886. *Reactions of Tin*(IV) *Halides with Ammonia Derivatives. Part II.*[1] *The Reaction of Liquid Ammonia with Tin*(IV) *Bromide, Diammonium Hexabromostannate*(IV), *and Tin*(IV) *Iodide.*

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The reaction between liquid ammonia and tin(IV) bromide or diammonium hexabromostannate(IV) gives ammonium bromide and the ammonobasic tin(IV) bromide, $SnBr(NH_2)_3$. Liquid ammonia and tin(IV) iodide react to give ammonium iodide and the ammonobasic tin(IV) iodide, $SnI_2(NH_2)_2$, but on washing with liquid ammonia further solvolysis occurs and $SnI(NH_2)_3$ can be isolated. The thermal decomposition of these substances has been examined.

The vapour pressures of ammonia adducts formed by ammonium bromide and ammonium iodide have been measured over a wide temperature range.

OUR study of the reaction of tin(IV) chloride [1] with liquid ammonia has now been extended to the analogous reactions of tin(IV) bromide and tin(IV) iodide. These reactions have previously received little attention, and with tin(IV) bromide, for instance, there is only an early report [2] of the formation of a diammine. With the tin(IV) iodide–ammonia system [3,4,5] work has been restricted to passing ammonia gas through solutions of the iodide in various organic solvents, and the isolation of compounds with overall formulæ SnI_4,xNH_3, where $x = 3$, 4, 6, and 8. No structure has been formulated for these compounds, which are probably mixtures of ammonolysis products, particularly in view of the formation [4] of unstable higher ammonia adducts; these could well be those ammonia adducts formed by the ammonium iodide produced on ammonolysis.

The systems formed by ammonia with tin(IV) bromide, diammonium hexabromostannate(IV), tin(IV) iodide, ammonium bromide, and ammonium iodide have been examined tensimetrically. In addition, the normal liquid-ammonia extraction procedure has been used to obtain ammonolysis products free from ammonium halides.

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[1] Part I, Bannister and Fowles, *J.*, 1958, 751.
[2] Rayman and Preis, *Annalen*, 1884, **223**, 326.
[3] Personne, *Compt. rend.*, 1862, **54**, 216.
[4] Ephraim and Schmidt, *Ber.*, 1909, **42**, 3856.
[5] Cooper and Wardlaw, *J.*, 1930, 1141.

EXPERIMENTAL

Materials.—Tin(IV) bromide (British Drug Houses) was distilled *in vacuo* and condensed into suitable containers.[6] Tin(IV) iodide (British Drug Houses) was recrystallised from anhydrous chloroform and stored *in vacuo.* Ammonia was purified as previously described.[1] Ammonium bromide and ammonium iodide (Hopkin and Williams) were recrystallised from doubly-distilled water and dried at 60° *in vacuo* for several hours before use.

Diammonium hexabromostannate(IV) was prepared by mixing concentrated solutions of ammonium bromide and tin(IV) bromide in 30% hydrobromic acid, the yellow precipitate being washed with ice-cold hydrobromic acid and dried (NaOH) [Found: Br, 75·6; N, 4·4. Calc. for $(NH_4)_2SnBr_6$: Br, 75·6; N, 4·4%]. Analogous attempts to make the corresponding diammonium and dirubidium hexaiodostannates(IV) reasonably pure were unsuccessful.

Analysis.—Tin and nitrogen were determined as described previously.[1] Bromine was determined by potentiometric titration with silver nitrate solution, and iodine by titration with potassium iodate in hydrochloric acid solution. Where products were difficult to remove from the reaction vessel, they were hydrolysed *in situ*; a ratio is then quoted.

Reactions and Tensimetric Studies.—These were carried out in a closed vacuum system similar to that used in Part I.

(i) *The ammonium bromide–ammonia and ammonium iodide–ammonia systems.* The pressure–composition isotherms obtained at −36° agree with those obtained by Watt and McBride [7] at −35·5°; they accordingly confirm the existence of the ammonia adducts NH_4Br,xNH_3, with $x = 1{\cdot}5$ and 3, and NH_4I,yNH_3, with $y = 1, 2, 3,$ and 4. The same adducts appeared to be formed at −63°, but because of their low dissociation pressures it was not possible clearly to distinguish between $NH_4I,2NH_3$ and NH_4I,NH_3. Since the equilibrium dissociation pressures were to be used diagnostically in the tin(IV) halide–ammonia systems, they were measured [8] over a fairly wide temperature range. Each equilibrium was clearly established at −36°, and then the temperature was varied and the equilibrium pressure of ammonia determined. The results, expressed as equations, are given in Table 1.

TABLE 1. *Equilibrium pressures in the ammonium bromide–ammonia and ammonium iodide–ammonia systems.*

	$\log_{10} P_{mm} = (-a/T) + b$			
Equilibrium	a	b	Temp. range	$-\Delta H$ (kcal./mole)
$NH_4Br,3NH_3 \rightleftharpoons NH_4Br,1{\cdot}5NH_3 + 1{\cdot}5NH_3$	2001·7	10·0844	− 64·5° to 0·0°	9·16
$NH_4Br,1{\cdot}5NH_3 \longleftarrow NH_4Br + 1{\cdot}5NH_3$	1866·4	9·3852	−64·5 to 0·0	8·54
$NH_4I,4NH_3 \rightleftharpoons NH_4I,3NH_3 + NH_3$	1970·1	10·0088	−62·3 to −17·8	9·02
$NH_4I,3NH_3 \rightleftharpoons NH_4I,2NH_3 + NH_3$	1753·3	8·9530	−60·3 to −23·0	8·02
$NH_4I,2NH_3 \rightleftharpoons NH_4I,NH_3 + NH_3$	2125·5	10·2024	−54·3 to 0·0	9·73
$NH_4I,NH_3 \rightleftharpoons NH_4I + NH_3$	2168·9	9·6922	−39·8 to 22·8	9·93

(ii) *Tin*(IV) *bromide–ammonia and tin*(IV) *iodide–ammonia reactions. Washing procedure.* After extensive washing of tin(IV) bromide with liquid ammonia (25 × 50 ml.) to remove ammonium bromide, a white solid remained undissolved (Found: Sn : Br : N = 1·00 : 0·95 : 3·05). It was allowed to come into contact with excess of ammonia and a pressure–composition isotherm was obtained, from which it appeared to contain no free ammonium bromide, although it did form simple ammonia adducts; these appeared to be a mono- and probably a di-adduct [cf. Fig. 1(*a*)] although it is difficult to establish these precisely because of their low dissociation pressures. The portion soluble in liquid ammonia (Found Sn : Br : N = 1·00 : 18·05 : 17·90) was mainly ammonium bromide.

With tin(IV) iodide, the white product initially formed was relatively soluble in liquid ammonia, and had entirely dissolved after about 15 washes. The residue after only 5 washes, which became pale yellow on pumping, had Sn : I : N = 1·00 : 1·30 : 3·30, but after a further

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[6] Fowles and Pleass, *J. Chem. Educ.*, 1956, **33**, 640.
[7] Watt and McBride, *J. Amer. Chem. Soc.*, 1955, **77**, 1317.
[8] Fowles and Pollard, *J.*, 1952 4938.

5 washes 1·00 : 1·01 : 2·99. The soluble portion after ten washes had Sn : I : N = 1·00 : 4·43 : 6·60. It seems, therefore, that the soluble portion has an overall composition $SnI_4,6NH_3$, corresponding to a mixture $SnI(NH_2)_3 + 3NH_4I$, but that a little excess of ammonium iodide is present, in agreement with the insoluble tin compound with Sn : I < 1 : 4.

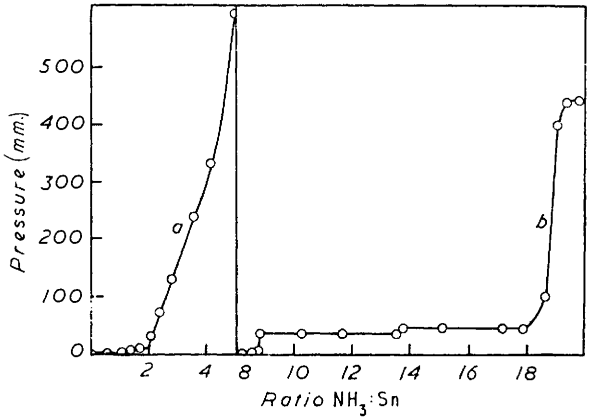


Fig. 1. *Tensimetry of* (*a*) $SnBr(NH_2)_3$ *and* (*b*) $SnBr_4$.

Fig. 2. *Tensimetry of* (*a*) SnI_4 *and* (*b*) $(NH_4)_2SnBr_6$.

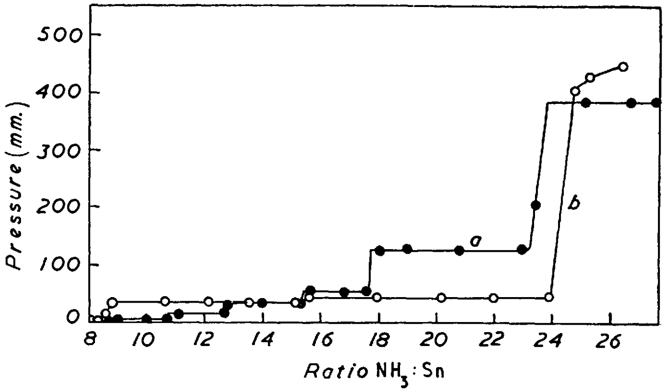
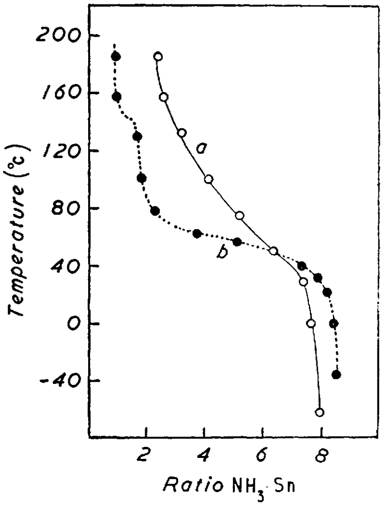


Fig. 3. *Tensimetry of* (*a*) $SnBr_4$ *and* (*b*) SnI_4.



The ammonobasic tin(IV) iodide, $SnI(NH_2)_3$, was fairly stable *in vacuo* up to 100°, but on heating to 180° lost 2 mol. of ammonia and formed an orange-red sublimate. The unsublimed rust-coloured residue reacted vigorously with dilute sulphuric acid, and completely dissolved in concentrated hydrochloric acid (Found: Sn : I : N = 1·00 : 0·77 : 1·05).

Tensimetry at $-36°$ *and* $-63°$.—The isotherms at $-36°$ for the tin(IV) bromide–ammonia and the tin(IV) iodide–ammonia system are shown in Figs. 1(*b*) and 2(*a*) respectively; the $-63°$ isotherms were very similar in general appearance, except that the univariant steps in the tin(IV) bromide–ammonia system were approximately 10% shorter. After removal of excess of ammonia, the materials remaining had overall compositions $SnX_4,8NH_3$; the results of the progressive thermal decomposition of these substances are shown in Figs. 3(*a*) and 3(*b*).

With $SnBr_4,8NH_3$, a *sublimate* started to form at 130° and by 180° almost all had sublimed into the cooler part of the tube (Found: Br, 66·3; N, 5·91. $SnBr_4,2NH_3$ requires Br, 67·7; N, 5·93%). With $SnI_4,8NH_3$, the decomposition was more complex, and at least two different sublimates were formed. Around 30° a dark red one was formed, but above 60° a yellow one, which gradually darkened on further heating. The unsublimed residue remaining at 180°, which contained about one-fifth of the tin originally used [as tin(IV) iodide] and had strong reducing properties in hydrochloric acid solution (Found Sn : I : N = 1·0 : 2·1 : 0·2), appears to be largely tin(II) iodide.

The isotherm obtained for the diammonium hexabromostannate(IV)–ammonia system at −36° is shown in Fig. 2(*b*). After removal of excess of ammonia at −36°, the solid remaining had an overall composition $(NH_4)_2SnBr_6,8NH_3$; the progressive thermal decomposition of this solid closely resembled that of $SnBr_4,8NH_3$ in that a sublimate of $SnBr_4,2NH_3$ was formed (Found: Sn : Br : N = 1·00 : 3·98 : 1·99); a residue of ammonium bromide remained at 180°.

DISCUSSION

In Part I we discussed the reaction of tin(IV) chloride with ammonia, and concluded that after initial co-ordination of an ammonia molecule, hydrogen chloride was eliminated, leaving as the final product a mixture of the ammonobasic tin(IV) chloride, $SnCl(NH_2)_3$, and ammonium chloride.

$$SnCl_4 + 2NH_3 \rightleftharpoons SnCl_3NH_2 + NH_4Cl$$
$$SnCl_3NH_2 + 2NH_3 \rightleftharpoons SnCl_2(NH_2)_2 + NH_4Cl$$
$$SnCl_2(NH_2)_2 + 2NH_3 \rightleftharpoons SnCl(NH_2)_3 + NH_4Cl$$

The pure ammonobasic tin(IV) chloride was obtained by washing out the soluble ammonium chloride with liquid ammonia. Now tin(IV) bromide and iodide should be ammonolysed analogously, except that the ammonolysis might go even further in view of the weaker tin–bromine and tin–iodine bonds. Our experiments show, however, that when the soluble ammonium halide is leached with liquid ammonia, the ammonolysis products remaining are analogous to that obtained with tin(IV) chloride; thus the ammonobasic tin(IV) halides, $SnBr(NH_2)_3$ and $SnI(NH_2)_3$, have been isolated. All the ammonobasic tin(IV) halides show some solubility in liquid ammonia, particularly the iodide. They are even more soluble in the presence of ammonium halides, and we attribute this to the formation of complex anionic tin species. Since the ammonobasic tin(IV) bromide, $SnBr(NH_2)_3$, forms ammonia adducts, its relatively poor acceptor properties are evidently not the reason for the last tin–bromine bond's not being ammonolysed. In view of the tendency for many tetrahalides to form compounds of the general formula $MX(NH_2)_3$, *e.g.*, with tin(IV) chloride, titanium(IV) chloride,[9] bromide,[10] and iodide,[10] and vanadium(IV) chloride,[11] it seems that the last halogen atom is particularly difficult to replace. Complete ammonolysis could, no doubt, be effected under more "alkaline" conditions, *i.e.*, with potassium amide, since early work by Fitzgerald[12] indicated that potassium amide in liquid ammonia completely replaced iodine atoms in tin(IV) iodide.

The thermal decomposition of the ammonobasic tin(IV) iodide appears to be analogous to that of the corresponding chloride,[13] the main reaction being $SnI(NH_2)_3 \longrightarrow SnIN + 2NH_3$. Side reactions such as $4SnIN \longrightarrow Sn_3N_4 + SnI_4$ evidently occur, however, and it is probable that the orange-red sublimate formed on heating to 180° is a mixture of tin(IV) iodide and its diammine.

Before considering the tensimetric results, we recall that although the ammonolysis of tin(IV) chloride at −63° gave a mixture of the ammonobasic tin(IV) chloride and ammonium chloride, $[SnCl(NH_2)_3 + 3NH_4Cl]$, 2 mol. of ammonium chloride could no longer be detected on raising the temperature to −36°. This was attributed to the formation of a complex, $[NH_4]_2[SnCl_3(NH_2)_3]$, which remained as a stable single phase in the solid state, so that the ammonium chloride could not be detected through the formation of its characteristic ammonia triadduct. Although tin(IV) bromide and tin(IV) iodide

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[9] Fowles and Pollard, *J.*, 1953, 2588.
[10] Fowles and Nicholls, unpublished observations.
[11] Fowles and Nicholls, *J.*, 1958, 1687.
[12] Fitzgerald, *J. Amer. Chem. Soc.*, 1907, **29**, 1693.
[13] Schwarz and Jeanmaire, *Ber.*, 1932, **65**, 1443.

resemble the chloride in giving analogous products in the washing experiments, [$SnBr(NH_2)_3$ and $SnI(NH_2)_3$], their tensimetric properties differ. With neither halide, for instance, does an increase in temperature appreciably alter the amount of ammonium halide found; at −63° and −36° 3 mol. of ammonium bromide and 2 of ammonium iodide can be detected in the appropriate tin(IV) halide–ammonia system. It seems that in the tin(IV) bromide–ammonia system any complex formed is unstable in the solid state. Thus 3 mol. of ammonium bromide are detected, and the product has an overall composition $SnBr_4,8NH_3$, so that the reaction at −36° must be $SnBr_4 + 8NH_3 \longrightarrow SnBr(NH_2)_3,2NH_3 + 3NH_4Br$. As we might expect, ammonolysis is not quite as extensive at −63°, and only 2·7 mol. of ammonium bromide are found. Moreover, the reaction cannot be

$$SnBr_4 + 8NH_3 \longrightarrow Sn(NH_2)_4 + 4NH_4Br \longrightarrow [NH_4][SnBr(NH_2)_4] + 3NH_4Br$$

because the amide is not formed even in the washing experiments, where conditions are much more favourable for maximum ammonolysis.

Further evidence for the non-formation of a stable complex is provided by the tensimetry of the diammonium hexabromostannate(IV)–ammonia system, where 5 mol. of ammonium bromide can be detected and the final product has an overall composition $(NH_4)_2SnBr_6,8NH_3$. In liquid ammonia the complex salt evidently behaves as a mixture of ammonium bromide and tin(IV) bromide, *i.e.*,

$$(NH_4)_2SnBr_6 \longrightarrow 2NH_4Br + SnBr_4 \xrightarrow{NH_3} 5NH_4Br + SnBr(NH_2)_3,2NH_3$$

The alternative explanation, a direct ammonolysis of five tin–bromine bonds in the anion, is ruled out because the final product would have an overall composition $(NH_4)_2SnBr_6,10NH_3$ {*i.e.* $[NH_4]_2[SnBr(NH_2)_5] + 5NH_4Br$}. Moreover, on thermal decomposition, the products of the reaction of ammonia with tin(IV) bromide and diammonium hexabromostannate(IV) behave very similarly:

$$SnBr_4,8NH_3 \longrightarrow SnBr_4,2NH_3 \text{ at } 180°; \quad (NH_4)_2SnBr_6,8NH_3 \longrightarrow SnBr_4,2NH_3 \text{ at } 180°$$

A sublimate of the diammine of tin(IV) bromide is formed in each case, but a residue of ammonium bromide remains, as would be expected from the decomposition of the product formed by the complex salt. In view of its volatility, the diammine of tin(IV) bromide is evidently a simple addition compound [similar to that formed by tin(IV) chloride] in which the tin atom achieves a covalency of six ($5s5p^35d^2$).

With tin(IV) iodide, only 2 mol. of ammonium iodide can be detected, even though three tin–iodine bonds can be ammonolysed in the washing experiments. In view of the results of the tin(IV) bromine–ammonia reaction, it is unlikely that formation of a stable complex can account for the " missing " mol. of ammonium iodide, particularly since the complex tin anions decrease in stability along the series $[SnCl_6]^{2-}$, $[SnBr_6]^{2-}$, $[SnI_6]^{2-}$. Under the conditions of the tensimetric studies, tin(IV) iodide is probably less ammonolysed than either of the other two halides. This may arise from the high solubility of ammonium iodide in liquid ammonia, leading to very acid conditions when tin(IV) iodide is ammonolysed with only a slight excess of ammonia. Under these conditions, the reaction would proceed only as far as the replacement of two iodine atoms by amino-groups: $SnI_4 + 8NH_3 \longrightarrow SnI_2(NH_2)_2,4NH_3 + 2NH_4I$.

The thermal decomposition of the reaction mixture is evidently quite complex, but in view of the residue of tin(II) iodide at 180° it seems that at least some of the product is reduced, with the liberation of iodine.

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