

592. The Reactions of Stannic Chloride with Alcohols.

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Reactions involving stannic chloride and the alcohols ROH, where R = Me, Et, Prⁿ, Prⁱ, Buⁿ, Buⁱ, Bu^s, Bu^t, or *tert.*-amyl, have been studied. With primary or secondary alcohols the products were either the volatile SnCl₄·2ROH or the non-volatile SnCl₃(OR)·ROH, or mixtures of the two. Ebullioscopic measurements in benzene showed that SnCl₃(OEt)·EtOH was dimeric whilst SnCl₄·2PrⁱOH was monomeric. With tertiary alcohols, products of the type SnCl₄·ROH, SnCl₃(OR)·ROH, or SnCl₃(OR) were obtained under various conditions. There was no evidence of the formation of alkyl chloride, olefin, and solvolysed metal chloride although this was typical of reactions involving tertiary alcohols and the tetrachlorides MCl₄ where M = Si, Ti, Zr, or Th.

IN 1886, Fischer¹ reported the isolation of stannic trichloride monoethoxide ethanolate SnCl₃(OEt)·EtOH from the reaction involving stannic chloride and ethyl alcohol. Rosenheim and Schnabel² later showed that by the addition of stannic chloride to ice-cold ethyl alcohol the alcoholate, SnCl₄·2EtOH could be isolated, and from reactions of stannic chloride with methyl, ethyl, or *n*-propyl alcohol obtained a series of compounds which they formulated as SnCl₂(OR)₂·HCl. Such substances have the same percentage composition as the trichloride monoalkoxide alcoholates SnCl₃(OR)·ROH. It seemed worthwhile to re-investigate these reactions as it would provide data for comparison with other metal chloride-alcohol systems and furnish information about the preparation of stannic alkoxides, of particular interest for branched-chain alcohols. We report results for stannic chloride and alcohols ROH where R = Me, Et, Prⁿ, Prⁱ, Buⁿ, Buⁱ, Bu^s, Bu^t, or *tert.*-amyl.

Primary Alcohols.—From the reaction of methyl or ethyl alcohol and the tetrachloride the alcoholate SnCl₃(OR)·ROH was obtained. *n*-Propyl, *n*-butyl, and *isobutyl* alcohol gave mixtures of the substances SnCl₄·2ROH and SnCl₃(OR)·ROH, the atomic ratio Cl : Sn being 3·4—3·5. Each mixture when heated gave a sublimate of the dialcoholate SnCl₄·2ROH. When SnCl₃(OMe)·MeOH was heated, the volatile SnCl₄·2MeOH was obtained, evidently owing to disproportionation under reduced pressure. Molecular weights showed that the trichloride monoethoxide ethanolate was dimeric in boiling benzene, tin having the co-ordination number 6 as in the volatile monomeric tetrachloride dialcoholates. In boiling ethyl alcohol SnCl₃(OEt)·EtOH had a lower molecular complexity (1·3), owing to solvation.

Secondary Alcohols.—The tetrachloride di(*isopropyl* alcoholate), SnCl₄·2PrⁱOH, was

¹ Fischer, *Monatsh.*, 1884, **5**, 426.

² Rosenheim and Schnabel, *Ber.*, 1905, **38**, 2777.

obtained by addition of stannic chloride to *isopropyl* alcohol. The alcoholate crystallised unchanged from *isopropyl* alcohol and sublimed completely at 45°/0.05 mm. Its molecular weight, determined ebulliometrically in benzene, agreed with the monomeric formula. In one experiment involving *isopropyl* alcohol evidence was obtained of the formation of a tetra-alcoholate $\text{SnCl}_4 \cdot 4\text{Pr}^i\text{OH}$. The addition of stannic chloride to *sec.*-butyl alcohol produced a crystalline solid which sublimed completely in the form of the dialcoholate.

Tertiary Alcohols.—From the reaction involving stannic chloride and *tert.*-butyl alcohol at *ca.* -80° the solid product was substantially the trichloride monoalcoholate $\text{SnCl}_3(\text{O}^t\text{Bu}) \cdot \text{Bu}^t\text{OH}$ and this was converted into the volatile tetrachloride monoalcoholate $\text{SnCl}_4 \cdot \text{Bu}^t\text{OH}$ by sublimation under reduced pressure. When stannic chloride was added to *tert.*-butyl alcohol without cooling and the volatile products and excess of alcohol were removed by distillation under atmospheric pressure, the solid product was the trichloride mono-*tert.*-butoxide $\text{SnCl}_3(\text{O}^t\text{Bu})$ and this gave some tetrachloride monoalcoholate at 60°/0.3 mm. When stannic chloride was added to ice-cold *tert.*-amyl alcohol a crystalline product was deposited, apparently a mixture of $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et})$ and $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et}) \cdot \text{EtMe}_2\text{C} \cdot \text{OH}$. Heating this at 50°/1 mm. gave a white crystalline sublimate which corresponded in analysis to a mixture of $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et})$ and $\text{SnCl}_4 \cdot \text{EtMe}_2\text{C} \cdot \text{OH}$. Similarly, reaction in benzene solution between *tert.*-amyl alcohol and the tetrachloride diisopropyl alcoholate gave substantially the trichloride mono-*tert.*-amyloxide which in turn produced a sublimate (75°/1 mm.) which consisted mainly of the tetrachloride monoalcoholate.

Discussion.—The “reactivity” of stannic chloride with alcohols is clearly low (“reactivity” is used in the sense of the degree of replacement of chloride by alkoxide groups) since the products are derivatives of either the tetrachloride or the trichloride monoalkoxide. For primary or secondary alcohols reactivity decreases as the electron-releasing tendency of the alkyl group increases. In terms of our theory for the reactivity of Group IV tetrachlorides³ the electron-release of the alkyl group should affect the reactivity of an alcohol in two ways. It should stabilise the co-ordinate link in $\text{R} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{H}^+ \text{M} \cdot \text{Cl}_4$ by delocalising the formal positive charge on the oxygen atom, and should promote reactivity by assisting in the expulsion of a chloride ion. On the other hand, by reducing the “acidity” of the alcohol, it should diminish reactivity owing to a reduction of the tendency for the proton to be expelled from the hydroxyl group. On this basis we should expect the order of reactivity to be: $\text{MeOH} > \text{EtOH} > \text{Pr}^i\text{OH} > \text{Pr}^o\text{OH}$ which resembles to some extent that found experimentally. The reaction concerned also involves the formation of alcoholic hydrochloric acid and this will undoubtedly be favoured in media of higher dielectric constant, *i.e.*, $\text{MeOH} > \text{EtOH} > \text{PrOH}$. The most remarkable feature of our results is the behaviour of the tertiary alcohols. The strong electron-releasing tendency of the *tert.*-alkyl group should cause tertiary alcohols to be less reactive than the secondary alcohols which is contrary to the observed behaviour. Moreover, we have found in connection with the reactivity of other metal tetrachlorides^{3,4} that tertiary alcohols react in a more complicated way involving the formation of alkyl chloride, olefin, water, hydrogen chloride, and a solvolyzed metal compound. This was not the case with stannic chloride and tertiary alcohols and it appears that this Group IVB tetrachloride behaves fundamentally differently from silicon tetrachloride or the Group IVA tetrachlorides. In this connection it is interesting that germanium tetrachloride⁵ is unusual in that it does not react with the lower alcohols or even form alcoholates. Thus in their reactions with an “ordinary” alcohol such as ethanol the reactivity of the tetrachlorides is in the order: $\text{SiCl}_4 \gg \text{TiCl}_4 > \text{ZrCl}_4 > \text{SnCl}_4 > \text{ThCl}_4 > \text{GeCl}_4$. This behaviour does not appear to be correlated in any simple general way with electronegativities, ionisation

³ Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

⁴ Bradley, Saad, and Wardlaw, *J.*, 1954, 2002.

⁵ Bradley, Kay, and Wardlaw, unpublished work.

energies, or metal-chlorine bond energies. Finally, we draw attention to the fact that stannic chloride gives volatile monoalcoholates $\text{SnCl}_4 \cdot \text{ROH}$ with tertiary alcohols, doubtless owing to the steric effect of the *tert.*-alkyl group in preventing the formation of the characteristic dialcoholate. It is probable that tin is exhibiting the unusual co-ordination number of 5 in the monoalcoholates.

EXPERIMENTAL

The general technique was similar to that employed in our earlier work on metal chloride-alcohol systems.^{3,4}

Analysis.—The sample was dissolved in 30% sulphuric acid, neutralised to methyl-orange with aqueous ammonia, diluted to 400 c.c. and, after the addition of macerated filter paper and ammonium nitrate (20 g.), boiled for about 2 min. The precipitate was collected on a filter paper (No. 41), washed with ammonium nitrate solution (2%), and ignited to tin dioxide. Chloride was determined gravimetrically on the filtrate.

Stannic Chloride.—The commercial anhydrous reagent was distilled immediately before use (Found: Sn, 45.8; Cl, 54.1. Calc. for SnCl_4 : Sn, 45.6; Cl, 54.4%).

Reactions of Alcohols.—Methyl alcohol. Stannic chloride (38 g.) was added to methyl alcohol (25 c.c.) and, after the initial vigorous reaction had subsided, benzene (100 c.c.) was added and the mixture was boiled for $\frac{1}{2}$ hr. The crystalline *trichloride monomethoxide methanolate* (20 g.) separated on cooling [Found: Sn, 41.5; Cl, 36.9. $\text{SnCl}_3(\text{OMe}) \cdot \text{MeOH}$ requires Sn, 41.2; Cl, 36.9%]. The alcoholate (10 g.), heated at 120°/1 mm., gave a crystalline sublimate of $\text{SnCl}_4 \cdot 2\text{MeOH}$ (1 g.) (Found: Sn, 36.9; Cl, 43.1. $\text{SnCl}_4 \cdot 2\text{MeOH}$ requires Sn, 36.6; Cl, 43.7%).

Ethyl alcohol. Stannic chloride (250 g.) was added to ice-cold ethyl alcohol (90 g.). The mixture solidified. Benzene (800 c.c.) was added and the solid dissolved at the b. p. The crystalline *trichloride monoethoxide ethanolate* obtained by cooling was separated and recrystallised from benzene. The final product (101 g.) was dried at room temperature and 0.1 mm. [Found: Sn, 37.6; Cl, 33.7; OEt, 28.0%; *M*, (in benzene) 667, (in ethyl alcohol) 412. $\text{SnCl}_3(\text{OEt}) \cdot \text{EtOH}$ requires Sn, 37.5; Cl, 33.7; OEt, 28.5%; *M*, 316.2].

n-Propyl alcohol. Stannic chloride (8.7 g.) was added to *n*-propyl alcohol (17.9 g.) and the mixture refluxed for 1 hr. Removal of solvent under reduced pressure left a white solid (13 g.) [Found: Sn, 32.8; Cl, 33.6. $\text{SnCl}_4 \cdot 2\text{PrOH}$ (1 mol.) + $\text{SnCl}_3(\text{OPr}) \cdot \text{PrOH}$ (1.38 mol.) requires Sn, 33.0; Cl, 33.7%]. The mixture (2 g.), heated at 40°/0.2 mm. in a short-path still, gave a sublimate of *stannic chloride dipropanolate* (1 g.) (Found: Sn, 31.1; Cl, 37.1. $\text{SnCl}_4 \cdot 2\text{PrOH}$ requires Sn, 31.2; Cl, 37.3%).

isoPropyl alcohol. Addition of stannic chloride (40 g.) to *iso*propyl alcohol (30 g.) produced a solid which was dissolved at the b. p. The solution rapidly deposited large hexagonal plates (58 g.) on cooling (Found: Sn, 31.6%). Recrystallisation from *iso*propyl alcohol gave hexagonal crystals (45 g.) of *stannic chloride dialcoholate* (Found: Sn, 31.3; Cl, 37.3; OPr^i , 29.9. $\text{SnCl}_4 \cdot 2\text{Pr}^i\text{OH}$ requires Sn, 31.2; Cl, 37.3; OPr^i , 31.0%). The product (1 g.) sublimed unchanged at 45°/0.05 mm. in a short-path still [Found: Sn, 31.7; Cl, 37.4%; *M* (in benzene), 373.2. $\text{SnCl}_4 \cdot 2\text{Pr}^i\text{OH}$ requires *M*, 380.7]. In several similar experiments the product was the dialcoholate but on one occasion when the tetrachloride (27 g.) and *iso*propyl alcohol (40 g.) were refluxed together for 1 hr. and allowed to cool overnight a crop of cubic crystals (19 g.) of *tetra-alcoholate* was deposited (Found: Sn, 23.9; Cl, 28.4; OPr^i , 46.1. $\text{SnCl}_4 \cdot 4\text{Pr}^i\text{OH}$ requires Sn, 23.7; Cl, 28.3; OPr^i , 47.2%). Evaporation of the mother-liquor to half bulk produced a crop of very small crystals which at room temperature slowly became cubic (Found: Sn, 27.1; Cl, 32.0; OPr^i , 39.9. Calc. for $\text{SnCl}_4 \cdot 3\text{Pr}^i\text{OH}$: Sn, 26.9; Cl, 32.2; OPr^i , 40.2%). This solid (1.5 g.) when heated in the short-path still at 55°/0.8 mm. gave a sublimate (1.0 g.) of the dialcoholate (Found: Sn, 31.4; Cl, 37.2; OPr^i , 30.5%). Another sample (5.0 g.) of " $\text{SnCl}_4 \cdot 3\text{Pr}^i\text{OH}$ " was dissolved in benzene (20 c.c.) and deposited small crystals of the dialcoholate (4.0 g.) (Found: Sn, 31.5; Cl, 37.0; OPr^i , 30.9%). These reactions indicate that the dialcoholate is the stable compound with evidence for a less stable tetra-alcoholate. There may also be an unstable trialcoholate but the compound obtained may be a mixture of the other two alcoholates.

n-Butyl alcohol. Stannic chloride (2.3 g.) was added to *n*-butyl alcohol (7.5 g.), and the solution evaporated to dryness, giving a solid (3.5 g.) (Found: Sn, 28.5; Cl, 29.1%; Cl: Sn,

3·42 : 1). The product (3 g.), heated at 70°/1·2 mm. in a short-path still, gave during 6 hr. a white sublimate (0·2 g.) of *stannic chloride dibutanolate* (Found : Sn, 29·4; Cl, 34·2. $\text{SnCl}_4 \cdot 2\text{BuOH}$ requires Sn, 29·0; Cl, 34·7%). The non-volatile residue was analysed (Found : Sn, 28·8; Cl, 28·9%; Cl : Sn, 3·36 : 1).

isoButyl alcohol. Stannic chloride (20 g.) was added to *isobutyl alcohol* (30 g.) and the mixture was boiled for $\frac{1}{2}$ hr. Evaporation of the solvent left a dark solid product (32 g.) (Found : Sn, 28·6; Cl, 29·7%; Cl : Sn, 3·48). This compound (2·5 g.), heated in a short-path still, gave the white crystalline dialcoholate (2·0 g.) (Found : Sn, 28·7; Cl, 33·9%) at 30°/0·01 mm.

sec.-Butyl alcohol. Stannic chloride (24 g.), added to ice-cold *sec.-butyl alcohol*, caused deposition of a white crystalline product (13 g.) (Found : Sn, 23·3; Cl, 27·5%). This (10 g.) sublimed completely at 50°/0·5 mm. in the short-path still as the dialcoholate (Found : Sn, 29·0; Cl, 34·2%).

tert.-Butyl alcohol. Stannic chloride (35 g.) was added to *tert.-butyl alcohol* (50 c.c.) at *ca.* -80°. The whole was allowed to attain room temperature and the resultant liquid evaporated under reduced pressure, leaving a white solid (44 g.) (Found : Sn, 33·4; Cl, 30·0%; Cl : Sn, 3·0 : 1). This was a mixture of $\text{SnCl}_3(\text{OBu}^t) \cdot \text{Bu}^t\text{OH}$ (Requires Sn, 31·9; Cl, 28·6%) and $\text{SnCl}_3(\text{OBu}^t)$ (Requires Sn, 39·8; Cl, 35·7%). A sample (17 g.), heated for 5 hr. in the short-path still at 60°/0·2 mm., gave a sublimate (8 g.) (Found : Sn, 35·5; Cl, 40·9; OBu^t , 23·3. Calc. for $\text{SnCl}_4 \cdot \text{Bu}^t\text{OH}$: Sn, 35·5; Cl, 42·4; OBu^t , 21·8%) which was substantially the tetrachloride monoalcoholate. In another experiment, stannic chloride (22 g.) was added to *tert.-butyl alcohol* (60 g.) without cooling. Volatile products were removed under atmospheric pressure (bath-temp. 140°) and left a pink solid product (25 g.) (Found : Sn, 39·9; Cl, 35·3%) which appeared to be the trichloride mono-*tert.-butoxide* without addendum. This solid (20 g.), heated for 8 hr. at 60°/0·3 mm., gave a sublimate (5 g.) (Found : Sn, 35·3; Cl, 40·6%) which was substantially $\text{SnCl}_4 \cdot \text{Bu}^t\text{OH}$.

tert.-Amyl Alcohol. Stannic chloride (29 g.) was added to *tert.-amyl alcohol* at *ca.* -20° and the mixture allowed to attain room temperature overnight. The crystalline product (18 g.) (Found : Sn, 34·7; Cl, 32·6%; Cl : Sn, 3·14) appeared to be mainly a mixture of $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et})$ (Requires Sn, 38·0; Cl, 34·1%) and $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et}) \cdot \text{EtMe}_2\text{C} \cdot \text{OH}$ (Requires Sn, 29·7; Cl, 26·6%). The product (8·7 g.), heated at 50°/1 mm. in a short-path still, gave some white sublimate (1·4 g.) (Found : Sn, 36·3; Cl, 39·0%; Cl : Sn, 3·6), evidently a mixture of $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et})$ and $\text{SnCl}_4 \cdot \text{CMe}_2\text{Et} \cdot \text{OH}$ (Requires Sn, 34·0; Cl, 40·7%). When the reactants were mixed without external cooling and then boiled under reflux for several hours and allowed to cool overnight, the crystalline product (Found : Sn, 38·0; Cl, 41·5%; Cl : Sn, 3·66) was a mixture of trichloride and tetrachloride complexes which sublimed unchanged under reduced pressure (Found : Sn, 37·8; Cl, 41·8%). Finally, *tert.-amyl alcohol* (4 g.) was caused to react in benzene (100 c.c.) with the tetrachloride *diisopropyl alcoholate* (10 g.). Alcohol interchange was promoted by azeotropic fractionation until benzene alone was collected, and the solvent was then removed by evaporation under reduced pressure. The white solid product (10·5 g.) (Found : Sn, 36·4; Cl, 30·8%) was evidently a mixture of $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et})$ and $\text{SnCl}_3(\text{O} \cdot \text{CMe}_2\text{Et}) \cdot \text{CMe}_2\text{Et} \cdot \text{OH}$. This product (1·0 g.) at 75°/1 mm. gave a white sublimate (0·3 g.) (Found : Sn, 31·0; Cl, 35·7%; Cl : Sn, 3·85) which was chiefly solvated tetrachloride.

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