TABLE 2

Conductimetric titrations in acetone solutions

Titre	Quantity (*g*)	Titrant	Concentration (M)	Breaks in conductance curve at $SOCl_2$: M * molar ratio	Composition of complex formed (solvation not shown)	Structure (solvation not shown)
$SOCl_2$	0·076	$AgNO_3$	0·03	1 : 2	$SO(NO_3)_2$	$SO^{2+}(NO_3^-)_2$
$SOCl_2$	0·123	$AgClO_4$	0·083	1 : 1,	$ClSO(ClO_4)$	$ClSO^+ClO_4^-$
				1 : 2	$SO(ClO_4)_2$	$SO^{2+}(ClO_4^-)_2$
$AgClO_4$	0·101	$SOCl_2$	0·017	1 : 2	$SO(ClO_4)_2$	$SO^{2+}(ClO_4^-)_2$
$SOCl_2$	0·129	$FeCl_3$	0·106	1 : 1,	$SOCl_2,FeCl_3$	$ClSO^+FeCl_4^-$
				1 : 2	$SOCl_2,2FeCl_3$	$SO^{2+}(FeCl_4^-)_2$
$FeCl_3$	0·173	$SOCl_2$	0·108	1 : 2,	$SOCl_2,2FeCl_3$	$SO^{2+}(FeCl_4^-)_2$
				3 : 2	$3SOCl_2,2FeCl_3$	$(SO^{2+})_3(FeCl_6^{3-})_2$
$SOCl_2$	0·108	PCl_3	0·096	1 : 1,	$SOCl_2,PCl_3$	$ClSO^+PCl_4^-$
				1 : 2	$SOCl_2,2PCl_3$	$SO^{2+}(PCl_4^-)_2$
PCl_3	0·134	$SOCl_2$	0·0966	1 : 2,	$SOCl_2,2PCl_3$	$SO^{2+}(PCl_4^-)_2$
				3 : 2	$3SOCl_2,2PCl_3$	$(SO^{2+})_3(PCl_6^{3-})_2$
$SOCl_2$	0·133	PCl_5	0·088	1 : 1,	$SOCl_2,PCl_5$	$ClSO^+PCl_6^-$
				1 : 2	$SOCl_2,2PCl_5$	$SO^{2+}(PCl_6^-)_2$
PCl_5	0·184	$SOCl_2$	0·112	1 : 2	$SOCl_2,2PCl_5$	$SO^{2+}(PCl_6^-)_2$
$SOCl_2$	0·118	$POCl_3$	0·098	1 : 1,	$SOCl_2,POCl_3$	$ClSO^+OPCl_4^-$
				1 : 2	$SOCl_2,2POCl_3$	$SO^{2+}(OPCl_4^-)_2$
$POCl_3$	0·151	$SOCl_2$	0·099	3 : 2	$3SOCl_2,2POCl_3$	$(SO^{2+})_3(OPCl_6^{3-})_2$
$SOCl_2$	0·113	$AsCl_3$	0·105	1 : 1,	$SOCl_2,AsCl_3$	$ClSO^+AsCl_4^-$
				1 : 2	$SOCl_2,2AsCl_3$	$SO^{2+}(AsCl_4^-)_2$
$AsCl_3$	0·190	$SOCl_2$	0·095	1 : 2,	$SOCl_2,2AsCl_3$	$SO^{2+}(AsCl_4^-)_2$
				3 : 2	$3SOCl_2,2AsCl_3$	$(SO^{2+})_3(AsCl_6^{3-})_2$
$SOCl_2$	0·112	$SbCl_3$	0·088	1 : 1,	$SOCl_2,SbCl_3$	$ClSO^+SbCl_4^-$
				1 : 2	$SOCl_2,2SbCl_3$	$SO^{2+}(SbCl_4^-)_2$
$SbCl_3$	0·202	$SOCl_2$	0·095	1 : 2,	$SOCl_2,2SbCl_3$	$SO^{2+}(SbCl_4^-)_2$
				3 : 2	$3SOCl_2,2SbCl_3$	$(SO^{2+})_3(SbCl_6^{3-})_2$
$SOCl_2$	0·0165	$SbCl_5$	0·017	1 : 1,	$SOCl_2,SbCl_5$	$ClSO^+SbCl_6^-$
				1 : 2	$SOCl_2,2SbCl_5$	$SO^{2+}(SbCl_6^-)_2$
$SbCl_5$	0·053	$SOCl_2$	0·014	3 : 2	$3SOCl_2,2SbCl_5$	$(SO^{2+})_3(SbCl_8^{3-})_2$
$SOCl_2$	0·160	$TiCl_4$	0·127	1 : 1	$SOCl_2,TiCl_4$	$ClSO^+TiCl_5^-$
				1 : 2	$SOCl_2,2TiCl_4$	$SO^{2+}(TiCl_5^-)_2$
$TiCl_4$	0·242	$SOCl_2$	0·14	1 : 2,	$SOCl_2,2TiCl_4$	$ClSO^+(TiCl_5^-)_2$
				3 : 2	$3SOCl_2,2TiCl_4$	$(SO^{2+})_3(TiCl_7^{3-})_2$
$SOCl_2$	0·122	$SnCl_4$	0·103	1 : 1,	$SOCl_2,SnCl_4$	$ClSO^+SnCl_5^-$
				1 : 2	$SOCl_2,2SnCl_4$	$SO^{2+}(SnCl_5^-)_2$
$SnCl_4$	0·268	$SOCl_2$	0·103	1 : 2	$SOCl_2,2SnCl_4$	$SO^{2+}(SnCl_5^-)_2$

* M = $AgNO_3$, $AgClO_4$, $FeCl_3$, PCl_3, PCl_5, $OPCl_3$, $AsCl_3$, $SbCl_3$, $SbCl_5$, $TiCl_4$, and $SnCl_4$.

EXPERIMENTAL

The experimental methods and the preparation of conductivity acetone were as described earlier.[2,3] Purified acetone was found to give no reaction to Karl Fischer reagent, which indicated a water content of less than 0·005%.[26] The conductance of various batches of acetone varied between $1{\cdot}22 \times 10^{-8}$ and $2{\cdot}0 \times 10^{-8}$ Ω^{-1} cm^{-1} at 25 °C. Extra-pure thionyl chloride (B.D.H.) was triply distilled; freshly distilled middle fractions were used. Other reagents were purified by standard procedures.

Silver(I) perchlorate was prepared by the method of Schumacher [27] and purified by recrystallisation from benzene.

For the preparation of solutions in acetone, both the solvent and thionyl chloride, or the Lewis acids, as the case may be, were precooled to 10—15 °C before mixing, and finally the volume made up at room temperature.[2,3] Potter's [10] argument against ionisability of thionyl chloride, on the ground of a possible slow reaction between acetone and thionyl chloride, is not valid in our case as all measurements were made on freshly prepared solutions. We observed no evidence of chemical reaction between acetone and thionyl chloride under these conditions.

Dry-nitrogen atmospheres were used during manipulation

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[26] L. G. Savedoff, *J. Amer. Chem. Soc.*, 1966, **88**, 664.

[27] J. C. Schumacher, 'Perchlorates,' Amer. Chem. Soc., Monograph Series, No. 146, Reinhold, New York, 1960, p. 52.

of sensitive materials and solutions; whenever required a glove-box was used. All conductance measurements and conductimetric titrations were carried out under dry-nitrogen atmospheres. Values of molar conductance obtained for thionyl chloride in acetone solutions are given in Table 1.

Conductimetric Titrations.—Freshly prepared acetone solutions of the titres (usually 30 cm^3) were titrated conductimetrically with acetone solutions of the titrants. Reverse titrations were carried out in most cases under similar conditions. A summary of data is given in Table 2. Conductimetric-titration curves for some of the systems are reproduced in Figures 1—4; the nature of such curves for all the other systems was similar.

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