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A SPECTROSCOPIC STUDY OF THE STRUCTURES AND EXCHANGE REACTIONS OF MONO- AND DI-ALKYLTIN ISOOCTYL THIOGLYCOLLATE STABILISERS OF PVC

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Summary

The structures of the alkyltin isooctyl thioglycollates $R_2SnCl_n(IOTG)_{2-n}$ ($n = 0,1$) and $RSnCl_n(IOTG)_{3-n}$ ($n = 0$–2) have been investigated by IR and ^1H NMR spectroscopy (R = Me, Bu, or Oct) and by ^{119}Sn NMR spectroscopy (R = Me or $BuOCOCH_2CH_2$). The ^{119}Sn NMR technique has been used to study the redistribution of the ligands Cl and IOTG between RSn and R_2Sn centres (R = Me and $BuOCOCH_2CH_2$), which proceeds to maximise the degree of ligand mixing and of chelating stabilisation by the groups $BuOCOCH_2CH_2$ and $SCH_2CO_2Oct^i$. These reactions are relevant to those which occur in a PVC matrix when mixtures of mono- and di-alkyltin isooctyl thioglycollates are incorporated as synergistic stabilisers.

Introduction

Alkyltin mercaptide stabilisers are widely used for preventing the formation of colour during high temperature (ca. 180°C) processing of poly(vinyl chloride) (PVC) [1]. Two classes of compound are used for this purpose, namely the dialkyltins, $R_2Sn(SR')_2$, and the monoalkyltins, $RSn(SR')_3$. Monoalkyltin compounds can be effective on their own (e.g. $(BuSnS_{1.5})_4$) [2], but, more commonly, they are used in synergistic admixture with the corresponding dialkyltin derivative [3–5].

The colouration results from degradation of the PVC by autocatalytic dehydrochlorination to give a coloured conjugated polyene. Investigations of the mode of action of the dialkyltin mercaptide stabilisers [1,6] have involved studies of their

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structures [7–10], and of their exchange reactions of SR′ for Cl with organic chlorides [1] in simulated tests [11], or with PVC [12]. It appears that there is more than one route by which stabilisation is effected, the two primary mechanisms being the scavenging of HCl to give the organotin chlorides $R_2Sn(SR')Cl$ and R_2SnCl_2 [13], and the exchange of SR′ for Cl at labile allylic chloride sites in the polymer at which the elimination of HCl is otherwise initiated [1,6].

Although similar principles may be assumed to control the stabilising effect of the monoalkyltin mercaptides, relatively few studies have been carried out on these compounds, and particularly on their synergistic action. In understanding the mechanism of synergism, it is important to know what exchange reactions may occur of the chloride and mercaptide ligands between the dialkyltin and monoalkyltin centres, and to identify the various species $R_2SnCl_n(SR')_{2-n}$ and $RSnCl_n(SR')_{3-n}$ which may be present.

We report here a study of the structures and exchange reactions of these compounds, using the techniques of IR and ^1H and ^{119}Sn NMR spectrometry. The organotin compounds were those used commercially [14], where R = Me, Bu, Oct or $BuOCOCH_2CH_2$ (the "estertin" compounds), and where SR′ = $SCH_2CO_2CH_2CH(C_2H_5)(C_4H_9)$ (IOTG, the "isooctyl" thioglycollates).

Experimental

The alkyltin chlorides, R_2SnCl_2 and $RSnCl_3$ (R = Me, Bu, and Oct), were commercial products and were used without further purification, and the "estertin" chlorides $(BuOCOCH_2CH_2)_2SnCl_2$, $BuOCOCH_2CH_2SnCl_3$, $(MeOCOCH_2CH_2)_2SnCl_2$, and $MeOCOCH_2CH_2SnCl_3$ were prepared by literature methods [15]. The isooctyl thioglycollates were obtained by treating these chlorides in ether with the appropriate amount of isooctyl thioglycollate, using aqueous sodium bicarbonate as a base to remove the HCl.

Infrared spectra were recorded on neat liquids using a Grubb Parsons Spectromaster Mark 1 or Pye Unicam SP2000 instrument.

^1H NMR spectra were recorded at 60 MHz on a Perkin–Elmer R10 spectrometer. ^{119}Sn NMR spectra of the methyltin compounds were obtained on a Varian XL200 instrument, and those of the "estertin" compounds on a JEOL FX 60Q instrument, using nuclear Overhauser suppressed conditions [16], with field-frequency lock to external D_2O.

Results and discussion

Structural studies

Previous studies of the structures of alkyltin thioglycollates $R_2Sn(IOTG)_2$ (R = Bu or Oct) [7], $Bu_2SnCl(IOTG)$ [9], and $RSnCl_{3-n}(IOTG)_n$ (R = Me or Bu, n = 1 or 2) [8,9] have largely been limited to IR and Mössbauer spectroscopy.

A "free" isooctyl thioglycollate shows a carbonyl stretching frequency at about 1735 cm^{-1}, but this shifts to lower frequency (down to about 1650 cm^{-1}) if chelation occurs, the degree of shift depending on the strength of the coordination. Both bands can be observed in compounds containing both free and chelated thioglycollate ligands. For all of the above compounds, it has been concluded that the carbonyl of one IOTG group coordinates intramolecularly to the tin, rendering it five-coordinate with an approximately trigonal bipyramidal geometry; we question this conclusion below.

Our values for the IR stretching frequencies of the carbonyl group in the compounds $RSnCl_{3-n}(IOTG)_n$ ($n = 1$–3) and $R_2SnCl_{2-n}(IOTG)_n$ (R = Me, Bu, or Oct) are given in Table 1. In general, these results agree with those for the methyl- and butyl-tin compounds which are in the literature [5,8,9], and the octyltin compounds follow a similar pattern. The two closely separated bands (ca. 1710 and 1735 cm^{-1}) in the carbonyl stretching region in the compounds $R_2Sn(IOTG)_2$ could be distinguished, but we were not able to resolve the two bands at ca. 1700 and 1735 cm^{-1} which have previously been reported for the tris-isooctyl thioglycollates, $RSn(IOTG)_3$.

Burley and Hutton have used these infrared bands to determine the species present in mixtures of organotin compounds [5]. ^1H NMR spectroscopy provides an alternative method [11], but the chemical shifts of the SCH_2 groups vary little between the different compounds (Table 2). ^{119}Sn NMR chemical shifts are much more sensitive to the nature of the ligands and to the coordination number at the tin; in a recent study of organotin chelates [17] it has been suggested that $\delta(^{119}Sn)$ usually moves to low frequency by 60–150 ppm as the coordination number changes from 4 to 5, and by another 130–200 ppm as it increases from 5 to 6. We have therefore concentrated attention on this technique.

The ^{119}Sn NMR chemical shifts of organotin thiolates have been studied by Kennedy and McFarlane [18–20]. The value of δ varies from $+144$ in $Me_2Sn(SMe)_2$ to $+75$ in $Me_2Sn(SBu^t)_2$, and from $+167$ in $MeSn(SMe)_3$ to $+65$ in $MeSn(SBu^t)_3$. These chemical shifts are not dependent on temperature or concentration when the compounds are dissolved in non-polar solvents, and they are only weakly affected by

TABLE 1

VALUES OF ν(C=O) (cm^{-1}) FOR ALKYLTIN ISOOCTYL THIOGLYCOLLATES

Compound [a]	R = Me	R = Bu	R = Oct
$R_2Sn(IOTG)_2$	1710, 1735 (1705, 1738) [b]	1709, 1730 (1708, 1734) [b] (1710, 1735) [c] (1708, 1733) [d]	1715, 1733
$R_2SnCl(IOTG)$	1667	1672 (1677) [c] (1676) [d]	1680
$RSn(IOTG)_3$	1724 (1700, 1738) [b]	1709 (1740) [c] (1700, 1737) [b] (1710, 1734) [d]	1709
$RSnCl(IOTG)_2$	1653, 1724 (1650, 1738) [b]	1658, 1724 (1666, 1737) [c] (1665, 1733) [d]	1666, 1737
$RSnCl_2(IOTG)$	1653 (1650) [b]	1677 (1667) [c] (1662) [d]	1667

[a] $HSCH_2CO_2Oct^i$, ν(C=O) 1724 cm^{-1}. [b] Ref. 8. [c] Ref. 9. [d] Ref. 5.

TABLE 2

^{1}H (SCH_2) CHEMICAL SHIFTS OF ALKYLTIN ISOOCTYL THIOGLYCOLLATES IN $CDCl_3$ [a]

Compound	R = Me	R = Bu	R = Oct
$R_2Sn(IOTG)_2$	3.40	3.40 (3.42) [b]	3.40
$R_2SnCl(IOTG)$	3.60	3.55 (3.59) [b]	3.55
$RSn(IOTG)_3$	3.50	3.55	3.55
$RSnCl(IOTG)_2$	3.65	3.65	3.65
$RSnCl_2(IOTG)$	3.70	3.80	3.75

[a] δ, relative to Me_4Si (error ±0.05 ppm). [b] Ref. 11.

the presence of polar solvents such as dimethyl sulphoxide. It is concluded that the organotin thiolates show little tendency to increase their coordination number above 4. This is supported by X-ray diffraction studies of organotin sulphides such as

TABLE 3

^{119}Sn NMR CHEMICAL SHIFTS OF ALKYLTIN ISOOCTYL THIOGLYCOLLATES

Compound	Solvent (Concentration (*M*))	$\delta(^{119}Sn)$ [a]
$MeSnCl_3$	$CHCl_3$ (0.4)	12.7
$MeSnCl_2(IOTG)$	$CHCl_3$ (0.4)	−56.0
$MeSnCl(IOTG)_2$	$CHCl_3$ (0.4)	−17.9
$MeSn(IOTG)_3$	$CHCl_3$ (0.4)	59.6
Me_2SnCl_2	$CHCl_3$ (0.4)	136.2
$Me_2SnCl(IOTG)$	$CHCl_3$ (0.4)	35.3
$Me_2Sn(IOTG)_2$	$CHCl_3$ (0.4)	72.8
$BuOCOCH_2CH_2SnCl_3$	CCl_4 (0.2)	−118.0
$MeOCOCH_2CH_2SnCl_3$	CCl_4 (0.5)	−108.0
$BuOCOCH_2CH_2SnCl_2(IOTG)$	CCl_4 (0.4)	−125.4
$BuOCOCH_2CH_2SnCl(IOTG)_2$	CCl_4 (0.4)	−21.9
$BuOCOCH_2CH_2Sn(IOTG)_3$	neat	64.5
$BuOCOCH_2CH_2Sn(IOTG)_3$	neat	32.1 [b]
$BuOCOCH_2CH_2Sn(IOTG)_3$	CCl_4 (0.3)	66.8
$(BuOCOCH_2CH_2)_2SnCl_2$	neat	−68.4
$(BuOCOCH_2CH_2)_2SnCl_2$	neat	−68.5 [b]
$(BuOCOCH_2CH_2)_2SnCl_2$	CCl_4 (0.3)	−49.6
$(MeOCOCH_2CH_2)_2SnCl_2$	$CDCl_3$ (0.6)	−64.5
$(BuOCOCH_2CH_2)_2SnCl(IOTG)$	neat	9.4
$(BuOCOCH_2CH_2)_2SnCl(IOTG)$	CCl_4 (0.4)	18.1
$(BuOCOCH_2CH_2)_2Sn(IOTG)_2$	neat	63.6
$(BuOCOCH_2CH_2)_2Sn(IOTG)_2$	neat	64.0 [b]
$(BuOCOCH_2CH_2)_2Sn(IOTG)_2$	CCl_4 (0.2)	67.1

[a] Relative to Me_4Sn (error ±0.2 ppm). [b] T.N. Mitchell in W.P. Neumann and M. Gielen (Eds.), 22 Deutscher Zinntag: Organozinnchemie, Rev. Si, Ge, Sn, and Pb Compds., Spec. Issue Freund Pub. House, Tel Aviv, 1980, p. 49.

$(Me_2SnS)_3$ [21], $(Ph_2SnS)_3$ [22], and $(MeSnS_{1.5})_4$ [23], which show these compounds to contain four-coordinate tin.

The ^{119}Sn NMR spectra of the methyltin and "estertin" compounds, $RSnCl_{3-n}(IOTG)_n$ and $R_2SnCl_{2-n}(IOTG)_n$ are listed in Table 3.

The chemical shift of $MeSn(IOTG)_3$ (59.6) is close to that of $MeSn(SBu^t)_3$ (65.0), and that of $Me_2Sn(IOTG)_2$ (72.8) is close to that of $Me_2Sn(SBu^t)_2$ (75). Similarly the chemical shifts of the "estertin" compounds $BuOCOCH_2CH_2Sn(IOTG)_3$ (64.5) and $(BuOCOCH_2CH_2)_2Sn(IOTG)_2$ (67.1) are similar to those of the corresponding methyltin compounds. These values are very much below the range (-90 to -330 ppm) which has been identified for fully five-coordinate tin [17], and we believe that it indicates that in solution these isooctyl thioglycollates are essentially four-coordinate: at most, the carbonyl group chelates only very weakly, or a small amount of the five-coordinate compounds is in equilibrium with the bulk which is four-coordinate. The Mössbauer spectra which have been reported do not differentiate clearly between four- and five-coordination, and, as described above, only small effects are observed in the infrared spectra. Further, only one ^{13}C NMR signal for the carbonyl groups is observed in the compounds $R_2Sn(IOTG)_2$ (R = Bu and Ph) and $Sn(IOTG)_4$ [7].

This conclusion that the compounds $R_2Sn(IOTG)_2$ and $RSn(IOTG)_3$ are essentially four-coordinate is important because some of the models for interpreting the details of the mechanism of stabilisation depend on the presence of five-coordination.

The compound $MeOCOCH_2CH_2SnCl_3$ has been shown crystallographically to contain five-coordinate tin [24], and shows $\delta(^{119}Sn) - 108$ ppm. This is in line with the low frequency shift (-118) which we observe for $BuOCOCH_2CH_2SnCl_3$. The compound $(MeOCOCH_2CH_2)_2SnCl_2$ has similarly been shown to contain tin with a six-coordinate octahedral geometry [24], but the chemical shift in solution which we find (-64.5) is much less than would be expected (-250 to -400) for six-coordinate tin. Simple dialkyltin dichlorides usually have chemical shifts in the range $+120$ to $+140$. The compound $(BuOCOCH_2CH_2)_2SnCl_2$ also showed a chemical shift of about -60, somewhat concentration-dependent. The evidence is inconclusive, but it suggests that whereas the "estertin" dichlorides are six-coordinate in the solid state, they are five-coordinate in dilute solution.

The chemical shifts of the compounds $Me_2SnCl(IOTG)$ (35.3) and $(BuOCOCH_2CH_2)_2SnCl(IOTG)$ (14.8) imply four-coordination in solution, but $MeSnCl(IOTG)_2$ (-17.9) and $BuOCOCH_2CH_2SnCl(IOTG)_2$ (-21.9) are probably weakly five-coordinate. Five-coordination is apparent also in the dichloride $MeSnCl_2(IOTG)$ (-56.0), but the much larger chemical shift in $BuOCOCH_2CH_2SnCl_2(IOTG)$ (-125.4) suggests that this has a different structure, involving coordination by the butoxycarbonyl group (cf. $BuOCOCH_2CH_2SnCl_3$, δ -118).

Exchange reactions

The facile exchange of electronegative ligands between organotin compounds, usually to give mixed-ligand derivatives (e.g. $R_2SnX_2 + R_2SnY_2 \rightarrow 2R_2SnXY$) is well established [14]. By ^1H and ^{13}C NMR spectroscopy, Parker and Carman [11] showed that dibutyltin dichloride and dibutyltin bis(isooctyl thioglycollate) reacted quantitatively and instantaneously to give $Bu_2SnCl(IOTG)$, and the same product has been identified by Mössbauer spectroscopy in PVC stabilised by the bis(isooctyl thioglycollate) [12].

A similar exchange between $BuSnCl_3$ and $Bu_2Sn(IOTG)_2$ was postulated by Bellenger et al. [25], and the exchange reactions involving Bu_2SnCl_2, $BuSnCl_3$, $Bu_2Sn(IOTG)_2$ and $BuSn(IOTG)_3$ were studied, using IR spectroscopy, by Burley and Hutton [5,9]. Mössbauer spectroscopy is of little use for studying exchange reactions involving the monoalkyltin compounds because the various derivatives $RSnCl_{3-n}(IOTG)_n$ show similar quadrupole coupling constants [26].

We have monitored the exchange of chloride and isooctyl thioglycollate ligands between dialkyltin and/or monoalkyltin centres. The reagents were mixed in the stoichiometries shown in the eqs. 1–10 in chloroform or carbon tetrachloride as solvent, and the products were identified by the integrated ^{119}Sn NMR spectra, or the ^1H NMR signals for the SCH_2 groups, using the data given in Tables 2 and 3.

The methyltin compounds were studied by both techniques giving concordant results. They show that the reactions illustrated in eqs. 1–10 (R = Me) take place rapidly and to completion at room temperature.

$$R_2SnCl_2 + R_2Sn(IOTG)_2 \rightarrow 2R_2SnCl(IOTG) \quad (1)$$

$$RSnCl_3 + 2RSn(IOTG)_3 \rightarrow 3RSnCl(IOTG)_2 \quad (2)$$

$$2RSnCl_3 + RSn(IOTG)_3 \rightarrow 3RSnCl_2(IOTG) \quad (3)$$

$$R_2SnCl_2 + RSn(IOTG)_3 \rightarrow R_2SnCl(IOTG) + RSnCl(IOTG)_2 \quad (4)$$

$$R_2SnCl_2 + RSnCl(IOTG)_2 \rightarrow R_2SnCl(IOTG) + RSnCl_2(IOTG) \quad (5)$$

$$R_2SnCl(IOTG) + RSn(IOTG)_3 \rightleftharpoons R_2Sn(IOTG)_2 + RSnCl(IOTG)_2 \quad (6)$$

$$R_2SnCl(IOTG) + RSnCl_3 \rightarrow R_2SnCl_2 + RSnCl_2(IOTG) \quad (7)$$

$$R_2Sn(IOTG)_2 + RSnCl_2(IOTG) \rightarrow R_2SnCl(IOTG) + RSnCl(IOTG)_2 \quad (8)$$

$$R_2Sn(IOTG)_2 + RSnCl_3 \rightarrow R_2SnCl(IOTG) + RSnCl_2(IOTG) \quad (9)$$

$$2R_2Sn(IOTG)_2 + RSnCl_3 \rightarrow 2R_2SnCl(IOTG) + RSnCl(IOTG)_2 \quad (10)$$

The reactions 1–4, 6, 9, and 10 were also studied by ^1H NMR for the butyl- and octyl-tin compounds, and with the exception of reaction 9 gave similar results to those obtained for the methyltin compounds, i.e. rapid exchange of the chloro and IOTG ligands occurred to give the products shown in the equations, and all except reaction 6 occurred to completion. In general, these results confirm those obtained by Burley and Hutton [5] using infra-red spectroscopy. Reaction 9, however, gave different results to those obtained for the methyltin compounds, since although $RSnCl_2(IOTG)$ (R = Bu, Oct) was produced, $R_2SnCl(IOTG)$ (R = Bu, Oct) was present as only a minor product. Unfortunately, because of the complexity of overlapping signals in the ^1H NMR spectra of reaction 9 (R = Bu, Oct), other products were not identified. However, it has previously been concluded [5] that when 3Cl and 2IOTG ligands were to be distributed between a Bu_2Sn and BuSn centre, some Bu_2SnCl_2 and $BuSnCl(IOTG)_2$ was present. The ^{119}Sn NMR signals for the species R_2SnCl_2 and $RSnCl(IOTG)_2$ (R = Me) were absent in our reactions 5 and 9, but it is not unusual for methyltin compounds to behave differently from their higher homologues.

At the temperature at which PVC is calendered, it seemed possible that the exchange of alkyl groups might occur between the tin centres (the Kocheshkov reaction). Mixtures of the various mono- and dialkyl-tin compounds (eq. 6, R = Me and Bu) were therefore kept at 180°C for 1–2 h, but examination by NMR spectroscopy showed that the products were the same as those obtained at room temperature.

We conclude from reactions 1–10 that rapid exchange occurs at room temperature between the chloro and IOTG ligands to maximise the possible degree of mixing at the two tin centres. One IOTG and 4 Cl ligands distribute themselves between R_2Sn and RSn to give $RSnCl_2(IOTG)$ probably because, as we have concluded above, it is stabilised by chelation. With 1 Cl and 4 IOTG ligands, the compound $RSnCl(IOTG)_2$ is formed, but any stabilising chelation is now relatively weak, and the equilibrium is more evenly balanced.

The reactions 1–4, 6, 9, and 10 were also studied for the butoxycarbonylethyl compounds by ^{119}Sn NMR spectroscopy. Only reaction 3 proceeded to completion, showing the spectrum of only $BuOCOCH_2CH_2SnCl_2(IOTG)$ in the product; again the presence of the two chloro ligands results in stabilising chelation by the butoxycarbonyl group, as discussed above.

Reactions 1, 2, and 4 gave the same type of products as were observed for the methyl, butyl, and octyltin compounds, but the reactions were only 50–80% complete. Again this incomplete reaction can be rationalised on the grounds that the reactant dichloride or trichloride can be stabilised by chelation by the alkoxycarbonyl group [27].

When the reagents $R_2Sn(IOTG)_2$ and $RSnCl_3$ were mixed in the molar ratios 1/1 and 2/1 the reactions did not proceed as shown in eqs. 9 and 10, but instead gave a mixture of R_2SnCl_2, $R_2SnCl(IOTG)$ and $RSnCl(IOTG)_2$, according to eqs. 11 and 12 respectively, the coefficients being those which gave the best fit with NMR intensities. Reaction 11 supports that proposed by Burley and Hutton [5] for the butyltin compounds, in that the R_2SnCl_2 and $RSnCl(IOTG)_2$ species are formed.

$$4R_2Sn(IOTG)_2 + 5RSnCl_3 \rightarrow 4R_2SnCl_2 + 3RSnCl(IOTG)_2 + 2RSnCl_2(IOTG) \tag{11}$$

$$3R_2Sn(IOTG)_2 + 2RSnCl_3 \rightarrow R_2SnCl_2 + 2R_2SnCl(IOTG) + 2RSnCl(IOTG)_2 \tag{12}$$

Conclusions

These results emphasise the ready exchange which occurs between chloro and thioglycollate groups bonded to monoalkyl and dialkyltin, and are in accord with the mechanism proposed by Burley and Hutton for the synergistic action of the mono- and di-alkyltin isooctyl thioglycollates. It is proposed that $BuSn(IOTG)_3$ is the most effective stabiliser, but it is thereby converted into $BuSnCl_3$ which, because of its Lewis acidity, is a prodegradant. The function of the $Bu_2Sn(IOTG)_2$ is, by exchange, to convert the prodegradant $BuSnCl_3$ into the $BuSn(IOTG)_3$ stabiliser; the Bu_2SnCl_2 which is also formed by this exchange is too weak a Lewis acid to act as a prodegradant [5].

We hope that the studies of ^{119}Sn NMR spectra in solution, reported here, will pave the way to similar studies by solid state ^{119}Sn NMR of organotin stabilisers in situ in the PVC matrix.

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