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REACTION OF HEXAMETHYLDITIN AND RELATED SPECIES WITH TRIMETHYLTIN CHLORIDE

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Summary

Despite unsuccessful attempts to trap it, evidence is presented that the polymeric "dimethyltin" obtained from hexamethyltin by reaction with trimethyltin chloride arises from monomeric dimethyltin as a reactive intermediate. Polymerisation proceeds either by insertion into Sn—Sn or into Sn—Cl bonds to yield mixtures of products of the type $(CH_3)_{2n+2}Sn_n$ and perhaps $(CH_3)_{2n}Sn_n$ with $n \geqslant 8$ as judged by mass spectrometry.

Introduction

In an earlier paper [1] we extended the previous study [2] of the reaction in methanol solution of trialkyltin halides with hexamethylditin, particularly the catalysed decomposition brought about by trimethyltin chloride.

$$(CH_3)_6Sn_2 \xrightarrow{(CH_3)_3SnCl} (CH_3)_4Sn + [(CH_3)_2Sn]$$

and confirmed that the reaction proceeds by rate controlling electrophilic Sn—CH_3 cleavage without concurrent Sn—Sn cleavage. Some speculation was also made on the mechanism of the formation of the presumed polymeric "dimethyltin" product.

The related substrates, tetramethyltin and trimethyl-t-butyltin, have now been studied so that rate constant comparisons can be made. Some investigations into the nature of the "dimethyltin" product have also been carried out with a view to clarifying its structure and the mechanism of its formation.

Experimental

Materials

Hexamethylditin, tetramethyltin, trimethyl-t-butyltin, trimethyltin chloride and dimethyl-t-butyltin chloride were purified and stored as previously described [1,3].

Perdeuterotetramethyltin was prepared following the method of Edgell and Ward [4] but using trideuteromethylmagnesium iodide, from CD_3I (20 g, 0.14 mol) and Mg (3.6 g, 0.15 mol), and stannic chloride (7.8 g, 0.03 mol) in dry di-n-butyl ether.

Perdeuterotrimethyltin chloride was obtained by reaction of perdeuterotetramethyltin (1.15 g, 0.006 mol) with stannic chloride (0.52 g, 0.002 mol) in a 10 ml flask fitted with a reflux condenser. The mixture was heated for 2 h at 150°C, allowed to cool and distilled from the reaction vessel, ca. 1.55 g of product being collected at 75—76°C/45 mmHg.

Methanol was AJAX UNIVAR dried for non-aqueous titrations which was further dried by the method of Lund and Bjerrum [5]. Methyl-d_3 iodide and benzyl chloride were from Koch-Light, and ^{13}C-Methyl iodide from Bio-Rad.

Product examination

Reactions were carried out either in NMR tubes sealed with pressure caps and studied by PMR spectroscopy [1,3], or, when the "dimethyltin" product was required, in foil-wrapped flasks closed with septum caps under nitrogen with magnetic stirring. The supernatant liquid was removed by syringe and the precipitated "dimethyltin" was washed several times with dry methanol before collection by filtration under nitrogen.

Kinetic measurements

These were carried out essentially as previously described [1,3] using peak height measurements in the PMR spectra at 100 MHz (JEOL PS-100 or MH-100) at 30 (±0.5)°C.

Results

(a) Hexamethylditin and trimethyltin chloride, rate studies

The previously reported [1] and some additional data examined in terms of both $(CH_3)_3SnCl$ and $(CH_3)_3Sn^+$, or a solvated form thereof, as catalytic reagents, yields:

$$k_{obs}/[(CH_3)_3SnCl]_s^{1/2} =$$

$$1.000\ (\pm 0.034) \times 10^{-4}\ [(CH_3)_3SnCl]_s^{1/2} + 0.552\ (\pm 0.141) \times 10^{-5}\ M^{-1/2}\ s^{-1}$$

where $[(CH_3)_3SnCl]_s$ is the stoichiometric concentration of the reagent, and k_{obs} is the first order rate constant for the disappeance of hexamethylditin.

If the second order rate constants for reaction of hexamethylditin with $(CH_3)_3SnCl$ and with $(CH_3)_3Sn^+$ are, respectively $6k_a$ and $6k'_a$ and the dissociation constant,

$$K_D = [(CH_3)_3Sn^+][Cl^-]/[(CH_3)_3SnCl]$$

is sufficiently small, then,

$$[(CH_3)_3Sn^+] \sim K_D^{1/2}[(CH_3)_3SnCl]_s^{1/2}$$

and

$$6k_a = 1.00\ (\pm 0.03) \times 10^{-4}\ M^{-1}\ s^{-1}\ (30°C)$$

$$6(k'_a - k_a)K_D^{1/2} = 5.5\ (\pm 1.4) \times 10^{-6}\ M^{-1/2}\ s^{-1}\ (30°C)$$

A value for K_D of 1.25×10^{-4} M (methanol, ionic strength 0.25 M, 25°C) has been reported [6] which gives $6k'_a \sim 6 \times 10^{-4}\ M^{-1}\ s^{-1}$. However, in our experiments the ionic strength arising from trimethyltin chloride dissociation will be much smaller. Hence $K_D \sim 1 \times 10^{-5}$ M might be more reasonable in which case $6k'_a \sim 2 \times 10^{-3}\ M^{-1}\ s^{-1}$.

(b) Tetramethyltin and trimethyltin chloride, rate studies

This reaction was made observable by the use of $(CD_3)_4Sn$, and was carried out with trimethyltin chloride in large excess so that a first order kinetic analysis could be applied and a single exchange would predominate at least in the early part of the reaction.

$$\begin{array}{lllll} (CD_3)_4Sn & + (CH_3)_3SnCl & \xrightarrow{4k_b} & (CD_3)_3SnCl & + (CD_3)_3SnCH_3 \\ A - X & B - X \sim B & & X & X \end{array}$$

Considering all species observable in the PMR specturm as a growing "tetramethyltin" peak to be $(CD_3)_3SnCH_3$, the data were processed as previously described for the tetramethyllead/trimethyllead chloride reaction [7] by the first order expression;

$$\log[1 - \frac{X}{A}] = 2.303 \times 4k_bBt$$

which is illustrated in Fig. 1.

For two kinetic runs:

$[(CH_3)_4Sn]_0$	$[(CH_3)_3SnCl]_0$	$4k_b$	
0.043 M	0.84 M	$7.5\ (\pm 0.2) \times 10^{-5}$	$7.2\ (\pm 0.4) \times 10^{-5}\ M^{-1}\ s^{-1}$
0.064 M	0.75 M	$6.8\ (\pm 0.2) \times 10^{-5}$	

(c) Trimethyl-t-butyltin and trimethyltin chloride, rate studies

As far as can be judged from the PMR spectrum at high gain there is exclusively Sn—CH_3 cleavage. The reaction was studied from both sides of the equilibrium.

$$(CH_3)_3SnC(CH_3)_3 + (CH_3)_3SnCl \underset{4k_{-c}}{\overset{3k_c}{\rightleftharpoons}} (CH_3)_2Sn[C(CH_3)_3]Cl + (CH_3)_4Sn$$

The reaction is rather slow in both directions and reaches an equilibrium for which

$$K = 3k_c/4k_{-c} = 0.09\ (\pm 0.01)$$

Second order treatment of the data yielded: $[(CH_3)_3SnC(CH_3)_3]_0$ 0.20 M;

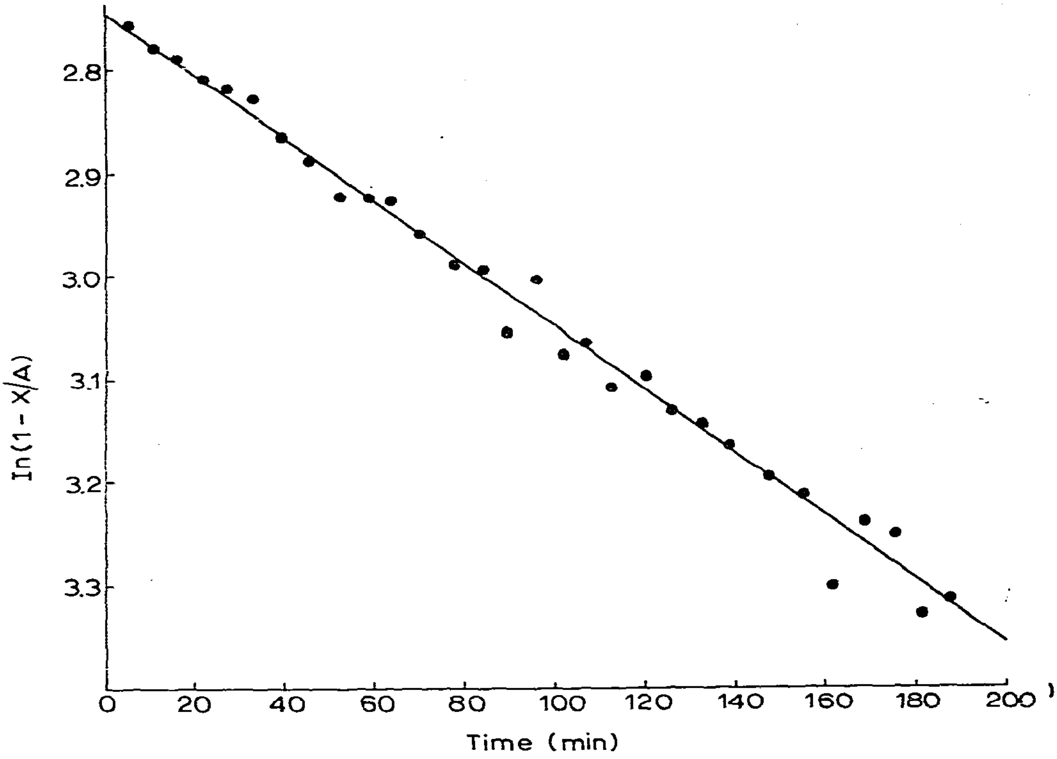


Fig. 1. First order plot for the reaction $(CD_3)_4Sn$ + $(CH_3)_3SnCl$.

$[(CH_3)_3SnCl]_0$ 0.20 M; $3k_c = 2.3\ (\pm 0.1) \times 10^{-6}\ M^{-1}\ s^{-1}$; and $[(CH_3)_4Sn]_0$ 0.37 *M*; $[(CH_3)_2SnC(CH_3)_3Cl]_0$ 0.35 *M*; $4k_{-c} = 3.8\ (\pm 0.2) \times 10^{-5}\ M^{-1}\ s^{-1}$, which with the equilibrium measurements give

$$3k_c = 2.9\ (\pm 0.6) \times 10^{-6},\ 4k_{-c} = 3.2\ (\pm 0.4) \times 10^{-5}\ M^{-1}\ s^{-1}$$

Over prolonged periods of the reaction the t-butyl species, particularly the chloride, underwent decomposition introducing inaccuracies in the analyses for which allowances could not be satisfactorily made.

(d) "Dimethyltin" from $(CH_3)_6Sn_2/(CH_3)_3SnCl$

Three samples of precipitated "dimethyltin" were collected from reactions on methanol at 25°C having $[(CH_3)_6Sn_2]_0 = [(CH_3)_3SnCl]_0 = 5.1 \times 10^{-2}$ *M A*; 0.101 *M B*; 0.305 *M C*. All three has essentially the same appearance and were yellow in colour. Table 1 summarises the mass spectra obtained in terms of the largest peak of each set corresponding to a single ion containing three or more tin atoms. These sets have the characteristic patterns arising from the various isotopes of tin.

(e) "Dimethyltin" from $(CH_3)_6Sn_2/(CD_3)_3SnCl$

The PMR spectrum of the methanol solution of these reagents, $[(CD_3)_3SnCl]$

TABLE 1

MASS SPECTRA OF DIMETHYLTIN SAMPLES EX $(CH_3)_3SnCl/(CH_3)_6Sn_2$

m/e	Probable ion	Relative intensity			*m/e*	Probable ion	Relative intensity		
		A	B	C			A	B	C
1220	$(CH_3)_{18}Sn_8^{+\cdot}$	0.5	0.8	1.2	669	$(CH_3)_5Sn_5^{+}$	11.1	2.7	8.6
1190	$(CH_3)_{16}Sn_8^{+\cdot}$	2.9	0.5	2.3	639	$(CH_3)_3Sn_5^{+}$	11.6		5.75
1175	$(CH_3)_{15}Sn_8^{+}$	0.8		0.7	624	$(CH_3)_2Sn_5^{+\cdot}$	66.4		
1160	$(CH_3)_{14}Sn_8^{+\cdot}$	0.9		1.3	626	$(CH_3)_{10}Sn_4^{+\cdot}$	9.5	19.2	12.8
1145	$(CH_3)_{13}Sn_8^{+\cdot}$	0.8		0.5	611	$(CH_3)_9Sn_4^{+}$	57.5	70.1	7.6
1072	$(CH_3)_{16}Sn_7^{+\cdot}$	3.2	3.8	3.2	596	$(CH_3)_8Sn_4^{+\cdot}$	60.0	40.7	42.8
1042	$(CH_3)_{14}Sn_7^{+\cdot}$	11.2	2.7	9.9	581	$(CH_3)_7Sn_4^{+}$	*100.0*	29.8	52.7
1027	$(CH_3)_{13}Sn_7^{+}$	9.3	1.1	5.3	566	$(CH_3)_6Sn_4^{+\cdot}$	22.7	4.4	
997	$(CH_3)_{11}Sn_7^{+}$	1.6		0.8	551	$(CH_3)_5Sn_4^{+}$	73.0	15.5	36.4
867	$(CH_3)_9Sn_7^{+}$			0.2	536	$(CH_3)_4Sn_4^{+\cdot}$	12.5		
922	$(CH_3)_{14}Sn_6^{+\cdot}$	8.4	8.8	9.1	521	$(CH_3)_3Sn_4^{+}$	39.2	10.5	22.3
907	$(CH_3)_{13}Sn_6^{+}$	48.4	3.8		506	$(CH_3)_2Sn_4^{+\cdot}$	25.0	7.8	11.9
892	$(CH_3)_{12}Sn_6^{+\cdot}$	33.4	10.8	38.5	476	$(CH_3)_8Sn_3^{+\cdot}$	13.1	15.1	9.1
877	$(CH_3)_{11}Sn_6^{+}$		8.2	25.8	461	$(CH_3)_7Sn_3^{+}$	92.8	*100.0*	*100.0*
774	$(CH_3)_{12}Sn_5^{+\cdot}$	11.1	17.3	17.8	446	$(CH_3)_6Sn_3^{+\cdot}$	50.4	54.7	54.5
759	$(CH_3)_{11}Sn_5^{+}$	26.5	28.7	28.9	431	$(CH_3)_5Sn_3^{+}$	69.5	33.5	48.7
744	$(CH_3)_{10}Sn_5^{+\cdot}$	75.7	19.2	51.8	416	$(CH_3)_4Sn_3^{+\cdot}$	45.3	21.6	32.4
729	$(CH_3)_9Sn_5^{+}$	70.8	21.3	50.4	401	$(CH_3)_3Sn_3^{+}$	13.7	26.5	39.1
714	$(CH_3)_8Sn_5^{+\cdot}$	11.6		7.3	386	$(CH_3)_2Sn_3^{+\cdot}$	18.0	17.0	22.7
699	$(CH_3)_7Sn_5^{+}$	16.0	3.1	9.8					

0.099 M, $[(CH_3)_6Sn_2]$ 0.120 M indicated that the reaction is exclusively

$$(CH_3)_6Sn_2 + (CD_3)_3SnCl \rightarrow (CD_3)_3SnCH_3 + [(CH_3)_2Sn] + (CH_3)_3SnCl$$

followed by

$$(CH_3)_6Sn_2 \xrightarrow{(CH_3)_3SnCl} (CH_3)_4Sn + [(CH_3)_2Sn]$$

However, a small loss of CH_3 groups from the solution could not be excluded, therefore the "dimethyltin" was examined by mass spectrometry. Table 2 summarizes the result.

(f) Reaction in the presence of benzyl chloride

The reaction of hexamethylditin and trimethyltin chloride (both 0.2 M) in methanol containing benzyl chloride (ca. 2 M) was allowed to proceed for several days during which time only the normal products were observed in the PMR spectrum. No resonances could be found corresponding to benzyltin species, furthermore the "dimethyltin" product gave a mass spectrum essentially the same as those in Table 1.

(g) Reaction in the presence of $^{13}CH_3I$

The reaction of hexamethylditin, 0.227 M and trimethyltin chloride (0.194 M) in methanol containing ^{13}C enriched methyl iodide, (1.838 M) was studied by PMR at 15 minute intervals during 6 h. No evidence of the formation of a ^{13}C enriched trimethyltin species was observed. However, after this time the

TABLE 2

MASS SPECTRUM OF DIMETHYLTIN EX $(CD_3)_3SnCl/(CH_3)_6Sn_2$

m/e	Probable ion	Relative intensity	*m/e*	Probable ion	Relative intensity
1042	$(CH_3)_{14}Sn_7^{+\cdot}$	9.8	566	$(CH_3)_6Sn_4^{+\cdot}$	41.7
1027	$(CH_3)_{13}Sn_7^{+}$	5.6	551	$(CH_3)_5Sn_4^{+}$	94.1
922	$(CH_3)_{14}Sn_6^{+\cdot}$	6.2	521	$(CH_3)_3Sn_4^{+}$	35.3
907	$(CH_3)_{13}Sn_6^{+}$	54.4	506	$(CH_3)_2Sn_4^{+\cdot}$	22.0
892	$(CH_3)_{12}Sn_6^{+\cdot}$	46.9	491	$CH_3Sn_4^{+}$	45.0
774	$(CH_3)_{12}Sn_5^{+}$	9.5	476	$(CH_3)_8Sn_3^{+\cdot}$	16.0
744	$(CH_3)_{10}Sn_5^{+\cdot}$	88.5	461	$(CH_3)_7Sn_3^{+}$	77.3
729	$(CH_3)_9Sn_5^{+}$	87.8	446	$(CH_3)_6Sn_3^{+\cdot}$	54.9
699	$(CH_3)_7Sn_5^{+}$	18.5	431	$(CH_3)_5Sn_3^{+}$	77.5
669	$(CH_3)_5Sn_5^{+}$	14.3	416	$(CH_3)_4Sn_3^{+\cdot}$	56.9
611	$(CH_3)_9Sn_4^{+}$	44.3	401	$(CH_3)_3Sn_3^{+}$	61.5
596	$(CH_3)_8Sn_4^{+\cdot}$	55.8	386	$(CH_3)_2Sn_3^{+\cdot}$	31.3
581	$(CH_3)_7Sn_4^{+}$	100.0	371	$CH_3Sn_3^{+}$	32.4

yellow "dimethyltin" became deep red. Similar red products can be obtained by reacting yellow "dimethyltin" with methyl iodide.

Discussion

A comparison of the rates of Sn—CH_3 cleavage by trimethyltin chloride is as follows:

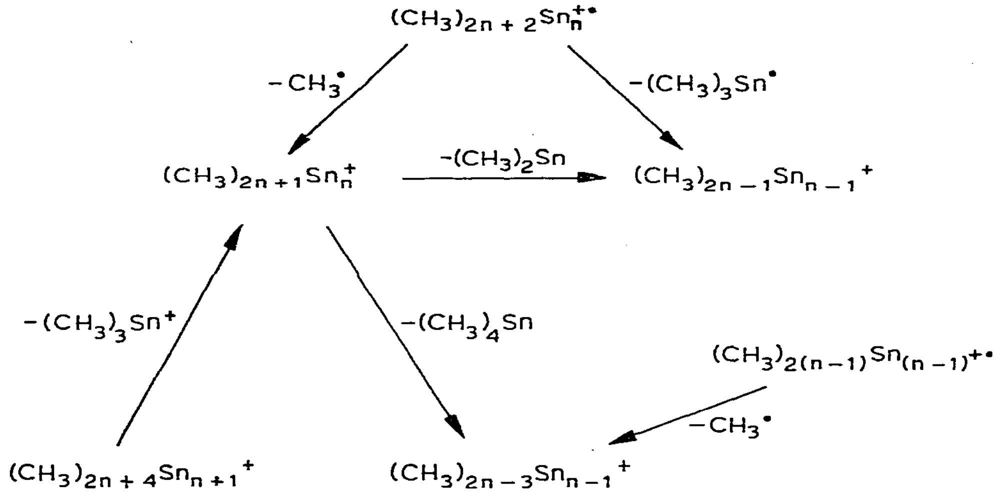
$(CH_3)_6Sn_2$ $\quad k_a = 1.67\ (\pm 0.05) \times 10^{-5}\ M^{-1}\ s^{-1}$

$(CH_3)_4Sn$ $\quad k_b = 1.8\ (\pm 0.1) \times 10^{-5}\ M^{-1}\ s^{-1}$

$(CH_3)_3SnC(CH_3)_3$ $\quad k_c = 0.77\ (\pm 0.04) \times 10^{-7}\ M^{-1}\ s^{-1}$

and the rate constant for the reaction of tetramethyltin with dimethyl-t-butyltin chloride is $k_{-c} = 0.95\ (\pm 0.05) \times 10^{-5}\ M^{-1}\ s^{-1}$. The above value for k_a is a maximum since, depending upon the mechanism of "dimethyltin" polymer formation, k_{obs} could be greater than $6k_a$ (see below). The similarity of k_a and k_b suggests, on the other hand, that essentially the same process is taking place since no steric retardation due to replacement of a methyl by a trimethylstannyl group is expected. (The relative sizes of these groups as indicated by conformational studies in cyclohexanes are $Me_3Sn < CH_3$ [8]). A t-butyl group in the substrate is responsible for a substantial rate reduction. (Similar behaviour is found for the corresponding reactions with trimethyllead chloride [7] and with methylmercuric chloride [3]). By contrast a t-butyl group in the reagent, c.f. k_{-c}, has a much smaller effect.

The "dimethyltin" produced in this reaction is rather unstable and air-sensitive. We have been unable to find a non-reacting solvent for it nor any fraction of it, so that our structural investigations to date rely solely on mass spectral examination. Molecular ions $(CH_3)_{2n+2}Sn_n^{+\cdot}$ and the fragments $(CH_3)_{2n+1}Sn_n^{+}$ are observed up to at least $n = 8$. Of particular importance is the absence of any chlorine containing ions. It would seem that the product is a mixture of non-cyclic species of the type $(CH_3)_{2n+2}Sn_n$, although the presence of cyclic compounds, $(CH_3)_{2n}Sn_n$, cannot be excluded. There are several resonable routes by which the various observed ions could be formed (see e.g. Scheme 1) which



makes it impossible to establish their origin and obtain an analysis of the mixture.

The molecular ions of methylpolygermanes, $(CH_3)_{2n+2}Ge_n$, are reported to lose a methyl radical followed by successive elimination of $(CH_3)_2Ge$ units [9]. Dodecaethylcyclohexastannane, $(C_2H_5)_{12}Sn_6$, yields substantial quantities of the ions $(C_2H_5)_{11}Sn_6^+$, $(C_2H_5)_7Sn_5^+$, $(C_2H_5)Sn_5^+$, $(C_2H_5)_5Sn_4^+$, $(C_2H_5)_4Sn_4H^+$, $(C_2H_5)_3Sn_4^+$ and $(C_2H_5)Sn_4^+$ (but no radical-cations other than the parent) suggesting that there can be eliminations of $(C_2H_5)_2Sn$, $(C_2H_5)_4Sn$, C_4H_8 and C_2H_6 [10]. Unfortunately, there are discrepancies between the two reported studies [11,12] of the mass spectrum of hexamethylditin, and our preliminary studies on this, the simplest alkylpolytin, have much in common but also much differing from both previous studies.

Dimethyltin is clearly indicated to be an intermediate in the thermal decomposition of pentamethylditin bromide reported by Grugel, Neumann and Seifert [13], thus:

$$\begin{tikzcd}
(CH_3)_5Sn_2H + (CH_3)_3CBr \arrow[r, "5^\circ C", "C_6H_6"'] & (CH_3)_5Sn_2Br \arrow[d, "20^\circ C;\ 1.5\ h"] \\
& (CH_3)_3SnBr + (CH_3)_2Sn
\end{tikzcd}$$

where the "dimethyltin" product is found to be a red, non-uniform polymer. Decomposition of the bromide in the presence of large amounts of methyl iodide suppresses the formation of "dimethyltin" and trimethyltin iodide is obtained. Insertion into the Sn—Sn bond of hexaalkylditins is also observed.

We could find no evidence of the trapping of dimethyltin in our system by means of benzyl chloride or methyl iodide, so that our case for its occurrence as an intermediate rests upon our analysis of the reaction between hexamethylditin and trimethyllead chloride [4]. It is instructive, however, to examine some possible mechanisms by which products of the type $(CH_3)_{2n+2}Sn_n$ could be formed and their influence on the observations so far made.

One of our earlier speculations [1] was that the initially formed pentamethylditin chloride might react with hexamethylditin by Sn—Sn cleavage.

$$(CH_3)_6Sn_2 + (CH_3)_5Sn_2Cl \rightleftharpoons (CH_3)_8Sn_3 + (CH_3)_3SnCl$$

or, in general,

$$(CH_3)_{2p+2}Sn_p + (CH_3)_{2q+1}Sn_qCl \rightleftharpoons$$

$$(CH_3)_{2(p-x)+1}Sn_{(p-x)}Cl + (CH_3)_{2(q+x)+2}Sn_{q+x}$$

to generate species with a high tin content without the intermediacy of dimethyltin. However there is no indication that the parent exchange reaction,

$$(CH_3)_6Sn_2 + (CD_3)_3SnCl \rightleftharpoons (CH_3)_3SnSn(CD_3)_3 + (CH_3)_3SnCl$$

takes place to a detectable extent, since CD_3 groups do not appear in polymeric "dimethyltin" ultimately obtained. Thus the key reaction of this mechanism appears to have been excluded.

Eliminating the above mechanism, it is difficult to envisage polytin formation without the intermediacy of dimethyltin, and two modes of reaction might be responsible.

A. Tin—tin bond insertion

$$(CH_3)_6Sn_2 + (CH_3)_3SnCl \underset{-1}{\overset{1}{\rightleftharpoons}} (CH_3)_4Sn + (CH_3)_5Sn_2Cl$$

$$(CH_3)_5Sn_2Cl \underset{-2}{\overset{2}{\rightleftharpoons}} (CH_3)_3SnCl + (CH_3)_2Sn$$

$$(CH_3)_6Sn_2 + (CH_4)_2Sn \overset{3}{\rightleftharpoons} (CH_3)_8Sn_3 \rightarrow \text{etc.}$$

$$(CH_3)_{2n}Sn_{n-1} + (CH_3)_2Sn \overset{n}{\rightleftharpoons} (CH_3)_{2n+2}Sn_n \rightarrow \text{precipitate}$$

Neglecting the reverse reactions (—1), which is observed to be unimportant, and (—2), the measured rate of reaction would be:

$$-d[(CH_3)_6Sn_2]/dt$$

$$= k_1[(CH_3)_6Sn_2][(CH_3)_3SnCl]\{1 + k_3[(CH_3)_6Sn_2]/\Sigma k_n[(CH_3)_{2n+2}Sn_n]\} \quad (n > 2)$$

$$\simeq 2k_1[(CH_3)_6Sn_2](CH_3)_3SnCl]$$

which would give $k_{obs} = 12k_a$ instead of the expected $6k_a$ (see above).

B. Tin—chlorine bond insertion

$$\underset{A}{(CH_3)_6Sn_2} + \underset{B}{(CH_3)_3SnCl} \underset{-1}{\overset{1}{\rightleftharpoons}} \underset{P_1}{(CH_3)_4Sn} + \underset{Y_2}{(CH_3)_5Sn_2Cl}$$

$$\underset{Y_2}{(CH_3)_5Sn_2Cl} \underset{-2}{\overset{2}{\rightleftharpoons}} \underset{Y_1 = B}{(CH_3)_3SnCl} + \underset{X}{(CH_3)_2}$$

$$\underset{Y_{p-1}}{(CH_3)_{2p-1}Sn_{p-1}Cl} + \underset{X}{(CH_3)_2Sn} \underset{\bar{k}_D}{\overset{\bar{k}_I}{\rightleftharpoons}} \underset{Y_p}{(CH_3)_{2p+1}Sn_pCl}$$

$$\underset{P_2}{(CH_3)_{2q+2}Sn_q} + \underset{Y_p}{(CH_3)_{2p+1}Sn_pCl} \underset{(2p+2)\bar{k}_R}{\overset{(2q+2)\bar{k}_R}{\rightleftharpoons}} \underset{P_p}{(CH_3)_{2p+2}Sn_p} + \underset{Y_q}{(CH_3)_{2q+1}Sn_qCl}$$

$\bar{k}_I \sim k_{-2}$, average rate of insertion of dimethyltin into Sn—Cl;
$\bar{k}_D \sim k_2$, average rate of dissociation to form dimethyltin;
$\bar{k}_R \sim 1/6\ k_1 \sim 1/4\ k_{-1}$ ($\sim 1.7 \times 10^{-5}\ M^{-1}\ s^{-1}$), average rate of Sn—CH$_3$ cleavage.

Provided that all the species, Y, except trimethyltin chloride are in relatively low concentrations (they are not observed in the PMR spectrum) then

$$-d[(CH_3)_6Sn_2]/dt = k_1[(CH_3)_6Sn_2][(CH_3)_3SnCl] + 6\bar{k}_R[(CH_3)_6Sn_2]\sum^{3} Y_n$$
$$\simeq k_1[(CH_3)_6Sn_2][(CH_3)_3SnCl]_0$$

These two mechanisms lead to different relative reactivities towards trimehtyltin chloride for hexamethylditin and tetramethyltin, i.e. 0.93/1 for B and 0.46/1 for A. We favour the former on the basis of the corresponding relative reactivities of 1.45/1 towards trimethyllead chloride [14] but find the distinction far from clear cut. Studies are in hand to determine the substituent effect of the trimethylstannyl group on other electrophilic aliphatic substitutions at carbon with the aim of clarifying this situation.

References

1 D.C. McWilliam and P.R. Wells, J. Organometal. Chem., 85 (1975) 165.
2 G. Tagliavini, G. Pilloni and G. Plazzonga, Ric. Sci., 36 (1966) 3.
3 D.C. McWilliam and P.R. Wells, J. Organometal. Chem., 85 (1975) 335.
4 W.F. Edgell and C.H. Ward, J. Amer. Chem. Soc., 76 (1954) 1169.
5 H. Lund and J. Bjerrm, Ber. Deut. Chem. Ges., A, 64 (1931) 210.
6 L. Doretti, P. Zanella and G. Tagliavini, J. Organometal. Chem., 22 (1970) 23.
7 D.P. Arnold and P.R. Wells, J. Organometal. Chem., 111 (1976) 285.
8 W. Kitching, H. Olszowy, J. Waugh and D. Doddrell, J. Org. Chem., 43 (1978) 898.
9 D.B. Chambers, F. Glocking and J.C.R. Light, Quart. Revs., 22 (1968 317.
10 W.P. Neumann and H.P. Ritter, J. Organometal. Chem., 56 (1973) 199.
11 M. Gielen, J. Nasielski and G. Vandendungen, Bull. Soc. Chim. Belges, 80 (1971) 175.
12 M. Lappert, J. Pedley, J. Simpson and T. Spalding, J. Organometal. Chem., 29 (1971) 195.
13 C. Grugel, W.P. Neumann and P. Seifert, Tetrahedron Lett., (1977) 2205.
14 D.P. Arnold and P.R. Wells, J. Organometal. Chem., 108 (1976) 345.