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Synthesis of Polymeric Alkoxides from Dialkyltin(IV) Oxides and Chloral, and their Characterization by Mössbauer and Infrared Spectroscopy

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The reaction of $(Alk_2SnO)_n$ with $OCH{\cdot}CCl_3$ gives compounds of elemental formula $Alk_2SnOCH(CCl_3)O$ (Alk = Bu^n, Oct^n), probably by addition of the Sn–O bond to the carbonyl group. Mössbauer parameters suggest the occurrence of five-coordinated Sn, and polymeric structures with bridging three-coordinating oxygens are proposed. The assumption that C_2SnO_3 units with trigonal bipyramidal type structures are present is consistent with point-charge model rationalization of the quadrupole splitting. Infrared spectra are in keeping with the proposed structures, suggesting, inter alia, *bent C Sn C skeletons, but the analysis of possible ν(Sn–O) modes does not provide conclusive evidence for the proposed meridional SnO_3 skeletal configuration. Osmometry in benzene is consistent with the presence of trimers or tetramers in solution, and the formation of these is rationalized in terms of the proposed solid state structures and of the IR spectra in solution.*

Introduction

The reaction of organometallic species with carbonyl compounds, having the carbonyl double bond activated by perhalo groups, usually involves addition of the metal–X bond (where X is an electronegative atom such as N,O, or carbon bound to substituents with –M effect) to the carbonyl group [1, 2]. In particular, organotin(IV) derivatives containing Sn–O bonds, *i.e.* alkoxides and stannoxanes, add to chloral to give new alkoxides, and this reaction seems to be initiated by nucleophilic attack of the tin-bound oxygen on the carbon atom of the carbonyl group [1]. Diorganotin(IV) oxides have apparently not been investigated in this context, although their reactions with organotin halides to form stannoxanes, which are presumably of analogous type, have been observed [1]. It thus seemed of interest to examine the interaction of diorganotin(IV) oxides with a carbonyl compound, and chloral was selected because of its enhanced reactivity. The formation of polymeric alkoxides could be expected, since chloral can insert into the Sn–O bonds of reactant oxides, which are probably cross-linked solid state polymers and seem to retain a certain degree of polymericity in solution [1]. The results are described below.

Experimental

Pure reagents and solvents (C. Erba, Milano) have been used. The reaction of $CCl_3{\cdot}CHO$ with several R_2SnO compounds (and also MeSn(O)OH) has been examined, and has been successful only for R = Bu^n, Oct^n. Equimolar amounts of chloral and Bu^n_2SnO or Oct^n_2SnO (the latter gifts from Schering AG, Bergkamen) have been refluxed together in benzene, and the products recovered as white powders by evaporation to dryness in a rotary evaporator. The products have been washed with solvent and dried in a vacuum desiccator. Analytical and physical data are listed in the Table; molecular weights have been measured with a Mechrolab 301A vapor pressure osmometer at 37 °C in benzene solutions, employing ΔR/C *vs.* C plots and graphical or least squares estimation of parameters.

Mössbauer spectra have been measured at constant acceleration, using both triangular and sawtooth waveforms in different spectrometers, with a $Ca^{119m}SnO_3$ source (R.C., Amersham, 10 mCi) at room temperature, using the apparatus, techniques and data reduction procedures described elsewhere [3]. Replicate spectra have been taken on different samples from independent preparations. The calculated parameters are in the Table.

Infrared spectra (reported in the Table) have been measured by a Perkin-Elmer mod. 457 spectrometer, calibrated with a polystyrene film, in the range 4000–250 cm^{-1}, in nujol and hexachlorobutadiene mulls between CsI disks. The Bu^n derivative has been also examined in CS_2 solution, using a 0.05 mm cell with CsI windows.

TABLE. Experimental Data for $[Alk_2SnOCH(CCl_3)O]_n$. Analytical found (calcd., n = 1).

Alk	M.p., °C	C%	H%	O%	Cl%	Sn%	Mol. wt.
Bu^n	115^a–120	30.49 (30.31)	4.98 (4.83)	8.18 (8.07)	26.77 (26.84)	29.81 (29.95)	1378 $(396.31)^b$
Oct^n	82–85	42.56 (42.52)	6.81 (6.94)	6.32 (6.29)	20.71 (20.92)	23.50 (23.34)	1852 $(508.53)^b$

Mössbauer parameters, mm s^{-1}, at liquid N_2 temperature: Alk = Bu^n : $\delta^c = 1.31$; $\Delta E^d = 3.21$. Oct^n : $\delta = 1.33$; $\Delta E = 3.24$.

Infrared absorptions[e] and tentative assignments[f]:

Alk = Bu^n	Oct^n	Assign.	Bu^n	Oct^n	Assign.
2965 s	2970 s	ν(C–H)	835 s	835 s	ν(C–Cl) and ν(C–C)
2930 s	2930 vs		800 s	800 s	
2870 m	2860 s		770 ms	770 ms	
1465 s	1470 s	δ(C–H)	720 w	720 mw	$\rho(CH_2)$?
1460 sh			675 ms	680 ms	ν(C–Cl)
1420 vw	1420 w		650 ms	650 ms	ν(C–Cl)? ν(Sn–O)?
1380 w	1380 w				
1345 ms	1350 ms		600 w	600 w	$\nu_{as}(SnC_2)$ and ν(Sn–O)
1295 w	1290 w		580 w	560 w	
1160 vvw	1160 sh	ν(C–O) and ν(C–C)	535 w	540 w	$\nu_s(SnC_2)$
1125 s	1125 s		445 mw	445 ms	ν(C–Cl) and skeletal bend
1085 w	1070 sh		410 vvw	420 sh	
1040 s	1040 s	ν(C–O) and ν(C–C)	385 ms	385 ms	$\delta(CCl_3)$?
			325 s	320 ms	ν(Sn–O)?
1000 ms	1005 w	δ(C–H)	295 m	285 mw	$\delta(CCl_3)$?
970 vw	985 vw		270 ms	260 mw	
875 w		$\rho(CH_3)$?			

[a] Softening point. [b] Formula weight, n = 1. [c] Isomer shift with respect to R. T. $CaSnO_3$. [d] Nuclear quadrupole splitting. Full widths at half height of the resonant peaks are around 1 mm s^{-1}. [e] For Alk = Bu^n, relevant bands here listed are detected also in CS_2 solution (except those masked by solvent vibrations); s = strong; m = medium; w = weak; sh = shoulder; v = very. [f] According to literature reports, see text.

Discussion

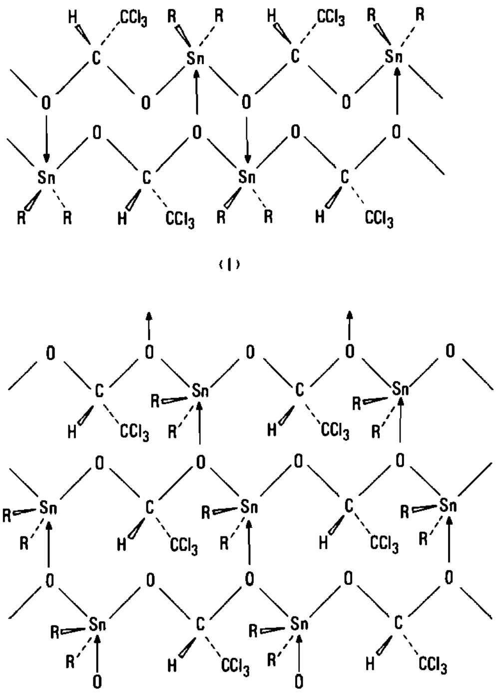
Analytical data clearly indicate that the elemental composition of the products corresponds to 1:1 ratio of the reagents. This would be consistent with the occurrence of the addition reaction of the Sn–O bond to the carbonyl group:

$$(Alk_2SnO)_n + nOCH{\cdot}CCl_3 \rightarrow n[Alk_2SnOCH(CCl_3)O]$$

where n represents eventual varying polymerization indexes of Alk_2SnO in solution [1].

Information about the solid state configurations of the products (indicated in the following as Alk_2Sn-chloral) is extracted from the spectroscopic investigations. Mössbauer isomer shift data, δ (see Table), are in the range typical of dialkyltin(IV) derivatives where Sn is bound to electronegative ligand atoms such as N,O, hal; besides, their magnitude excludes a *cis*-octahedral structure [4, 5]. Quadrupole splittings, ΔE (see Table), are inconsistent with tetrahedral, *cis*- and *trans*-octahedral configurations of dialkyltin(IV) linked to N, O, hal [5, 6]. It is instead observed that the Mössbauer parameters of Alk_2Snchloral are in excellent agreement with those pertaining to trigonal bipyramidal type species $Alk_2Sn(ONO)$ and $Alk_2Sn(NNO)$, with equatorial C, C, N and axial O, O or O, N atoms, where ligands are the dianions of 3-(*o*-hydroxyphenylamino)crotonophenone, N-(2-hydroxyphenyl)salicylaldimine and glycylglycine (δ = 1.21–1.37; ΔE = 3.15–3.43 mm s^{-1}) [7–10].

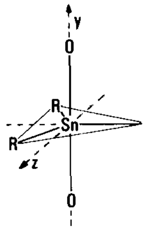
Five-coordination of Sn in Alk_2Snchloral, in a trigonal bipyramidal type structure, may be due to three-coordinating oxygens, cross-linking two (str.I) or more (str. II) polymeric alkoxide chains with tin atoms in the backbone (*i.e., catena-μ-*[2,2,2-trichloro-1,1-ethanediolato(2-)-*O,O'*]-di-n-alkyltin(IV)). It must be recalled here that intermolecular association through three-coordinating oxygen is a common



(I)

(II)

Figure 1. Possible structures of polymers $(R_2Sn\ chloral)_n$. I: cross-linking between two chains of *catena*-μ-[2,2,2-trichloro-1,1-ethanediolato(2-)-O,O′]-di-n-alkyltin(IV). II: extended cross-linked network.



(III)

Figure 2. Ideal regular trigonal bipyramidal configuration of tin(IV) neighbourhood in R_2Sn chloral. x, y, z are the principal components of the electric field gradient according to partial quadrupole splitting values used in the point-charge calculations (see text).

feature for alkoxides, stannoxanes and diorganotin oxides, originating oligomers as well as cross-linked polymers [1, 11].

In order to test the reliability of the hypotheses above, we have effected a point-charge model calculation of ΔE for Alk_2Snchloral in the regular trigonal bipyramidal configuration III. For this structure, the use of different sets of partial quadrupole splitting values for equatorial and axial substituents, p.q.s.(tbe) and p.q.s.(tba), is required, and pertinent data have been extracted by a linear regression method on ΔE of octahedral and trigonal bipyramidal organotins [12]. According to structures I and II, R_2Sn^{IV} moieties would be bridged by oxygens of a 1,1-diol; tin compounds of this class apparently have not been reported, so that the method in [12] cannot be employed in order to calculate the desired p.q.s. values for $CCl_3{\cdot}CHOO$. On the other hand, diol bridges in I, II would correspond in some way to acetate bridges in $R_3Sn(OCOCH_3)$ [13]. For the latter case the p.q.s.(tba) of acetate oxygens, $\{CH_3COO\}^{tba} = \frac{1}{2}e^2|Q|([CH_3COO]^{tba} - [hal]^{tba})$, has been estimated as +0.075 mm s^{-1} [12]; this value could be attributed also to p.q.s. $\{CCl_3{\cdot}CHOO\}^{tba}$ in the case oxygens of both compounds show comparable σ donor power (which governs p.q.s. magnitude [14]), which would occur whether electron delocalization in acetate carboxyl and inductive effect due to the CCl_3 radical in chloral hydrate are comparable in dictating partial charges on oxygen atoms of both compounds. These have been reported for CH_3COOH as Q = –0.234 and –0.208 for carbonyl and OH oxygens respectively, the average being –0.221 [15]; we have calculated the charge on chloral hydrate oxygens, Q = –0.228, by the same procedure as in [15], using the CHELEQ program, and formal charges = 0.00, bond orders = 1.00 as input parameters for all atoms and bonds in the valence bond structural formula of $Cl_3C{\cdot}CH(OH)_2$ [15, 16].

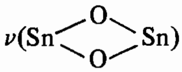
In view of the near correspondence of Q values above, we have assumed $\{CH_3COO\}^{tba} = \{CCl_3{\cdot}CHOO\}^{tba}$; besides, by the relationship [12]:

$$3\{CCl_3{\cdot}CHOO\}^{tbe} - 4\{CCl_3{\cdot}CHOO\}^{tba} \sim 0.58\ \mathrm{mm\ s^{-1}}$$

the value $\{CCl_3{\cdot}CHOO\}^{tbe}$ = +0.29(3) mm s^{-1} has been obtained. With these data of p.q.s.(tbe) and p.q.s.(tba), and $\{Alk\}^{tbe}$ = –1.13 mm s^{-1} [12], we have calculated ΔE = +3.35 mm s^{-1} for Alk_2Sn-chloral in structure III, using the pertinent point-charge equation (eqn. 42 of Ref. 12). Experimental (ΔE_{av} = 3.225 mm s^{-1}, Table) and calculated ΔE are in excellent agreement, well below the accepted Δ(ΔE) limit of 0.4 mm s^{-1} [17], so that it is concluded that the environment of tin in our compounds is of the type depicted in III. Besides, the point-charge model treatment strongly suggests the real occurrence of different oxygen sites, tba and tbe, and this favours the extended polymeric structure II where three-coordinating oxygens can be considered axial and the divalent ones equatorial.

The infrared spectra (see Table) also give indications on the occurrence of the reaction and the nature of the solid products. The carbonyl stretching mode of chloral, occurring at 1749–1762 (solid) and 1758 (liquid) cm^{-1} [18] disappeared in R_2Sn chloral, where two ν(C–O) bands are observed in correspondence to analogous vibrations occurring in chloral hydrate (1110 and 1086 cm^{-1}) [19, 20] and polychloral (1122–1070, 975 cm^{-1}) [21]; this is consistent with the proposed reaction pathway and with the advanced structures I and II. It may be mentioned that ν(C–O) in Bu$_2^n$Sn(OR)$_2$ have been attributed to absorptions in the ranges 1027–1066 [22], 1063–1076 cm^{-1} [23].

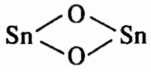
For the regular trigonal bipyramidal structure III, point group C$_{2v}$, eleven I.R. active skeletal modes are expected, *i.e.*, two ν(SnC$_2$), three ν(Sn–O) and six deformation vibrations [24]. Tin–carbon stretchings have been easily identified, see Table [23, 25, 26], there being uncertain only the choice for ν_{as}(SnC$_2$) between the two bands at 600–580, 560 cm^{-1}. Attributions in the table concerning ν(Sn–O) modes are very tentative. The 650 and 600–560 cm^{-1} bands would be consistent with existing Sn–O assignments concerning R$_2$SnO, R$_2$Sn(OR′)$_2$ and others [22, 23, 27–30], but the 650 cm^{-1} absorption could be very probably associated to a ν(CCl$_3$) mode of the chloral residue, occurring at 582 cm^{-1} in polychloral [21]. As to the 325–320 cm^{-1} band of Alk$_2$Snchloral (which, owing to his intensity, is the only absorption below 400 cm^{-1} not attributable to eventual bending modes, δ(CCl$_3$) [18, 21] and others), it could correspond in some way to the 320–305 cm^{-1} band we observed to occur in (Bu$_2^n$SnO)$_n$ and (Oct$_2^n$SnO)$_n$. On the other hand, ν(Sn–O) bands are often weak and difficult to identify, as in Alk$_2$Sn(OR)$_2$ [23], where only two ν(SnO) modes have been attributed although four, IR active, skeletal Sn–O stretchings [24] would be expected in these *cis*-octahedral solid state polymers [11]. The absence in R$_2$Snchloral of the strong, broad 400 cm^{-1} band of (R$_2$SnO)$_n$, attributed to



[31], would again rule out structure I, according to Mössbauer results.

Other bands in the spectra, not discussed in the preceding, have been attributed by analogy with chloral and related compounds, including CHCl$_3$, and from known ranges for vibrational modes in aliphatic chains [18–21, 32].

Concluding about solid state characterization of Alk$_2$Snchloral, Mössbauer spectroscopy indicates five-coordinated Sn in the trigonal bipyramidal type configuration III, from which the extended cross-linked polymeric structure II is advanced, in the light also of the structures of reactant (Alk$_2$SnO)$_n$ and of the proposed reaction mechanism. Infrared data confirm the 1,1-diolate nature of the chloral residue, as well as the bending of the CSnC skeleton, while no definite information is extracted on the advanced meridional SnO$_3$ skeleton; the presence of



groups, and consequently structure I, seem to be excluded.

In benzene solution, osmometric data (Table) suggest that Alk$_2$Snchloral are trimers or tetramers, molecular weights corresponding to 3.5, 3.6 formula units. Formation of cyclic tetramers, in solution, would be easily understood on the basis of both solid structures (I and II), with retention of at least one R$_2$SnO$_3$ unit. Whether the same would occur in CS$_2$ solution, the presence of R$_2$SnO$_3$ units in the tetramer would justify the near correspondence of IR bands, attributed to ν(Sn–O) modes, of Bu$_2^n$Sn chloral in the solid state and in CS$_2$ solution (in a special way for the 325 and 675 cm^{-1} absorptions).

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