A STUDY OF MERCAPTOESTER/CHLORINE EXCHANGE EQUILIBRIA EXHIBITED BY β-CARBOALKOXYETHYLTIN COMPOUNDS

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Summary

60 MHz proton NMR data confirms that Cl/mercaptoester exchange reactions in butyl- and β-carbobutoxyethyltin compounds occur readily in deuterochloroform at 35°C. The positions of dibutyl-, monobutyl- and mixed mono-/dibutyltin equilibria are dictated by intramolecular carbonyl to tin coordination from the mercaptoester groups. In the analogous β-carbobutoxyethyltin systems the corresponding equilibria are perturbed by the competing carbonyl to tin coordination from the β-carbobutoxyethyl groups. These results are correlated with the activity of alkyltin and β-carboalkoxyethyltin stabilisers in PVC.

Introduction

Alkyltin mercaptoesters such as dibutyltin bis(2-ethylhexylthioglycollate) (Bu$_2$Sn(2-EHTG)$_2$) and butyltin tris(2-ethylhexylthioglycollate) (BuSn(2-EHTG)$_3$) are established stabilisers for PVC [1]. The corresponding mercaptoester/chlorides are intermediates in the stabilisation process, and are generated when the stabilisers react with HCl liberated from the polymer or when the stabilisers react with active chlorine groups within the polymer [2]. These organotin mercaptoester/chlorides have been shown to exist in equilibrium with the corresponding alkytin chlorides and alkyltin mercaptoesters as demonstrated by IR and NMR spectroscopies [3–5]. The positions of these equilibria are dictated by carbonyl to Sn coordination involving the mercaptoester carbonyl groups. Not only do these equilibria exist within the dialkyltin and monoalkyltin types but similar exchange equilibria exist between dialkyltin and monoalkyltin compounds [6]. We have also suggested that equilibria of this type may provide an explanation for the phenomenon of synergism which is observed between mono- and dialkyltin mercaptoester stabilisers.

Relatively recently a new class of organotin compounds, namely "estertins" (β-carboalkoxyethyltins), have been developed as PVC stabilisers [7]. Equilibria involving the estertin mercaptoester chlorides are potentially susceptible to perturbation by the competing carbonyl to tin coordination arising from the β-carboalkoxyethyl group. We present here the results of ^{1}H NMR studies on butyltin compounds which complements our previous IR study [6] and the results of IR and ^{1}H NMR studies of equilibria involving estertin compounds.

Results and discussion

IR studies

Our previous studies of mercaptoester/chlorine exchange equilibria were performed with IOTG (iso-octylthioglycollate) based compounds. Since commercially available IOTG is derived from the isomerically impure alcohol iso-octanol, these
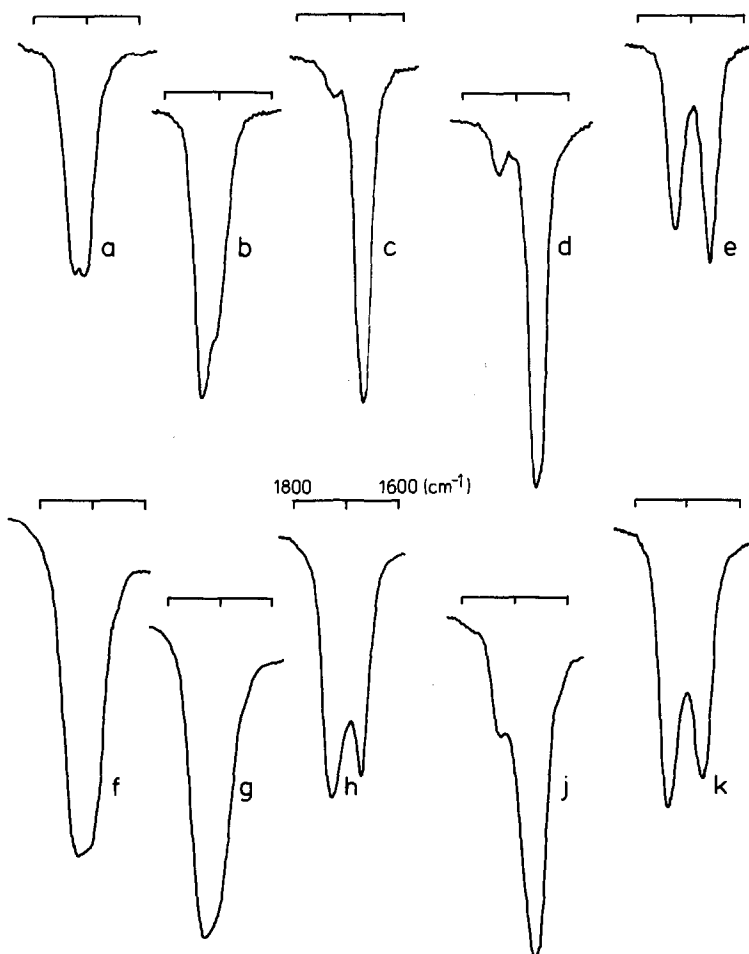

Fig. 1. The carbonyl region infra-red spectra of organotin mercaptoesters: (a) $Bu_2Sn(2\text{-EHTG})_2$, (b) $BuSn(2\text{-EHTG})_3$, (c) $Bu_2SnCl(2\text{-EHTG})$, (d) $BuSnCl_2(2\text{-EHTG})$, (e) $BuSnCl(2\text{-EHTG})_2$, (f) $(\beta CBE)_2Sn(2\text{-EHTG})_2$, (g) $\beta CBESn(2\text{-EHTG})_3$, (h) $(\beta CBE)_2SnCl(2\text{-EHTG})$, (j) $\beta CBESnCl_2(2\text{-EHTG})$, (k) $\beta CBESnCl(2\text{-EHTG})_2$.

compounds were found to be less suitable than the isomerically pure 2-EHTG (2-ethylhexylthioglycollate) for ^{1}H NMR studies. We have therefore repeated our previous IR work with 2-EHTG-based compounds and have obtained identical IR spectra. Figure 1 shows the carbonyl region IR spectra of butyltin and estertin 2-ethylhexylthioglycollates and the 2-ethylhexylthioglycollate chlorides; ν(C=O) values for these compounds are also listed in Table 1.

The electronegativity of the central tin atom in organotin mercaptoesters is perturbed by the presence of electron-withdrawing (Cl or S) or -donating (alkyl) groups. Consequently all compounds show some degree of intramolecular carbonyl to tin coordination. This results in a lowering of the carbonyl bond order, which is reflected in a lowering of the carbonyl stretching frequency. Hence, ν(C=O) values in the region of 1733–35 cm^{-1} correspond to un-coordinated or 'free' carbonyl groups and those in region of 1662–1710 cm^{-1} represent intramolecularly coordinated carbonyl groups. From this information the structures of the butyltin compounds have been deduced [3] and are presented below.
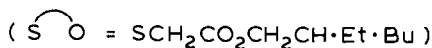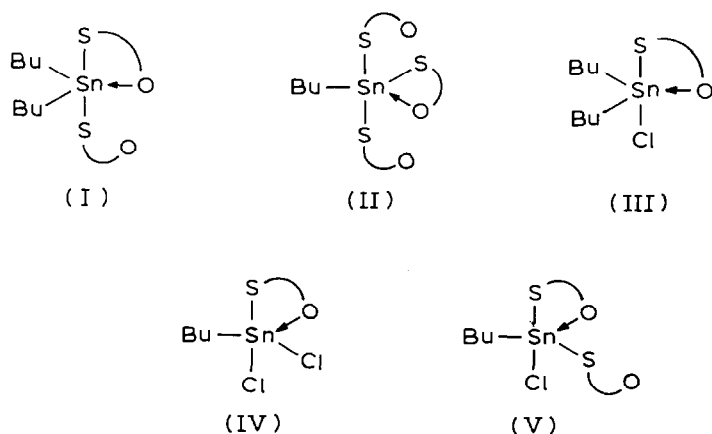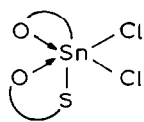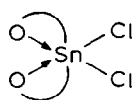
(I)   (II)   (III)

(IV)   (V)

(S O = SCH$_2$CO$_2$CH$_2$CH·Et·Bu)

TABLE 1

IR DATA FOR ORGANOTIN MERCAPTOESTERS

Compounds		ν(C=O) (± 2 cm^{-1})			
		R = Bu		R = CH$_2$CH$_2$CO$_2$Bu	
R$_2$Sn(2-EHTG)$_2$		1733	1708	1735v.br	
RSn(2-EHTG)$_3$		1734	1710sh	1733br	
R$_2$SnCl(2-EHTG)	[R$_2$SnCl$_2$/R$_2$Sn(2-EHTG)$_2$]	1734w	1676	1734	1679
RSnCl$_2$(2-EHTG)	[2RSnCl$_3$/RSn(2-EHTG)$_3$]	1733w	1662	1733w	1665
RSnCl(2-EHTG)$_2$	[RSnCl$_3$/2RSn(2-EHTG)$_3$]	1733	1665	1735	1671
RSnCl$_3$/R$_2$SnCl(2-EHTG)		1733vw	1662	1736w	1677
RSnCl(2-EHTG)$_2$/R$_2$SnCl$_2$		1733	1670	1734	1680
⎰ RSn(2-EHTG)$_3$ + R$_2$SnCl$_2$		1733	1674		
⎨ RSnCl$_2$(2-EHTG)					
⎱ + R$_2$Sn(2-EHTG)$_2$				1736	1680
RSn(2-EHTG)$_3$			1677,		
+ R$_2$SnCl(2-EHTG)		1733	1710sh	1735	1682

The IR spectra of the corresponding estertin compounds are, however, less informative. For $(\beta CBE)_2Sn(2\text{-EHTG})_2$ (bis(β-carbobutoxyethyl)tin-bis(2-ethyl-hexylthioglycollate)) and $\beta CBESn(2\text{-EHTG})_3$ there appears to be little evidence for any intramolecular carbonyl coordination to tin although this may be masked by the higher ratio of 'free' to coordinated carbonyl groups in these compounds. For the estertin compounds containing chlorine, in only one case, namely $\beta CBESnCl_2(2\text{-EHTG})$, can any co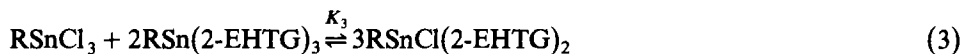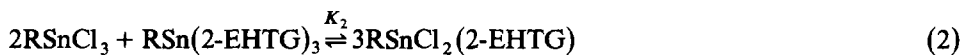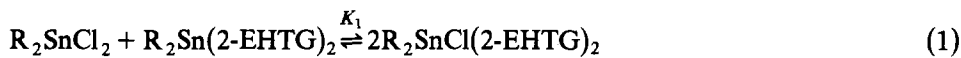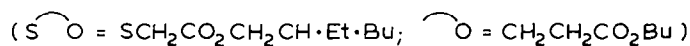nclusion be reached with regard to the structures of the estertin mercaptoester/chlorides. A mixture of $\beta CBESnCl_3$ and $\beta CBESn(2\text{-EHTG})_3$ corresponding to equilibrium (2) exhibits one main carbonyl absorption at 1665 cm^{-1}. This suggests that equilibrium (2), as in the case of butyltins, lies far to the r.h.s. (right hand side) and that in $\beta CBESnCl_2(2\text{-EHTG})$ both ester containing groups are strongly coordinated to tin (VI). Structurally this compound may be similar to $(\beta CBE)_2\,SnCl_2$, which also contains two coordinated carbonyl groups (VII) [8].

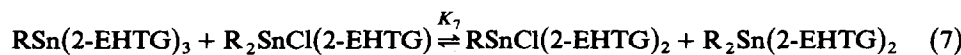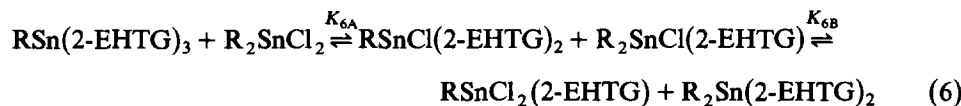(VI)   (VII)

$(\overset{\frown}{S\ O} = SCH_2CO_2CH_2CH\cdot Et\cdot Bu;\ \overset{\frown}{\ O} = CH_2CH_2CO_2Bu)$

$$R_2SnCl_2 + R_2Sn(2\text{-EHTG})_2 \overset{K_1}{\rightleftharpoons} 2R_2SnCl(2\text{-EHTG})_2 \tag{1}$$

$$2RSnCl_3 + RSn(2\text{-EHTG})_3 \overset{K_2}{\rightleftharpoons} 3RSnCl_2(2\text{-EHTG}) \tag{2}$$

$$RSnCl_3 + 2RSn(2\text{-EHTG})_3 \overset{K_3}{\rightleftharpoons} 3RSnCl(2\text{-EHTG})_2 \tag{3}$$

$(R = Bu, CH_2CH_2CO_2Bu)$
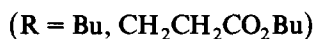
IR spectroscopy is also a useful tool for the study of equilibria involving both mono- and di-alkyltin compounds (eqs. 4–7) (R = Bu). Indeed, the spectra of these systems involving different mercaptoester/chlorine ratios are sufficiently well defined that the positions of the equilibria can be determined with reasonable confidence [6].

$$RSnCl_2(2\text{-EHTG}) + R_2SnCl_2 \overset{K_4}{\rightleftharpoons} RSnCl_3 + R_2SnCl(2\text{-EHTG}) \tag{4}$$

$$RSnCl(2\text{-EHTG})_2 + R_2SnCl_2 \overset{K_{5A}}{\rightleftharpoons} RSnCl_2(2\text{-EHTG}) + R_2SnCl(2\text{-EHTG}) \overset{K_{5B}}{\rightleftharpoons}$$

$$RSnCl_3 + R_2Sn(2\text{-EHTG})_2 \tag{5}$$

$$RSn(2\text{-EHTG})_3 + R_2SnCl_2 \overset{K_{6A}}{\rightleftharpoons} RSnCl(2\text{-EHTG})_2 + R_2SnCl(2\text{-EHTG}) \overset{K_{6B}}{\rightleftharpoons}$$

$$RSnCl_2(2\text{-EHTG}) + R_2Sn(2\text{-EHTG})_2 \tag{6}$$

$$RSn(2\text{-EHTG})_3 + R_2SnCl(2\text{-EHTG}) \overset{K_7}{\rightleftharpoons} RSnCl(2\text{-EHTG})_2 + R_2Sn(2\text{-EHTG})_2 \tag{7}$$
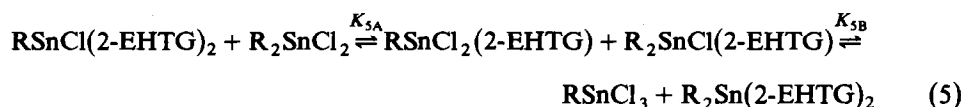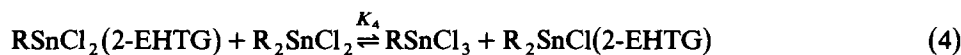
Fig. 2. The carbonyl region infra-red spectra of mixed mono-/di-organotin mercaptoesters: (a) BuSnCl$_3$ + Bu$_2$SnCl(2-EHTG), (b) BuSnCl(2-EHTG)$_2$ + Bu$_2$SnCl$_2$, (c) BuSn(2-EHTG)$_3$ + Bu$_2$SnCl$_2$, (d) BuSn(2-EHTG)$_3$ + Bu$_2$SnCl(2-EHT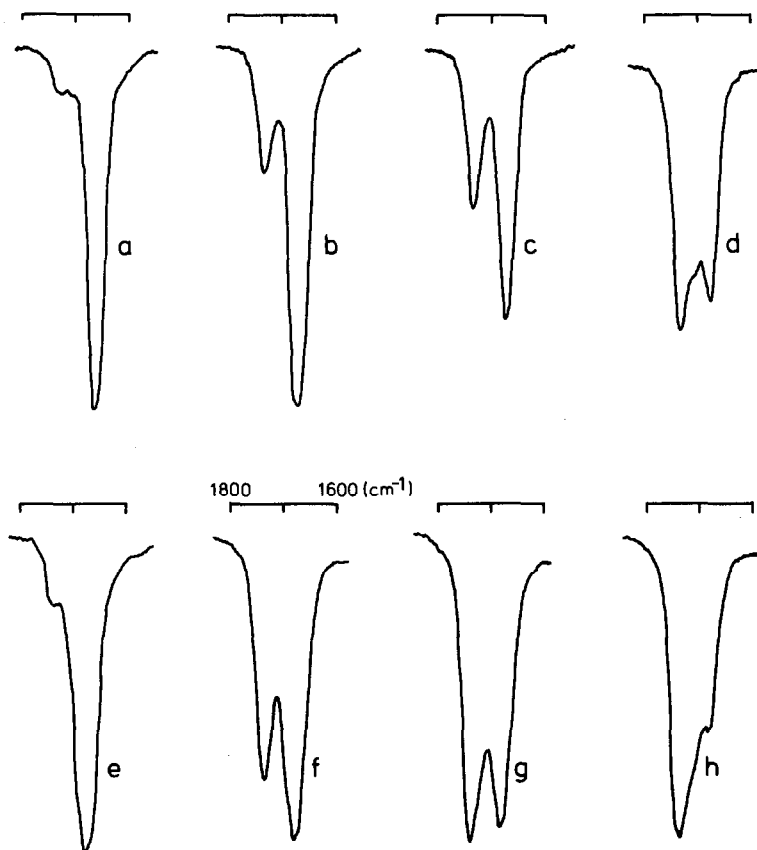G), (e) βCBESnCl$_3$ +(βCBE)$_2$SnCl(2-EHTG), (f) βCBESnCl(2-EHTG)$_2$ +(βCBE)$_2$SnCl$_2$, (g) βCBESnCl$_2$(2-EHTG)+(βCBE)$_2$Sn(2-EHTG)$_2$ (h) βCBESn(2-EHTG)$_3$ +(βCBE)$_2$SnCl(2-EHTG).

Similar studies with mixed mono- and di-estertin 2-EHTG/Cl compounds were much less informative because of the presence of the additional ester group of the β-carboalkoxyethyl moiety. These spectra are presented in Fig. 2, and for comparison the spectra of the corresponding butyltin systems are also included. It is impossible to judge the positions of equilibria 4–7 (R = CH$_2$CH$_2$CO$_2$Bu) from this data and ^{1}H NMR spectroscopy has proved to be a much more useful tool.

^{1}H NMR studies

Proton NMR data confirms that equilibria 1 and 2 (R = Bu) lie strongly to the r.h.s. since single sharp peaks are obtained in each case in the SCH_2CO$_2$ region of the spectrum, however a mixture of BuSnCl$_3$ and BuSn(2-EHTG)$_3$ in the ratio 1/2 exhibited, not only, a strong signal at 3.66 ppm (BuSnCl(2-EHTG)$_2$) but also a much weaker signal at 3.55 ppm, due to a small but significant concentration of BuSn(2-EHTG)$_3$. Equilibrium 3 is, therefore, displaced to the r.h.s., in keeping with the IR result for this system. K_3(Bu) was found to be 4.2 × 10^2. Our data for butyl-

TABLE 2

^{1}H NMR DATA FOR ORGANOTIN MERCAPTOESTERS

Compounds		Chemical shift (δ(ppm)) ^{a} SCH$_2$CO$_2$	
		R = Bu	R = CH$_2$CH$_2$CO$_2$Bu
R$_2$Sn(2-EHTG)$_2$		3.39	3.42
RSn(2-EHTG)$_3$		3.55	3.59
R$_2$SnCl(2-EHTG)	[R$_2$SnCl$_2$/R$_2$Sn(2-EHTG)$_2$]	3.57	3.42, *3.55* ^{b}
RSnCl$_2$(2-EHTG)	[2RSnCl$_3$/RSn(2-EHTG)$_3$]	3.77	3.82
RSnCl(2-EHTG)$_2$	[RSnCl$_3$/2RSn(2-EHTG)$_3$]	3.55, *3.66*	3.60, *3.69*, 3.83
RSnCl$_3$/R$_2$SnCl(2-EHTG)		3.77	3.82
RSnCl(2-EHTG)$_2$/R$_2$SnCl$_2$		3.58, 3.76	3.56, *3.69*, 3.83
⎰ RSn(2-EHTG)$_3$ + R$_2$SnCl$_2$		3.57, 3.67	
⎱ RSnCl$_2$(2-EHTG)			
+ R$_2$Sn(2-EHTG)$_2$			3.56, 3.59, 3.68
RSn(2-EHTG)$_3$			
+ R$_2$SnCl(2-EHTG)		3.39, *3.55*, 3.67	3.43, *3.56, 3.60*, 3.69

^{a} Downfield from internal TMS. ^{b} Figures in italics indicate most prominent peaks.

and ester-tins are listed in Table 2; the results for butyltins compare favourably with those reported by Michel and co-workers [5].

The strength of carbonyl to tin coordination in these organotin mercaptoesters is governed by the electronegativity of the central tin atom. This coordination reduces not only the C=O bond order but also the charge density on the carbonyl C atom. This results in a deshielding effect on the protons of the SCH$_2$CO$_2$ group and the magnitude of the deshielding is therefore directly related to the strength of the carbonyl to tin coordination and to the electronegativity of the tin atom. Hence the position of the SCH$_2$CO$_2$ signal is governed by the electronegativity of the tin atom to which the mercaptoester group is attached.

Diestertin mixtures

The NMR spectrum of an equimolar mixture of (βCBE)$_2$SnCl$_2$ and (βCBE)$_2$Sn(2-EHTG)$_2$ exhibits two signals in the SCH$_2$CO$_2$ region (3.42 and 3.56 ppm), in contrast to the spectrum of the similar butyltin mixture. The former peak is

TABLE 3

EQUILIBRIUM CONSTANT DATA AT 35°C

K	R = Bu	R = CH$_2$CH$_2$CO$_2$Bu
K_1	$> 10^3$	18
K_2	$> 10^3$	$> 10^3$
K_3	4.2×10^2	–
K_4	$< 10^{-3}$	$< 10^{-3}$
K_{5A}	$> 10^3$	0.32
K_{5B}	$< 10^{-3}$	$< 10^{-3}$
K_{6A}	$> 10^3$	2.25
K_{6B}	$< 10^{-3}$	$< 10^{-3}$
K_7	0.22	0.04
K_8	–	22

due to $(\beta CBE)_2 Sn(2\text{-EHTG})_2$ and by analogy with the spectrum of $Bu_2 SnCl(2\text{-}$EHTG) the latter peak represents the presence of $(\beta CBE)_2 SnCl(2\text{-EHTG})$. Equilibrium constant data is presented in Table 3.

Monoestertin mixtures

The spectrum of a 2/1 mixture of $\beta CBESnCl_3$ and $\beta CBESn(2\text{-EHTG})_3$, corresponding to the l.h.s. of equilibrium 2 ($R = CH_2 CH_2 CO_2 Bu$), exhibits a single signal at 3.82 ppm representing the formation of $\beta CBESnCl_2$ (2-EHTG). This result is in agreement with the IR result for this system. The 1/2 mixture of $\beta CBESnCl_3$ and $\beta CBESn(2\text{-EHTG})_3$ exhibits signals at 3.59 and 3.82 ppm, due to $\beta CBESn(2\text{-}$EHTG)$_3$ and $\beta CBESnCl_2(2\text{-EHTG})$ respectively, and a major signal at 3.69 ppm corresponding to $\beta CBESnCl(2\text{-EHTG})_2$. This mixture is therefore most aptly described by equilibrium 8. The position of this equilibrium again contrasts sharply with the corresponding butyltin case.

$$\beta CBESnCl_2(2\text{-EHTG}) + \beta CBESn(2\text{-EHTG})_3 \overset{K_8}{\rightleftharpoons} 2\beta CBESnCl(2\text{-EHTG})_2 \qquad (8)$$

Mixed mono-/di-systems

(a) One 2-EHTG group. NMR evidence (Table 2) confirms that equilibrium 4 ($R = Bu$) lies strongly to the l.h.s., since the equimolar mixtures of $BuSnCl_2(2\text{-}$EHTG)/$Bu_2 SnCl_2$ and $BuSnCl_3/Bu_2 SnCl(2\text{-EHTG})$ exhibited identical spectra, namely a single sharp peak at 3.77 ppm corresponding to $BuSnCl_2(2\text{-EHTG})$. Similarly an equimolar mixture of $\beta CBESnCl_3$ and $(\beta CBE)_2 SnCl(2\text{-EHTG})$ exhibited a single signal at 3.82 ppm suggesting that equilibrium 4 ($R = CH_2 CH_2 CO_2 Bu$) also lies strongly to the l.h.s. $K_4(Bu)$ and $K_4(\beta CBE)$ are estimated to be $< 10^{-3}$.

(b) Two 2-EHTG groups. Data presented in Table 2 confirms our previous conclusion from IR studies that $BuSnCl_2(2\text{-EHTG})$ and $Bu_2 SnCl(2\text{-EHTG})$ are the major constituents of equilibrium 5 (see Fig. 3b). Levels of $BuSnCl(2\text{-EHTG})_2$ and $Bu_2 SnCl(2\text{-EHTG})_2$ were below the detection limit. Equilibrium 5A(Bu), therefore, lies strongly to the r.h.s. suggesting that $K_{5A}(Bu)$ is greater than 10^3 whilst $5_B(Bu)$ lies strongly to the l.h.s. and $K_{5B}(Bu)$ less than 10^{-3}.

For the analogous estertin mixture ($\beta CBESnCl(2\text{-EHTG})_2$ and $(\beta CBE)_2 SnCl_2$) NMR spectroscopy indicates the presence of $\beta CBESnCl(2\text{-EHTG})_2$ (3.69 ppm) as well as $\beta CBESnCl_2(2\text{-EHTG})$ (3.83 ppm) and $(\beta CBE)_2 SnCl(2\text{-EHTG})$ (3.56 ppm) (see Fig. 3a). Clearly $(\beta CBE)_2 Sn(2\text{-EHTG})_2$ is absent from this spectrum and $K_{5B}(\beta CBE)$ must be very similar to $K_{5B}(Bu)$. On the other hand $K_{5A}(\beta CBE)$ is calculated to be 0.32 which is 3–4 orders of magnitude smaller than $K_{5A}(Bu)$.

The positions of equilibria 5A and 5B ($R = Bu$) are dictated by carbonyl to tin coordination from the mercaptoester groups. $BuSnCl_2(2\text{-EHTG})$ and $Bu_2 SnCl(2\text{-}$EHTG) predominate (exclusively) since they contain the most strongly coordinated mercaptoester groups. However, for $R = CH_2 CH_2 CO_2 Bu$ the mercaptoester coordination is outweighed by stronger carbonyl to tin coordination from the β-carbobutoxyethyl group (in $(\beta CBE)_2 SnCl_2$) and equilibrium 5A is displaced strongly to the l.h.s.

(c) Three 2-EHTG groups. An equimolar mixture of $BuSn(2\text{-EHTG})_3$ and $Bu_2 SnCl_2$ exhibited only signals at 3.67 and 3.57 ppm confirming that $BuSnCl(2\text{-}$
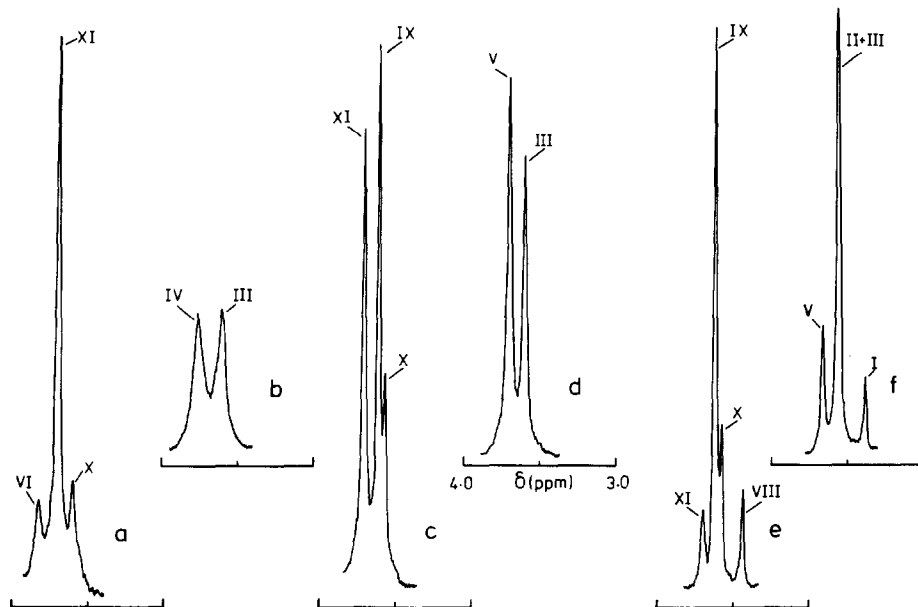
Fig. 3. The SCH_2CO_2 region ^1H NMR spectra of mixed mono-/di-organotin mercaptoesters: (a) $\beta CBESnCl(2\text{-}EHTG)_2$ + $(\beta CBE)_2SnCl_2$, (b) $BuSnCl(2\text{-}EHTG)_2$ + Bu_2SnCl_2, (c) $\beta CBESnCl_2(2\text{-}EHTG)$ + $(\beta CBE)_2Sn(2\text{-}EHTG)_2$, (d) $BuSn(2\text{-}EHTG)_3$ + Bu_2SnCl_2, (e) $\beta CBESn(2\text{-}EHTG)_3$ + $(\beta CBE)_2SnCl(2\text{-}EHTG)$, (f) $BuSn(2\text{-}EHTG)_3$ + $Bu_2SnCl(2\text{-}EHTG)$. $(Bu_2Sn(2\text{-}EHTG)_2$ = I, $BuSn(2\text{-}EHTG)_3$ = II, $Bu_2SnCl(2\text{-}EHTG)$ = III, $BuSnCl_2(2\text{-}EHTG)$ = IV, $BuSnCl(2\text{-}EHTG)_2$ = V, $\beta CBESnCl_2(2\text{-}EHTG)$ = VI, $(\beta CBE)_2Sn(2\text{-}EHTG)_2$ = VIII, $\beta CBESn(2\text{-}EHTG)_3$ = IX, $(\beta CBE)_2SnCl(2\text{-}EHTG)$ = X, $\beta CBESnCl(2\text{-}EHTG)_2$ = XI).

$EHTG)_2$ and $Bu_2SnCl(2\text{-}EHTG)$ are the only constituents of equilibrium 6. However, the corresponding estertin system (derived from $\beta CBESnCl_2(2\text{-}EHTG)$ and $(\beta CBE)_2Sn(2\text{-}EHTG)_2)$, in contrast to the butyltin case also contains $\beta CBESn(2\text{-}EHTG)_3$ as well as $\beta CBESnCl(2\text{-}EHTG)_2$ and $(\beta CBE)_2SnCl(2\text{-}EHTG)$ (see Figs. 3c and 3d). In both cases K_{6B} is of the order of 10^{-3}, whereas $K_{6A}(Bu)$ is approximately 10^3 and K_{6A} (βCBE) is 2.25. This difference of 2 to 3 orders of magnitude in K_{6A} values must again reflect the influence of carbonyl to tin coordination in $(\beta CBE)_2SnCl_2$ upon the position of equilibrium 6.

(d) Four 2-EHTG groups. An equimolar mixture of $BuSn(2\text{-}EHTG)_3$ and $Bu_2SnCl(2\text{-}EHTG)$ generates small equilibrium concentrations of $BuSnCl(2\text{-}EHTG)_2$ and $Bu_2Sn(2\text{-}EHTG)_2$ and the mixture can be represented by equilibrium 7. Our conclusion from IR work that the equilibrium lies to the l.h.s. is confirmed and $K_7(Bu)$ was determined to be 0.22. In the estertin case $K_7(\beta CBE)$ was found to be 0.04. These equilibrium constants are more similar than are the K_{5A} and K_{6A} values for the butyl and estertin systems which are markedly different. However, qualitatively equilibrium 7 is displaced in a similar fashion to (5A) and (6A) by the additional ester coordination from the β-carbobutoxyethyl group.

Presumably, equilibrium 4 is also displaced to the l.h.s. in the estertin case relative to the butyltin system but $K_4(Bu)$ is very small ($< 10^{-3}$) and hence from this simple study it is impossible to verify this hypothesis.

PVC stabilisation

Dialkyltin bis(2-ethylhexylthioglycollates) are effective stabilisers for PVC and undergo conversion initially to the corresponding dialkyl chlorotin 2-ethyl-hexylthioglycollates (eq. 9). This transformation has been monitored by Mössbauer spectroscopy for the dibutyltin compound [9] and by IR spectroscopy for the

$$R_2Sn(2\text{-EHTG})_2 + HCl \text{ (or PCl)} \rightarrow R_2SnCl(2\text{-EHTG}) + H \text{ 2-EHTG(P2-EHTG)}$$

$$(9)$$
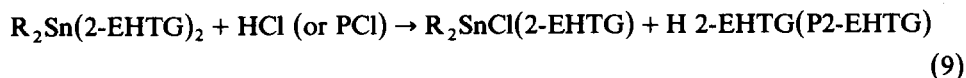
(R = Me, Bu, Oct or $CH_2CH_2CO_2Bu$; P = polymer)

dioctyl- and diester-tin compounds [10]. Comparative studies revealed that the estertin compound is more efficient than the dioctyltin compound at minimising the generation of unsaturation within the polymer during the early stages of stabilisation. The IR study also revealed that the diestertin stabiliser is more rapidly consumed during these early stages, which explains the better early colour (lower unsaturation).

For the dialkyltin bis(2-ethylhexylthioglycollates) at 35°C equilibrium 1 lies far to the r.h.s., however, for the diestertin stabiliser this equilibrium lies further to the l.h.s. Assuming that this effect will also be important at 190°C (the temperature of the PVC stabilisation tests [10]) displacement of equilibrium 1 to the l.h.s. will result in a higher effective concentration of $(\beta CBE)_2Sn(2\text{-EHTG})_2$ relative to $Oct_2Sn(2\text{-EHTG})_2$ during the early stages of the stabilisation process and hence more efficient stabilisation is the result. Since $(\beta CBE)_2SnCl_2$, which is also generated along with the effective stabiliser, has no detrimental effect on the degradation process the formation of this compound does not counteract the beneficial effect produced by the regeneration of $(\beta CBE)_2Sn(2\text{-EHTG})_2$.

Several workers [11,12], including ourselves [6], have concluded that the origin of synergism in mixtures of dialkyltin 2-ethylhexylthioglycollates lies in Cl/2-EHTG exchange reactions between the stabiliser and the mercaptoester chlorides. Regeneration of the monoalkyltin stabiliser and removal of the prodegradent alkyltin trichlorides are the two processes believed to give rise to synergism [6]. An example of this type of process is presented in reaction 10.

$$RSnCl_3 + R_2Sn(2\text{-EHTG})_2 \rightarrow RSn(2\text{-EHTG})_3 + R_2SnCl_2 \qquad (10)$$

During the stabilisation process a mixture of mono- and di-alkyltin 2-ethyl-hexylthioglycollates is converted stepwise to the corresponding mixed alkyltin chlorides and equilibria such as 4–7 become important in the stabilisation process. Our present NMR study reveals that equilibria 4–7, and in particular 5 and 6, are markedly sensitive to the presence of the carboalkoxyethyl group in the estertin stabilisers. Hence, the distribution of Cl and 2-EHTG groups between the mono- and di-estertin compounds will be markedly different to that in the alkyltin system at the same extent of conversion and this perturbation will have a corresponding influence upon the performance of the stabiliser mixture.

More detailed studies of equilibria 4–7 (R = Bu, $CH_2CH_2CO_2Bu$) are required at elevated temperatures to provide information which is more relevant to PVC processing conditions (160–200°C).

Experimental

Compounds

Butyltin 2-ethylhexylthioglycollates and 2-ethylhexylthioglycollate chlorides were prepared as described in a previous publication [3]. Bis(β-carbobutoxyethyl) tin dichloride was prepared by the transesterification of the corresponding methyl ester with n-butanol [13]. Bis(β-carbomethoxyethyl)tin dichloride was prepared by the hydrostannation method previously described [14]. β-Carbobutoxyethyltin trichloride was prepared by the reaction between $HSnCl_3$ ($HCl + SnCl_2$) and butyl acrylate [15]. Bis(β-carbobutoxyethyl)tin-bis(2-ethylhexylthioglycollate) was prepared from the dichloride as described in a recent article [10] and β-carbobutoxyethyltin tris(2-ethylhexylthioglycollate) was prepared by the same technique. Mixtures of estertin chlorides and 2-ethylhexylthioglycollates corresponding nominally to (βCBE)$_2$SnCl(2-EHTG). βCBESn$_2$Cl(2-EHTG) and βCBESnCl(2-EHTG)$_2$ were prepared by simply stirring together the appropriate molar quantities of the organotin compounds.

Spectroscopy

Infra-red spectra were obtained as neat liquid films on a Perkin–Elmer 577 grating spectrophotometer. ^{1}H nuclear magnetic resonance spectra were recorded at 35°C in deuterochloroform on a Perkin–Elmer R12B 60 MHz instrument. TMS was used as internal standard.

Equilibrium constants

Equilibrium constants were determined from the NMR data by the cut and weigh method from spectra recorded on a 10 min scan time.

For equilibria such as 4 (Bu), where the concentration of one of the possible constituents (in this case Bu$_2$SnCl(2-EHTG)) was below the detection limit (1–2%), K_4(Bu) was estimated to be $< 10^{-3}$. For an equilibrium displaced to the same extreme extent to the r.h.s, (e.g. 5A(Bu)) the equilibrium constant was assumed to be $> 10^3$.

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