Journal of Organometallic Chemistry, 51 (1973) 181–187
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VIBRATIONAL SPECTRA AND STRUCTURE OF SOME TRIVINYLTIN CARBOXYLATES

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

(Received September 11th, 1972)

SUMMARY

IR spectra of the trivinyltin carboxylates, $(CH_2{=}CH)_3SnOCOX$, with X being CH_3, CH_2Cl, $CHCl_2$ and CF_3 have been re-examined and measurements extended into the far-infrared region. Carboxylate group frequencies change significantly through this series of compounds from values characteristic of ionic $CH_3CO_2^-$ to the ester-type $CF_3C({=}O)O-$. Both solid state and solution data are analysed, marked differences between these being attributed to depolymerisation processes. Assignment of Sn–C and Sn–O stretching frequencies are proposed and interpreted in terms of the geometry about the metal centre. Supplementary evidence for the assignments is provided by Raman spectra for some of the solid compounds, though an intense and persistent fluorescence marked all but the most intense bands. It is suggested that the origin of this fluorescence may lie in an extended π-conjugation brought about by involvement of tin d-orbitals with the surrounding vinyl groups, this proposal being consistent with infrared evidence based on the vinyl group frequencies.

INTRODUCTION

This study represents an extension of our previous work on organotin carboxylates[1,2] and is complimentary to the work of Peruzzo, Plazzogna and Tagliavini[3]. The objective was a better understanding of the structure and bonding in the novel vinyltin carboxylates of general formula $(CH_2{=}CH)_3SnOCOX$. In particular, we aimed at a characterisation of the nature of changes in structure accompanying dissolution of the solid (believed polymeric[3]) compounds and the effect of changing the nature of the group X from CH_3, to CH_2Cl, to $CHCl_2$ and finally to CF_3. By measuring far-IR spectra we hoped to determine the characteristics of the Sn–O bonding in these compounds.

EXPERIMENTAL

The trivinyltin carboxylates, $(CH_2{=}CH)_3SnOCOX$, with X being CH_3, CH_2Cl, $CHCl_2$ and CF_3 all were prepared from tetravinyltin and the appropriate sodium carboxylates by an electrochemical technique described in detail earlier[3]. The compounds were purified by recrystallisation from dry tetrahydrofuran. Solutions for spectroscopy were prepared at approx. 5% w/v in dry chloroform.

IR spectra were obtained from the solid compounds 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 purging unit to enable frequencies to be determined down to 200 cm^{-1}. Far IR spectra were obtained from vaseline dispersions of the solid compounds held between high density polyethylene discs in an evacuated Grubb Parsons Cube Interferometer. Spectra were obtained in the range 50–400 cm^{-1}, an ICL 4130 computer being used to perform the fourier transforms of interferogram data. Raman spectra were obtained using an instrument comprising a Hilger model D330/331 double monochromator coupled

TABLE 1

INFRARED FREQUENCIES[a] FOR $(CH_2{=}CH)_3SnOCOX$

$X{=}CH_3$	$X{=}CH_2Cl$	$X{=}CHCl_2$	$X{=}CF_3$
82 m[b]	78 m[b]		66 m[b]
120 m[b]	122 m[b]		118 m[b]
196 s[b]	150 m[b]		158 (sh)[b]
294 m[b]	202 s(br)[b]	285 w	282 m[b]
304 m[b]	308 m[b]	300 w	304 m[b]
485 s	330 s[b]	320 w	405 w
510 (sh)	490 s	340 vw	430 (sh)
539 s	510 (sh)	450 m	450 (sh)
590 (sh)	540 s	490 s	485 m
610 s	570 m	518 w	510 m
672 s	705 s	565 w	531 m
802 w	755 w	630 s	598 w
822 w	798 s	710 (sh)	635 m
947 s	830 w	720 s	722 s
967 (sh)	935 m	770 m	795 m
1000 s	958 s	800 w	840 m
1015 (sh)	1000 s	821 s	855 (sh)
1050 w	1095 w	950 s	955 m
1130 w	1210 w	985 s	975 w
1225 w	1238 m–s	1095 w	995 m
1240 m	1260 s	1215 (sh)	1025 w
1285 m	1390 m	1225 m	1145 s
1345 m	1402 m	1240 m	1190 vs
1395 m	1425 vs	1260 w	1240 w
1410 m	1510 w	1350 s	1390 (sh)
1440 vs	1560 vs	1390 vs	1415 s
1540 vs	1580 w	1410 w	1460 w
1560 s	1598 s	1585 m	1585 w
1589 m	2940 m	1620 vs	1660 m
1900 w	2980 s	1650 s	1695 vs
2938 m	3000 w	1910 w	1710 m, (sh)
2980 s	3050 m		2940 m
3000 w			2985 s
3040 m			3050 s
			3100 m

[a] All frequencies in cm^{-1}. Intensities described by s strong, m medium, w weak, v very, (sh) shoulder, (br) broad. [b] These frequencies obtained from interferometry.

with a Brookdeal amplification/phase sensitive detection system and a Coherent Radiation model 52A argon ion laser. The solid compounds all tended to fluoresce strongly, but satisfactory spectra could be obtained from pressed discs held in the laser beam at ca. 45° such that direct scatter of the beam occurred at the disc surface remote from the monochromator entrance slit. IR frequencies are reported to $\pm 1\ \mathrm{cm}^{-1}$, and Raman frequencies to $\pm 2\ \mathrm{cm}^{-1}$.

RESULTS AND DISCUSSION

Tables 1 and 2 contain listings of IR and Raman bands recorded from the solid compounds. For molecules of this complexity, rigorous assignments of all the bands to the many normal modes of vibration is not possible and the only suitable procedure is the usual group frequency approach. Relative intensities of bands are seen to differ greatly between the Raman and IR spectra, the strongest features in the former occurring in the regions around $290\ \mathrm{cm}^{-1}$ and $520\ \mathrm{cm}^{-1}$ and in the latter in the carbonyl stretching region. These data provide clues which are helpful in making assignments. On the basis of IR intensities and group frequency correlation tables[4] bands arising from C–O stretching frequencies have been assigned and are presented so as to display the trends with changing X group in Fig. 1. The multiplet structures of the bands are presumed to be due to solid state effects, but in spite of these the major trends are clearly visible. As the X group in $(CH_2{=}CH)_3SnOCOX$ is changed from CH_3 through CH_2Cl and $CHCl_2$ to CF_3 there is a marked increase in the separation of the two main components of the C–O stretching bands. The first two compounds give bands which correlate well with those expected for the ionised RCO_2^- group[4] and also are of similar frequencies to those recorded for the compound $(CH_3)_3Sn$-$OCOCH_3$[1,5]. As with the trimethyltin carboxylates, the implication is that these first

TABLE 2

RAMAN FREQUENCIES FOR $(CH_2{=}CH)_3SnOCOX$

$X{=}CH_3$	$X{=}CH_2Cl$	$X{=}CHCl_2$	$X{=}CF_3$
		274 w	
291 vs		285 w	285 s
		420 w	
515 vs	513 w	520 s	520 s
541 w		712 w	549 w
		768 w	768 w
		816 m	
		885 w	
945 w		944 w	
997 w		988 w	
		1073 w	
		1167 w	
1250 m	1253 w	1243 m	1250 m
1352 w	1365 vw	1388 m	1394 m
1393 m	1401 w	1436 m	1449 w
1442 w	1590 w	1581 m	1587 w
1589 w	1644 vw	1622 m–w	

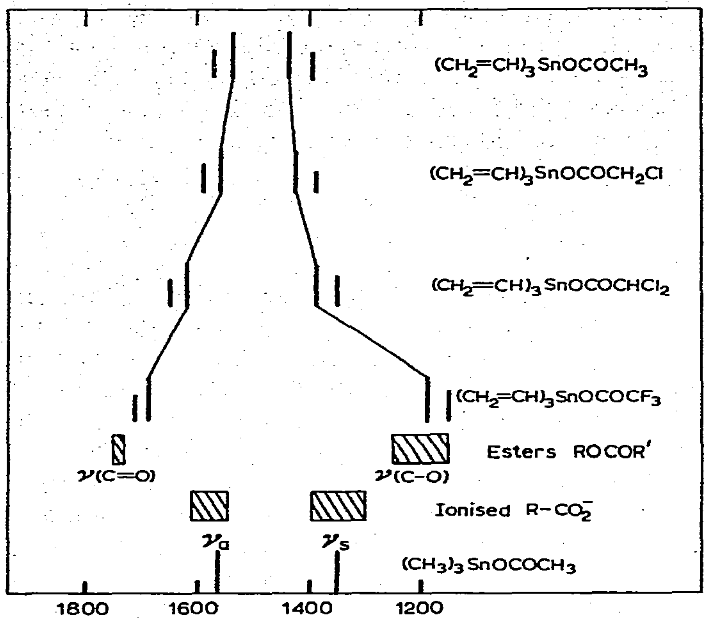

Fig. 1. Correlations between the C–O stretching frequencies of the trivinyltin carboxylates and standard group frequencies for esters, carboxylate salts, and trimethyltin acetate.

TABLE 3

INFRARED BANDS (in cm^{-1}) IN THE C–O STRETCHING REGION FROM SOLIDS AND CHCl$_3$ SOLUTIONS OF (CH$_2$=CH)$_3$SnOCOX

X	*Solid state*		*CHCl$_3$ solution*	
CH$_3$	1560 s. 1540 vs	1440 vs, 1395 m	1645 vs, 1618 s	1315 vs
CH$_2$Cl	1598 s. 1560 vs	1424 vs, 1390 m	1670 s, 1640 s	1390 m, 1345 s
CHCl$_2$	1650 s, 1620 vs	1390 vs, 1350 s	1670 s, 1625 vs	1390 s, 1335 s
CF$_3$	1710 m, 1695 vs	1190 vs, 1145 s	1710 m, 1690 vs	1185 vs, 1155 s

two compounds at least are polymeric in the solid state, with (CH$_2$=CH)$_3$Sn groups being associated through symmetrical bidentate carboxylate groups. However, for X=CHCl$_2$ the separation of the C–O stretching band components is greater, and for X=CF$_3$ much greater. The latter resembles that normally produced by organic esters, the lower frequency component then being assigned to the C–O single bond stretch and the higher to the C=O double bond stretch[3]. The dichloro compound data are of intermediate form. The implication that the perfluoromethyl compound differs from the CH$_2$ and CH$_2$Cl compounds in being monomeric in the solid state is supported by the results obtained from chloroform solutions of the compounds. These are given in Table 3, in which a comparison of solid state and solution frequencies in the C–O stretching region is made. It is seen that with X=CH$_3$ and CH$_2$Cl there is a marked increase in the separation of C–O band components on dissolution, but very little change for the X=CHCl$_2$ and CF$_3$ compounds. Previous molecular weight determinations[3] have shown that the CF_3 and CH_2Cl compounds are monomeric in $CHCl_3$, but that the acetate is trimeric. The present data suggest that with $X=CHCl_2$, as well as for $X=CF_3$, the compounds are monomeric in the solid state, while with $X=CH_3$ and CH_2Cl the compounds exist as polymeric solids.

Previous work with trimethyltin carboxylates[1] has provided data which are helpful in making assignments of the skeletal stretching modes about the metal centre in these analogous vinyl compounds. Unlike the $(CH_3)_3Sn$ group however, the $(CH_2{=}CH)_3Sn$ group appears to generate three bands in the Sn–C stretching region[3,6] (400–600 cm^{-1}) of all the solid state spectra. These occur in the IR at approx. 490, 510 and 540 cm^{-1}, while the Raman spectra show a single strong band at approx. 520 cm^{-1}. The analogy with the $(CH_3)_3Sn$ group suggests the assignment of the strong, Raman-active band to the symmetric stretching mode of the SnC_3 group[1,7]. However, unlike the case of the $(CH_3)_3Sn$ group, there is no simple correspondence of this Raman band with an IR band from $(CH_2{=}CH)_3Sn$, unless it be the weakest component of the triplet at 510 cm^{-1}, recognising that factor group splitting might produce 10 cm^{-1} frequency shift[8]. This Raman–IR comparison, taken together with the relative complexity of the Sn–C stretching region in the IR and the further fact that solid and solution IR spectra are essentially identical in this region for all compounds, supports the earlier suggestion[3] that the SnC_3 moiety here is of lower symmetry than that established for trimethyltin carboxylates in the solid state. If the vinyl groups occupy one equatorial and both axial positions in the coordination trigonal bipyramid about the tin atom[3] then three normal stretching modes of vibration will result from the SnC_3 group of C_{2v} symmetry. This contrasts with the situation where the carbon groups all are equatorial, when the D_{3h} local symmetry gives rise to only two ν(Sn–C) modes, one of which is doubly degenerate. In the case of axial distortion of this latter configuration also, when C_{3v} local symmetry in the SnC_3 skeleton results, only two distinct modes are generated. The case for axially oriented vinyl groups evidently is quite strong, based on the Sn–C stretching region. Further support is found in the SnC_3 deformation region[7] (ca. 150 cm^{-1}) where the absence of a strong Raman band in the trivinyltin spectra contrasts sharply with the trimethyltin data, indicating fundamental structural differences between these compounds.

The other spectral region of particular interest for these compounds is that associated with Sn–O stretching. In the region previously assigned to these modes[1] intense Raman bands are found at 291 and 285 cm^{-1}, respectively, for the methyl and perfluoromethyl compounds. Again this contrasts with the trimethyltin carboxylate spectra where only the SnC_3 deformation mode (at ca. 150 cm^{-1}) gave an intense Raman band below 500 cm^{-1}. If the above bands are assigned to symmetric Sn–O stretching it may be speculated that their relatively high intensities and frequencies are indicative of stronger and more covalent Sn–O bands in the trivinyltin carboxylates than in the trimethyltin carboxylates[8], though it must be stated that these assignments can only be tentative.

Finally, the vinyl group frequencies are worthy of comment. Fig. 2 presents a summary of the principal bands assignable to the vinyl group and correlates them with the normal group frequencies characteristic of organic molecules[4]. The spectra all are closely similar to one another and to those previously reported for the vinyl group bonded to a metal[9,10], but it is clear from Fig. 2 that there are distinct differences from the normal organic vinyl group spectrum. For example the band characteristic

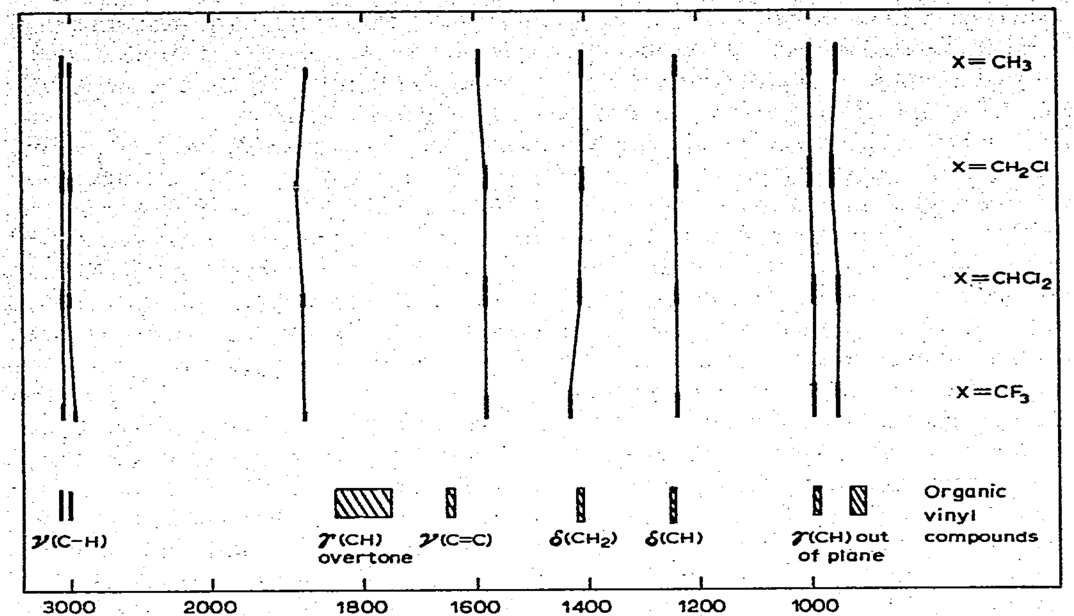

Fig. 2. Correlations between the vinyl group frequencies from the trivinyltin carboxylates $(CH_2{=}CH)_3Sn{-}OCOX$, and standard group frequencies from organic vinyl compounds.

of C=C stretching is shifted ca. 60 cm^{-1} to lower frequency in the trivinyltin carboxylate spectra, suggesting a weakening of the C=C bond. This effect conceivably could arise from delocalisation of the vinyl group π-electrons through the tin-centre, this presumably involving the tin $5d$-orbitals. This π-electron delocalisation similarly could extend to the carboxylate group and account in part for the substantial differences in structure and bonding established here between the trivinyltin and the trimethyltin carboxylate molecules. The persistent nature of the fluorescence recorded for these trivinyltin compounds might also be due to the unusual electronic structure involving an extended π-conjugation.

ACKNOWLEDGEMENTS

We thank Professor Tagliavini and his colleagues at the University of Padua for their very practical cooperation in this study. We also thank Reuben Girling for recording spectra, and N.A.T.O. for financial support through Research Grant Number 374.

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