*Contribution from the Laboratory for General and Inorganic Chemistry (B), University of Ghent, Belgium**

A Study of the Structure of Trimethyl-tinhaloacetates by N.M.R. and I.R. Spectroscopy

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The p.m.r. IR spectra of trimethyltinchloro- and -fluoroacetates have been studied. It could be established that these compounds in the solid state most probably are of a polymeric structure with five coordinated tin. In solution however, the molecules are mainly monomeric and tetragonal, but also some associated species must be present for the dichloro-, trichloro-, and trifluoroacetate. In the case of the monochloro- and dichloroacetate also the existence of rotational isomers could be established.

Introduction

The structures of methyltincarboxylates have been investigated by several authors. In 1958 an ionic structure was proposed by Freeman[1] for di-n-butyltinacetate from IR spectral data. Okawara *et al.*[2] interpreted the IR spectra of some methyltincarboxylates as a superposition of the carboxylate anion and the methyltincation spectra. On the other hand in 1961 Beattie and Gilson[3] argued that the IR data of $(CH_3)_3SnAc$ could as well be explained by a structure with bridging acetate groups and five coordinated tin.

This was confirmed by Janssens, Luyten, and Van der Kerk[4] for the solid compound. In dilute solutions in apolar solvents, however, the structure should be monomeric and tetrahedral; only at very high concentrations and in the liquid state just above the melting point could association occur. A similar conclusion was drawn by these authors[5,6] from IR investigations on the structure of trimethyltinhydroxyde and trimethyltinformiates.

IR spectra of tributyltinchloro- and -fluoroacetates were investigated by Vilarem *et al.*[7] They concluded that the structure should be monomeric and tetragonal. This survey of actual data clearly shows the existence of certain ambiguities in the structural propositions for alkyltincarboxylates. We therefore decided to investigate the IR and N.M.R. spectra of the complete series of trialkyltin-chloro- and fluoroacetates $(CH_3)_3SnOOCCH_nX_{3-n}$ (X = Cl, F) in order to obtain an homogeneous pattern of experimental information.

Experimental Section

Synthesis of Compounds. All the compounds studied in this work were obtained by neutralization of $(CH_3)_3SnOH$ with the corresponding acid. They were purified by sublimation. For the fluoroderivatives which were not previously reported the melting points and the yields obtained are:

$(CH_3)_3SnOOCCH_2F$	m.p. 198°C,	yield: 60%
$(CH_3)_3SnOOCCHF_2$	m.p. 150°C,	yield: 70%
$(CH_3)_3SnOOCCF_3$	m.p. 129°C,	yield: 85%

Nuclear Magnetic Resonance Spectra. The p.m.r. spectra were recorded with a Varian dual-purpose n.m.r. spectrometer V-4300 B at 56.4 Mc. The compounds were examined in diluted $CHCl_3$ solutions (3-5% by weight) and as melts if possible. In the molten state no TMS reference was used and only the internal chemical shifts are reported. Because of the low solubility of the compounds no C^{13}–H coupling could be observed in solution.

The n.m.r. data are reported in Table I.

Infrared Spectra. IR spectra were recorded with a Perkin-Elmer model 225 double-beam grating spectrofotometer.

The spectra of the solid compounds in KI disks were recorded between 4000-200 cm^{-1}, those of the solutions from 4000 to 400 cm^{-1}, using matched liquid cells of 1-mm pathlength with KBr windows. CCl_4 was used as the solvent in the region 4000-1300 cm^{-1}, CS_2 in the region 1300-400 cm^{-1}. The spectra of the solid sodium chloro- and -fluoroacetates were also recorded in KI disks to allow comparisons with the spectra of the $(CH_3)_3Sn$-compounds.

The infrared absorption frequency values relevant to the discussion and their assignments are collected in Tables II, III, and IV. Tentative band assignments are indicated with "?".

The assignments were mainly done by comparison with those for $(CH_3)_3SnOOCCH_3$ and trimethyltinchloroacetates as solids in KBr by Okawara,[2] for mono-di- and trichloroacetic acid by Kagarise,[10] and for NaAc by Wilmshurst.[11]

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Table I. Chemical Shifts and Coupling Constants of $(CH_3)_3SnOOCR$ Compounds

Solutions in $CHCl_3$					Melts				
	τ					Internal chem. shift			
R	$(CH_3)_3Sn$	R	$J_{Sn^{117}-C-H}$	$J_{Sn^{119}-C-H}$	R	$\Delta(CH_3)Sn{-}R$	$J_{Sn^{117}-C-H}$	$J_{Sn^{119}-C-H}$	$J_{C^{13}-H}$
CH_3	9.415	7.961	55.3	57.7	CH_2Cl	187	60.1	63.4	133
CH_2Cl	9.346	5.922	55.7	58.7	$CHCl_2$	292	60.7	63.3	130.3
$CHCl_2$	9.281	4.043	55.8	58.9	CF_3		62.7	65.9	117
CCl_3	9.220	—	56.2	58.5					
CH_2F	9.309	5.497	55.4	58.3					
CHF_2	9.309	3.529	56.4	59.2					
CF_3	9.274	—	57.1	59.5					

Table II. IR data of $(CH_3)_3SnOOCR$ as solid in KI

R=CH_3	R=$CHCl_2$	R=$CHCl_2$	R=CCl_3	Assignment
1560 vs (br)	1610	1615	1655	ν_{as}(COO)
1410 vs (br)	1380	1375	1342	ν_s(COO)
770 vs (br)	780 vs (br)	785 vs (br)	790 s	ρ(CH_3—Sn)
			748	ν(C—Cl)
660 vs	675 m 665 sh	675 m 665 sh	682 vs 668 sh	δ(COO)
550 vs	550 s	550 s	550 s	ν_{as}(Sn—C)
495 s	495 s	495 m	493 m	ρ(COO)
			340 w	δ(C—Cl)
250 m (br)	265 w	267 w	285 w	ν(Sn---O)?
	245 w	245 w	215 w	τ(COO)?

Table III. IR data of $(CH_3)_3SnOOCR$ in solution

R=CH_3	R=CH_2Cl	R=$CHCl_2$	R=CCl_3	R=CF_3	Assignment
1648 s	1690 s 1660 s	1700 s 1680 s	1702 s	1720 vs 1660 vs	ν_{as}(COO)
		1622 m	1650 m		
1360 m	1335 vs	1324 vs	1290 s	1400 vs	ν_s(COO)
780 sh	780 s	785 s	760 vs	790 m	ρ(CH_3)
758 vs					
670 w	715 w (br)			730 m	δ(COO)
				680 m 670 m	ρ(COO)?
542 m	540 s	542 m	547 m	550 w	ν_{as}(Sn—C)
515 w	512 w	515 w	515 w	515 vw	ν_s(Sn—C)
430 w (br)	420 (br)	425 w (br)	430 w (br)		ν(Sn--O)?

Table IV. IR data of $(CH_3)_3SnOOCR$ as solid in KI

R=CH_2F	R=CHF_2	R=CF_3	Assignment
1590 vs (br)	1630 vs	1680 vs	ν_{as}(COO)
1445 vs	1460 s	1435 s	ν_s(COO)
1430 vs	1445 sh		
	810 vs	840 vs	δ(COO),
775 s	780 vs	805 vs	ρ(CH_3—Sn)
		725 vs	δ(COO)
690		680 w	
575 m	595 m	600 w	δ(R-group)
555 sh	555 m	550 m	ν_{as}(Sn—C)
545 s	545 s		
510 w	515 v vw	520 s	ρ(COO), δ(C—F)
	490 w		δ(C—F),
215 m	355 vw	270 s	ν(Sn--O),?
	300 w		τ(COO)?

Cryoscopic Measurements. For the compounds that were sufficiently soluble in benzene *i.e.* the three chloro compounds and the trifluoro compounds, the molecular weights were determined by cryoscopy in benzene. The molecular weights agreed to within 5% with the monomeric formula.

Results and Discussion

(1) *Nuclear Magnetic Resonance Spectra*

Solution Data. There is a regular decrease of the chemical shift for the RCOO-protons with increasing number of chloro or fluoro substituents. This trend is easily understood on account of the increasing inductive effect with increasing number of halogen atoms.

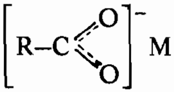
For the $(CH_3)_3Sn$ protons however, the shielding is apparently insensitive to the number of fluorine atoms, whereas for the chlorine-substituted compounds there is a decreasing shielding with increasing number of halogen atoms. A comparison of these results therefore suggests that the inductive effect is probably of minor importance and that for the chloro-compounds there might arise some contribution from the neighbouring anisotropy effect of the chloromethylgroups.

The tin-proton coupling constants over two bonds show a slight increase (1-2 c.p.s.) with increasing number of halogen substituents. These variations, however, are of little structural significance. Nevertheless it is worth-while to note that these coupling constants are about equal to those of the methyltinhalides in $CHCl_3$ solution.[8] Therefore a tetragonal structure can be forwarded for these compounds in solution implying that they are monomeric in solution as is confirmed by the cryoscopic measurements in benzene.

P.M.R. Data for the Compounds as Pure Liquids. The tin-proton coupling constant values show a remarkable increase with respect to those for the compounds in solution. This situation is most probably caused by a change in the hybridisation state of the tin atom. With regard to the possible structures, mentioned in the introduction, and n.m.r. spectroscopic investigations on five- and six-coordinated tin,[9] these data suggest the existence of a linear polymer in which Sn has the coordination number 5.

(2) *Infrared Spectra*

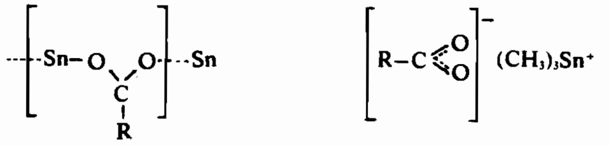
Trimethyltinchloroacetates : Solid in KI Matrix. Vibrations of the *(CH_3)$_3$Sn-group.* The 550 cm^{-1} absorption peak observed in the spectra of the four compounds is ascribed to ν_{as}Sn–C. In none of the four spectra is there a band at around 510 cm^{-1} which could be assigned to ν_s(Sn–C). In the region from 500 to 200 cm^{-1}, it is difficult to state wether or not there is a ν_{Sn-O} band since C–Cl deformation and COO torsion vibrations also yield absorptions in this region. Nevertheless the 250 cm^{-1} band in $(CH_3)_3$SnAc might tentatively be ascribed to ν_{Sn-O} because no absorption occurs in this region in the spectrum of NaAc. For the chlorine-substituted compounds the situation is obviously more complex as can be seen by comparison of the data of Tables II and III.

Vibrations of the COO-group. ν_{as}COO and ν_sCOO yield broad and very strong bands between 1655 and 1342 cm^{-1}, indicating the absence of a C=O bond. In the spectra of the sodium salts the corresponding bands are found between 1345 and 1660 cm^{-1}. Ch. Duval *et al.*[12] suggested that the two CO bonds of the COO-group are identical in the sodium salts, the actual structure being  $\left[R{-}C\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}\right]^- M^+$. Therefore in the trimethyltinchloroacetates also two identical CO bonds might be present. These two CO frequencies are reported to be rather insensitive to structural changes but very strongly influenced by electronegative groups. Therefore the increase of ν_{as}COO and the decrease of ν_sCOO with increasing number of Cl substituents could be explained by a dominating inductive effect on ν_{as}COO with a strengthening of the CO bond, and a dominating mass effect on ν_sCOO with a corresponding decrease of this frequency. The great mass effect on ν_sCOO has also been observed by Vilarem *et al.*[7] in the spectra of tributyltinhaloacetates. δCOO increases from 660 cm^{-1} to 682 cm^{-1} in going from $(CH_3)_3SnOOCCH_3$ to $(CH_3)_3SnOOCl_3$. A similar observation was made by Kagarise[10] in the series CH_3COOH to CCl_3COOH.

It is interesting to note that δCOO in $(CH_3)_3$SnAc is increased by 15 cm^{-1} *versus* δCOO in NaAc. Because an analogous increase of δCOO in going from monomeric acetic acid to dimeric and polymeric forms has been observed, it is delieved that this increase also can be ascribed to an association along the COO group in $(CH_3)_3$SnAc. This increase however is not observed for di- and trichloroacetate. As an explanation we suppose that δCOO (associated) is much less influenced by electronegative substituents than is δCOO (non associated). Therefore in the $(CH_3)_3$Sn compounds δCOO only should increase from 660 cm^{-1} to 682 cm^{-1}, while in the soidum salts it goes from 645 to 740 cm^{-1}.

Conclusion. The absence of ν_sSn–C suggests the $(CH_3)_3$Sn-group in these compounds to be planar. This can be achieved either by a $(CH_3)_3Sn^+$ cation or by five coordination around tin with sp^{3}d hybridization. The coupling constant data in the p.m.r. spectra for the melts are however too small for an ion and on the other hand they are considerably larger than for a normally sp^3 hybridized tin atom carrying one electronegative substituent. Thus both sets of data suggest formation of sp^{3}d hybrid orbitals around tin.

The general aspect and the position of ν_{as}COO and V_sCOO must be correlated with two equivalent CO bonds in the COO-group. In the region 800-200 cm^{-1}, the spectra cannot be explained by a simple superposition of the $(CH_3)_3Sn^+$ cation and the acetate- or chloroacetate anion. On the contrary it is possible to explain certain changes by supposing formation of associated molecular groups by bridging COO-group. We could not determine with certainty the position of ν_{Sn-O}, although it is very probable that one of the weak absorption peaks between 350 and 200 cm^{-1} is to be assigned to this vibration. In $(CH_3)_3SnOOCH$, $(C_2H_5)_3SnOOCH$ and $(C_4H_9)_3SnOOCH$[6] this vibration was attributed to the 300, 283 and 270 cm^{-1} absorption band respectively. In view of all these considerations it seems to us that trimethyltinchloroacetates in the solid state are of a polymeric structure (A), contrasting with an ionic structure (B) first proposed by R. Okawara *et al.*



(A) (B)

(3) *Trimethyltinchloroacetates in Solution*

Vibrations of the *(CH_3)$_3$Sn-group.* The weak absorption band at 425 cm^{-1} is most probably due to ν_{Sn-O}. Solutions of $(CH_3)_3SnOOCH$ and $(C_2H_5)_3SnOOCH$[6] showed also an absorption band at 425 cm^{-1} which has been attributed to this vibration. With respect to the ν_{Sn-O} frequency in the solid-state spectra, there is a remarkable increase. This is easily understood if it is recalled that in the solid state the COO group is a bridging group so that we actually observe the vibration of an O–Sn–O group rather than that of an ⋗Sn–O– group.

Vibrations of the COO-group. In the region of absorption of ν_{as}COO we observe for $(CH_3)_3$SnAc one strong absorption band at 1648 cm^{-1}, but respectively 2,3 and 2 absorption bands for mono-, di- and trichloroacetate. With respect to the single absorption band in the spectra of the solid compounds these bands are shifted to higher frequencies with the exception of the band with the lowest frequency in di- and trichloroacetate. These shifts only can be ascribed to the formation of a CO double bond in the CCO-group. The presence of this C=O double bond allows the assumption of a rotational *cis-trans* isomerism of the

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[12] Ch. Duval, J. Lecomte, and F. Douville, *Bull. Soc. Chim.*, 9, 263 (1942).

$-CH_2Cl$ and $-CHCl_2$ groups *versus* the C=O group. Consequently the C=O absorption band should be split up in two bands that could be correlated with the 1690, 1660 cm^{-1} and 1700, 1680 cm^{-1} frequencies of the monochloro- and dichloroacetate. Such isomeric splittings have also been observed in the spectra of butyltinhaloacetates.[7]

The 1622 cm^{-1} band in the dichloroacetate and the 1650 cm^{-1} band in the trichloroacetate obviously should be ascribed to some associated molecules still present in solution. Indeed, their frequency is about the same as that for ν_{as}COO for di- and trichloroacetate in the solid state (1610 and 1645 cm^{-1}). Therefore the strengthening of one CO bond in the COO-group should be reflected in a decrease of the strength of the other CO bond, the latter receiving more single bond character. Indeed a decrease of this frequency with respect to the frequency of the same band in the solid compound is observed. On the other hand, the decreasing trend of this frequency with increasing chlorine substitution suggests that also in solution the mass effect is the dominating factor.

Conclusion. The occurrence of ν_sSn–C at 515 cm^{-1} together with ν_{as}Sn–C and the formation of a CO double bond in the COO-group accompanied by the appearance of rotational isomers, indicate that these compounds should have a tetragonal (monomeric) structure in solution. Moreover solutions of trimethyltindi- and -trichloroacetate apparently still contain dimeric or linear polymeric molecules.

(4) *Trimethyltinfluoroacetates*

Because of the very low solubility of the monofluoro- and difluoroacetate only the spectrum of the trifluoroacetate could be recorded in solution.

Sn–C-stretching Vibrations. In the spectra of the solid compounds only ν_{as}Sn–C is observed at 555 cm^{-1}. In solution however, also ν_sSn–C appears in the spectra as was also observed in the spectra of the chloro compounds. With reference to the data of the n.m.r. spectra it therefore follows that the structure of the fluoro-compounds must be analogous with that of the chloro compounds.

COO Stretching Vibrations. In the solid state these vibrations are found as strong absorption bands between 1680 and 1430 cm^{-1} suggesting the absence of a C=O double bond. The frequencies are in close agreement with those of the Na salts. With increasing fluorine substitution ν_{as}COO increases, indicating a dominating inductive effect on this vibration. Since this effect is greater for fluorine than for chlorine the observed increase of the frequency is also steeper. On the other hand ν_sCOO increases for the first two members of the series and then decreases for the trifluoroacetate. This can be explained by a dominating inductive effect for the former compounds and a dominating mass effect for the latter. In the chloro-compounds it was seen that the mass effect was dominating throughout the whole series.

In the spectrum of trifluoroacetate in solution, the 1660 cm^{-1} band can be attributed, as in the case of the chlorocompound, to polymeric species still present in solution.

Conclusion. Apparently the structural conclusions drawn for the chlorocompounds may be extended to the fluorocompounds. Only in the relative contribution of inductive and mass effects on the COO-frequencies a slight difference could be observed.