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REACTIONS OF HEXAMETHYLDITIN WITH ALKYLMERCURIC SALTS

II. REACTIONS OF TRIMETHYLSTANNYLMERCURY INTERMEDIATES

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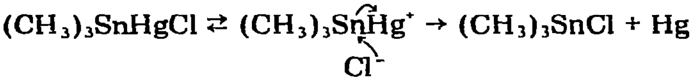
Summary

The kinetics of the formation of two kinds of products from the intermediate $(CH_3)_3SnHgCH_3$, postulated to be formed by reaction of hexamethylditin with methylmercuric salts, have been studied. The two processes are suggested to be electrophilic attack at mercury by methylmercuric halide, and at mercury bound carbon by trimethyltin halide. When pure, the intermediate may be more stable than has been previously supposed.

Introduction

In the preceding paper [1] we described the reactions of hexamethylditin with mercuric chloride and a number of alkylmercuric salts. In the case of mercuric chloride we suggested that trimethylstannylmercuric chloride was formed as a transient intermediate which rapidly decomposed as an ion pair by way of nucleophilic substitution at the highly reactive tin, expelling the good leaving group, mercury (eqns. 1 and 2).

$$(CH_3)_6Sn_2 + HgCl_2 \rightarrow (CH_3)_3SnCl + (CH_3)_3SnHgCl \qquad (1)$$



$$(CH_3)_3SnHgCl \rightleftarrows \underset{Cl^-}{(CH_3)_3Sn\overset{\frown}{}Hg^+} \rightarrow (CH_3)_3SnCl + Hg \qquad (2)$$

One may similarly account for the absence of trialkylsilyl- and trialkylgermylmercuric salts due to their rapid decomposition in reactions that might have been expected to produce them, e.g.,

$[(CH_3)_3Si]_2Hg + HgX_2 \rightarrow 2(CH_3)_3SiX + 2Hg$ (ref. 2)

$[(C_2H_5)_3Ge]_2Hg + HgX_2 \rightarrow 2(C_2H_5)_3GeX + 2Hg$ (ref. 3)

and the results of the following reactions:

$(C_2H_5)_3SnH + C_2H_5HgCl \rightarrow (C_2H_5)_3SnCl + Hg + C_2H_6$ (ref. 4)

$(C_2H_5)_3SnH + C_2H_5HgOCOCH_3 \rightarrow (C_2H_5)_3SnOCOCH_3 + Hg + C_2H_6$ (ref. 5)

When the above decompostion route is unavailable, the mercurials of the Group IV elements can be isolated as is the case for the species $(R_3M)_2Hg$, although low temperature must be maintained for the tin compound [6, 7].

We postulate that the reaction of hexamethylditin with alkylmercuric salts yields transient trimethylstannylmercurials and that these are the source of the final products (eqns. 3-5).

$$(CH_3)_6Sn_2 + RHgX \rightarrow (CH_3)_3SnX + (CH_3)_3SnHgR \qquad (3)$$

$$(CH_3)_3SnHgR \begin{cases} \rightarrow (CH_3)_3SnR \rightarrow & (4) \\ \rightarrow (CH_3)_3SnX + R_2Hg & (5) \end{cases}$$

Mitchell [7] has reported the preparation of t-butyl(trialkylstannyl)mercurials and has demonstrated that radical decomposition leading to CIDNP occurs in benzene solution at 37°. Presumably due to its instability methyl(trimethylstannyl)mercury could not be isolated. It has been tentatively suggested that its rapid decomposition to tetramethyltin and mercury might follow an intramolecular process, but that this is prevented by steric crowding in the case of the t-butyl derivative giving it greater stability.

Experimental

Details of the materials and techniques employed are given in the preceding paper [1].

Since we are particularly interested in the relative rates of formation of tetramethyltin and dimethylmercury, initial concentrations were chosen such that both were formed in substantial quantities. This in general requires that there be more hexamethylditin than required according to the stoichiometry:

$$(CH_3)_6Sn_2 + (1+x)\, CH_3HgX \rightarrow (1+x)\, (CH_3)_3SnX + (1-x)\, (CH_3)_4Sn + x\, (CH_3)_2Hg + Hg$$

Figure 1 of the preceding paper illustrates a typical PMR spectrum during reaction. The variations in concentration of hexamethylditin, methylmercuric halide, and trimethyltin halide are readily determined, but dimethylmercury always appears close to hexamethylditin so that a precise determination is not possible when its peak is small and that of hexamethylditin very large. Having verified the above stoichiometry for several systems the following calculation was employed when direct measurement was not feasible:

$$[(CH_3)_2Hg]_t = \tfrac{1}{2}\{[(CH_3)_3SnX]_t - [(CH_3)_4Sn]_t\}$$

Since its peak was always small, the concentration of methylmercuric halide was generally determined with greater precision from:

$$[CH_3HgX]_t = [CH_3HgX]_0 - [(CH_3)_3SnX]_t$$

Results and discussion

Figure 1 for a methylmercuric bromide reaction, like Fig. 2 of the preceding paper for a methylmercuric chloride reaction, shows that the rate of formation of dimethylmercury is initially greater than that of tetramethyltin. This would accord with two decomposition pathways for the intermediate,

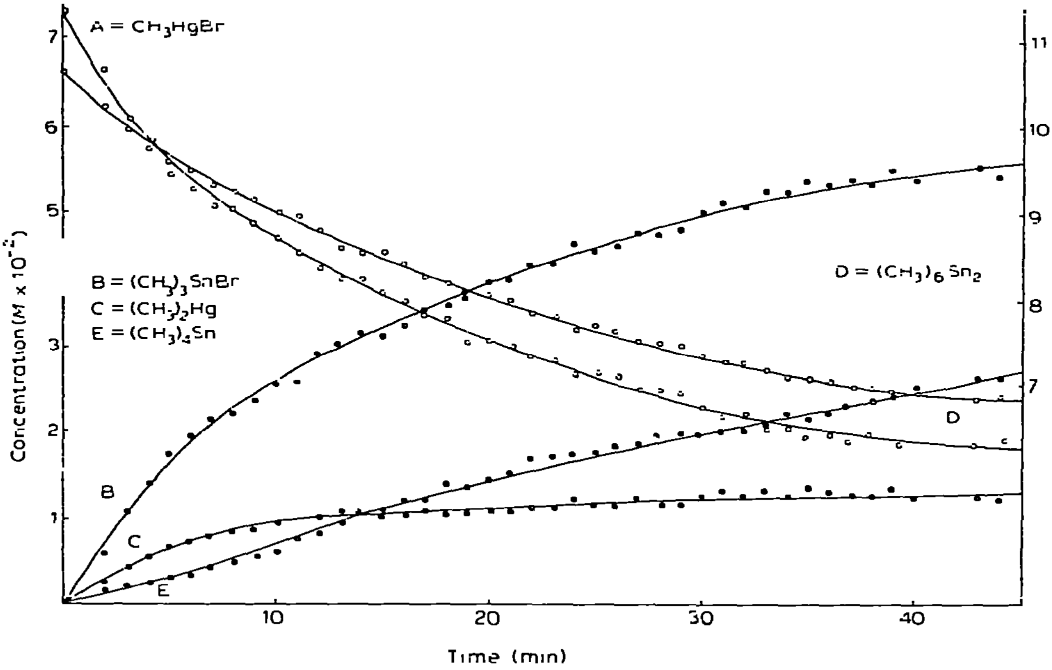


Fig. 1. Concentration vs. time curves for (CH$_3$)$_6$Sn$_2$/CH$_3$HgBr reaction B2.

one dependent and one independent of the methylmercuric halide concentration (eqns. 4 and 5).

$$(CH_3)_3SnHgCH_3 \rightarrow (CH_3)_4Sn + Hg \qquad (4)$$

$$(CH_3)_3SnHgCH_3 + CH_3HgX \rightarrow (CH_3)_3SnX + (CH_3)_2Hg + Hg \qquad (5)$$

We examined first the situation where reaction 4 is intramolecular and

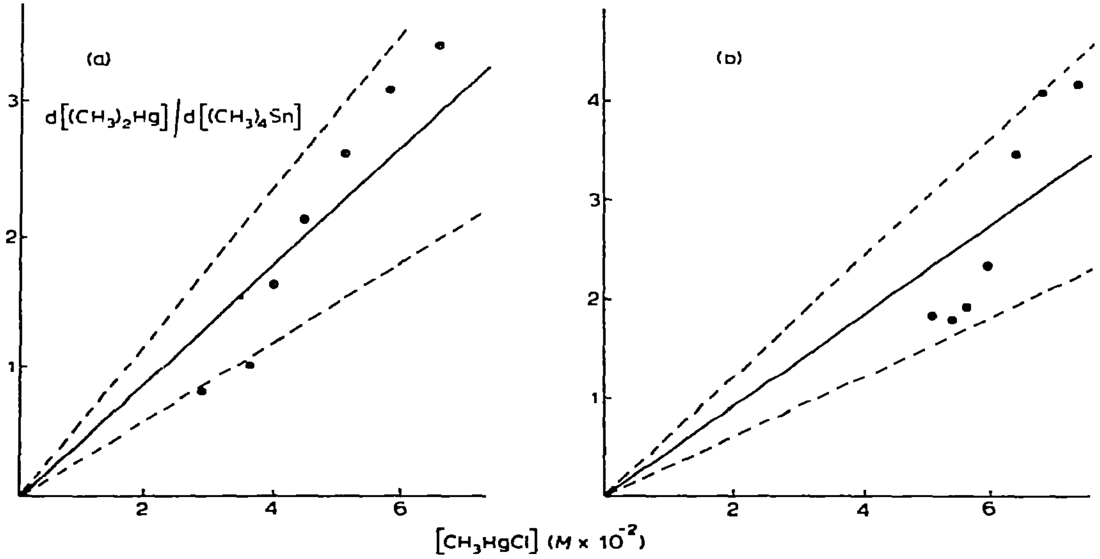


Fig. 2. Performance of eqn. 6 (a) reaction C1; (b) reaction C2 (see Table 1).

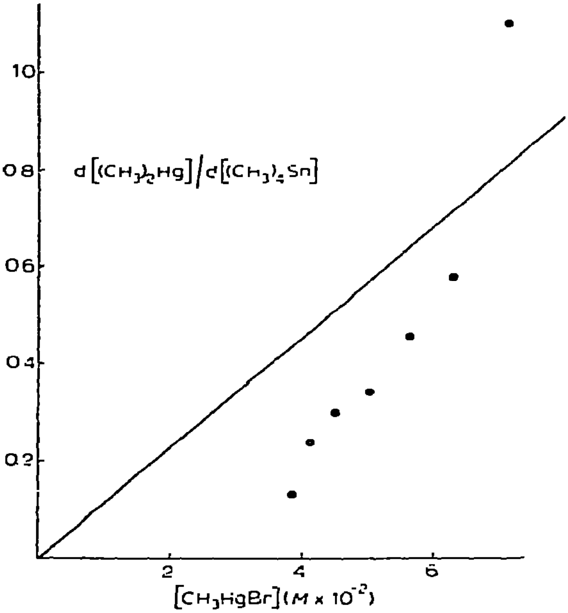


Fig. 3. Performance of eqn. 6 for reaction B1.

unimolecular while reaction 5 is first order in methylmercuric halide. In this case, rate equation 5 would hold, which is illustrated graphically in Fig. 2 for

$$\left\{\frac{d[(CH_3)_2Hg]/dt}{d[(CH_3)_4Sn]/dt}\right\}_t = \left\{\frac{d[(CH_3)_2Hg]}{d[(CH_3)_4Sn]}\right\}_t = \frac{k_5[CH_3HgX]_t}{k_4^0} \qquad (6)$$

two of the methylmercuric chloride reactions, and Fig. 3 for a methylmercuric bromide reaction. Evidently the experimental data do not conform to the expectations of eqn. 6. However, the left hand side of eqn. 6 cannot be determined without indeterminate and probably large uncertainties.

A better test employs directly measured concentrations in the integrated form of eqn. 6, although this is not a simple expression amenable to graphical treatment (eqn.7). Starting from an initial estimate of $k_4^0/2k_5$ eqn. 7 was solved

$$\ln\left\{[CH_3HgX]_t + \frac{k_4^0}{2k_5}\right\} = \ln\left\{[CH_3HgX]_0 + \frac{k_4^0}{2k_5}\right\} - \frac{2k_5}{k_4^0}[(CH_3)_4Sn]_t \qquad (7)$$

iteratively [8] using data from several experiments. The results are summarised in Table 1 for initial estimates of 1.25×10^{-2} and 3.0×10^{-2} M in the cases of chloride and bromide respectively. (These estimates were obtained from the examination of eqn. 6 as indicated in Figs. 2 and 3.) The computer programme employed was checked against a set of hypothetical concentration data conforming to eqn. 7 and was found to converge satisfactorily to the true value of $k_4^0/2k_5$. Also the computation was found to be quite sensitive to errors artificially introduced into the data but still converge satisfactorily.

It is evident then that the experimental data do not fit eqn. 7. The nature of the deviation from eqn. 7 is such that $k_4^0/2k_5$ tends to be found larger for larger initial concentration of methylmercuric halide or of hexamethylditin.

TABLE 1

CALCULATION OF $k_4^0/2k_5$

Reaction No.	X	$[CH_3HgX]_0$ (M) (× 10^2)	$[(CH_3)_6Sn_2]_0$ (M) (× 10^2)	$k_4^0/2k_5$ (M) (× 10^2)
C1	Cl	7.89	7.67	1.535
C2	Cl	8.01	3.71	1.33
C3	Cl	8.60	2.97	0.86
C5	Cl	7.55	12.52	1.33
C6	Cl	3.86	10.36	0.72
C7	Cl	2.80	10.70	0.37
B1	Br	8.32	10.10	7.40
B2	Br	7.32	10.66	4.82
B3	Br	3.78	10.39	2.25

This suggests that reaction 4 may be catalysed by the product of their reaction, i.e. trimethyltin halide. If this were so then eqn. 8 would apply, which is illus-

$$\left\{\frac{d[(CH_3)_2Hg]}{d[(CH_3)_4Sn]}\right\}_t = \frac{k_5[CH_3HgX]_t}{k_4^{\mathrm{c}}[(CH_3)_3SnX]_t} \qquad (8)$$

trated in Figs. 4 and 5. Although there appears to be linear behaviour in this case, yielding $k_5/k_4^{\mathrm{c}} \approx 1.0$ and 0.25 in the cases of chloride and bromide respectively, one must be aware that experimental uncertainties, particularly in the relative rates of product formation, prevent a definitive conclusion being drawn with confidence.

The corresponding integrated relative rate expression is eqn. 9. Iterative

$$\ln\{(1-2k_5/k_4^{\mathrm{c}})[(CH_3)_3SnX]_t + 2k_5/k_4^{\mathrm{c}}[CH_3HgX]_0\} = \ln\{2k_5[CH_3HgX]_0/k_4^{\mathrm{c}}\}$$
$$+ k_4^{\mathrm{c}}/2k_5(1-2k_5/k_4^{\mathrm{c}})/[CH_3HgX]_0\{[(CH_3)_3SnX]_t-(1-2k_5/k_4^{\mathrm{c}})[(CH_3)_4Sn]_t\} \qquad (9)$$

treatment of the data was again applied [8] although with a hypothetical data set it was found that convergence was rather slow, particularly from a value of k_5/k_4^{c} that was too small. On the other hand, treatment through eqn. 9 is twice as sensitive to errors in the input data than is treatment through eqn. 7. Equation 9 satisfactorily reproduces the observed data for $k_5/k_4^{\mathrm{c}} = 1.1$ (±0.35) for chloride and 0.26 (±0.05) for bromide.

With both the uncatalysed and catalysed pathways available for decomposition of the intermediate, one would have eqn. 10:

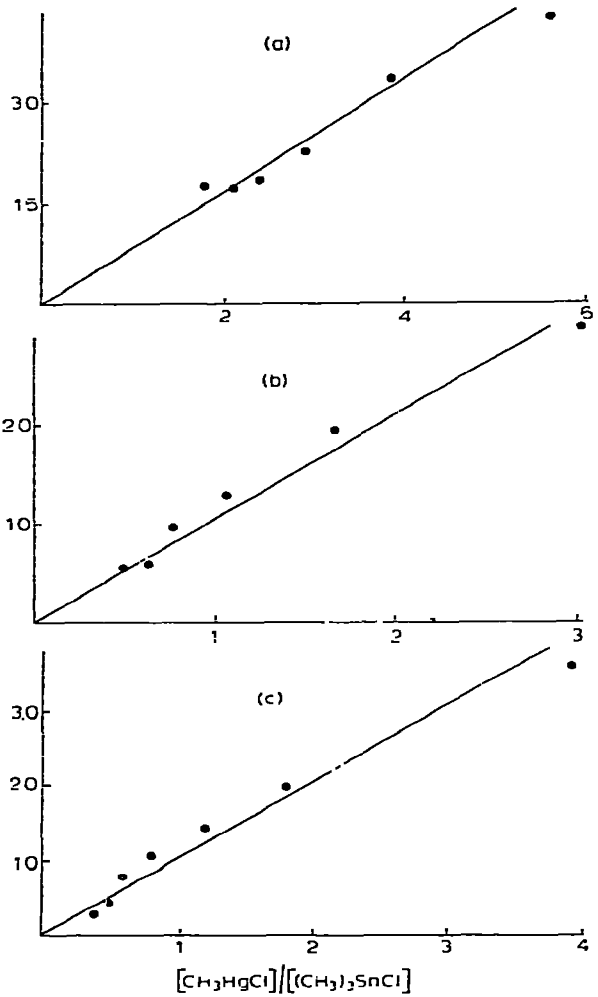
$$\frac{d[CH_3)_4Sn]}{d[(CH_3)_2Hg]} = \frac{k_4^0 + k_4^{\mathrm{c}}[CH_3HgX]_0}{k_5[CH_3HgX]_t} - \frac{k_4^{\mathrm{c}}}{k_5} \qquad (10)$$

since

$$[(CH_3)_3SnX]_t = [CH_3HgX]_0 - [CH_3HgX]_t.$$

An even more complex integrated rate expression (eqn. 11) is obtained,

$$(1-2k_5/k_4^{\mathrm{c}})[(CH_3)_4Sn]_t = \{[CH_3HgX]_0-[CH_3HgX]_t\} +$$
$$\frac{(k_4^0/k_4^{\mathrm{c}} + [CH_3HgX]_0)}{(1-k_4^0/2k_5)} \ln\left\{\frac{k_4^0 + k_4^{\mathrm{c}}[CH_3HgX]_0 - (k_4^{\mathrm{c}}-2k_5)[CH_3HgX]_t}{k_4^0 + 2k_5[CH_3HgX]_0}\right\} \qquad (11)$$



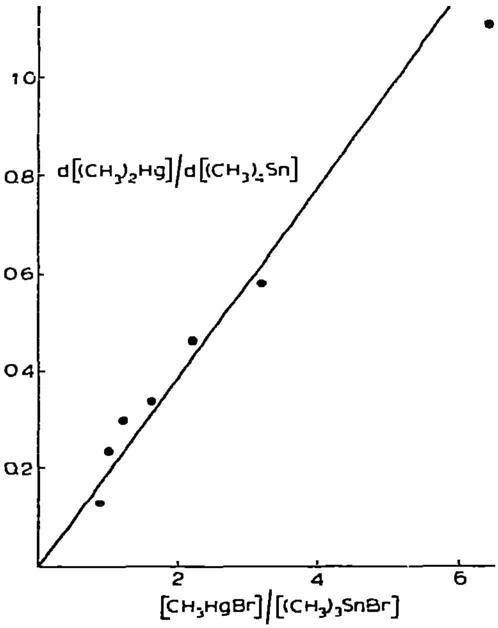


Fig. 4. Performance of eqn. 8 (a) reaction C2; (b) reaction C5; (c) reaction C6.

Fig. 5. Performance of eqn. 8 for reaction B1.

which contains too many adjustable parameters for iterative solution.

Figure 6 illustrates the behaviour of the experimental data with respect to eqn. 10, and Fig. 7 shows the relationship of the slopes of the approximate lines obtained to the initial concentration of reagent. The values of k_5/k_4^{c} are quite similar to those found by the iterative treatment and the value of k_4^0/k_4^{c} is not different from zero by more than the experimental uncertainty.

Our data are best accounted for by a single catalysed decomposition path of the intermediate competing with methylmercuric halide reaction, and we are unable to detect a significant uncatalysed decomposition. The implication of this is that methyl(trimethylstannyl)mercury might be rather more stable than has been supposed [7] provided that it is free of decomposition catalysts, and hence that further attempts at its synthesis and isolation will be worthwhile.

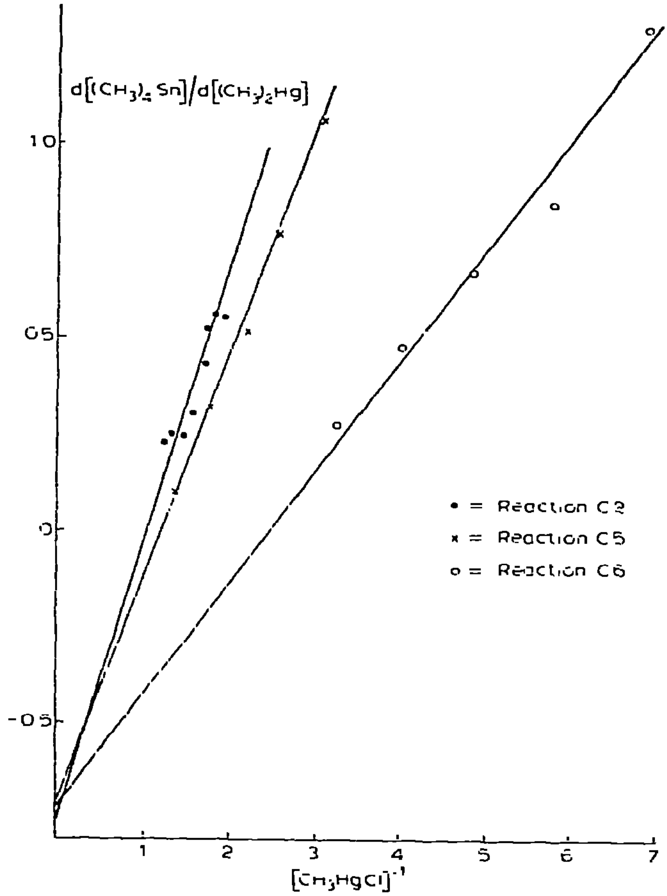


Fig. 6. Performance of eqn. 10.

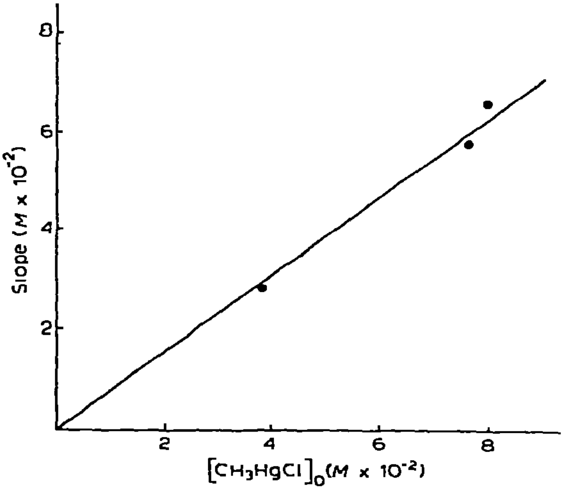


Fig. 7. Dependence of slopes of eqn. 10 on initial concentration.

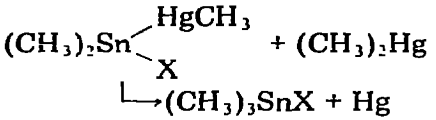
In the case of methylmercuric iodide we were unable to detect dimethylmercury as a product. Considering the maximum concentration that would have escaped detection one may estimate that in this case $k_5/k_4^{c} <$ *ca.* 0.025. On the other hand dimethylmercury is formed to the exclusion of tetramethyltin in the case of methylmercuric acetate, requiring that $k_5 >> k_4^{c}$.

Concerning the mechanisms of the reactions removing the trimethylstannyl mercurial from the system one may speculate that the methylmercuric halide reaction 5 involves steps A-C.

S_E on mercury-bound carbon yielding

$$(CH_3)_3SnHgX + (CH_3)_2Hg \hookrightarrow (CH_3)_3SnX + Hg \qquad (5A)$$

or S_E on tin-bound carbon yielding



$$(CH_3)_2Sn(HgCH_3)X + (CH_3)_2Hg \hookrightarrow (CH_3)_3SnX + Hg \qquad (5B)$$

or S_E on mercury yielding

$$(CH_3)_3SnX + [CH_3HgHgCH_3] \hookrightarrow (CH_3)_2Hg + Hg \qquad (5C)$$

(the S_E reaction at tin will be trivial).

There appears to be no reason for expecting reactions 5A and 5B to be particularly rapid since they correspond to the reactions of methyl groups in an alkylmethylmercury and an alkyltrimethyltin, and indeed, in the case of the chloride, reaction 5B does not occur since CH_3HgCD_3 is not formed from CD_3HgCl [1]. Hence we favour reaction 5C even though yet another unknown intermediate, a mercurous organic derivative, is postulated to be formed. Such species have been postulated on other occasions [9].

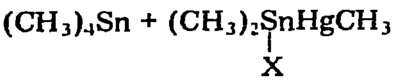
The trimethyltin halide catalysed decomposition 4 presumably follows a path resembling reaction 12 the catalysed decomposition of hexamethylditin [10], i.e., by carbon—metal bond cleavage.

$$(CH_3)_6Sn_2 + (CH_3)_3SnX \rightarrow (CH_3)_4Sn + (CH_3)_5Sn_2X \qquad (12)$$

This could be by S_E at mercury-bound carbon yielding

$$(CH_3)_3SnHgX + (CH_3)_4Sn \hookrightarrow (CH_3)_3SnX \qquad (4A)$$

or S_E at tin-bound carbon yielding



$$(CH_3)_4Sn + (CH_3)_2Sn(X)HgCH_3 \qquad (4B)$$

Of these alternatives we prefer 4A, on the grounds that the product in 4B is unlikely to yield trimethyltin halide exclusively, and the reaction is unlikely to be faster than the observed rate-controlling step which itself is considerably faster than reaction 12.

If 5B and 4A are indeed the competing reactions for the destruction of methyl(trimethylstannyl)mercury one might expect the ratio k_5/k_4^{c} to parallel the ratio k_3/k_{12} since they refer to similar reactions (S_E at the metal and car-

TABLE 2

X	$k_3 (M^{-1}s^{-1})^a$ ($\times 10^3$)	$k_{12} (M^{-1}s^{-1})^b$ ($\times 10^4$)	k_5/k_5^{Cl}	k_3/k_{12}
Cl	5.2	1.0	1.0	52 (1)
Br	3.8	2.4	0.25	16 (0.32)
I	2.5	5.8	<0.025	4.3 (0.08)

[a] See ref. 1 [b] See ref. 10.

bon, respectively, in hexamethylditin). Table 2, which summarises the results of the present study, indicates that this is indeed the case.

Acknowledgement

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