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TRIALKYLTIN HALIDE CATALYSED DECOMPOSITION OF HEXAMETHYLDITIN

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Summary

In the trialkyltin halide-catalysed decomposition of hexamethylditin to tetramethyltin and "dimethyltin" the halide itself is the electrophilic reagent, not the dissociated cation, as previously suggested. Studies with trivinyltin chloride show that trivinyltrimethylditin is not formed during the decomposition.

Introduction

The decomposition of hexaalkylditins according to eqn. 1 can be brought about by a variety of Lewis acid catalysts, such as boron trifluoride, dimethylboron fluoride and diborane [1]. Organic derivatives of tin(II) are not obtained

$$R_6Sn_2 \rightarrow R_4Sn + [R_2Sn] \qquad (1)$$

as such however, and all the products arising from this and other reactions having or approximating to this empirical formula have been shown to be polymeric and/or cyclic derivatives of tin(IV) [2].

Tagliavini, Pilloni and Plazzogna [3] have reported a study of the trialkyltin chloride-catalysed reaction of hexamethylditin, in which they provide evidence that the tin—carbon undergoes attack by a species equivalent to the trialkyltin cation, since there is a half-order kinetic dependence upon catalyst concentration.

We have further examined this reaction, since it occurs as a possible complication in the alkylmercuric halide cleavage of hexamethylditin, trimethyltin chloride being one product [4]. Futhermore, the reactions of hexamethylditin with mercuric salts [4], alkylmercuric salts [4], iodine [5, 6] and silver complexes [7] all appear to involve tin—tin bond cleavage without tin—carbon bond cleavage.

Experimental

Materials

Hexamethylditin (Alfa Inorganics) was purified by distillation under reduced pressure with a nitrogen bleed, and small samples, ca. 0.25 g, were sealed under vacuum in ampoules flushed with dry nitrogen. These were stored at 0°.

Trivinyltin chloride was prepared from tetravinyltin and stannic chloride according to Rosenberg [8] and purified by distillation under reduced pressure B.p. 90-91°/20 Torr (lit. [9] 59°/6 Torr). Trimethyltin chloride (Alfa Inorganics) was purified by distillation at atmospheric pressure. B.p. 153° (lit [9] 152-154°). Trimethyltin bromide was prepared from tetramethyltin and stannic bromide as described by Van den Berghe and Van der Kelen [10], and purified by distillation at atmospheric pressure. B.p. 165° (lit. [9] 165°). Trimethyltin iodide was prepared from the chloride by the action of sodium iodide in acetone solution. It was purified by distillation under reduced pressure. B.p. 86-88°/48 torr (lit. [9] 68°/15 Torr).

Methanol (analytical reagent grade UNIVAR) was purified by distillation from magnesium methoxide and stored over Type 3A molecular sieves.

Product examination

All reactions were conducted in NMR tubes sealed with pressure caps, and the composition of the reaction mixtures derived from the proton magnetic

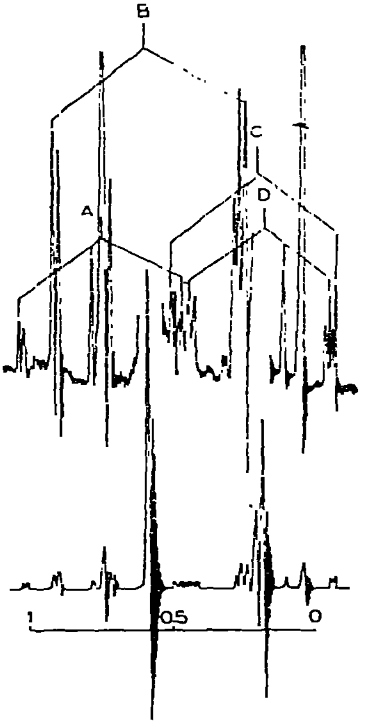


Fig. 1. 100 MHz spectrum of trivinyltin chloride/hexamethylditin system (methyl region). A, $[(CH_3)_2Sn]_n$; B, $(CH_3)_3Sn(C_2H_3)_2$; C, CH_3SnCl; D, $(CH_3)_6Sn_2$.

resonance spectra obtained at 100 MHz (JEOL PS-100). The most complex system, illustrated in Fig. 1, is the trivinyltin chloride/hexamethylditin reaction. The polymeric "dimethyltin" product appears as a yellow precipitate during the reaction and can be removed by centrifugation. A product presumably of low molecular weight remaining in solution is visible in the PMR spectra with chemical shifts and coupling constants similar to those described by Brown and Morgan [11].

Kinetic measurements

Standard solutions in methanol of hexamethylditin and of the reagent were prepared in 5 ml standard flasks. The reagent solution, 0.3 ml, was added by syringe to a previously weighed NMR tube fitted with a pressure cap, and the tube reweighed. After equilibration at the probe temperature (30 ± 1°), hexamethylditin solution, 0.3 ml, was added, the tube was tightly restoppered and shaken for about half a minute. The amount of hexamethylditin solution added was determined by weighing at completion of the experiment. Progress of reaction was followed by examining the methyl group region of the spectrum. In the case of the trivinyltin chloride reaction experiments with an internal cyclohexane reference showed that $[(CH_3)_6Sn_2]_t + [(CH_3)_3SnCl]_t = [(CH_3)_6Sn_2]_0$ which provided a reference for the system. In the catalysed reactions $[(CH_3)_3SnX]$ remains constant and was employed as reference.

A small amount of oxygen can enter the system during the setting-up period as shown by experiments conducted with the trialkyltin halide absent. This results in a loss of hexamethylditin which is converted to a trimethyltin species, presumably the methoxide. Typically this amounted to ca. 1% which is within experimental uncertainty, so that no corrections were applied.

Results

Trivinyltin chloride-induced decomposition

A system composed initially of hexamethylditin (0.28 *M*) and trivinyltin chloride (1.16 *M*) conforms to eqn. 2.

$$(CH_3)_6Sn_2 + (CH_2{=}CH)_3SnCl \rightarrow (CH_2{=}CH)_3SnCH_3 + (CH_3)_3SnCl + 1/n\,[(CH_3)_2Sn]_n \qquad (2)$$

The trivinylmethyltin subsequently reacts thus:

$$(CH_2{=}CH)_3SnCH_3 + (CH_2{=}CH)_3SnCl \rightarrow (CH_2{=}CH)_4Sn + (CH_2{=}CH)_2Sn(CH_3)Cl \qquad (3)$$

Figure 2 illustrates the progress of reaction (n.b. the concentration of trivinylmethyltin can be determined with much less precision than the other two species). The large excess of trivinyltin chloride ensures that this species alone induces the decomposition and that catalysis by trimethyltin chloride is negligible. The data give an excellent fit to the integrated second-order rate expression (see Fig. 3) arising from

$$-d[(CH_3)_6Sn_2]/dt = k[(CH_3)_6Sn_2][(CH_2{=}CH)_3SnCl]$$

with $k = 2.8 \times 10^{-4}\ M^{-1}\ s^{-1}$ (30°)

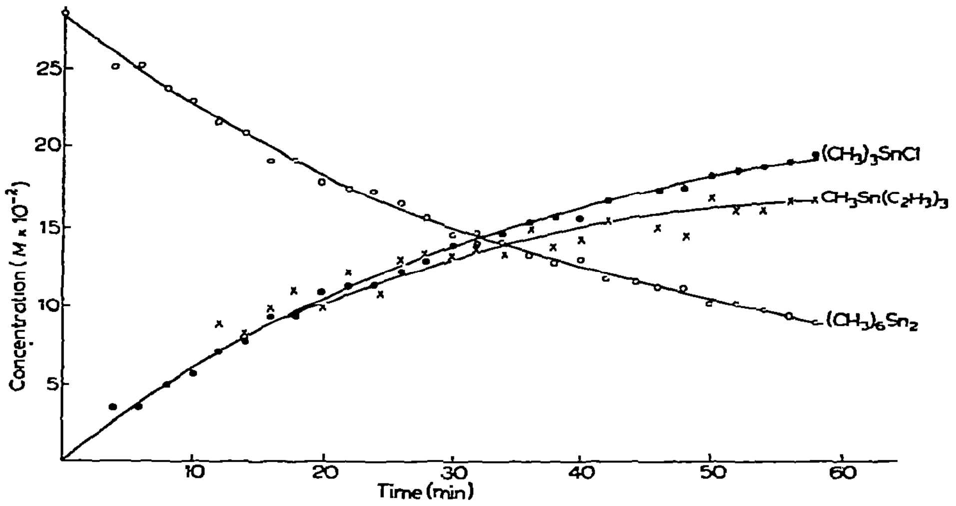


Fig. 2. Concentration vs. time curves for trivinyltin chloride/hexamethylditin system.

The precipitated "dialkyltin" polymer reacted with mercuric chloride to yield only dimethyltin dichloride with no detectable vinyl species present.

Trimethyltin halide catalysis

Several systems were investigated, using $[(CH_3)_6Sn_2]_0$ 0.13 to 0.19 *M* and $[(CH_3)_3SnX]_0$ 0.05 to 0.40 *M* (X = Cl,Br or I), and all gave excellent corres-

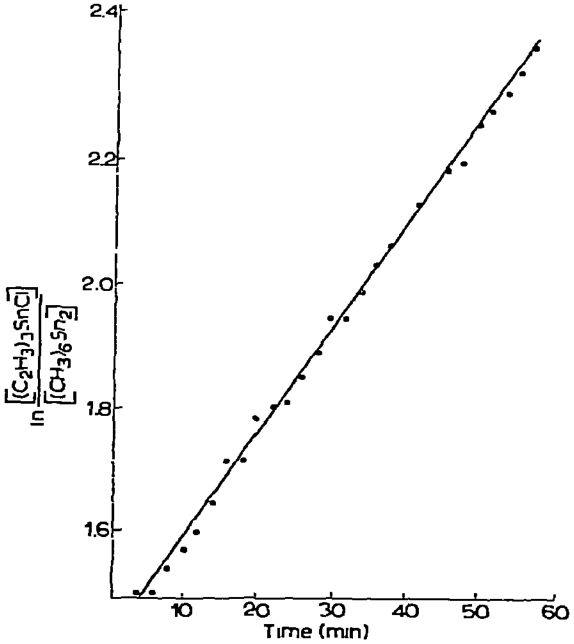


Fig. 3. Second order plot for the trivinyltin chloride/hexamethylditin system.

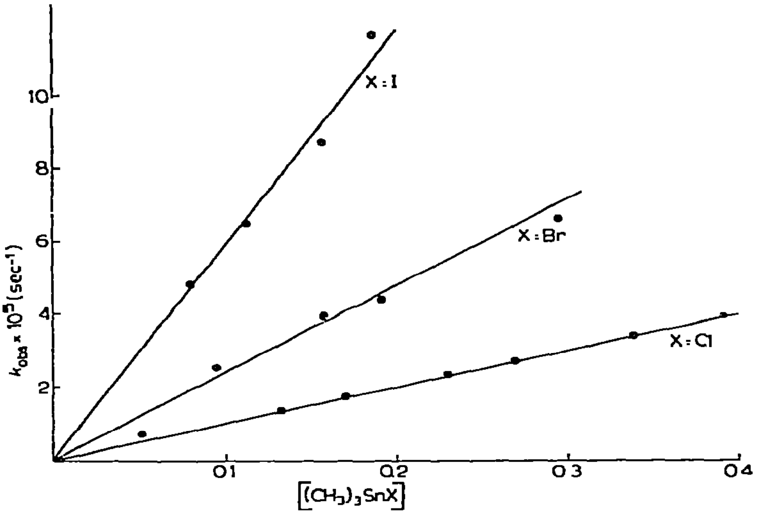


Fig. 4. Dependence of first order rate constant upon catalyst concentration.

pondence for first-order kinetics in hexamethylditin. The observed first-order rate constants are not linear with $[(CH_3)_3SnX]^{1/2}$ but depend upon the first power of the catalyst concentration, as indicated in Fig. 4. Table 1 summarises the results obtained.

A further series of data were obtained for trimethyltin chloride catalysis overlapping the catalyst concentration range previously reported [3]. Correlation according to eqn. 4 is shown in Fig. 5.

$$k_{obs}[(CH_3)_3SnCl]^{-1/2} = a[(CH_3)_3SnCl]^{1/2} + b \qquad (4)$$

Least squares analysis yields $a = 0.999(\pm 0.153) \times 10^{-4}\ M^{-1}\ s^{-1}$; $b = 0.193$ (± 0.686).

Discussion

Evidence that the catalysis involves tin—carbon bond cleavage is provided by the report [3] that triethyltin chloride yields initially triethylmethyltin. This product does not arise from reaction between tetramethyltin and triethyltin chloride, which is a process known to occur at a very much slower rate.

TABLE 1

TRIMETHYLTIN HALIDE-CATALYSED DECOMPOSITION OF HEXAMETHYLDITIN

Methanol solution; 30±1°

Halide	$[(CH_3)_3SnX]_0$ (M)	k (M^{-1} s^{-1})($\times 10^4$)
Chloride	0.050 to 0.393	1.0
Bromide	0.094 to 0.295	2.4
Iodide	0.080 to 0.187	5.8

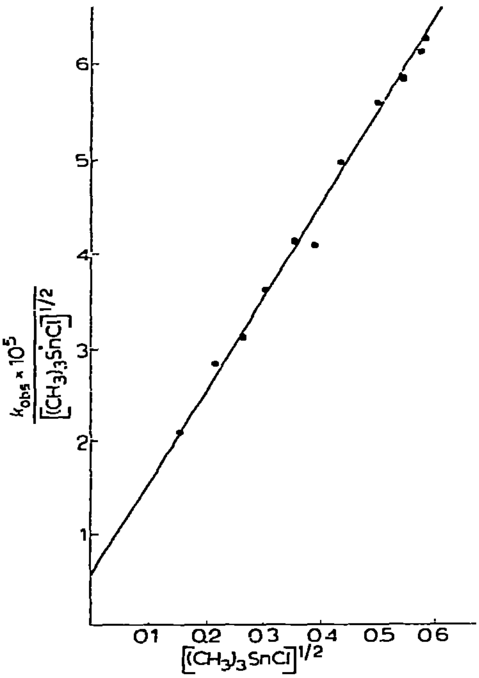


Fig. 5. Correlation by means of eqn. 4.

The possibility that tin—tin bond cleavage also takes place in this reaction was not ruled out by the use of triethyltin chloride, since formation of trimethyltriethylditin could have occurred, as follows,

$(CH_3)_6Sn_2 + (C_2H_5)_3SnCl \rightarrow (CH_3)_3SnSn(C_2H_5)_3 + (CH_3)_3SnCl$

but have escaped detection. This is because electrophilic tin—methyl cleavage generally occurs so much faster than tin—ethyl cleavage that the same overall reaction would be observed. Tetramethyltin is, for example, five hundred times more reactive than tetraethyltin towards mercury chloride [12].

$(CH_3)_3SnSn(C_2H_5)_3 + (C_2H_5)_3SnCl \rightarrow (C_2H_5)_3SnCH_3 + (C_2H_5)_3SnCl + [(CH_3)_2Sn]$

$(CH_3)_3SnSn(C_2H_5)_3 + (CH_3)_3SnCl \rightarrow (CH_3)_4Sn + (C_2H_5)_3SnCl + [(CH_3)_2Sn]$

However if a trialkyltin halide, R_3SnX, in which the alkyl group is more readily cleaved from tin were employed as reagent then the intermediacy of the tin—tin cleavage product would be revealed both in the appearance of R_4Sn and $RSn(CH_3)_3$ and in the formation of polymer containing the alkyl group.

$(CH_3)_3SnSnR_3 + R_3SnX \rightarrow R_4Sn + (CH_3)_3SnX + [R_2Sn]$

$(CH_3)_3SnSnR_3 + (CH_3)_3SnX \rightarrow RSn(CH_3)_3 + (CH_3)_3SnX + [R_2Sn]$

Divinylmercury is ca. 200 times more reactive than dimethylmercury towards hydrogen chloride [13] and a vinyl group in a tetraalkyltin reacts much more rapidly with electrophiles than do methyl and other alkyl groups [8, 14]. Thus if trivinyltrimethylditin were formed from hexamethylditin and trivinyltin chloride then its presence would lead to the formation of tetravinyltin, vinyltrimethyltin and vinyl components in the dialkyltin polymer. Of these, only the former is observed and it does not appear until late in reaction when it is clearly being formed at the expense of methyltrivinyltin. (A further example of the greater reactivity of the vinyl group.)

A feature of the reaction which was unexpected is the kinetic dependence on the reagent concentration, instead of its half power. The half power dependence previously reported [3] has been ascribed to dissociation yielding a low concentration of the effective reagent, trialkyltin cation or a solvated species derived therefrom.

$$R_3SnX \overset{(K)}{\rightleftarrows} R_3Sn^+ + X^-$$

$$[R_3Sn^+] \approx K^{1/2}\,[R_3SnX]_0^{1/2}$$

$$\text{if } [R_3Sn^+] << [R_3SnX]_0, \text{ arising from } K << 4[R_3SnX]_0 \qquad (5)$$

Under the conditions we used, for trimethyltin halides also the rate is dependent upon the first power of the catalyst concentration and not its half power. The major difference between ours and the previous experiments [3] is that the concentrations we used are generally much larger. It is thus possible that both the cation and halide function as catalysts then:

$$\begin{aligned} k_{obs} &= k_x\,[(CH_3)_3SnX] + k_+\,[(CH_3)_3Sn^+] \\ &= k_x\,[(CH_3)_3SnX]_0 + (k_+ - k_x)[(CH_3)_3Sn^+] \\ &\approx k_x\,[(CH_3)_3SnX]_0 + (k_+ - k_x)K^{1/2}[(CH_3)_3SnX]_0^{1/2} \end{aligned} \qquad (6)$$

At high concentrations one could have the first term of eqn. 6 dominant, while at low concentration the second term could be the more important. In the case of trimethyltin chloride this has been tested through the use of eqn. 4 but a contribution by the second term does not exceed experimental uncertainty.

Figure 6 indicates that the previously reported results [3] do not follow the pattern established in the present work. In particular, reaction appears to occur considerably more rapidly when the reagents are in lower concentration. Furthermore, with $K = 1.25 \times 10^{-4} M$ (methanol 25°) reported [14] for tri-

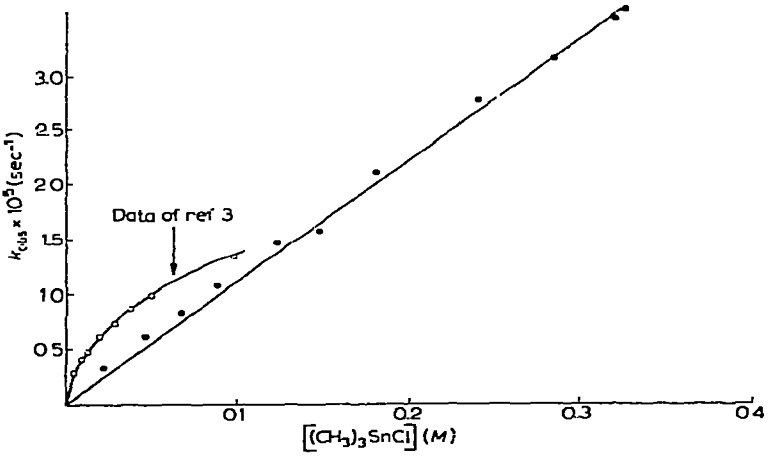
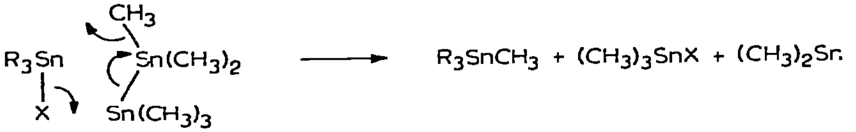


Fig. 6. Dependence of first order rate constant upon catalyst concentration.

methyltin chloride one obtains from the data of ref. 3, $k_+ \approx 4 \times 10^{-3} M^{-1} s^{-1}$ (30°) which appears rather small for cationic electrophile relative to the trimethyltin halides (see Table 1).

Trialkyltin halides presumably function as electrophiles in this reaction by an $S_E i$ process in which the nucleophilic halide assistance increases in the order Cl < Br < I. The mechanism may involve a single step cleavage of both the tin—carbon and the tin—tin bond thus:



(7)

In this case dimethyltin would be formed as a discrete intermediate and undergo polymerisation by some subsequent rapid, unknown process. However a reasonable polymerisation process can be described that does not involve dimethyltin at any stage.

$$R_3SnX + (CH_3)_6Sn_2 \rightarrow R_3SnCH_3 + (CH_3)_5Sn_2X \qquad (8)$$

$$(CH_3)_5Sn_2X + (CH_3)_6Sn_2 \rightarrow (CH_3)_8Sn_3 + (CH_3)_3SnX \qquad (9)$$

$$(CH_3)_{2n-1}Sn_{n-1}X + (CH_3)_{2m+2}Sn_m \rightarrow (CH_3)_{2n+2}Sn_n + \qquad (10a)$$

$$\searrow \text{ and/or } (CH_3)_{2n}Sn_n + \qquad (10b)$$

$$(CH_3)_{2p+1}Sn_pX \rightarrow (CH_3)_{2p-2}Sn_{p-1} + (CH_3)_3SnX \qquad (11)$$

Reactions 10a and 10b provide for the formation of linear polymers while reaction 11 is envisaged as the source of cyclic products. However the key reaction, 9, involves a tin—tin cleavage of a type we have already shown to be unimportant.

Clearly a detailed study of the nature of the polymer formed in these reactions and its dependence on the concentrations of the various reactants is the most likely source of information on the polymerisation process. We are currently investigating this aspect of the reaction.

References

1 A.B. Burg and J.R. Spielmann, J. Amer. Chem. Soc., 83 (1961) 2667.
2 W.P. Neumann, The Organic Chemistry of Tin, Wiley-Interscience, New York, 1970, Ch. 14.
3 G. Tagliavini, G. Pilloni and G. Plazzogna, Ric. Sci., 36 (1966) 3.
4 D.C. McWilliam and P.R. Wells, J. Organometal. Chem., 85 (1975) 335, 347.
5 M. Gielen, J. Nasielski and G. Vandendunghen, Bull. Soc. Chim. Belg., 80 (1971) 165.
6 G. Tagliavini, S. Faleschini, G. Pilloni and G. Plazzogna, J. Organometal. Chem., 5 (1966) 136.
7 G. Tagliavini, S. Faleschini and E. Genero, Ric. Sci., 36 (1966) 717.
8 S.D. Rosenberg, A.J. Gibbons and H.E. Ramsden, J. Amer. Chem. Soc., 79 (1957) 2138.
9 R.K. Ingham, S.D. Rosenberg and H. Gilman, Chem. Rev., 60 (1960) 459.
10 E.V. Van den Berghe and G.P. Van der Kelen, J. Organometal. Chem., 6 (1966) 522.
11 T.L. Brown and G.L. Morgan, Inorg. Chem., (1963) 736.
12 M.H. Abraham and G.F. Johnston, J. Chem. Soc. A (1970) 188.
13 R.E. Dessy and J.Y. Kim, J. Amer. Chem. Soc., 83 (1961) 1167
14 D. Seyferth, J. Amer. Chem. Soc., 79 (1957) 2133.
15 L. Doretti, P. Zanella and G. Tagliavini, J. Organometal. Chem., 22 (1970) 23.