962. *The Preparation and Properties of Stannic Alkoxides.*

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Reactions involving alcoholic solutions of stannic chloride with either sodium alkoxides or ammonia were investigated and for different reasons found unsuitable for preparing stannic alkoxides. The last were obtained by alcohol interchange involving the *iso*propoxide *iso*propyl alcoholate $Sn_2(OPr^i)_8,2Pr^iOH$ which was itself obtained by a four-stage process involving the double alkoxide $Na\,Sn_2(OEt)_9$ and the *tert.*-amyloxide as intermediates. The properties of stannic alkoxides are compared with those of the corresponding titanium and zirconium compounds.

LITTLE is known about stannic alkoxides. Meerwein and Bersin [1] claimed to have isolated the tetraethoxide from the reaction of stannic chloride with the requisite quantity of sodium ethoxide although they mentioned that a double alkoxide $Na\,H_3[Sn(OEt)_6]_2$ was sometimes obtained. Thiessen and Koerner [2] reported that the same reaction gave the alkoxy-acid $H_2[Sn(OEt)_6]$. In reinvestigating this system we obtained none of these compounds, but obtained quantitatively the double alkoxide $NaSn_2(OEt)_9$ by reaction (1). The analogous *iso*propoxide was also obtained. In view of the successful preparation of alkoxides of titanium, germanium, zirconium, and hafnium through the tetrachloride, alcohol, and ammonia we tried this method with stannic chloride. Using either ethyl or *iso*propyl alcohol, we obtained substances containing appreciable amounts of chloride and ammonia (or amido-groups), and the method did not yield pure stannic alkoxides. The affinity of nitrogen for co-ordination with tin was further emphasised by the preferential formation of the complex $SnCl_4,2C_5H_5N$ in the reaction of stannic chloride, pyridine, *tert.*-amyl alcohol, and ammonia in an attempt to prepare tin *tert.*-amyloxide. Stannic alkoxides were eventually obtained pure by the following route:

$$2SnCl_4 + 9NaOEt = NaSn_2(OEt)_9 + 8NaCl \quad \dots\dots\dots\dots \quad (1)$$

$$Na\,Sn_2(OEt)_9 + HCl = 2Sn(OEt)_4 + NaCl + EtOH \quad \dots\dots\dots \quad (2)$$

$$Sn(OEt)_4 + 4CMe_2Et{\cdot}OH = Sn(O{\cdot}CMe_2Et)_4 + 4EtOH \quad \dots\dots\dots \quad (3)$$

$$Sn(O{\cdot}CMe_2Et)_4 + 5Pr^iOH = Sn(OPr^i)_4,Pr^iOH + 4CMe_2Et{\cdot}OH \quad \dots\dots \quad (4)$$

$$Sn(OPr^i)_4,Pr^iOH + 4ROH = Sn(OR)_4 + 5Pr^iOH \quad \dots\dots\dots \quad (5)$$

The stannic ethoxide produced by reaction (2) is impure owing to some hydrolysis and the presence of sodium chloride. As the stannic *iso*propoxide obtained in an analogous reaction was more hydrolysed the hydrolysis is probably caused by water produced in a side reaction involving alcohol and hydrochloric acid. In an attempt to avoid hydrolysis a reaction was tried with tin trichloride monoethoxide ethanolate in place of hydrochloric acid:

$$SnCl_3(OEt),EtOH + 3Na\,Sn_2(OEt)_9 = 7Sn(OEt)_4 + 3NaCl + EtOH$$

However, the stannic ethoxide was still contaminated with sodium chloride. These difficulties were overcome by subjecting the impure stannic ethoxide to reaction (3) and distilling out the volatile tin tetra-*tert.*-amyloxide. Reaction (4) was facilitated by the small solubility of stannic *iso*propoxide *iso*propyl alcoholate in *iso*propyl alcohol from which it is readily crystallised; the crystalline *iso*propyl alcoholate was an excellent starting material for the preparation of several stannic alkoxides [reaction (5), R = Me, Et, Pr^n, Bu^s, Bu^t, n-C_5H_{11}, *tert.*-C_5H_{11}, and $EtMe_2C$]. None of the primary alkoxides could be volatilised even under very low pressure without decomposition and in this respect they differ remarkably from the primary alkoxides of titanium, germanium, and zirconium. On the

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[1] Meerwein and Bersin, *Annalen*, 1929, **476**, 113.

[2] Thiessen and Koerner, *Z. anorg. Chem.*, 1931, **195**, 88.

other hand there is a striking similarity in the volatilities of the *monomeric* tertiary alkoxides as shown in Table 1.

TABLE 1. *Boiling points of tertiary alkoxides.*

R in $M(OR)_4$	Ti	Sn	Zr
Me_3C	91°/4·2 mm.	99°/4·0 mm.	85·5/4·0 mm.
Me_2EtC	98/0·1	102/0·2	95/0·1
$MeEt_2C$	128/0·1	140/0·4	128/0·1

The stannic *iso*propoxide *iso*propyl alcoholate was dimeric in boiling benzene and thus resembles in structure as well as crystalline form the corresponding derivatives of zirconium and cerium. Moreover, there is a further resemblance because a series of sodium zirconium alkoxides, with the formula $Na\,Zr_2(OR)_9$ analogous to the sodium tin alkoxides, have been prepared.[3] The lower thermal stability of tin alkoxides than of zirconium alkoxides applies also to the sodium double alkoxides. Thus although the sodium zirconium alkoxides could be volatilised unchanged under reduced pressure the tin compounds decomposed under similar conditions.

A similar reaction to that of stannic chloride, alcohol, and ammonia, giving stannic chloride alkoxide ammoniates (or amides), occurred when stannic chloride was replaced by the iodide. Further information was obtained by treating stannic *iso*propoxide with ammonium chloride in boiling benzene; a chloride *iso*propoxide ammoniate was produced suggesting that the final stage of dechlorination (eqn. 6) is reversible:

$$SnCl(OR)_3 + NH_3 + ROH \longrightarrow Sn(OR)_4 + NH_4^+ + Cl^- \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This equation also explains why the product of the ammonia reaction has a lower chloride content when alcohol–benzene rather than alcohol alone is used, because ammonium chloride is less soluble, so promoting the forward reaction. The stannic *iso*propoxide also reacted with liquid ammonia giving an ammoniate or amido-compound and this explains the presence of ammonia in the above products, *viz.*:

$$NH_3 + Sn(OR)_4 \longrightarrow Sn(OR)_4,NH_3 \text{ or } SnNH_2(OR)_3,ROH$$

EXPERIMENTAL

General experimental details were similar to those described previously.[4, 5] Stannic chloride was refluxed for several hours with a little thionyl chloride and then fractionally distilled.

Analysis.—Compounds containing tin and chlorine but no sodium were analysed as previously described.[5] As this method was unsuitable for sodium, owing to the presence of a large amount of ammonium salts, the tin was precipitated with " Cupferron." Then the filtrate was evaporated to dryness, the organic matter carefully burnt off, and the sodium determined as sulphate. Ammonia was determined volumetrically in the distillate after a sample was distilled with sodium hydroxide in a Kjeldahl apparatus.

Reactions involving Stannic Chloride and Sodium Ethoxide.—(*a*) To tin trichloride monoethoxide ethanolate (3·62 g., 1 mol.) in ethyl alcohol (50 c.c.) was added sodium ethoxide (from 0·78 g. of Na, 3 mol.) in alcohol (20 c.c.) and the system was boiled for 3 hr. The sodium chloride was filtered off, and the filtrate evaporated to dryness to give the *double ethoxide* as a white solid [Found: Sn, 35·7; $Na\,Sn_2(OEt)_9$ requires Sn, 35·7%].

(*b*) The trichloride (47·3 g., 1 mol.) was caused to react with sodium ethoxide (from 12·14 g. of Na, 3·5 mol.) in boiling alcohol (100 c.c.). Removal of the sodium chloride by filtration followed by evaporation of the filtrate to dryness left a solid (38 g.) [Found: Sn, 35·6; EtO, 59·7; Na, 3·6. Calc. for $Na\,Sn_2(OEt)_9$: Sn, 35·7; EtO, 60·91; Na, 3·5%]. The double alkoxide was very soluble in benzene or carbon tetrachloride and less soluble in ether or light petroleum. It crystallised from alcohol. When heated in a short-path still under 0·1 mm. it did not sublime or melt below 260°, whereat it decomposed.

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[3] Bartley and Wardlaw, to be published.

[4] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204.

[5] Bradley, Caldwell, and Wardlaw, *J.*, 1957, 3039.

Attempts to prepare Stannic Ethoxide by the Sodium Method.—(a) *By the action of alcoholic hydrogen chloride on* Na $Sn_2(OEt)_9$. The sodium tin ethoxide (10 g.) was caused to react with the requisite quantity of alcoholic hydrogen chloride (*ca.* 1% w/v) at the b. p. After filtering off the sodium chloride and evaporating the filtrate under reduced pressure we obtained the white solid *tetraethoxide* (7·1 g.) [Found: Sn, 38·7; EtO, 54·4. $Sn(OEt)_4$ requires Sn, 39·7; EtO, 60·3%].

(b) *By the reaction of* $SnCl_3(OEt),EtOH$ (1 *mol.*) *and* Na $Sn_2(OEt)_9$ (3 *mol.*). The sodium tin ethoxide (6·1 g.) and tin trichloride monoethoxide ethanolate (0·98 g.) were caused to react in boiling alcohol (100 c.c.). The solid product (4 g.) (Found: Sn, 36·9; EtO, 54·2%), obtained after filtering off the precipitate and evaporating the filtrate to dryness, was contaminated with sodium chloride.

Stannic tert.-*Amyloxide.*—(a) *By the pyridine–ammonia method.* Stannic chloride (23 g.) reacted exothermically with *tert.*-amyl alcohol (44·2 g.), pyridine (38 g.), and benzene (115 g.). Treatment with ammonia caused no apparent change; the initially formed precipitate was stannic chloride dipyridinate (Found: Sn, 29·3; Cl, 33·2. Calc. for $SnCl_4,2C_5H_5N$: Sn, 28·3; Cl, 33·9%).

(b) *From tin chloride alkoxide ammoniates.* Stannic chloride (20 c.c.) was added slowly with stirring to ethyl alcohol (300 c.c.) and the solution then treated with excess of ammonia. After the ammonium chloride was filtered off the filtrate gave on evaporation a white solid (37 g.) (Found: Sn, 39·6; EtO, 50·8; Cl, 3·5; NH_3, 5·1%). This was caused to react with *tert.*-amyl alcohol (52 g.) in benzene (204 g.) and the ammoniacal ethyl alcohol–benzene azeotrope was removed by fractional distillation. Evaporation of solvent under reduced pressure left a dark brown viscous liquid (38·5 g.) which on distillation at 127°/0·1 mm. gave a yellow distillate (17 g.) [Found: Sn, 25·6; Cl, 0·3. Calc. for $Sn(OC_5H_{11})_4$: Sn, 25·4%]. The black non-volatile residue contained stannous tin. In a similar experiment with a tin chloride ethoxide ammoniate containing more chloride (38·2 g.; Sn, 38·7; EtO, 50·1; Cl, 6·4; NH_3, 5·8%) and *tert.*-amyl alcohol (48·5 g.) in benzene (500 c.c.), a viscous brown product (45 g.) was obtained but this decomposed when heated under reduced pressure and gave no tetra-*tert.*-amyloxide. Starting with a chloride-free tin ethoxide ammoniate (Sn, 38·3; EtO, 55·6%) we finally distilled out pure *stannic tetra*-tert.-*amyloxide* 106°/0·4 mm., and this was monomeric in boiling benzene [Found: Sn, 25·5%; *M*, 471·4. $Sn(OC_5H_{11})_4$ requires Sn, 25·4%; *M*, 467·3]. Similar results were obtained by starting from tin chloride *iso*propoxide ammoniates. For example, from the reaction involving the chloride *iso*propoxide ammoniate (29·1 g.; Sn, 31·5; Pr^iO, 62·7; Cl, 3·3; NH_3, 2·7%), and *tert.*-amyl alcohol (35·2 g.) in benzene (200 c.c.) a viscous residue was obtained which at 128°/0·8 mm. gave a yellow distillate (16·6 g.) (Found: Sn, 26·1; Cl, 0·7%) and a black residue (14 g.).

(c) *By the method involving sodium tin ethoxide.* This method gave the purest product. Sodium tin ethoxide (32·62 g.) was treated with the requisite boiling alcoholic hydrochloric acid (136 g.) for 2½ hr. The product (30·6 g.) obtained after filtering off sodium chloride and evaporating solvent from the filtrate still contained sodium chloride (Found: Sn, 37·9; EtO, 54·9; Cl, 4·1; Na, 2·5%). The impure ethoxide (28·1 g.) was then treated with *tert.*-amyl alcohol (50 g.) in benzene (200 c.c.). During this alcohol interchange more sodium chloride was deposited. After filtration and evaporation of the filtrate a viscous liquid (41·5 g.) was left. This was distilled at 100°/0·2 mm. and gave a colourless distillate (31·6 g.) (Found: Sn, 25·5%).

Stannic iso*Propoxide.*—Addition of *iso*propyl alcohol (100 c.c.) to stannic *tert.*-amyloxide (31·0 g.) caused immediate deposition of crystals which dissolved when refluxed for 2 hr. A crystalline mass appeared on cooling. Two further recrystallisations from *iso*propyl alcohol afforded the *stannic* iso*propoxide* iso*propyl alcoholate* (Found: Sn, 28·8; Pr^iO, 71·4%; *M*, 833·4. $Sn_2(OPr^i)_8,2Pr^iOH$ requires Sn, 28·6; Pr^iO, 71·2%; *M*, 830·4). The alcoholate (3 g.), heated at 90° under reduced pressure, lost *iso*propyl alcohol and the viscous residue was distilled at 131°/1·6 mm. giving a viscous distillate which set to a wax of *stannic tetra*iso*propoxide* (1·2 g.) [Found: Sn, 34·0; Pr^iO, 66·1; $Sn(OPr^i)_4$ requires Sn, 33·4; Pr^iO, 66·6%].

Stannic Alkoxides prepared from the iso*Propoxide.*—Several *stannic alkoxides* were obtained by alcohol interchange of the *iso*propoxide *iso*propyl alcoholate. The reactions were conducted in benzene and, except for the preparations of the methoxide and ethoxide, were facilitated by the azeotropic removal of the *iso*propyl alcohol by fractional distillation. In the cases involving alcohols less volatile than *iso*propyl, the fractional distillation was replaced by a rapid evaporation of the mixed alcohols under reduced pressure. This process was repeated with fresh quantities of the less volatile alcohol until analysis of the product showed that interchange was complete. The results are shown in Table 2.

TABLE 2.

R in $Sn(OR)_4$	$Sn(OPr^i)_4,Pr^iOH$ (g.)	C_6H_6 (g.)	ROH (g.)	$Sn(OR)_4$ (g.)	Sn (%) Found	Sn (%) Required
Pr^n	4·2	160	11·0	2·8 [a]	33·6	33·4
Bu^s	7·2	150	15·3	7 [b]	29·2	28·9
Bu^t	10·0	—	*c*	8·8 [d]	29·2	28·9
Me	4·0	80	30 + 30 + 30	2·9 [e]	48·0	48·8
Et	4·0	—	50 + 50 + 50	3·5 [f]	39·9	39·7
Me_2EtC	5·0	100	8·5	6·0 [g]	25·7	25·4
Et_2MeC	4·8	100	5·9	4·0 [h]	22·9	23·2

[a] Viscous liquid appearing to boil at 120°/0·03 mm. (decomp.). [b] Solid, m. p. *ca.* 100°/0·2 mm. and sublimed (decomp.) at 154°/0·2 mm. [c] Three successive amounts (500 c.c.) of benzene–*tert.*-butyl alcohol azeotrope used. [d] Solid, m. p. *ca.* 40°, distilled at 50°/0·1 mm. and at 99°/4·0 mm. (Found: Bu^tO, 70·3. Required: Bu^tO, 71·1%). [e] Solid, decomp. at 180°/0·1 mm. [f] Solid, decomp. at 175°/0·05 mm. (Found: EtO, 59·1. Required: EtO, 60·3%). [g] Viscous liquid appearing to boil at 160°/0·1 mm. (decomp.). [h] Liquid, distilled at 140°/0·4 mm.

Reaction between Stannic iso*Propoxide and Ammonium Chloride.*—Stannic *iso*propoxide (5 g.) was caused to react with ammonium chloride (2 g.) in boiling benzene (100 c.c.). After 20 min. ammonia was detected and after 6 hr. the system was cooled, unchanged ammonium chloride filtered off, and the filtrate evaporated to leave a solid (3 g.) (Found: Sn, 41·6; Cl, 10·1; NH_3, 3·9%. Cl/Sn, 0·69; NH_3/Sn, 0·82). A separate experiment confirmed that ammonium chloride was negligibly soluble in benzene and that the presence of chloride and ammonia in the product resulted from a reaction between the alkoxide and ammonium chloride.

Reaction between Stannic iso*Propoxide and Liquid Ammonia.*—Ammonia was condensed on stannic *iso*propoxide at *ca.* −80° and allowed to stand for 1 hr. Removal of ammonia under reduced pressure left a white solid (Found: Sn, 37·1; NH_3, 4·5%. NH_3/Sn, 0·89).

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