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REACTION OF HEXAMETHYLDITIN WITH TRIMETHYLLEAD CHLORIDE

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Summary

Unlike the trimethyltin chloride-catalysed decomposition of hexamethylditin to tetramethyltin and polymeric "dimethyltin", reaction with trimethyllead chloride initially yields tetramethyllead, trimethyltin chloride and lead(II) chloride. Concurrently and subsequently tetramethyllead and trimethyltin chloride react together. A mechanism involving dimethyltin formation and insertion into trimethyllead chloride is suggested.

Introduction

Trialkyltin halides react with hexamethylditin by initial electrophilic Sn—CH_3 cleavage, ultimately yielding a tetraalkyltin and a polymeric form of "dimethyltin" according to [1,2]:

$$CH_3)_6Sn_2 + R_3SnX \rightarrow CH_3SnR_3 + [(CH_3)_2Sn] + (CH_3)_3SnX$$

$$CH_3)_6Sn_2 \xrightarrow[\text{catalytic}]{(CH_3)_3SnX} (CH_3)_4Sn + [(CH_3)_2Sn]$$

Despite the fact that other reagents, e.g. mercuric salts and alkylmercuric salts [3], silver salts and complexes [4] and iodine [5], appear to react exclusively with the Sn—Sn bond, there is no detectable cleavage in this sense by trialkyltin electrophiles [2,6].

The structure and the mechanism of the formation of the polymeric "dimethyltin" are still uncertain. However, a mixture of species of the type $(CH_3)_{2n+2}Sn_n$ is indicated, and a series of insertions of transient dimethyltin into Sn—Sn or Sn—X bonds appears to be involved [6].

Trimethyllead chloride would appear to be a similar, although somewhat more reactive, electrophile towards trimethyltin chloride. Nevertheless, its reaction with hexamethylditin does not yield polymeric "dimethyltin" but rather a lower valence state product of lead, i.e. lead(II) chloride, is formed. This reaction clear-

ly can provide important clues as to the nature of the steps subsequent to Sn—CH_3 cleavage of hexamethylditin.

Experimental

Materials

Hexamethylditin and tetramethyltin were purified and stored as previously described [2,3]. Tetramethyllead (Alfa Inorganics) was supplied and used as an 80% solution in toluene. Trimethyllead chloride was obtained from the Organisch Chem. T.N.O. Utrecht, and was recrystallised from chloroform/hexane. Dimethyl-t-butyltin chloride was prepared in 80% yield by addition of mercuric chloride (1.63 g, 0.006 mol) to trimethyl-t-butyltin (1.33 g, 0.006 mol) in about 20 ml methanol. Most of the methylmercuric chloride separated immediately as a white fluffy solid, which was filtered off. The solution was cooled to —25°C, and a second crop of methylmercuric chloride was collected. Removal of the solvent left a low-melting solid. This was distilled up a glass tube at 100°C/38 mmHg, giving a clear oil, which solidified when touched with a spatula (m.p. 36°C). NMR showed the absence of methylmercuric chloride. The compound has a foul odour, is extremely soluble in methanol and anhydrous ether, and is slightly light-sensitive, precipitating a white solid. Found: C, 29.7; H, 6.1. $C_6H_{15}SnCl$ calcd.: C, 29.9; H, 6.3%. Methanol was AJAX UNIVAR "dried for non-aqueous titrations".

Product examination

All reactions were conducted in NMR tubes sealed with serum caps, and the composition of the reaction mixtures derived from PMR peak height measurements at 100 MHz (JEOL PS-100 or MH-100) as in previous studies [2,3]. Fig. 1 illustrates a typical spectrum with the components clearly resolved. Table 1 summarises the chemical shift and coupling constant data for methanol solutions. By the use of an internal reference, e.g. a known amount of acetone, it was established that no metal-bound methyl groups were lost from the system. The individual corrected peak heights could thus be compared with their sum and related to a constant determined by the initial concentrations. (Methyl group balance.)

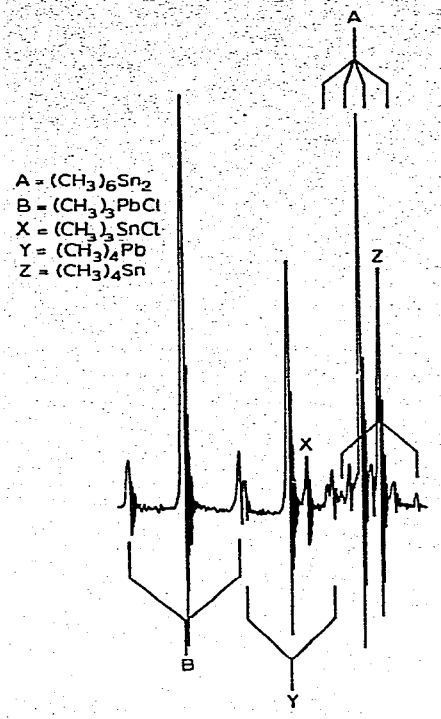
Lead(II) chloride, which precipitates during the reaction, was identified by its dissolution in boiling water, and the precipitation of black lead sulphide on the addition of aqueous sodium sulphide, but was nor normally determined. (In one case an 87% recovery was achieved.)

Kinetic measurements

These were carried out essentially as previously described [2,3], and a typical set of data points is illustrated in Fig. 2. Calculated concentration vs. time curves (see below) are also shown.

(a) $(CH_3)_6Sn_2/(CH_3)_3PbCl$. In all cases the ratio of hexamethylditin : trimethyllead chloride was in excess of the stoichiometric requirement and the reactions were followed until the latter was essentially all consumed. (The slow reaction of hexamethylditin with the low concentration of trimethyltin chloride was inconsequential throughout.)

(b) $(CH_3)_4Pb/(CH_3)_3SnCl$. The reaction between tetramethyllead and trimethyltin chloride was allowed to proceed to equilibrium, $K = 4k_1/4k_{-1} = 75$ (±10).



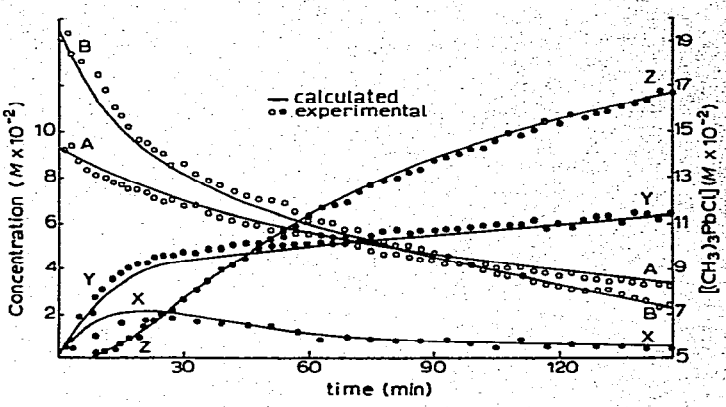


Fig. 1. 100 MHz NMR spectrum of a reaction mixture initially 0.071 *M* in $(CH_3)_6Sn_2$ and 0.145 *M* in $(CH_3)_3PbCl$ (after 40 min).

Fig. 2. Comparison of calculated and experimental concentration/time data for reaction $(CH_3)_6Sn_2$ + $(CH_3)_3PbCl$.

$$(CH_3)_4Pb + (CH_3)_3SnCl \underset{4k_{-1}}{\overset{4k_1}{\rightleftharpoons}} (CH_3)_3PbCl + (CH_3)_4Sn \qquad (1)$$

Employing the usual second order function for different initial concentrations the data show good linearity with evidence of the reverse reaction at latter stages. The mean of three runs gave $4k_1 = 3.4\ (\pm 0.4) \times 10^{-2}\ M^{-1}\ s^{-1}$ (30°C) and hence $4k_{-1} = 4.7\ (\pm 1.2) \times 10^{-4}\ M^{-1}\ s^{-1}$.

The concentration vs. time data for the overall reaction were corrected for reaction 1 in the following manner. The species involved are symbolized thus:

TABLE 1

METHYL GROUP RESONANCES [a]

	$\delta(CH_3)$ [b] (ppm)	J (Hz)		$\delta(CH_3)$ [b] (ppm)	J (Hz)
$(CH_3)_6Sn_2$	0.20	46, 48 [c] 15, 16 [d]	$(CH_3)_6Pb_2$	0.97	43 [e] 23 [f]
$(CH_3)_4Sn$	0.06	52, 54 [c]	$(CH_3)_4Pb$	0.73	62.5 [e]
$(CH_3)_3SnCl$	0.58	64, 67 [c]	$(CH_3)_3PbCl$	1.50	78 [e]

[a] In methanol. [b] Chemical shifts positive to low field of TMS. [c] ^{117}Sn—C—H and ^{119}Sn—C—H coupling. [d] ^{117}Sn—Sn—C—H and ^{119}Sn—Sn—C—H coupling. [e] ^{207}Pb—C—H coupling. [f] ^{207}Pb—Pb—C—H coupling.

$(CH_3)_3PbCl = B$; $(CH_3)_3SnCl = X$; $(CH_3)_4Pb = Y$; $(CH_3)_4Sn = Z$. The concentrations of each species are known at a series of times at equal intervals, Δt. At time t_i, the concentrations are B_i, X_i, Y_i, Z_i. At the mean times $\bar{t}_i = \frac{1}{2}(t_i + t_{i-1})$, the increments in each concentration, divided by Δt, are the approximate rates at the times t_i, viz. $(\Delta B/\Delta t)_i$, etc.

If the rate constant for reaction 1 is k_R, $(=4k_1)$, then the contribution to the overall rate due to this reaction is:

$$R_i = -(\Delta Y/\Delta t)_i = -(\Delta X/\Delta t)_i = (\Delta B/\Delta t)_i = (\Delta Z/\Delta t)_i = k_R \bar{X}_i \bar{Y}_i$$

The overall rates for each species may now be modified by this quantity, e.g.:

$$(\Delta B/\Delta t)'_i = (\Delta B/\Delta t)_i - R_i, \text{ etc.}$$

By a reverse procedure, using the initial concentrations and the modified rates, four series of points were generated, being the corrected concentration vs. time curves, e.g.:

$$B_i = (\Delta B/\Delta t)'_i \cdot \Delta t + B_{i-1}, \text{ etc.}$$

(c) $(CH_3)_3SnC(CH_3)_3/(CH_3)_3PbCl$. The reaction of tetramethyllead with dimethyl-t-butyltin chloride was studied to obtain the rate constant for the reverse reaction, i.e. that of trimethyl-t-butyltin with trimethyllead chloride (reaction 2).

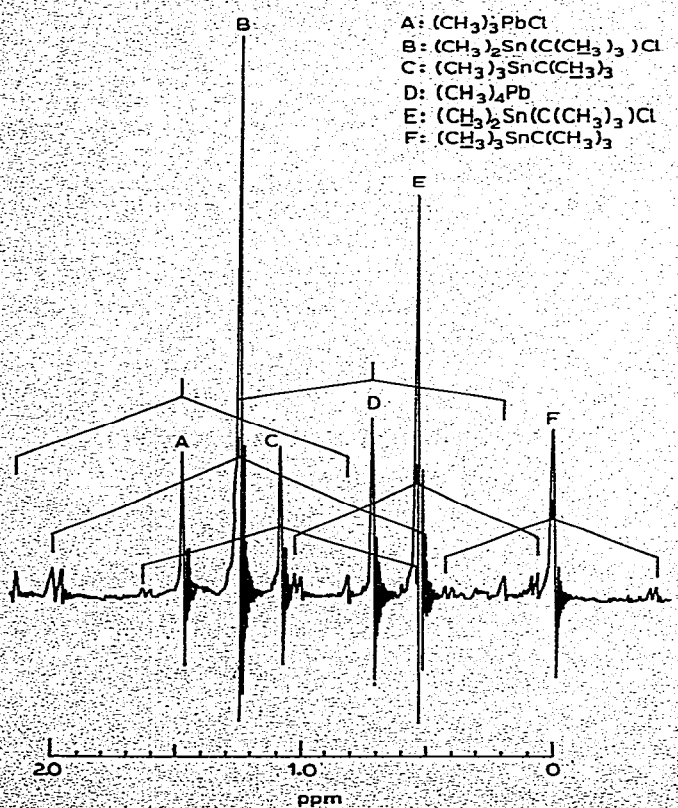


Fig. 3. 60 MHz NMR spectrum of reaction mixture $(CH_3)_4Pb + (CH_3)_2Sn[C(CH_3)_3]Cl$.

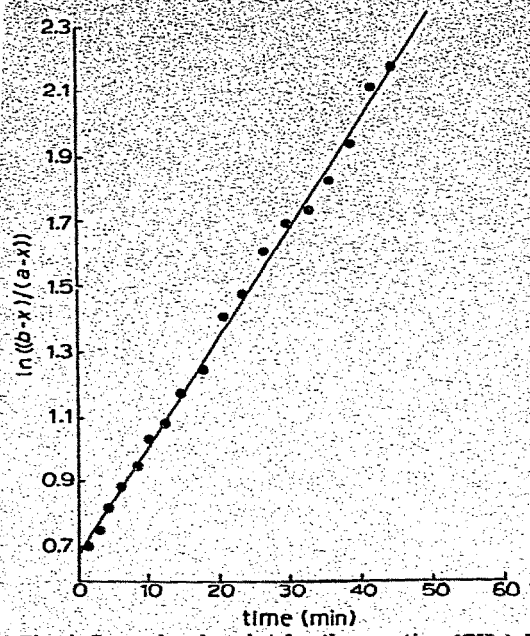


Fig. 4. Second order plot for the reaction $(CH_3)_4Pb + (CH_3)_2Sn[C(CH_3)_3]Cl$.

$$(CH_3)_3SnC(CH_3)_3 + (CH_3)_3PbCl \underset{4k_{-2}}{\overset{3k_2}{\rightleftharpoons}} (CH_3)_2Sn[C(CH_3)_3]Cl + (CH_3)_4Pb \qquad (2)$$
$$x \qquad\qquad x \qquad\qquad b-x \qquad\qquad a-x$$

A 60 MHz NMR spectrum is shown in Fig. 3, with the resonances and satellites indicated. The kinetics were analysed using a methyl group balance. The sum of one-quarter of the corrected height of the $(CH_3)_4Pb$ peak, and one-third of the corrected height of the $(CH_3)_3Sn$ peak of the $(CH_3)_3SnC(CH_3)_3$, represents the known initial tetramethyllead concentration, a. Thus $(a-x)$ can be calculated, and thence $(b-x)$. The normal second order functions exhibited good correlations (Fig. 4). The mean value from two runs was $4k_{-2} = 1.8\ (\pm 0.1) \times 10^{-2}\ M^{-1}\ s^{-1}$. The equilibrium constant was found to be $K = 4k_{-2}/3k_2 = 550 \pm 50$, which enabled calculation of the required $3k_2 = 3.3\ (\pm 0.5) \times 10^{-5}\ M^{-1}\ s^{-1}$.

Results and discussion

The concentration vs. time curves for the hexamethylditin/trimethyllead chloride reaction, cf. Fig. 2, display a number of interesting features. For an initial reactant ratio of 1 : 2 the overall reaction, neglecting a small yield of trimethyltin chloride, is:

$$(CH_3)_6Sn_2 + 2(CH_3)_3PbCl \rightarrow 2(CH_3)_4Sn + (CH_3)_4Pb + PbCl_2$$

However, it is evident that initially trimethyllead chloride is being consumed at about four times the rate of hexamethylditin. Furthermore, most of the total tetramethyllead arises early in the reaction, after which its rate of formation levels off while tetramethyltin becomes the major product. Also an almost steady state in trimethyltin chloride is quite rapidly attained. These features are

all consistent with the consecutive formation and destruction of tetramethyllead and trimethyltin chloride. When the appropriate corrections are made to the various concentrations allowing for reaction 1 it is found that all of the tetramethyltin product in fact arises from reaction 1 and the stoichiometry of the primary reaction is found to be:

$$(CH_3)_6Sn_2 + 4(CH_3)_3PbCl \rightarrow 3(CH_3)_4Pb + 2(CH_3)_3SnCl + PbCl_2$$

To obtain the rate constant for the primary reaction, presumed to be first order each in hexamethylditin and trimethyllead chloride, i.e. eq. 3, the concen-

$$(CH_3)_6Sn_2 + (CH_3)_3PbCl \xrightarrow{6k_3} \quad (3)$$

tration vs. time data for hexamethylditin were fitted to a fourth degree polynomial employing a curve-fitting least squares program (kindly provided by Dr. V. Lucchini). The first derivative of this function gives the instantaneous rate at each point, which, when divided by the appropriate concentrations of hexamethylditin and trimethyllead chloride, yields many values for the second order rate constant. The set of values for each kinetic run oscillated about the mean just as the experimental points oscillated about the polynomial expression. The distribution about the mean was, however, random, and the mean values from four kinetic runs at different initial concentrations are in excellent agreement (Table 2).

To test that the system was properly represented by the two rate processes, the rate equations were integrated using a Runge—Kutta program (a modified version of a PDP-10 Library Program) yielding a set of calculated concentration vs. time curves. One result is illustrated in Fig. 2 based upon the above value of $6k_3$ and a value of $4k_1$ that is 85% of the value independently determined. No allowance was made for the reaction of hexamethylditin with trimethyltin chloride ($1.0 \times 10^{-4}\ M^{-1}\ s^{-1}$) [2]. It is probably not significant that the required value of $4k_1$ is slightly lower since the reaction conditions are not identical. Full optimisation of k_1 and k_3 was not considered to be justified in view of experimental uncertainties and the possibility of neglected minor rate steps.

It is interesting to compare the reactivities summarised in Table 3. For Sn—CH_3 cleavage, trimethyllead chloride is about ten times as reactive as trimethyltin chloride. The methyl groups of tetramethyltin have about the same reactivity as those of hexamethylditin indicating no significant activating effect arising from the trimethylstannyl group. On the other hand the t-butyl group is responsible for a substantial reduction in cleavage rate, which is presumably steric in origin.

TABLE 2

RATE CONSTANTS FOR REACTION 3

$[(CH_3)_6Sn_2]_0$ (M)	$[(CH_3)_3PbCl]_0$ (M)	$6k_3$ (30°C) ($\times 10^{-3}\ M^{-1}\ s^{-1}$)
0.071	0.145	1.11 (±0.02)
0.055	0.162	1.03 (±0.01)
0.082	0.164	1.00 (±0.02)
0.094	0.200	1.05 (±0.01)
average value	$6k_3 = 1.05\ (\pm 0.06) \times 10^{-3}\ M^{-1}s^{-1}$.	

TABLE 3

STATISTICALLY CORRECTED RATE CONSTANTS FOR Sn—CH_3 CLEAVAGE (30 ± 0.5°C)

Substrate	$(CH_3)_3SnCl$	$(CH_3)_3PbCl$
$(CH_3)_6Sn_2$	$1.7 \times 10^{-5}\ M^{-1}s^{-1}$ [a]	$k_3 = 1.75 \times 10^{-4}\ M^{-1}s^{-1}$ [c]
$(CH_3)_4Sn$	$1.8 \times 10^{-5}\ M^{-1}s^{-1}$ [b]	$k_{-1} = 1.2 \times 10^{-4}\ M^{-1}s^{-1}$ [c]
$(CH_3)_3SnC(CH_3)_3$	$1 \times 10^{-6}\ M^{-1}s^{-1}$ [b]	$k_2 = 1.1 \times 10^{-5}\ M^{-1}s^{-1}$ [c]

[a] Ref. 2. [b] Ref. 6. [c] This work.

For the mechanism of the primary reaction a rate controlling step can be written [1,2,6], thus:

$$(CH_3)_6Sn_2 + (CH_3)_3PbCl \underset{4k_{-3}}{\overset{6k_3}{\rightleftharpoons}} (CH_3)_4Pb + (CH_3)_5Sn_2Cl \qquad (3)$$

and thereafter is speculation. However, in order that intermediates can be formed from which lead(II) chloride can ultimately be derived, it appears necessary that the following ensue:

$$(CH_3)_5Sn_2Cl \underset{-4}{\overset{4}{\rightleftharpoons}} (CH_3)_3SnCl + (CH_3)_2Sn \qquad (4)$$

$$(CH_3)_3PbCl + (CH_3)_2Sn \xrightarrow{5} (CH_3)_3PbSn(CH_3)_2Cl \qquad (5)$$

Presuming $(CH_3)_5Sn_2Cl$ to have a reactivity similar to that of $(CH_3)_3SnCl$, and this is the case for $(CH_3)_3CSn(CH_3)_2Cl$ [6], then $4k_{-3}$ can be estimated as 3×10^{-2} $M^{-1}\,s^{-1}$ (i.e. $\simeq 4k_1$). This means that the equilibrium of reaction 3 is actually quite unfavourable in the observed direction and hence that the further reaction of its product, $(CH_3)_5Sn_2Cl$, must be sufficiently rapid, i.e.:

$$k_4 \gg 3 \times 10^{-2}\,[(CH_3)_4Pb]_{av} \simeq 2 \times 10^{-4}\ s^{-1}$$

to prevent the reverse step being apparent in the kinetics. (There will be no similar problem with step 4 since until the end of the reaction $[(CH_3)_3PbCl] \gg [(CH_3)_3SnCl]$ and the former is probably more reactive, i.e. $k_5 > k_{-4}$.)

Several relatively rapid reactions are possible for the leadtin product of reaction 5 which now possesses easily cleaved Pb—CH_3 bonds. Perhaps the simplest suggestion, however, is that dimethyllead extrusion follows an intramolecular methyl—chlorine exchange and that the dimethyllead rapidly reacts with trimethyllead chloride [7] driving the overall reaction to completion.

$$(CH_3)_3PbSn(CH_3)_2 \rightleftharpoons (CH_3)_2PbSn(CH_3)_3 \rightleftharpoons (CH_3)_2Pb + (CH_3)_3SnCl \xrightarrow{2(CH_3)_3PbCl}$$

(Cl under the first Sn; Cl under the second Pb)

$$2(CH_3)_4Pb + PbCl_2$$

In our view then the reactions of hexamethylditin with trimethyltin and trimethyllead halides have in common the initial Sn—CH_3 cleavage followed by the formation of the intermediate dimethyltin. In the one case this intermediate enters a sequence of reactions leading to polymer formation, while in the other case the more reactive dimethyllead is generated and cleaved to lead(II) chloride.

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