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RAMAN AND INFRARED SPECTRA OF TRIMETHYLTIN CARBOXYLATES

RONALD E. HESTER
Department of Chemistry, University of York (Great Britain)

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SUMMARY

Raman spectra over the frequency range 50–4000 cm^{-1} and IR spectra over the range 200–4000 cm^{-1} have been recorded for the solid trimethyltin carboxylates $(CH_3)_3SnOCOX$, with X being H, CH_3, CH_2Cl, and CH_2CH_3. The spectra have been analysed, and C–O, Sn–C, and Sn–O bond stretching modes have been assigned. The IR spectra of the carboxylates in chloroform solutions also have been determined, and the band assignments shown to be consistent with solution depolymerisation of carboxylate-bridged solid state structures.

INTRODUCTION

Trialkyl- and triaryltin carboxylates and their simple derivatives have received considerable attention in recent years, and a number of IR and Mössbauer spectroscopic studies have been made of series of compounds wherein the nature of the alkyl/aryl group has been changed in a systematic way, or the carboxylate group has been changed[1–5]. Much evidence has been accumulated to show that these compounds, of general formula $R_3SnOCOR'$, are commonly polymeric in the solid state, but that depolymerisation (complete except for formates) occurs on dissolving in an organic solvent. The planarity of the R_3Sn groups in the solid polymers has been inferred from the inactivity in the IR spectrum of the symmetric SnC_3 stretching mode, though an X-ray diffraction study of tribenzyltin acetate has established with certainty the essential planarity in this case[6]. Further insight into the stereochemical features of these molecules can be obtained from Raman spectroscopy, which provides convenient access to the symmetrical (IR inactive) vibrational modes.

Since the $(R_3SnOCOR')_n$ polymer chains must be linked by bidentate carboxylate groups[7], the C–O stretching frequencies can be classified as symmetric and asymmetric vibrations of the OCO group, so that Raman spectra also can be helpful here in determining assignments. Furthermore, a key feature in the structure determination is the identification of the Sn–O stretching frequencies, and these evidently occur in the region below 300 cm^{-1} which has been little studied by IR methods[1].

EXPERIMENTAL

The compounds $(CH_3)_3SnOCOX$, with X being H, CH_3, CH_2Cl, and CH_2CH_3, were prepared from tetramethyltin and the appropriate sodium carboxylate by an electrochemical technique described in detail earlier[8]. All of these compounds were appreciably soluble in chloroform at ambient temperatures.

IR spectra were obtained from the solids as both nujol and hexachlorobutadiene mulls, and from the $CHCl_3$ solutions, using cells with CsI windows. The instrument used was a Perkin–Elmer model 621, equipped with a dry-air flushing unit to enable frequencies to be determined down to 200 cm^{-1}. Raman spectra were obtained from the solids with a considerably modified Perkin–Elmer model LR-1 instrument, using a Spectra Physics model 125 He-Ne laser light source. IR frequencies are reported to ± 1 cm^{-1}, and Raman frequencies to ± 2 cm^{-1}.

RESULTS AND DISCUSSION

Raman and IR spectra obtained from the solid compounds are shown over the full frequency region in diagramatic form in Fig. 1. The relative band intensities shown are experimental, no corrections having been made for spectral sensitivity variations.

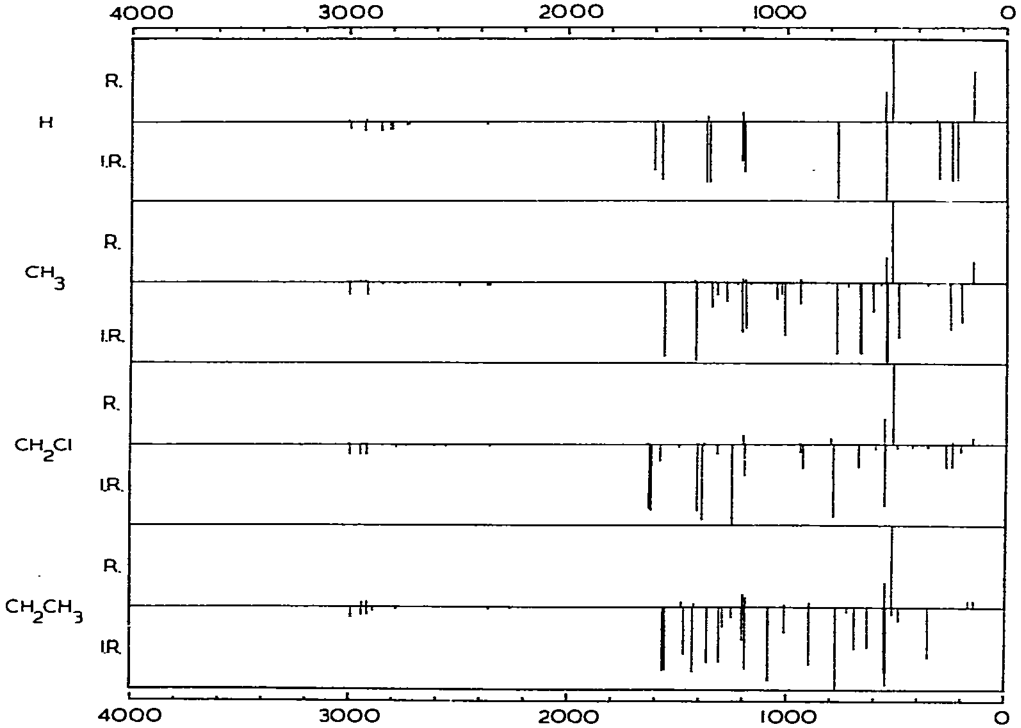

Fig. 1. Raman and IR spectra (schematic) of trimethyltin carboxylates, $(CH_3)_3SnOCOX$, with X=H, CH_3, CH_2Cl or CH_2CH_3.

Although completely rigorous assignments of the bands to their respective normal modes is impossible for systems of this complexity, much can be achieved by the usual type of group frequency designation procedure. For this it is helpful to consider the full frequency assignment made for the trimethyltin group in $(CH_3)_3SnCl$ by Edgell and Ward[9], from Raman and IR spectra considered together. Since the intention here is to establish reasonable assignments in the C–O, Sn–C, and Sn–O bond stretching regions, the relevant parts of the $(CH_3)_3Sn$ group spectrum have been abstracted and are presented in Table 1, together with some group frequency correlation data taken from Bellamy[10]. While both the symmetric and the asymmetric SnC_3 stretching modes are IR active in $(CH_3)_3SnCl$, due to its pyramidal (C_{3v}) symmetry, the former mode has been shown to be absent from IR spectra of solid trimethyltin carboxylates, signifying planarity (D_{3h} local symmetry) of the $(CH_3)_3Sn$ groups in carboxylate-linked polymeric chain structures. The present work shows (Fig. 1) the symmetric SnC_3 modes as strong Raman bands for each of the compounds studied. For the $CHCl_3$ solution spectra, in each case the 516 cm^{-1} symmetric SnC_3 mode was IR active, though still very weak. Moreover, the frequencies of all SnC_3 modes were found to be remarkably insensitive to the group shape (planar or pyramidal) and to its environment (polymeric or monomeric carboxylate, or even chloride).

TABLE 1

FREQUENCIES FOR $(CH_3)_3Sn$ AND SOME CARBOXYLATE AND HYDROCARBON GROUPS

Description	Frequency (cm^{-1})	Ref.
$(CH_3)_3Sn$ group		
SnC_3 symmetric stretch	518	9
SnC_3 asymmetric stretch	548	9
SnC_3 deformation	150	9
$Sn–CH_3$ rocking	787	9
$Sn–CH_3$ symmetric deformation	1193	9
$Sn–CH_3$ asymmetric deformation	1400	9
C–H deformations		
CH_3 sym. deformation in $CH_3–C$	1370–1380	10
CH_3 asym. deformation in $CH_3–C$	1430–1470	10
$–CH_2–$ deformation	1445–1485	10
CH_2 deformation in $C–CH_2–CO_2H$	1420	10
CH_2 rocking, twisting, wagging	720	10
$O_2C–H$ deformation in plane	1378	1
$O_2C–H$ deformation out-of-plane	1073	1
Carboxylate modes		
a. Ionized $R–CO_2^-$		
OCO asymmetric stretch	1550–1610	10
OCO symmetric stretch	1300–1400	10
b. Esters		
C=O stretch	1735–1750	10
C–O stretch in formates	1180–1200	10
C–O stretch in acetates	1230–1250	10
C–O stretch in propionates	1150–1200	10

The C–O stretching frequencies appear to be more sensitive to the structure and bonding in the carboxylates. The frequencies assigned to these modes in Table 2 are substantially in agreement with previous work. It will be seen that the $CHCl_3$ solution spectra differ significantly from the solid state (mull) spectra in this region, and that two strong IR bands have to be assigned to the asymmetric OCO (or C–O) stretch in several cases. For the solutions, the explanation is clear, in that it has been

TABLE 2

ASSIGNMENTS FOR TRIMETHYLTIN CARBOXYLATES IN THE SOLID STATE AND IN CHLOROFORM SOLUTION

Frequencies in cm^{-1}

Mode	$(CH_3)_3SnOCOX$, with X =			
	H	CH_3	CH_2Cl	CH_2CH_3
Solids				
ν_s(Sn–O)	252, 227	208	247	
ν_a(Sn–O)	310	258	277	355
ν_s(Sn–C)	522	521	518	519
ν_a(Sn–C)	554	554	555	552
ν_s(OCO)	1357	1346	1386	1364
ν_a(OCO)	1575, 1603	1564	1621, 1630	1555, 1565
Solutions				
ν_s(Sn–C)	516	517	515	516
ν_a(Sn–C)	555	548	548	595
ν_s(OCO) or ν(C–O)	1352	1314	1348	1344
ν_a(OCO) or ν(C=O)	1585, 1648	1645	1660, 1682	1644

established[8] that the higher frequency bands grow in intensity at the expense of the lower ones as the solutions are diluted, thus establishing the former as monomer bands, the latter as dimer or higher polymer bands. For the solid state spectra the explanation of the doublet structure in the asymmetric OCO stretching region is more obscure, though a partial solubility (with depolymerisation) in the mulling agents could conceivably provide an explanation. In this respect it is worth noting that quite substantial differences between KBr and nujol mull IR spectra of trimethyltin carboxylates have been reported previously, though without comment[11]. In line with the previous molecular weight determinations[8], however, the comparison of C–O stretching frequencies between Tables 1 and 2 establish the essential point that a change from polymeric (bidentate carboxylate groups resembling ionized RCO_2^-) to monomeric (monodentate, ester-like carboxylate groups) structures occurs.

The only previous study[1] of low frequency bands from $R_3SnOCOR'$ compounds was devoted to IR spectra of formates, and extended only to 35 μ (286 cm^{-1}). In agreement with that work, a strong IR band at 310 cm^{-1} has been established for solid trimethyltin formate, but it is not immediately obvious that this must be assigned to an Sn–O stretching mode, since two other strong IR bands which also might be due to Sn–O motion occur at somewhat lower frequencies (see Fig. 1). The Raman spectrum is not particularly helpful here, since only the SnC_3 deformation mode is strongly active in the region below 400 cm^{-1}. The absence of a strong Sn–O Raman band is in itself indicative of a highly ionic character in the tin–carboxylate bond, since covalent metal–ligand vibrations usually generate intense Raman spectra[12]. This suggestion of highly ionic character is in line with the form of the carboxylate group frequencies resembling that of ionized RCO_2^- systems, as seen earlier. An Sn–O frequency as low as 310 cm^{-1} (or lower) also suggests an unusually weak bond, since the Sn–O modes in compounds such as $(CH_3)_2Sn(OR)_2$, with R being an alkyl group, occur in the 600 cm^{-1} region[13]. The highest frequency bands in this lowest frequency region are tentatively assigned to asymmetric SnO_2 stretching modes for each of the carboxylates in Table 2, though it would seem unwise to read much significance into their considerable frequency variations at this stage. Symmetric SnO_2 stretching modes similarly are assigned to the lower frequency strong IR bands. The activity of these modes would be in keeping with non-linear C_{2v} O–Sn–O groups, as already established by X-ray work[6] for tribenzyltin acetate in the solid state.

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