146. *Reactions of Tin*(IV) *Halides with Ammonia Derivatives. Part I. The Reaction of Tin*(IV) *Chloride with Liquid Ammonia.*

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The reaction of tin(IV) chloride with liquid ammonia gives mainly ammonium chloride and the ammonobasic tin(IV) chloride, $SnCl(NH_2)_3$; the latter can be prepared pure by thorough washing with liquid ammonia. A tensimetric study of the reaction shows that ammonium chloride and $SnCl(NH_2)_3$ are formed at −63°, but that at higher temperatures (−45° and −36°) there is further reaction with the formation of a complex tin species, $[NH_4]_2[SnCl_3(NH_2)_3]$. The progressive thermal decomposition of all the initial products shows the existence of various intermediate mixtures, with the eventual production of a readily sublimable diammine of tin(IV) chloride, ($SnCl_4,2NH_3$).

The mechanism of the various reactions is discussed.

STUDIES of the ammonolysis of the chlorides of the Group IVB elements show that although carbon tetrachloride does not react with liquid ammonia at its boiling point,[1] silicon(IV) chloride [2] and germanium(IV) chloride [3] are completely ammonolysed to the amide and imide respectively, while tin(IV) chloride forms an ammonobasic chloride. No evidence has been presented for the ammonolysis of lead(IV) chloride.

Early investigators [4] showed that tin(IV) chloride reacted with gaseous ammonia at room temperature to give a white compound $SnCl_4,4NH_3$, which gave a sublimate $SnCl_4,2NH_3$ when heated. Both substances were simply formulated as addition compounds. Schwarz and Jeanmaire [5] considered that the reaction of tin(IV) chloride with ammonia might give a mixture of ammonium chloride and an ammonobasic tin(IV) chloride, and proved this by washing their product with liquid ammonia to extract the soluble ammonium chloride, leaving the insoluble ammonobasic tin(IV) chloride $SnCl(NH_2)_3$. Our investigations confirm Schwarz and Jeanmaire's observations except that we found it unnecessary to heat the product to 100° between washes to remove ammonium chloride completely.

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[1] Watt and Hahn, *J. Amer. Chem. Soc.*, 1955, **77**, 312.
[2] Vigoureux and Hugot, *Compt. rend.*, 1903, **135**, 1670.
[3] Thomas and Pugh, *J.*, 1931, 60.
[4] Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, Vol. VII, 1927, p. 445.
[5] Schwarz and Jeanmaire, *Ber.*, 1932, **65**, 1443.

We consider that the ammonolysis proceeds in a number of stages:

$$SnCl_4 + 2NH_3 \rightleftharpoons SnCl_3NH_2 + NH_4Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$
$$SnCl_3NH_2 + 2NH_3 \rightleftharpoons SnCl_2(NH_2)_2 + NH_4Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$
$$SnCl_2(NH_2)_2 + 2NH_3 \rightleftharpoons SnCl(NH_2)_3 + NH_4Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii)$$
$$SnCl(NH_2)_3 + 2NH_3 \rightleftharpoons Sn(NH_2)_4 + NH_4Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iv)$$

and that the removal of the ammonium chloride by washing pulls over the equilibria until $SnCl(NH_2)_3$ is left as the main product. Each stage will follow the usual solvolysis pattern of the initial co-ordination of ammonia molecules followed by the elimination of hydrogen chloride under the influence of the solvent ammonia molecules :

$$SnCl_4 + 2NH_3 \longrightarrow [SnCl_4,2NH_3] \longrightarrow SnCl_3NH_2 + NH_4Cl$$

With the replacement of chlorine atoms by amino-groups the tin will become a much poorer acceptor so that the reaction will not go completely to the tin(IV) amide.

Now if there is any ammonium chloride present it will form a triammoniate with a distinctive dissociation pressure,[6] and a tensimetric study of the $SnCl(NH_2)_3$–NH_3 system will show us if ammonium chloride is present; each three moles of ammonia present at the known dissociation pressure of the ammonium chloride triammoniate correspond to the presence of one mole of ammonium chloride. From Fig. 1(*a*) we see that there is no appropriate univariant portion, so that no ammonium chloride can be present.

The tensimetric study of the tin(IV) chloride–ammonia reaction at –63° [cf. Fig. 1(*c*)] shows that 2·6 mol. of ammonium chloride are produced in the initial equilibrium reaction, so that the product is largely $SnCl(NH_2)_3$ together with a little $SnCl_2(NH_2)_2$. This agrees with the washing experiments, where removal of ammonium chloride left $SnCl(NH_2)_3$.

At reaction temperatures of –36° and –45°, however [cf. Fig. 1(*b*)], only slightly more than 1 mol. of ammonium chloride can be detected. Now an increase in temperature should tend to increase the amount of ammonolysis and produce more ammonium chloride, so it appears that some of the ammonium chloride is not being detected tensimetrically. A reasonable interpretation would be that some ammonium chloride interacts with the ammonobasic tin chloride to form one single phase; this ammonium chloride would then remain undetected since it could not form its characteristic triammoniate. One obvious explanation is the formation of an anionic tin(IV) complex between the ammonobasic tin chloride and ammonium chloride:

$$SnCl(NH_2)_3 + 2NH_4Cl \longrightarrow [NH_4]_2[SnCl_3(NH_2)_3]$$

Some evidence for this behaviour is afforded by the washing runs, where a considerable amount of tin is found together with the ammonium chloride in the filtrate. In the washing experiments, we would expect some of the ammonobasic tin chloride to form a complex and be carried over with the ammonium chloride; all the tin would not be in the form of a complex because the ammonium chloride concentration is relatively low—a large excess of liquid ammonia being present. This type of complex-forming action is quite common, and experiments with the insoluble ammonobasic chlorides of titanium(IV), vanadium(IV), and molybdenum(V) [7] have shown that solution is readily affected by the addition of ammonium salts.

This complex-formation is evidently irreversible, because after the excess of ammonia has been removed at –36°, the product can be cooled to –63° in the presence of further ammonia, and a new tensimetric study again shows only 1 mol. of ammonium chloride to be present. On the other hand, in the similar repetition of a –63° run at –36°, the amount of ammonium chloride found changes from almost 3 mol. to the 1 mol. usually found at –36°.

Therefore we must account for complex-formation's occurring only at –45° and –36°

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[6] Fowles and Pollard, *J.*, 1952, 4938.

[7] Fowles, unpublished observations.

and not at −63°. A probable explanation is that at −63° the solubility of ammonium chloride (and the ammonobasic tin chloride) is so low that complex-formation would be very slight, whereas at the higher temperatures the much greater solubility of ammonium chloride and correspondingly acidic solution produces complex-formation.

There should, on our simple theory, be 3 mol. of ammonium chloride detectable at −63° and one at −36°, and the slightly greater amount of ammonium chloride at −36° must be accounted for either in terms of a somewhat greater ammonolysis with the increased temperature or incomplete complex-formation; we should, for instance, expect complex-formation to be incomplete if the ammonobasic tin chloride was polymeric (caused by elimination of hydrogen chloride between neighbouring molecules).

Fig. 1.

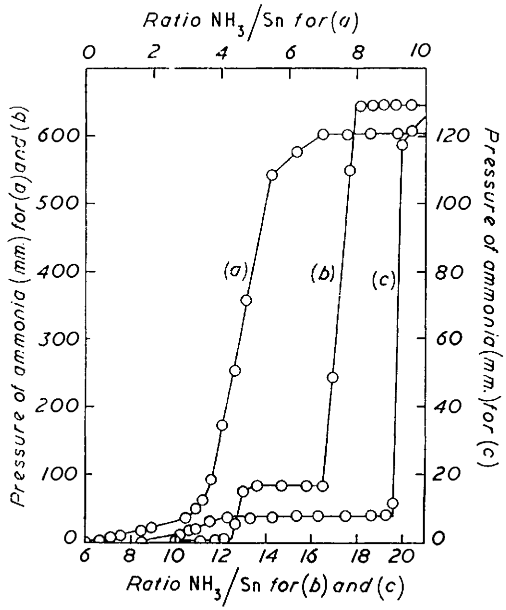
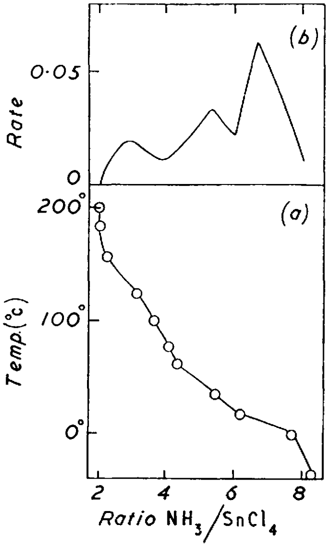


Fig. 2.



The thermal decomposition between 0° and 200° of the products formed at all three temperatures gives very similar results (Fig. 2), which strongly suggest intermediate compounds of some stability. Since the liberated ammonia diffuses only slowly through the solid, successive decompositions will tend to overlap, and the decomposition curves show slope changes rather than vertical portions at the more stable intermediate compositions.

These intermediate compounds have the overall formula $SnCl_4,xNH_3$, with $x = 6$, 4, and 2. Assuming that the product of the tin(IV) chloride–ammonia reaction at −63° contains a mixture of ammonium chloride and an ammonobasic tin chloride, we explain the stepwise decomposition of the ammonolysis products as follows:

$SnCl(NH_2)_3 + 3NH_4Cl$ corresponding to $SnCl_4,6NH_3$

$\downarrow$

$SnCl_2(NH_2)_2 + 2NH_4Cl$ ($+\ 2NH_3\uparrow$) corresponding to $SnCl_4,4NH_3$

$\downarrow$

$SnCl_3(NH_2) + NH_4Cl$ ($+\ 2NH_3\uparrow$) corresponding to $SnCl_4,2NH_3$

$\downarrow$

$SnCl_4 + 2NH_3$ which react immediately outside the hot zone to give $SnCl_4,2NH_3$

We consider that complex anionic tin species have been formed in the reactions at −45° and −36°, and the subsequent thermal decompositions will follow the scheme:

$$\begin{array}{l}
[NH_4]_2[SnCl_3(NH_2)_3] + NH_4Cl \text{ corresponding to } SnCl_4,6NH_3 \\
\downarrow \\
[NH_4][SnCl_3(NH_2)_2] + NH_4Cl\ (+\ 2NH_3\uparrow) \text{ corresponding to } SnCl_4,4NH_3 \\
\downarrow \\
SnCl_3(NH_2) + NH_4Cl\ (+\ 2NH_3\uparrow) \text{ corresponding to } SnCl_4,2NH_3
\end{array}$$

This again reacts to form the diammine of tin(IV) chloride.

In these thermal decompositions, the tin–nitrogen bonds break, in contrast to the tin–chlorine bond rupture found in the base-catalysed reactions in liquid ammonia.

To provide further evidence about the nature of the anionic tin complexes, we studied the ammonolysis of diammonium and dipotassium hexachlorostannate(IV). With the diammonium salt at −36°, 2·8 mol. of ammonium chloride can be detected, suggesting that three of the six chlorine atoms can be replaced to give $[NH_4]_2[SnCl_3(NH_2)_3] + 3NH_4Cl$; the complex anion is thus the same as that postulated as being formed in the tin(IV) chloride–ammonia reaction, but the liberated ammonium chloride cannot take part in further complex-formation and is therefore detected tensimetrically. The solution is more acidic than in the case of tin(IV) chloride, because of the extra ammonium chloride, and ammonolysis does not go quite as far, so that rather less than 3 mol. of ammonium chloride are formed. With the dipotassium hexachlorostannate(IV) 1·2 mol. of ammonium chloride are detected. This suggests that three of the chlorine atoms are first replaced in the hexachlorostannate ion, with the formation of 3 moles of ammonium chloride and the replacement of two of the potassium ions by ammonium ions (so that only 1 mol. of ammonium chloride remains to be detected) giving a mixture of potassium chloride and the diammonium triamminotrichlorostannate(IV):

$$K_2SnCl_6 \xrightarrow{NH_3} K_2[SnCl_3(NH_2)_3] + 3NH_4Cl \longrightarrow [NH_4]_2[SnCl_3(NH_2)_3] + NH_4Cl + 2KCl$$

This replacement is facilitated by the insolubility of potassium chloride in liquid ammonia.

Further evidence for these reaction schemes is provided by the thermal decomposition of the mixtures formed by the ammonolysis of the complex salts. The diammonium salt behaves just as tin(IV) chloride itself, except that whereas at 200° virtually all the tin(IV) chloride product has sublimed, giving $SnCl_4,2NH_3$, a very considerable quantity of ammonium chloride still remains behind from the complex salt product. Thus although the sublimate of diamminotin(IV) chloride forms readily, the massive ammonium chloride sublimes only very slowly at 200°. With the dipotassium product, a similar thermal decomposition is observed, but the substantial residue remaining at 200° is now potassium chloride.

EXPERIMENTAL

Materials.—Tin(IV) chloride (Messrs. British Drug Houses) was distilled *in vacuo* into suitable ampoules.[8] Ammonia (from Imperial Chemical Industries Limited) was dried (Na) and condensed into the vacuum line. The ammonium and potassium hexachlorostannate(IV) were prepared by the reaction of tin(IV) chloride (1 mol.) and the appropriate chloride (2 mol.) in dilute hydrochloric acid [Found: Cl, 57·4; N, 7·6. Calc. for $(NH_4)_2SnCl_6$: Cl, 57·9; N, 7·6. Found: Sn, 29·0; Cl, 52·0. Calc. for K_2SnCl_6: Sn, 29·0; Cl, 51·9%].

Analysis.—Complete analyses were normally carried out, but whenever the product firmly adhered to the reaction vessel it was hydrolysed with dilute sulphuric *in situ*, so that subsequent analysis gave only the Sn : Cl : N ratio.

Nitrogen was determined as ammonia by distillation from an alkaline solution into boric acid solution,[9] followed by titration with standard hydrochloric acid solution (B.D.H. 4·5 indicator).

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[8] Fowles and Pleass, *J. Chem. Educ.*, 1956, **33**, 640.

[9] " Standard Methods of Analysis of Iron, Steel and Ferroalloys," The United Steel Companies, Ltd., Sheffield, 1951, 4th edn., p. 55.

Tin was determined as the oxide[10] by ignition of the precipitated hydroxide. Chlorine was determined potentiometrically as chloride by titration with standard silver nitrate solution, by use of lead–lead sulphate and silver–silver chloride half-cells.

Reactions and Tensimetric Studies.—All reactions were carried out in the usual type of closed vacuum system.[6, 11]

The voluminous white solid produced by the direct reaction of tin(IV) chloride and ammonia at −33·5° was washed extensively (15 × 50 ml.) with liquid ammonia to remove ammonium chloride; the solid remaining was pumped for several hours at room temperature before analysis [Found: Sn, 57·9; Cl, 18·3; N, 20·1%; Sn : Cl : N, 1 : 1·06 : 2·94. $SnCl(NH_2)_3$ requires Sn, 58·7; Cl, 17·5; N, 20·8%].

This *product* was allowed to come into contact with excess of ammonia at −36°, and a tensimetric study was made of the $SnCl(NH_2)_3$–NH_3 system [Fig. 1(*a*)].

The $SnCl_4$–NH_3 system was studied tensimetrically at −36°, −45°, and −63°, and the results of the −36° and −63° investigations are shown in Figs. 1(*b*) and 1(*c*) respectively.

Thermal Decompositions.—These were carried out on the products remaining after removal of excess of ammonia at the reaction temperature, by heating the sample *in vacuo* for 2 hr. at successive intervals of about 20°, the ammonia liberated at each temperature being condensed and measured.[6] In this way the following compounds were thermally decomposed: $SnCl_4,8NH_3$, $(NH_4)_2SnCl_6,8NH_3$, and $K_2SnCl_6,8NH_3$. (Only the overall compositions are quoted.) The results of these decompositions are illustrated in Fig. 2 (rate in moles of ammonia deg.$^{-1}$ hr.$^{-1}$). The white sublimate which was formed above 120° was analysed in each case, Sn : Cl : N being 1·0 : 3·88 : 2·10, 1·0 : 4·10 : 2·10, and 1·0 : 3·99 : 2·06 respectively.

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[10] Hillebrand, Lundell, Bright, and Hoffman, "Applied Inorganic Analysis," Wiley, New York, 1953, 2nd edn., p. 287.

[11] Fowles and Pleass, *J.*, 1957, 1674.