

REDISTRIBUTION REACTIONS OF β -CARBOALKOXYETHYL TIN COMPOUNDS

JOSEPH W. BURLEY and RONALD E. HUTTON

Akzo Chemie (UK) Ltd., Research Centre, Hollingworth Road, Littleborough, Greater Manchester OL15 0BA (Great Britain)

(Received February 10th, 1981)

Summary

Carboalkoxyethyltin compounds undergo redistribution reactions at faster rates than similar unsubstituted alkyltin compounds. In redistribution reactions between SnCl_4 and carboalkoxyethyltin compounds stable intermolecular complexes are formed. Rate enhancement is explained in terms of intra- and intermolecular coordination effects. Where strong intermolecular coordination effects are observed, specific electrophilic cleavage of the carboalkoxyethyl group can occur in preference to alkyl cleavage in mixed carboalkoxyethyl-alkyltin compounds. The presence of a β -ester function can catalyse both alkyl/chlorine and alkyl/alkyl' exchange reactions.

Introduction

The redistribution (disproportionation) reactions discovered by Kozeschkow [1] have long been utilised for the synthesis of alkyl- and phenyltin halides. Reactions 1, 3 and 5 proceed essentially as described by Kozeschkow, except for reaction 1 which does not proceed to completion since the final step (2) does not proceed at a reasonable rate if the reaction is uncatalysed [2]. Indeed, only few examples exist of successful "catalysis" of reaction 2, and then only



(R = Me, Bu, Oct, Ph)

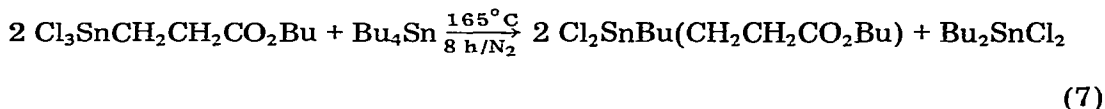
in polar solvent media such as dimethyl sulphoxide ($R = \text{Me}$) [3] and $\text{P}_2\text{O}_5/\text{PCl}_3$ ($R = \text{Et}$) [2]. Reactions 4 and 6 represent the final steps in the overall reactions described by equations 3 and 5, respectively.

In spite of the fact that reactions 1–6 have attained significant commercial importance for the synthesis of intermediates to PVC stabilisers (R_3SnCl and R_2SnCl_2 ; $R = \text{Me, Bu, Oct}$) and biocides and fungicides (R_3SnCl ; $R = \text{Bu, Ph}$) and also aroused considerable academic interest, there appears to have been no systematic study of the mechanisms of many of them. Reactions 2, 4 and 6 proceed at the slowest rates (very slow in the case of 2) and, therefore, present the greatest scope for kinetic modification by functional substitution. It is these reactions which form the basis of the present study of the redistribution reactions of "estertin" (β -carboalkoxyethyltin) compounds. Studies of the redistribution equilibria of functionally substituted organotin compounds are extremely rare. Omae [4] has described one example of this type of reaction with ester-substituted alkyltin halides and Kuivila has compared the rates of the redistribution reactions of β - and γ -keto-substituted compounds with the corresponding unsubstituted butyltin derivative [5]. Kuivila observed considerable kinetic and thermodynamic enhancement for the keto-substituted compounds, which he interpreted in terms of intramolecular catalysis of the redistribution reaction.

Experimental

Compounds

$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{R}$ ($R = \text{Me, Bu}$) and $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_2$ ($R = \text{Me, Bu}$) were prepared by published methods [6–8]. $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_3$ ($R = \text{Me, Bu}$) were prepared from the corresponding carboalkoxyethyltin trichlorides by reaction with metallic zinc and $\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_4$ ($R = \text{Me, Bu}$) were prepared from the corresponding bis(β -carboalkoxyethyl)tin dichlorides, also by reaction with metallic zinc [9]. $\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})$ was prepared according to eq. 7.



$\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})$ was separated from the reaction mixture by fractional distillation. The yield was 76%.

$\text{ClSnBu}_2(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})$ was prepared by the hydrostannation of methyl acrylate with Bu_2SnHCl at 40°C , according to the method of Pedain [10]. Bu_2SnHCl [11] was easily prepared from equimolar quantities of Bu_2SnCl_2 and Bu_2SnH_2 which was prepared by reduction of Bu_2SnCl_2 with LiAlH_4 [12].

SnCl_4 (B.D.H.), BuSnCl_3 (Aldrich), Bu_2SnCl_2 (B.D.H.), Bu_3SnCl (Aldrich) and Bu_4Sn (Scheering — distilled grade) were commercially available and were used without further purification. $\text{Oct}_2\text{SnCl}_2$ was prepared by reaction between dioctyltin oxide (Scheering) and excess hydrochloric acid.

Reactions

All redistribution reactions were performed under dry nitrogen. Equimolar

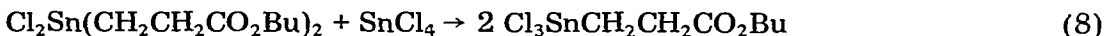
quantities of the appropriate reagents were mixed and heated quickly to the required reaction temperature. All reactions involving the consumption or formation of alkyltin halides or SnCl_4 were followed by GLC where these compounds were quantitatively converted to the corresponding alkyl methyltin compounds and SnMe_4 , respectively, by reaction with MeMgI in Et_2O . A Perkin Elmer F11 hot wire-detector GC system was utilised in conjunction with a Sigma 10 Data Station. The methylated tin compounds were separated on a $24'' \times 1/4''$ stainless steel column packed with 15% Dexsil 300 on Chromosorb WAW DMCS 80–100 mesh. The injection temperature was 275°C and temperature profile was $60 \rightarrow 300^\circ\text{C}$ at $15^\circ/\text{min}$. The carrier gas was helium (flow rate $60 \text{ cm}^3/\text{min}$) and the detector temperature was 300°C .

Reactions involving only carbomethoxyethyltin halides were monitored by NMR spectroscopy. Several reactions involving carboalkoxyethyltin halides were also monitored by IR spectroscopy. NMR spectra were recorded on a Perkin-Elmer R12B 60 MHz spectrometer and IR spectra were recorded largely as neat liquids on a Perkin-Elmer 577 grating spectrophotometer.

Results and discussion

Reactions leading to alkyltin trihalides

In contrast to simple dialkyltin dihalides, $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$ undergoes redistribution with SnCl_4 at a reasonable rate at 100°C . The conversion/time curve for this reaction 8 is presented in Fig. 1 (a) along with the rate curve



for the reaction between $\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})$ and SnCl_4 , which proceeds at a much slower rate. However, the rate of the latter reactions is still significantly faster than that of the corresponding reaction between Bu_2SnCl_2 and SnCl_4 , where the formation of BuSnCl_3 could not be detected within the time scale of the reactions described by Fig. 1. Infrared spectroscopy has been used to complement the chromatographic study of these reactions. This technique is particularly useful for the study of reactions involving estertin compounds since the carbonyl stretching frequency ($\nu(\text{C}=\text{O})$) of the ester carbonyl group is sensitive to molecular environment [13]. This effect is caused by carbonyl coordination to tin, which may be intra- or intermolecular in origin, and which results in lower carbonyl-stretching frequencies than those expected for simple alkyl esters. The $\nu(\text{C}=\text{O})$ values for $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$, $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_2$, $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$ and $\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_4$ are presented in Table 1 and illustrate the coordination phenomenon. The data for $\text{CH}_3\text{CH}_2\text{CO}_2\text{Me}$, a good model for the carboalkoxyethyl groups, is also included in Table 1. This IR data is consistent with the structures illustrated in Fig. 2 (a–d) for the four carbomethoxyethyltin compounds. Structures a and b have also been verified by X-ray crystallography [14]. Structure c, with one coordinated carbonyl group and two uncoordinated carbonyl groups, is consistent with the pentacoordinate geometry of coordination complexes of trialkyltin halides [15]. Finally, the IR spectrum of $\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_4$ shows again a single peak in the same position as $\text{CH}_3\text{CH}_2\text{CO}_2\text{Me}$, consistent with the total absence of coordination to

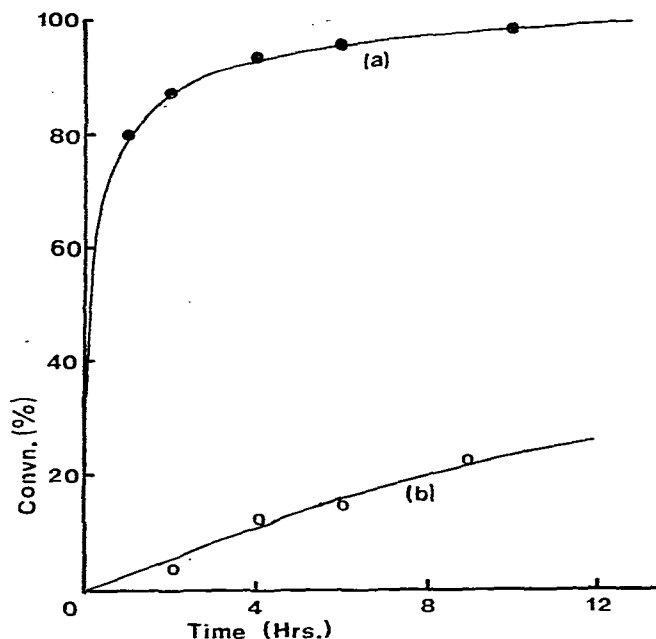


Fig. 1. Conversion/time curves for the reactions between (a) SnCl_4 and $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$, and (b) SnCl_4 and $\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})$.

tin in this compound. IR data for a number of other carboalkoxyethyltin compounds are also contained in Table 1.

The IR spectrum of $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$ shows a single peak at 1674 cm^{-1} . Addition of an equimolar quantity of SnCl_4 to this compound at ambient temperature results in the formation of a new carbonyl frequency at 1602 cm^{-1} . Such a low carbonyl stretching frequency suggests coordination to SnCl_4 [16]

TABLE 1

CARBONYL STRETCHING FREQUENCIES FOR CARBOALKOXYETHYL TIN COMPOUNDS

Compound	$\nu(\text{C}=\text{O})$ (cm^{-1}) ($\pm 2\text{ cm}^{-1}$)	
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$	1660	^a
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_2$	1677	^a
$\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$	1680	1735
$\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_4$		1735
$\text{CH}_3\text{CH}_2\text{CO}_2\text{Me}$		1735
$\text{Cl}_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2)\text{Bu}$	1652	
	1638	^a
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$		1674
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2 + \text{SnCl}_4$	1602	1674
$\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})$		1673
$\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu}) + \text{SnCl}_4$	1620	1673
$\text{ClSnBu}_2(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})$		1686
$\text{ClSnBu}_2(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}) + \text{SnCl}_4$	1637	1680
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me} + \text{Bu}_2\text{SnCl}_2$		1655

^a Spectra recorded as Nujol mulls; all other spectra recorded as neat liquids.

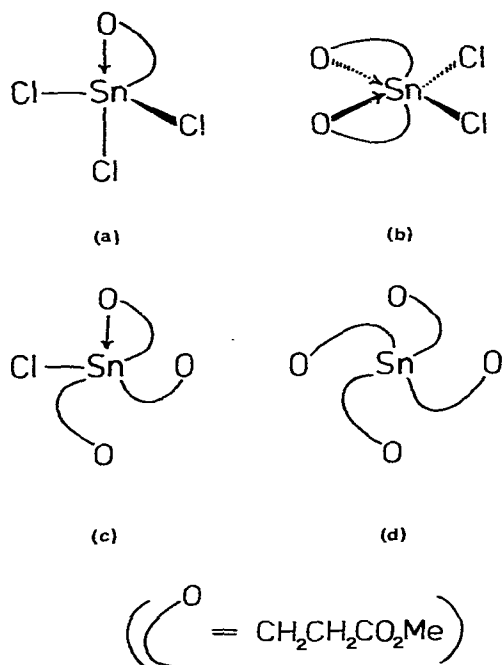
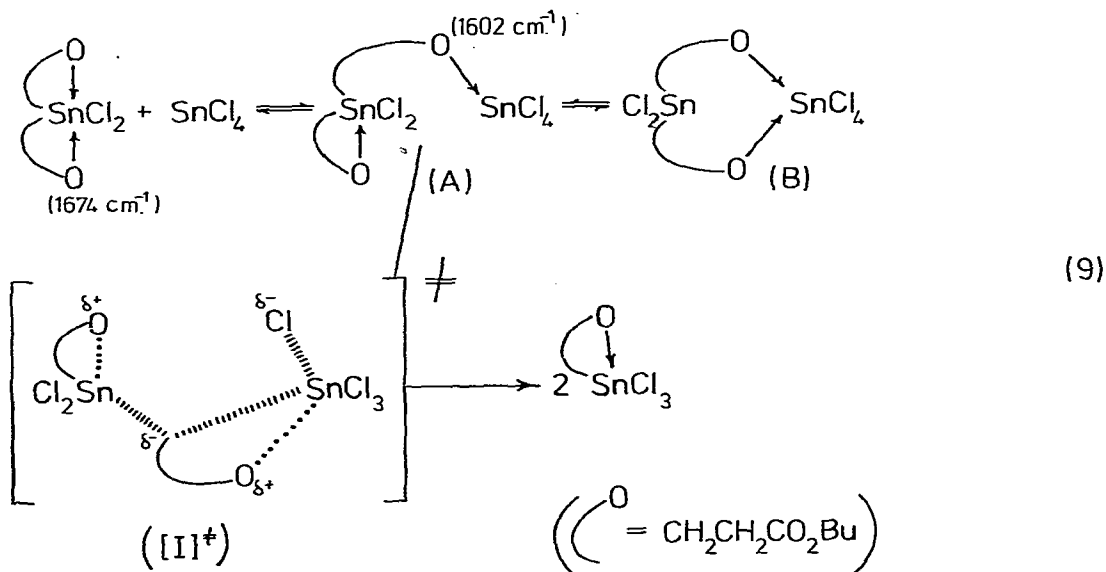


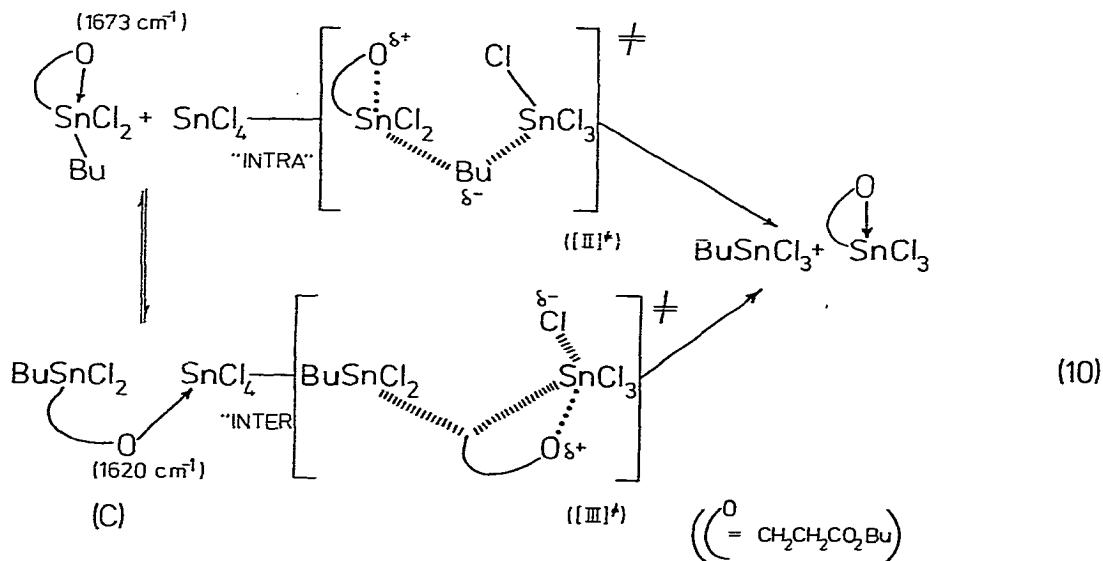
Fig. 2. Molecular structures for carbomethoxyethyltin compounds (a) $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$, (b) $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_2$, (c) $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$ and (d) $\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_4$.

and the formation of complex A, which is presumably in equilibrium with the constituent species. In the resulting spectrum the two peaks at 1674 and 1602 cm^{-1} are of similar intensity, suggesting that complex A constitutes the majority of the reaction mixture; however, the occurrence of a small equilibrium concentration of B, where both ester groups are coordinated to the Sn atom of SnCl_4 , cannot be excluded. Raising the temperature of the reaction mixture to 100°C causes the disappearance of the peak at 1602 cm^{-1} and the formation of



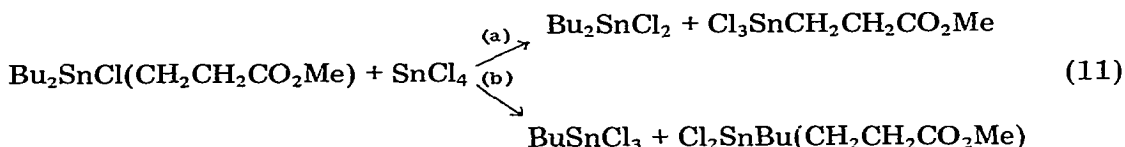
a new peak at 1652 cm^{-1} corresponding to the formation of $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Bu}$ (eq. 9). Giving due consideration to the coordination geometries of the reactants and product species it is not unreasonable to propose that complex A is the intermediate which gives rise to the transition state to the reaction. It is possible that activation for this reaction, in comparison to the reaction between simple dialkyltin dihalides and SnCl_4 , stems from complex formation. If, when the reactants are held in close proximity, the correct molecular geometry for alkyl/chlorine exchange is achieved, then complex formation alone could explain the rate enhancement. However, rate enhancement may also stem from the coordination effects which are present in complex A and, therefore, present also in the transition state to the products. Firstly, intramolecular coordination by one ester group will result in the enhanced polarisation of the Sn—C bond of the other ester-substituted alkyl group in $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$, since the induced positive charge on Sn will be stabilised by delocalisation onto the coordinating ester group. This will result in increased nucleophilicity of the transferring alkyl group. Secondly, intermolecular coordination will facilitate the ionisation of a Sn—Cl bond in SnCl_4 , thereby increasing the activity of the Cl atom in the redistribution process.

A similar IR study has been performed on the reaction between SnCl_4 and $\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})$. Again, mixing the reagents at room temperature gives rise to a new carbonyl absorption, this time at 1620 cm^{-1} , which must reflect the same phenomenon of carbonyl coordination to SnCl_4 . Coincidentally, a similar situation arises in the IR spectrum where the two peaks, one corresponding to intramolecular coordination in $\text{Cl}_2\text{SnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})$ and one due to intermolecular coordination to SnCl_4 , have again similar intensities. In this case, however, this observation is consistent with approximately equal concentrations of the reacting species and the complex C. If the rate enhancement in this reaction is due to intramolecular carbonyl coordination to Sn, as in the reacting entities, it would seem most likely that butyl group transfer to SnCl_4 would occur since this requires the least further molecular reorientation after the alkyl transfer step (transition state $[\text{II}]^\ddagger$). This explanation is consistent



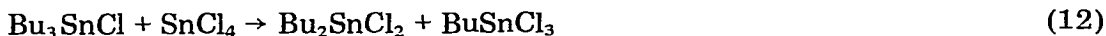
with the electrophilic cleavage of mixed alkyl/ester-substituted alkyl tin compounds by bromine [17] where specific stepwise cleavage of alkyl groups occurs. However, if catalysis in this reaction is due to intermolecular carbonyl coordination, as in complex C, it is then more likely that transition state [III][‡] is involved, which requires the transfer of the carbobutoxyethyl group to SnCl₄. Again, transfer of this group would require the least further molecular reorientation after alkyl transfer, since the carbonyl group is already coordinated to the Sn atom to which the carbobutoxyethyl group is transferred. Since the same products are evolved via both possible transition states it is not easily possible to determine which alkyl group is transferred in the reaction.

In an attempt to gain some insight into this type of redistribution reaction it was decided to react SnCl₄ with the trialkyltin compound ClSnBu₂-(CH₂CH₂CO₂Me), since, if butyl group transfer to SnCl₄ occurs (resulting from intramolecular catalysis), BuSnCl₃ and Cl₂SnBu(CH₂CH₂CO₂Me) will be produced and if carbomethoxyethyl group-transfer occurs (originating from intermolecular catalysis) Cl₃SnCH₂CH₂CO₂Me and Bu₂SnCl₂ will be produced (eq. 11). ClSn(Bu)₂(CH₂CH₂CO₂Me) was prepared as described in the experi-

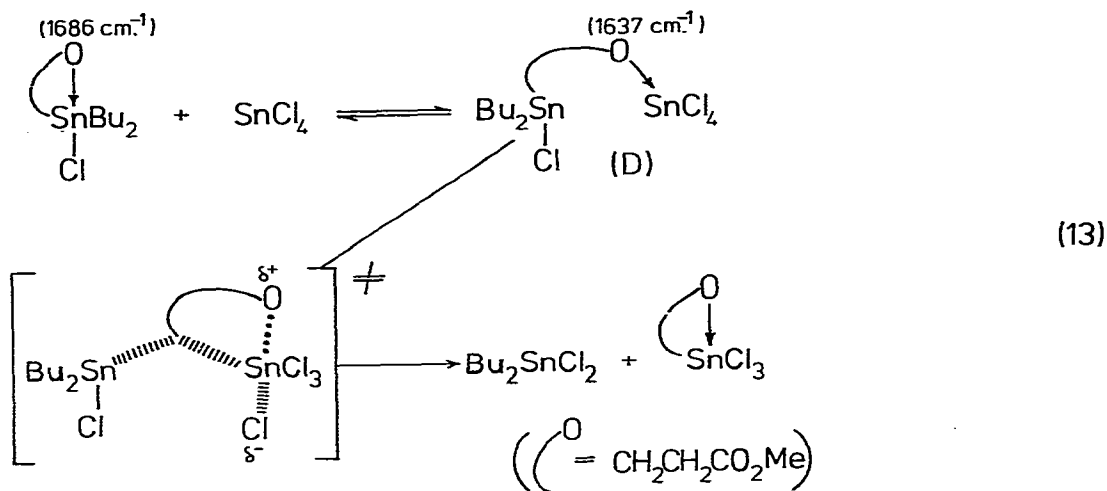


mental section.

When SnCl₄ was mixed with an equimolar quantity of ClSnBu₂(CH₂CH₂CO₂Me) at room temperature (~20°C) a very exothermic process ensued. The reaction temperature reached 100°C within a few minutes and, upon cooling, the mixture quickly crystallised. GLC analysis of the products revealed the presence of 46% Bu₂SnCl₂ and 3.5% BuSnCl₃ with no SnCl₄ detectable. This reaction was, therefore, complete after a few minutes at 100°C, again suggesting that significant rate enhancement had occurred due to the presence of a carbomethoxyethyl group. (The reaction between SnCl₄ and Bu₃SnCl (eq. 12) proceeds to completion at 100°C, but within a few hours [18]). Supportive evidence for the GLC data on the products was obtained from an infrared study of the reaction.



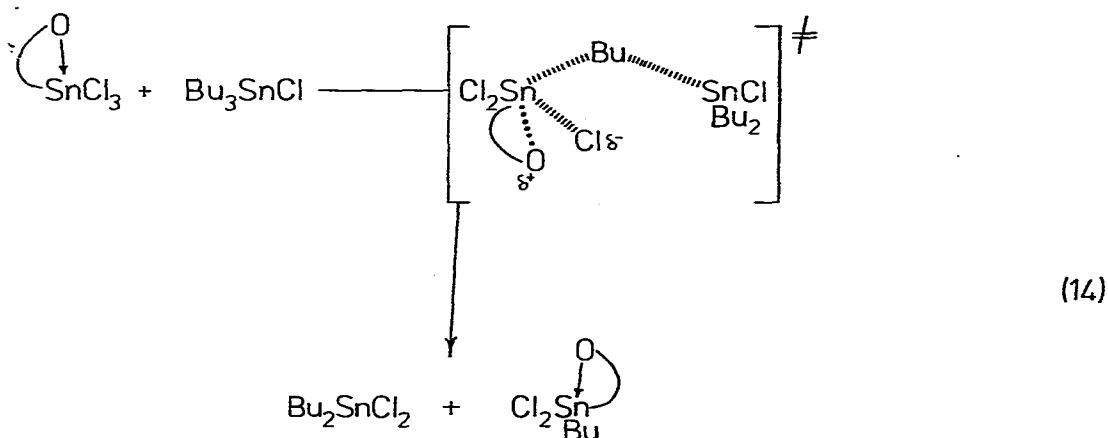
In this case the reagents, SnCl₄ and ClSnBu₂(CH₂CH₂CO₂Me), were both cooled to 0°C and mixed quickly at this temperature. When the IR spectrum of this mixture was recorded immediately the carbonyl region showed two peaks; one at 1680 cm⁻¹ which is presumably due largely to unreacted ClSnBu₂(CH₂CH₂CO₂Me), and one at 1637 cm⁻¹ which quickly disappeared, and is probably due to the intermolecular coordination complex D. After a few minutes in the beam of the spectrophotometer the spectrum of the mixture had collapsed to a single peak at 1655 cm⁻¹, which is identical to the spectrum of an authentic mixture of Bu₂SnCl₂ and Cl₃SnCH₂CH₂CO₂Me (see Table 1). The quantities of BuSnCl₃ and Bu₂SnCl₂ produced in the initial reaction are consistent with approximately 93% selectivity in terms of reaction 11(a) vs. 11(b). Hence it would appear that where strong intermolecular complex formation is possible



almost specific cleavage of the carboalkoxyethyl group in mixed alkyl/carboalkoxyethyl-tin compounds by SnCl_4 can occur. Here, therefore, is the first example of intermolecular nucleophilic catalysis of an electrophilic displacement reaction. Kuivila has, however, previously described an example of intramolecular nucleophilic catalysis of a similar type of electrophilic displacement reaction [5].

Reactions leading to dialkyltin dihalides

Conversion/time data for the reaction between Bu_3SnCl and BuSnCl_3 at 170°C is illustrated in Fig. 3 along with data for the reaction between Bu_3SnCl and $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$. Determination of the initial rates of these reactions shows a rate enhancement of approximately 6-fold for the reaction involving the estertin compound. Catalysis of this reaction must stem from intramolecular carbonyl coordination since there is little or no tendency for intermolecular coordination between the two reagents. A suggested transition state for this reaction is represented in eq. 14. More dramatic is the rate enhancement



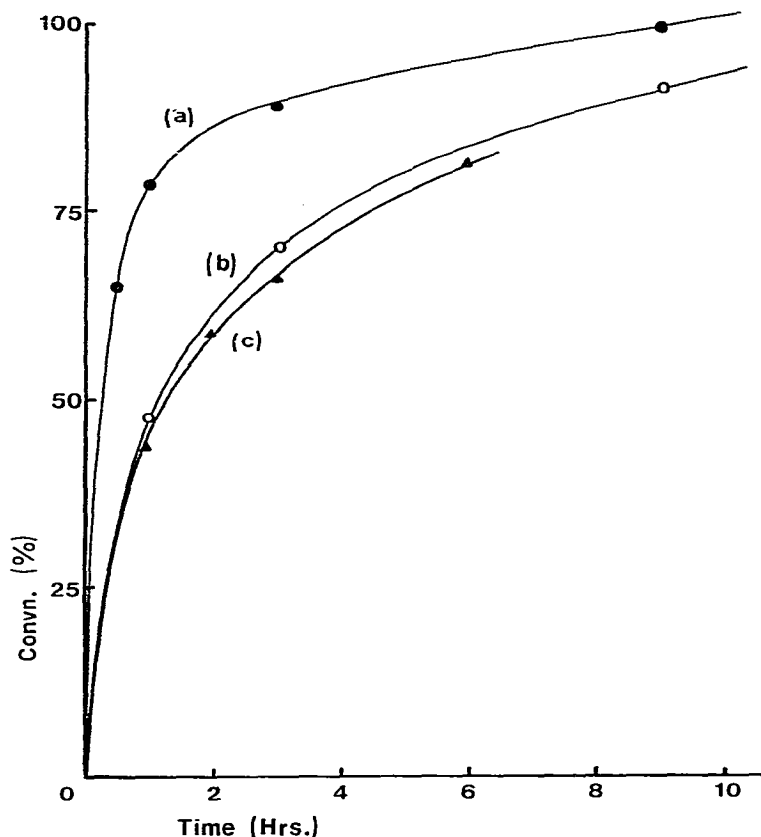
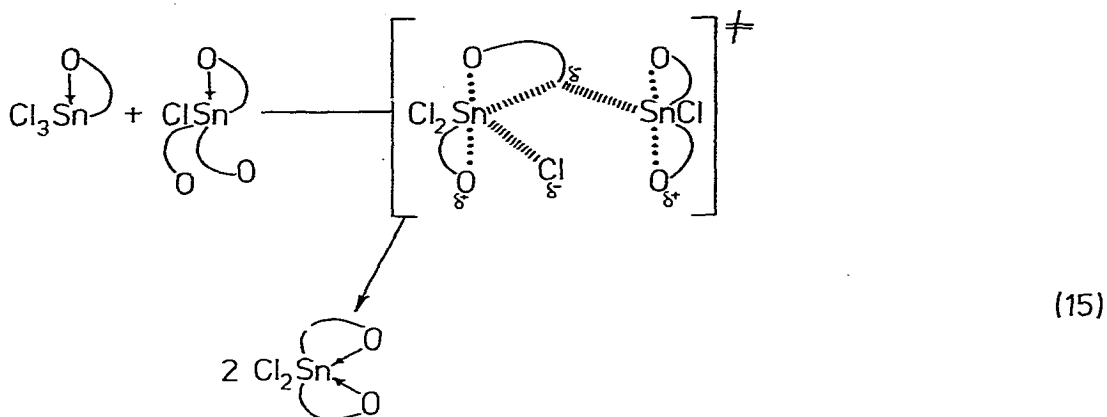


Fig. 3. Conversion/time curves for the reactions between (a) Bu_3SnCl and $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$ (at 170°C), (b) Bu_3SnCl and BuSnCl_3 (at 170°C) and (c) $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$ and $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$ (at 50°C).

observed for the reaction between $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$ and $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$ in comparison to the simple butyltin compounds. The two reactions proceed at essentially similar rates at widely different temperatures; the estertin reaction at 50°C and the alkyltin reaction at 170°C . Such temperature differences suggest a factor of very approximately 4×10^3 in initial reaction rates. The probable transition state for the estertin reaction is illustrated in eq. 15, and shows that there is a combination of 4 inter- and intramolecular carbonyl coordination effects which are likely to give rise to rate enhancement. However, intramolecular carbonyl coordination in $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$, giving rise to enhanced polarisation of the Sn—Cl bonds, and intramolecular coordination in $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$, giving rise to enhanced polarisation of the Sn—C bonds, are probably the two main rate-enhancing effects. Incoming intermolecular carbonyl coordination from $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$ to $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{Me}$ and intramolecular carbonyl coordination within $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3$ are probably less significant.



Reactions leading to trialkyltin halides

Conversion/time data for reaction 16 ($R = \text{Bu}, \text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$) is presented in Fig. 4. From these curves it can be estimated that there is approximately a

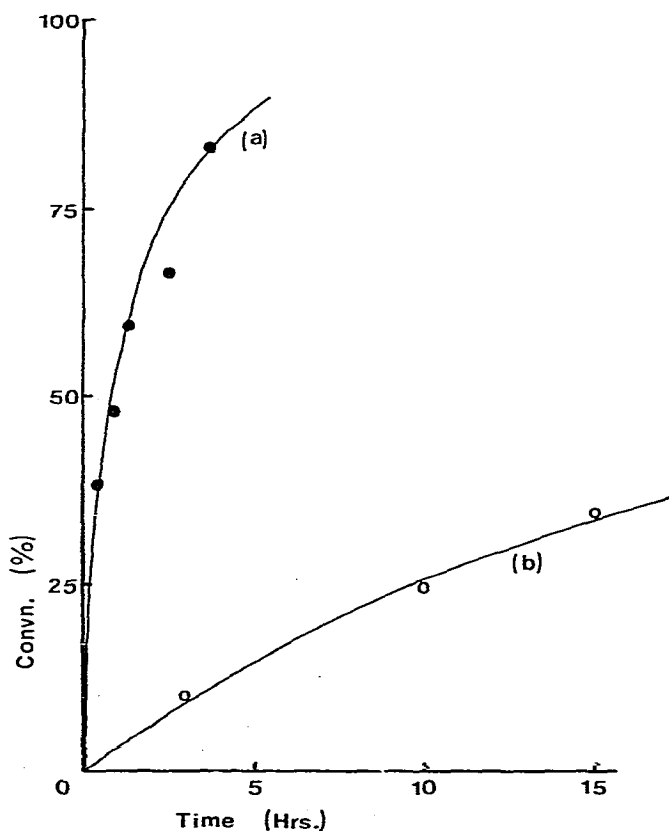


Fig. 4. Conversion/time curves for the reactions between (a) $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_2$ and $\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_4$, and Bu_2SnCl_2 and Bu_4Sn .

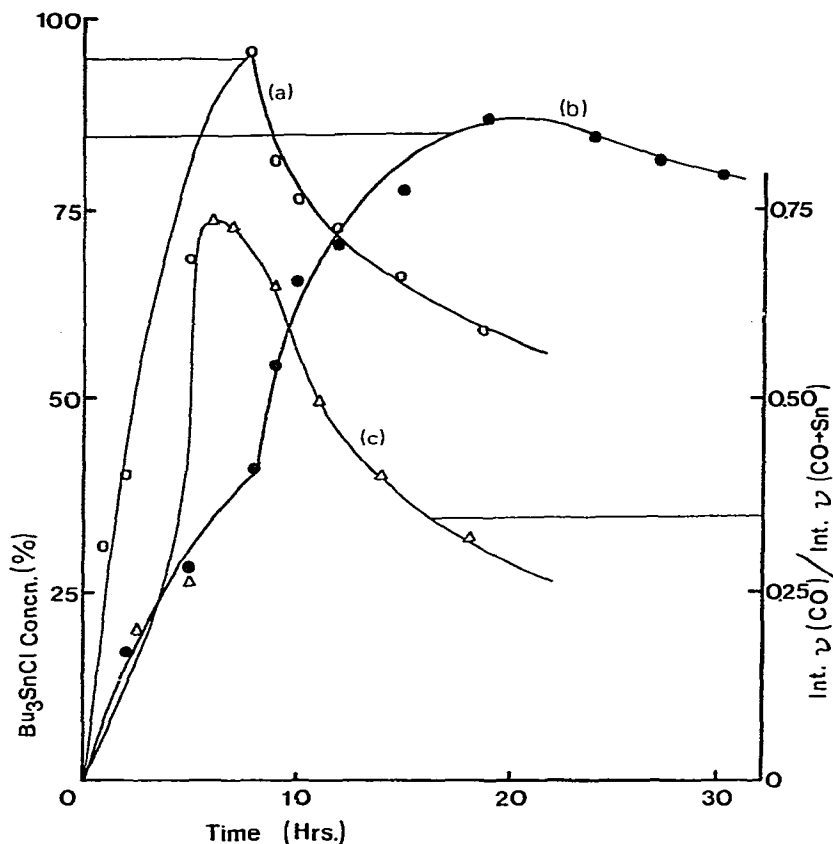


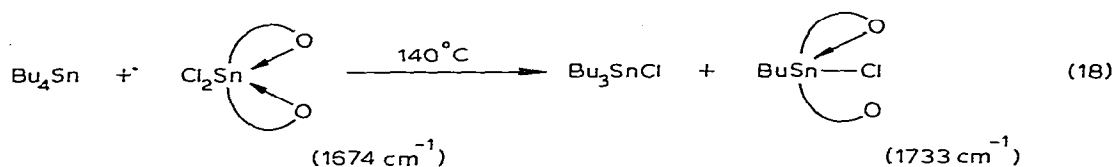
Fig. 5. Concentration of Bu_3SnCl (%) / time curves for the reactions between (a) $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$ and Bu_4Sn and (b) $\text{Oct}_2\text{SnCl}_2$ and Bu_4Sn . (Maximum concentrations of Bu_3SnCl were calculated according to eq. 17). Curve (c) represents the change in the ratio of the intensity of $\nu(\text{C}=\text{O})$ (uncoordinated) to that of $\nu(\text{CO}\rightarrow\text{Sn})$ (intramolecularly coordinated) with time.

40-fold difference in initial rates. Again it is not unreasonable to propose that carbonyl coordination (probably mainly intramolecular in origin, since any intermolecular interaction will be very weak) is responsible for the rate enhancement.

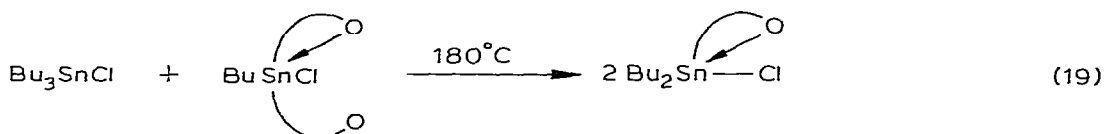
More interesting, perhaps, is the study of reaction 17 where $\text{R} = \text{Bu}$ and $\text{R}' = \text{CH}_2\text{CH}_2\text{CO}_2\text{Bu}$ and Oct . The concentration of Bu_3SnCl was monitored in these



reactions and the concentration/time curves are presented in Fig. 5. At 140°C the reaction between $\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$ and Bu_4Sn approaches completion relatively quickly and in preliminary experiments the concentration then appeared to fall slowly. In an attempt to verify this the reaction temperature was raised after 8 hours at 140°C to 180°C . As Fig. 5(a) shows, a marked decrease in the concentration of Bu_3SnCl occurs under these conditions. If eq. 17 correctly represents the principal reaction there should be an overall decrease in carbonyl coordination to Sn, since only one carbonyl group in $\text{ClSnBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu})_2$ will be intramolecularly bound: see eq. 18. (This assumption is based



upon the expected 5-coordinate geometry of complexed trialkyltin halides [11].) Hence a plot of $\text{int. } \nu(\text{C=O})/\text{int. } \nu(\text{CO}\rightarrow\text{Sn})$ (the ratio of the intensity of the free (uncoordinated) carbonyl absorption to that of the intramolecularly coordinated carbonyl absorption) against time should also indicate the extent of reaction. This data is illustrated in Fig. 5(c) and, since a similar reaction profile is obtained from the spectroscopic study, almost certainly this and the chromatographic study relate to the same series of reactions. A decrease in the ratio $\nu(\text{C=O})/\nu(\text{CO}\rightarrow\text{Sn})$ indicates a change back towards complete carbonyl coordination to Sn and reaction 19 is proposed to account for this change. This reaction also accounts for the consumption of Bu_3SnCl GLC data for reaction



17 ($\text{R}' = \text{Oct}$) suggest that the same stepwise reactions occur and that the limited data available indicates that the Bu/Oct exchange is again slower than the Bu/ $\text{CH}_2\text{CH}_2\text{CO}_2\text{Bu}$ exchange. Hence carbonyl coordination can also catalyse alkyl/alkyl' exchanges as well as alkyl/chlorine exchanges.

Acknowledgement

Thanks are due to C.J. Groenenboom, Akzo Research Laboratories, Arnhem (The Netherlands) for obtaining the NMR spectra.

References

- 1 K.A. Kozeschkow, Ber. Dtsch. Chem. Ges., 62 (1929) 996.
- 2 W.P. Neumann and G. Burkhardt, Annalen, 663 (1963) 11.
- 3 H.G. Langer, Tetrahedron Letts., 1 (1967) 43.
- 4 I. Omae, K. Yamaguchi and S. Matsuda, J. Organometal. Chem., 24 (1970) 663.
- 5 H.G. Kuivila, J.E. Dixon, P.L. Maxfield, N.M. Scarpa, T.M. Topka, K. Tsai and K.R. Wursthorn, J. Organometal. Chem., 86 (1975) 89.
- 6 R.E. Hutton and V. Oakes, Adv. in Chem. Series, 157 (1976) 123.
- 7 J.W. Burley, R.E. Hutton and V. Oakes, J. Organometal. Chem., 156 (1978) 369.
- 8 J.W. Burley, P. Hope, R.E. Hutton and C.J. Groenenboom, J. Organometal. Chem., 170 (1979) 21.
- 9 C.J. Groenenboom, J.W. Burley, M.R.J. Jolley and R.E. Hutton, 22nd Deutschen Zinntag, Düsseldorf, 1978.
- 10 J. Pedain, Dissertation, Univ. of Giessen, 1965.
- 11 A.K. Sawyer and H.G. Kuivila, Chem. and Ind., (1961) 260.
- 12 G.J.M. van der Kerk, J.G. Noltes and J.G.A. Luijten, J. Appl. Chem., 7 (1957) 366.
- 13 I. Omae, Reviews on Si, Ge, Sn and Pb compounds, 1 (1972) 50.
- 14 P.G. Harrison, T.J. King and M.A. Healy, J. Organometal. Chem., 182 (1979) 17.
- 15 A.K. Sawyer (Ed), Organotin Compounds, Vol. 1, M. Dekker Inc. New York, 1971, p. 123.
- 16 V.I. Gaivoronskii and O.A. Osipov, J. Gen. Chem. U.S.S.R., 33 (1963) 2901.
- 17 D. Seyferth and E.G. Rochow, J. Amer. Chem. Soc., 77 (1955) 1302.
- 18 J.G.A. Luijten and F. Rijkers, Rec. Trav. Chim. Pays-Bas, 8 (1964) 857.