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STUDIES OF ORGANOTIN CHEMISTRY
II* AN INFRARED AND NMR SPECTROSCOPIC STUDY OF THE TRIMETHYLTIN CHLOROACETATES

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INTRODUCTION

An interesting property of trialkyltin carboxylates is their tendency to associate through bridging carboxylate groups, with the formation of five-coordinate tin. The association is normally considered to be complete in the solid state, but an equilibrium between free and associated forms is often found in solution[1,2]. Association in the solid state is assumed to take the form of linear infinite chains (thus accounting for the unexpected insolubility of simple compounds such as trimethyltin formate and acetate), and the associated form in solution is likewise usually taken to be linear in structure.

Tri*methyl*tin carboxylates should be of special interest as the simplest members of the series, but studies have been restricted to the solid state in view of their reported insolubility[3] (trimethyltin laurate is an exception, its infrared spectrum having been studied in carbon tetrachloride[1]). We recently reported that the known insoluble forms of trimethyltin formate and acetate could be converted to distinct, new soluble forms by the simple process of heating in a sealed tube with cyclohexane[4]. The value of solution infrared and NMR studies on these compounds has led us to reexamine the solubilities of other simple methyltin carboxylates. We describe in this paper our observations on trimethyltin chloroacetate, dichloroacetate, and trichloroacetate.

EXPERIMENTAL

The trimethyltin chloroacetates were prepared by reaction of trimethyltin hydroxide (obtained by the method of Luijten[5]) with the corresponding halogenated acetic acid in water. The procedure was straightforward, but because of the faint possibility that the compounds may exist in two forms (*vide infra*) a typical preparation is described in great detail: Dichloroacetic acid (0.91 g; 7 mmole) dissolved in water (10 ml) was added to a water solution of trimethyltin hydroxide (1.268 g; 7 mmole). The clear, colorless solution was stirred approximately 15 min at room temperature. No precipitate formed. The solution was poured into a 10 cm Petri dish and evaporated to dryness on a steam bath. The resulting white solid residue was dried overnight in a calcium chloride dessicator and sublimed twice in high vacuum. Yield 1.184 g white needles. Microanalyses were carried out by Alfred Bernhardt Mikroanalytisches

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* For Part I see ref. 4.

Laboratorium, Mülheim, Germany, with results as given in Table 1. Molecular weights were determined using a Mechrolab Osmometer in the Microanalytical Laboratory of this Department and the results are given in Table 2. Nuclear magnetic resonance and infrared spectra were determined as previously described[4].

TABLE 1

ANALYTICAL RESULTS AND MELTING POINTS[a]

Compound	*C*	*H*	*O*	*Cl*	*M.p.*[b] (°C)
$ClCH_2COOSn(CH_3)_3$	22.5 (23.4)	4.1 (4.3)	12.3 (12.4)	13.5 (13.8)	143–145 (lit.[3] 148°)
$Cl_2CHCOOSn(CH_3)_3$	20.6 (20.6)	3.4 (3.4)	10.8 (11.0)	24.3 (24.3)	138–140 (lit.[3] 135°)
$Cl_3CCOOSn(CH_3)_3$	18.4 (18.4)	2.9 (2.8)	9.8 (9.8)	32.5 (32.6)	175–176 (lit.[3] 179°)

[a] Calculated value in parentheses. [b] Gallenkamp apparatus, sealed capillary, uncorrected.

TABLE 2

MOLECULAR WEIGHT DATA[a]

Compound	*Dibromomethane*		*Carbon tetrachloride*		*Calcd.*
	Concn.[b]	*Mol. wt.*	*Concn.*[b]	*Mol. wt.*	
$ClCH_2COOSn(CH_3)_3$	9.3	272	4.3	296	257
	14.2	266	8.9	300	
	20.0	270			
$Cl_2CHCOOSn(CH_3)_3$	8.6	307	3.8	315	292
	16.8	299	7.0	302	
	26.8	301	11.0	328	
$Cl_3CCOOSn(CH_3)_3$	11.1	359	Not		326
	16.5	329	sufficiently		
	25.2	320	soluble		

[a] Mechrolab Osmometer, benzil calibration, 37°. [b] As mg per ml of solvent.

RESULTS AND DISCUSSION

The previously known and reportedly insoluble[3] trimethyltin chloroacetates have been prepared and found to be soluble. It is possible that the key factor in obtaining these soluble materials, as was the case with soluble trimethyltin formate and acetate[4], is the heating of the compounds in a suitable liquid for a suitable period of time. However, in the course of our work, we have not observed insoluble forms of any of the chloroacetates. The estimated solubilities of our compounds in chloroform at room temperature are as follows: monochloroacetate, 96 mg/ml; dichloroacetate, 83 mg/ml; trichloroacetate, 70 mg/ml.

Values for the molecular weights of the three trimethyltin chloroacetates are given in Table 2. All compounds show a small degree of association, between 1.0 and 1.2, the values in carbon tetrachloride tending to be somewhat higher. The precision of the osmometric measurements was rather poor, and was not sufficient to detect the expected trend to increasing association at higher concentration.

The association equilibrium can also be studied by infrared and NMR spectroscopy, and these results will next be discussed. In what follows, we use the term "association" without implication as to whether the associated species is linear (as normally assumed, and supported by an investigation of tripropyltin formate[2]) or cyclic (as postulated in trimethyltin formate[4]) or a mixture of both.

Infrared spectra

In the original infrared study of the three trimethyltin chloroacetate esters, Okawara, Webster, and Rochow[3] reported that the compounds were insoluble, and therefore restricted their investigation to KBr disc and Nujol mull examination of the solid phase. As already noted, we have found the chloroacetate esters to be amply soluble for infrared investigation in both carbon tetrachloride and chloroform. We discuss first the infrared spectrum of the dichloroacetate, since it raises a number of interesting questions.

The spectrum of trimethyltin dichloroacetate in carbon tetrachloride solution (Fig. 1) is strongly concentration dependent, and reveals much information regarding probable assignments and structures. Such dependence has earlier been observed in trimethyltin laurate[1] and trimethyltin formate[4]; it is attributed to an equilibrium between associated and unassociated forms, in which both ester-like and bridging carboxylate groups are present. The principle effect of increasing concentration is to increase the intensity of the bands at 1652 cm^{-1} and 1368 cm^{-1} relative to the 1708–1687 cm^{-1} doublet and the 1330 cm^{-1} band. The bands which gain intensity at higher concentration are most probably due to an associated form, and we therefore assign the 1652 and 1368 cm^{-1} bands as the asymmetric and symmetric carbon–oxygen stretching modes of the dichloroacetate group in bridging position between the two tin atoms. These values differ from the values 1570 and 1420 cm^{-1} found in un-

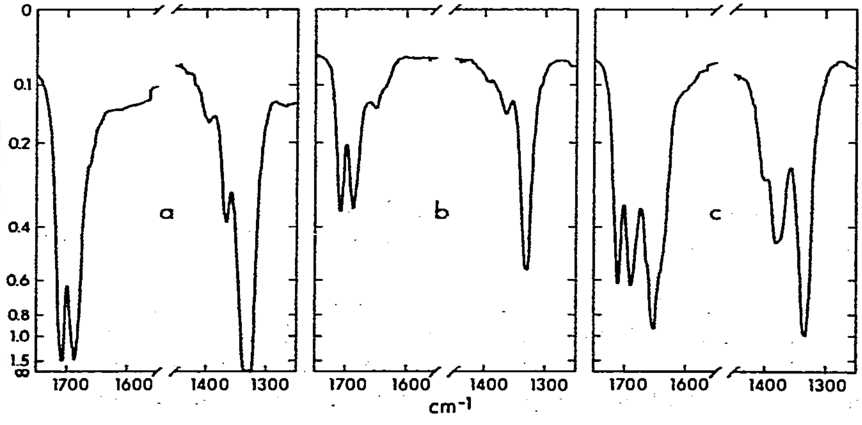
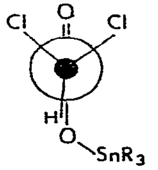


Fig. 1. Infrared spectra of trimethyltin dichloroacetate in carbon tetrachloride: a, 2.8 mg/ml CCl_4, 5.0 mm cell; b, 11 mg/ml CCl_4, 0.5 mm cell; c, 18 mg/ml CCl_4, 0.1 mm cell.

substituted trialkyltin acetates[1,4,6], and a similar trend is observed in the sodium salts of the corresponding acids[6].

The 1708–1687 cm^{-1} doublet and the 1330 cm^{-1} band (Fig. 1) are identified with the unassociated form of trimethyltin dichloroacetate. The occurrence of a doublet requires comment, and is considered to be due to the presence of two conformational isomers of the molecule. Cummins has explained in this way his observations on tributyltin chloroacetate esters[7], in which doublets with similar separation occur. Two possible conformations are shown in Newman projection as (I) and (II).



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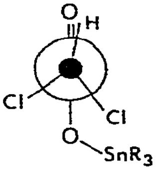

II

In chloroform solution (Fig. 2a), trimethyltin dichloroacetate exhibits two broad bands at 1680 and 1330 cm^{-1}, and there is very little change with concentration. The broadening of carbonyl bands in chloroform, a phenomenon well established in the metal carbonyl field[8], presumably obscures the detail visible in carbon tetrachloride. Indistinct shoulders around 1660 cm^{-1} and 1370 cm^{-1} may be due to a low concentration of an associated form.

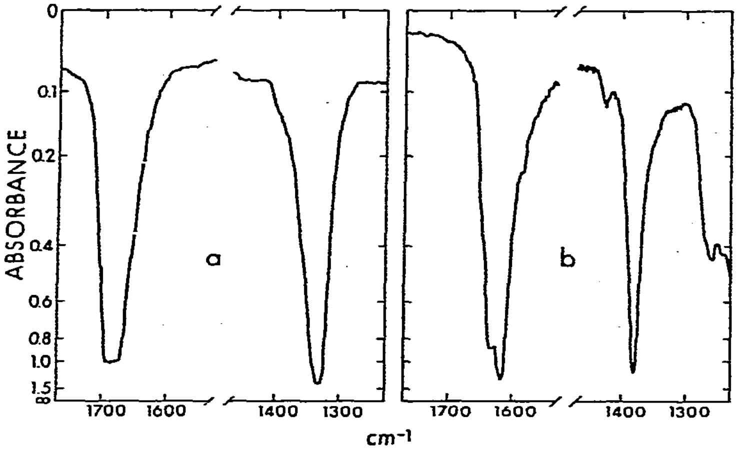

Fig. 2. Infrared spectra of trimethyltin dichloroacetate: a, 17 mg/ml in CHCl$_3$, 0.5 mm cell; b, mull in halocarbon oil.

In the solid state (Halo-oil mull, Fig. 2b), the dichloroacetate shows strong bands at 1620 and 1380 cm^{-1}, with definite shoulders at 1650 and 1635 cm^{-1}. Similar bands have been observed by other workers[3]. The general position suggests they are due to a bridging dichloroacetate group, and the multiplicity of bands may again be due to a conformational effect.

Spectra of mono-, di-, and trichloroacetates are compared in Fig. 3, in the

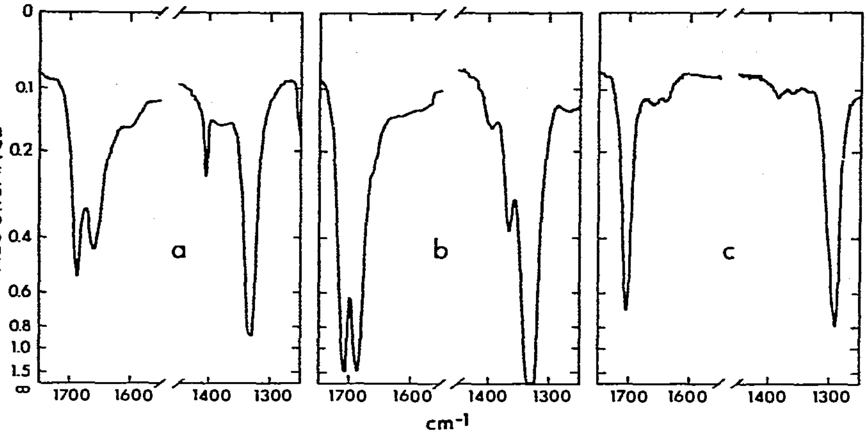

Fig. 3. Infrared spectra in carbon tetrachloride: a, trimethyltin monochloroacetate; b, trimethyltin dichloroacetate; c, trimethyltin trichloroacetate.

TABLE 3

CARBONYL–CARBOXYL ASSIGNMENTS IN TRIALKYLTIN ACETATES AND CHLOROACETATES

Compound	*Solvent*[a]	*Free, ester-like*		*Associated, bridging*		*Ref.*
		ν (CO) asym.	*ν (CO) sym.*	*ν (CO) asym.*	*ν (CO) sym.*	
$CH_3COOSn(CH_3)_3$	$CHCl_3$	1658	1318			4
	Nujol			1570	1425	4
$CH_3COOSn(C_2H_5)_3$	CCl_4	1655	1302			1
	Nujol			1572	1412	1
$ClCH_2COOSn(CH_3)_3$	CCl_4	1688–1660[b]	1333			[f]
	Halo oil			1615	1378[e]	[f]
$ClCH_2COOSn(C_4H_9)_3$	CCl_4	1688–1661[b]				7
	(?)			1596	1404	6
$Cl_2CHOOSn(CH_3)_3$	CCl_4	1708–1687[b]	1330	1652	1368	[f]
	Halo oil			1620[c]	1380	[f]
$Cl_2CHOOSn(C_4H_9)_3$	CCl_4	1698–1679[b]				7
	(?)			1627	1364	6
$Cl_3COOSn(CH_3)_3$	CCl_4	1704	1290			[f]
	$CHCl_3$	1702	1305			
	Nujol			1648[d]	1348	[f]
$Cl_3COOSn(C_4H_9)_3$	CCl_4	1705				7
	(?)			1646	1340	6

[a] Solid when in nujol, halo oil, and (?). [b] Doublet due to conformational effect, *cf.* text. [c] With shoulders at 1650 and 1635 cm^{-1}. [d] Shoulder at 1662 cm^{-1}. [e] With sharp weaker band at 1400 cm^{-1}. [f] This work.

carbon–oxygen stretching region, and assignments are given in Table 3. The doublet due to conformational effects is of course lacking in trimethyltin trichloroacetate (Fig. 3c). The assignments are in reasonable accord with those of others which have been reported.

The possibility should be borne in mind that the carboxylate group could be bidentate (and the tin five-coordinate) even in the absence of association if chelation is invoked. However, the concentration dependence observed in carbon tetrachloride would only be expected for an equilibrium involving association. The presence of small amounts of chelate monomer cannot be ruled out on the basis of the present results, and an extensive study of molecular weight and band intensity data would be required to do so.

In chloroform solution, the three chloroacetate derivatives show bands near 546 cm^{-1} (strong) and 512 cm^{-1} (weak); these can be assigned with confidence to the asymmetric and symmetric tin–carbon stretching modes. In accord with well-established principles, this shows the presence of tetrahedral trimethyltin groups, and is consistent with the non-bridging chloroacetate groups indicated by the carbonyl–carboxyl region of the spectrum. In one series of experiments, increasing amounts of pyridine added to a trimethyltin dichloroacetate solution eliminated the 512 cm^{-1} band, presumably by making the tin atom five-coordinate with a planar SnC_3 group. This confirms the identity of the 512 cm^{-1} band, and the results are entirely comparable with those in the trimethyltin formate–pyridine system[4].

Nuclear magnetic resonance spectra

As pointed out in the initial paper of this series[4], methyltin derivatives are particularly suitable for NMR study, because of the ease with which proton tin coupling constants may be determined. The coupling constants $J(^{119}Sn\text{–}CH_3)$ and $J(^{117}Sn\text{–}CH_3)$* provide uniquely valuable information concerning the hybridization and coordination number of the tin atom. As a result of the general misconception that trimethyltin chloroacetates are insoluble, there has been no previous investigation of this kind.

The principles underlying the use of J values in the study of methyltin carboxylates have already been discussed[4]. Briefly, in four-coordinate tin, there is a small variation of J with electronegativity of the substituents: for tetramethyltin, $J = 54.0$ cps and for trimethyltin chloride, $J = 58.5$ cps. In an established[9] five-coordinate tin compound such as the pyridine adduct of trimethyltin chloride (doubtless the principle species in a pyridine solution of trimethyltin chloride), J rises to 67.0 cps[10]. A value of 70.0 cps is also found for a solution of trimethyltin chloride in tetramethylene sulfoxide, where five-coordinate tin is also the predominant species[11]. *The J value can be regarded as diagnostic of the coordination state of trimethyltin derivatives.*

Coupling constants under various conditions are given in Table 4. The most striking feature is that in chloroform solutions from −30° to +50°, *J values for all three compounds are close to 59 cps.* This is close to the value for trimethyltin chloride, and suggests that the molecules are essentially unassociated, with four-coordinate tin. If associated, five-coordinate tin were present, one would expect to observe an increased J, the weighted average of ~ 59 and ~ 69 cps, values characteristic of the two coordination states. In the case of trimethyltin formate, J values indicated the presence of appreciable amounts of five-coordinate tin and increased at lower temperatures where association is also expected to increase. In chloroform solutions of the trimethyltin chloroacetates, both the value of J and the lack of a significant temperature effect indicate the absence of association. It may be noted, however, that the weighted value of J is not a very sensitive measure of association, since a 5% change in the

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* For convenience in the following discussion we refer only to the ^{119}Sn coupling constant, denoted simply as J.

TABLE 4

PROTON MAGNETIC PARAMETERS FOR TRIMETHYLTIN CHLOROACETATES[a]

Solvent	*Temp.*	$ClCH_2COOSn(CH_3)_3$[b]		$Cl_2CHCOOSn(CH_3)_3$[c]		$Cl_3CCOOSn(CH_3)_3$[d]	
		J_1	J_2	J_1	J_2	J_1	J_2
$CDCl_3$	50	58.8	56.2	58.7	56.2		
$CDCl_3$	33.5	58.9	56.4	59.6	56.9	59.0	56.5
$CDCl_3$	0	59.3	56.7	59.3	56.4	59.6	56.9
$CDCl_3$	−30	59.0					
$CDCl_3/C_5D_5N$	50	67.4	64.4	68.2	65.2		
$CDCl_3/C_5D_5N$	33.5	67.9	64.8	68.3	65.3	68.3	65.2
$CDCl_3/C_5D_5N$	−10	68.1	65.1	68.4	65.3	68.3	65.3

[a] Solutions saturated at room temperature. Coupling constants in cps; $J_1 = J(^{119}Sn\text{–}CH_3)$; $J_2 = J(^{117}Sn\text{–}CH_3)$. τ values for $CDCl_3$ solutions. [b] $(CH_3)_3Sn$ at τ 9.39, $ClCH_2$ at τ 5.83. [c] $(CH_3)_3Sn$ at τ 9.33, Cl_2CH at τ 4.13. [d] $(CH_3)_3Sn$ at τ 9.28.

population of the four and five coordinate states would change J by only about 0.5 cps.

A single NMR measurement on a *carbon tetrachloride* solution of trimethyltin dichloroacetate (approximately 30 mg/ml, 33.5°) showed $J = 61.4$ cps, a value which implies that some 20–25% of the tin is five-coordinate in this solvent. This is in qualitatively good agreement with the infrared results in carbon tetrachloride (Fig. 1c). As observed previously[4], chloroform tends to reduce the degree of association of the trimethyltin carboxylates, perhaps by a hydrogen bonding effect.

As is apparent from the last three entries of Table 4, addition of excess pyridine increases J to values in the five-coordinate range. The value for all compounds at 33.5° is close to 68 cps, slightly higher than the 65.8 cps observed for soluble trimethyltin acetate. This is very likely due to the higher electron withdrawing ability of the chloroacetate ligands, which increases the acceptor ability of the tin atom, and stabilizes the pyridine adduct.

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SUMMARY

Trimethyltin monochloroacetate, dichloroacetate, and trichloroacetate have been prepared and found to be soluble. Solution infrared spectra and molecular weights, and proton NMR spectra are reported and discussed. The compounds are essentially monomeric in chloroform and very slightly associated in carbon tetrachloride. Infrared spectra of the mono- and dichloroacetate suggest that conformational isomers of these molecules are present[*].

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[*] *Note added in proof*: We thank one of the referees for drawing attention to the work on conformational isomers in a series of tributyltin haloacetates by M. Vilarem and J. C. Maire, *Compt. Rend. Ser. C*, 262 (1966) 480.

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