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Some Effects of Boron Lewis Acids upon Methyltin Compounds[1]

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The salt $NaSn(CH_3)_3$ in liquid ammonia reacts with $H_3NB(CH_3)_3$ in such a manner that yields of $Sn_2(CH_3)_6$ above 90% are obtained upon warming to room temperature. However, when $NaSn(CH_3)_3$ reacts with BF_3 or $(CH_3)_2BF$ in diethyl ether, the yields of $Sn_2(CH_3)_6$ are far smaller. The main reason is found in the catalytic disproportionation of $Sn_2(CH_3)_6$ by these Lewis acids, producing methyltin polymers and tetramethyltin; then BF_3 reacts with the latter to make CH_3BF_2 and the new compound $(CH_3)_3SnBF_4$ (m.p. 89°; dissociable with liberation of BF_3). The decomposition of $(CH_3)_3SnH$ to H_2 and $Sn_2(CH_3)_6$ is catalyzed by diborane, which also is an effective catalyst for the disproportionation of $Sn_2(CH_3)_6$.

Recent studies have indicated that alkyltin compounds are reactive toward Lewis acids. For example, R_4Sn compounds react with tin tetrahalides to make alkyltin halides[2]; or boron trichloride exchanges chloride for a C_2H_3 or C_2F_3 group from tin.[3] Similarly, BF_3 attacks $(CH_3)_3SnCF_3$ to make $(CH_3)_3Sn(CF_3BF_3)$, leading to salts of the $CF_3BF_3^-$ ion.[4]

The results of the present study are summarized

$$(CH_3)_4Sn + 2BF_3 \longrightarrow CH_3BF_2 + (CH_3)_3SnBF_4 \qquad (1)$$

$$Sn_2(CH_3)_6 \longrightarrow (CH_3)_4Sn + \frac{1}{n}[Sn(CH_3)_2]_n \qquad (2)$$

(catalyzed by BF_3, $(CH_3)_2BF$ or B_2H_6)

$$[Sn(CH_3)_2]_n \longrightarrow m(CH_3)_4Sn + [Sn(CH_3)_{2-x}]_y \qquad (3)$$

(same catalysts)

$$2(CH_3)_3SnH \longrightarrow H_2 + Sn_2(CH_3)_6 \qquad (4)$$

(catalyzed by B_2H_6)

$$2NaSn(CH_3)_3 + H_3NB(CH_3)_3 \longrightarrow Sn_2(CH_3)_6 + \text{solids} \qquad (5)$$

(in liquid ammonia)

$$2NaSn(CH_3)_3 + BF_3 \text{ or } (CH_3)_2BF \longrightarrow Sn_2(CH_3)_6 + \text{solids} \qquad (6)$$

(in diethyl ether)

The work actually began with reactions (5) and (6), which represented attempts to form a covalent Sn–B bond. It was assumed that the lone-pair electrons on tin would have enough base strength to form such a bond (at least as the first of a series of reactions), but we found no way to demonstrate this. The solid by-product of (5) was far from simple, behaving like a source of methide ion and apparently including B–B bonded polymers. The reason for a low yield of $Sn_2(CH_3)_6$ from (6) was found through experiments leading to equations (1) through (4).

Reaction (1) evidently is related to the addition of BF_3 to $(CH_3)_3SnCF_3$[4] but ends differently because CH_3BF_2 is a weaker Lewis acid than BF_3,[5] whereas CF_3BF_2 is stronger.[6] The resulting $(CH_3)_3SnBF_4$ melts near 89° in a sealed tube; or *in vacuo* at 100° it forms a white sublimate with loss of BF_3 and a sharp decrease of equilibrium pressure. It reacts with diethyl ether to form two liquid phases; and its high solubility in water doubtless also includes a chemical reaction.

The low m.p. of $(CH_3)_3SnBF_4$ is an argument against the ionic structure $(CH_3)_3Sn^+BF_4^-$; however, we have no basis for choosing among structures having one, two or three Sn–F–B bridge bonds. Some relation to the very unstable $(CH_3)_3SiBF_4$[7] might be considered.

Reactions (2) and (3) describe the metastability of hexamethyldistannane relative to tetramethyltin and methyltin polymers. Some of the solids were white, while others had the yellow color of the long-known dimethyltin polymer,[8] suggesting that reaction (2) occurred even though the stoichiometry would imply much destruction of this polymer by reactions described by equation (3). In one experiment, indeed, the solid product contained only 0.7 CH_3 per tin atom. With BF_3 as a catalyst, of course, reaction (1) also was extensive.

Reaction (4) represents an attempt to make the hypothetical $(CH_3)_3SnBH_4$. Again the equation is idealized, for the actual results were complicated by extensive occurrence of reaction (2).

Experimental Part

The experimental work here reported was performed by means of a high-vacuum manifold, permitting quantitative monitoring of reactions involving volatile substances. Samples of well purified reactants and products were either measured as gases or weighed in detachable stop-cock tubes. The volatile products all were known substances, which could be identified by their molecular weights and other physical properties.

Reaction (1): Trimethyltin Fluoborate.–Measured samples of $(CH_3)_4Sn$ and BF_3 were sealed in glass tubes and brought to reaction under the conditions indicated in Table I. The product CH_3BF_2 showed the vapor tensions 69.5 mm. at −97.4° and 286.9 mm. at −78.5° (calcd., 70.1 and 287.2 mm.)[9] and mol. wt. 62.8 (calcd., 63.8). The non-volatile residue of expt. 1, presumably a mixture of $(CH_3)_3SnF$ and $(CH_3)_3SnBF_4$, melted at 90–92°; that from expt. 4 at 89.0–89.4° under 20 mm. pressure of BF_3. Another preparation (not listed in Table I) melted in a small sealed tube at 88.9–89.4°. Pressure measurements for the dissociation $(CH_3)_3SnBF_4 \rightarrow (CH_3)_3SnF + BF_3$ were complicated by the changing composition of the liquid phase as BF_3 came off to register higher equilibrium pressures at higher temperatures. The effect was to diminish the slope of the log P *vs.* $1/T$

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TABLE I

THE $(CH_3)_4Sn-BF_3$ REACTION

Expt. no.	Reactants (mmole) $(CH_3)_4Sn$	BF_3	Time (hr.)	Temp. (°C.)	Volatile components (mmole) $(CH_3)_4Sn$	BF_3	CH_3BF_2	Sn:B Ratio in residue
1	0.693	0.803	2	100	0.194	Nil	0.473	1.51
2	(Residue of No. 1)	0.739	2	100	Nil	0.556	Nil	0.99
3	0.586	1.260	16	20	0.322	0.732	0.264	1.00
4	0.582	1.283	2	100	0.168	0.451	0.401	0.98

TABLE II

CATALYTIC DISPROPORTIONATION OF $Sn_2(CH_3)_6$

Expt. no.	Starting materials (mmoles)		Temp. (°C.)	Time (hr.)	Volatile components (mmoles)	
1	$Sn_2(CH_3)_6$	0.113	100	38	$Sn_2(CH_3)_6$	0.111
2	$Sn_2(CH_3)_6$	1.096	20	24	$Sn(CH_3)_4$	0.780
	BF_3	2.699			CH_3BF_2	0.756
					BF_3	1.118
3	$Sn_2(CH_3)_6$	0.122	100	36	$Sn_2(CH_3)_6$	0.020
	$(CH_3)_2BF$	.131			$Sn(CH_3)_4$	.124
					$(CH_3)_2BF$	.131
4	$Sn_2(CH_3)_6$	.330	100	1	$Sn(CH_3)_4$	.459
	B_2H_6	.565			B_2H_6	.491
					H_2	.062

curve, giving an absurdly low ΔH value, when the vapor-phase volume was not small relative to the size of the sample. However, in a relatively small tensimeter, a sublimate having the composition $(CH_3)_3SnF \cdot 0.80BF_3$ was measured in the range 2.8 mm. at 102° to 33 mm. at 163°, with results conforming very well to the equation $\log P_{\text{mm.}} = 8.1028 - 2870/T$. From this, $\Delta H = 13.1$ kcal./mole and $\Delta H/T_{760} = 23.8$ cal./deg. mole. These values could represent the detachment and vaporization of the single component BF_3 from the liquid phase but would be too low if any $(CH_3)_3SnF$ also were being vaporized.

It appears from the results of Table I that the equation $(CH_3)_4Sn + BF_3 \rightarrow CH_3BF_2 + (CH_3)_3SnBF_4$ is virtually exact in terms of the reactants consumed, provided that enough BF_3 is present.

Reaction (2): Disproportionation of the Distannane.—The air-sensitive hexamethyldistannane was prepared by the action of sodium on trimethyltin chloride in liquid ammonia[10,11] and purified by high-vacuum sublimation; m.p. 23.5° (known value);[12] vapor tension 1.0 mm. at 25°. The conditions and results of the sealed-tube experiments on its catalytic disproportionation are shown in Table II.

Experiment 1 showed that the disproportionation of $Sn_2(CH_3)_6$ does not occur readily without a catalyst. Experiment 2 may be understood in terms of equation (2) if it is assumed that much of the yellow dimethyltin polymer disproportionated to a far less methylated tin material and tetramethyltin, with the latter reacting further according to equation (1). Thus the final solid residue, still showing a yellow color indicative of the dimethyltin polymer and containing 1.412 mmoles of Sn, 2.700 mmoles of CH_3 groups, 0.825 mmole of B and 3.231 mmoles of F, could be interpreted as 0.825 mmole of $(CH_3)_3SnBF_4$ with a methyltin material written empirically as $[Sn_5(CH_3)_2]_x$.

In Expt. 3 the catalyst evidently was less effective for reaction (2), since some $Sn_2(CH_3)_6$ survived; however, it seems that some process of type (3) was important, for the solid product, empirically written as $[Sn(CH_3)_{1.45}]_x$ was white and so could not have included much dimethyltin polymer. Here there was no boron compound capable of reacting in the manner of equation (1), so that the yield of tetramethyltin was higher than demanded by equation (2), having been derived partly from reaction (3) and recovered without further reaction.

Experiment 4 showed that diborane is a relatively effective catalyst, for it destroyed the whole sample of $Sn_2(CH_3)_6$ in one hour at 100° and left a methyltin residue relatively poor in methyl groups. The formation of hydrogen corresponded to the normal decomposition of diborane, the loss of which should not be attributed to any net contribution of material to the main methyltin reactions; its function was purely catalytic.

Reaction (4): Condensation of Trimethylstannane.—A 1.129 mmole sample of $(CH_3)_3SnH$ was heated with 1.112 mmoles of B_2H_6 in a sealed tube at 70° for 1.5 hr., after which the B_2H_6 was wholly recovered (measured, 1.112 mmoles). The recovery of 0.603 mmole of $(CH_3)_3SnH$ meant that 0.526 mmole had been used up. Then the formation of H_2 was nearly in accord with equation (4): found, 0.255 mmole; calcd., 0.263. The yield of $Sn_2(CH_3)_6$ was 0.083 mmole, or 32% of the calcd. 0.263; the rest was accountable by reactions (2) and (3), forming 0.155 mmole of $(CH_3)_4Sn$ and a non-volatile yellow residue having the empirical formula $[Sn(CH_3)_{2.24}]_x$. This would correspond to an open-chain polymer averaging seven $Sn(CH_3)_2$ units per two $(CH_3)_3Sn$ end-groups. Thus under milder conditions than in Expt. 4 of Table II, reaction (2) was extensive while reaction (3) occurred only to a small extent if at all.

Reaction (5).—The salt $NaSn(CH_3)_3$ was made by treating $(CH_3)_3SnCl$ with sodium in liquid ammonia.[10,13] A solution containing 2.85 mmoles of this salt with 3.90 mmoles of $H_3NB(CH_3)_3$ was warmed from −77 to −35° without apparent change; but after evaporation of the liquid ammonia and further warming to room temperature, 0.4 mmole of CH_4 and 1.18 mmoles of $Sn_2(CH_3)_6$ (0.8 mm. at 23°; m.p. 23.5°; density 1.55 at 25° *vs.* known 1.57)[10] were removed *in vacuo*. The residue was warmed slowly to 90°, bringing the total CH_4 to 4.2 mmoles and the final yield of $Sn_2(CH_3)_6$ to 1.30 mmoles, representing 91% of the original $Sn(CH_3)_3$ groups. Thus the residue contained material equivalent to 0.25 mmole of $NaSn(CH_3)_3$, along with 3.90 mmoles of boron, 7.5 mmoles of CH_3 groups and 2.60 mmoles of sodium, presumably in the form of amide to which the methylated boron material was attached. This residue was treated with as much HCl as would react at room temperature, liberating 0.15 mmole of $(CH_3)_3SnCl$, 0.38 mmole of $B(CH_3)_3$, 0.50 mmole of CH_4 and 0.59 mmole of H_2. Thus it seems that the boron had several forms: aside from the indicated complex of $B(CH_3)_3$ there must have been some methidic $B-CH_3$ material (doubtless enhanced by amide complex-formation), and probably there were some B–B bonds whose HCl-cleavage would account for the formation of H_2. Yet another probable component would be a relatively inert and highly condensed methylboron polymer.

Reaction (6).—For the experiments in ether solution, the $NaSn(CH_3)_3$ was made from tetramethyltin with sodium in liquid ammonia.[10] The ammonia solution was filtered and most of the ammonia was removed by high-vacuum sublimation, with warming to −25°. Then the product was dissolved in diethyl ether at that temperature and treated with BF_3 or $(CH_3)_2BF$,[14] with warming to 0°. When the ratio of BF_3 to $NaSn(CH_3)_3$ was close to 2:1, the reaction gave a white precipitate and a yellow solution, but no appreciable yield of $Sn_2(CH_3)_6$, evidently because reaction (2) destroyed any of it which might have been formed. With a 1:1 ratio, however, $Sn_2(CH_3)_6$ was produced in a 19.7% yield. This result may represent a genuinely effective action of BF_3 for conversion of $NaSn(CH_3)_3$ to $Sn_2(CH_3)_6$, for a dry sample of $NaSn(CH_3)_3$ decomposed at room temperature to give only a 10% yield of $Sn_2(CH_3)_6$. However, the less catalytically destructive $(CH_3)_2BF$ led to higher yields of $Sn_2(CH_3)_6$. For example, 1.53 mmoles of $NaSn(CH_3)_3$ and 0.67 mmole of $(CH_3)_2BF$ produced 0.32 mmole of $Sn_2(CH_3)_6$, representing 42% of the originally-present $Sn(CH_3)_3$ groups.

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