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MONOMERIC AND ASSOCIATED FORMS OF TRIVINYLTIN FORMATE IN SOLUTION

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Summary

The preparation and properties of trivinyltin formate are described. Molecular weight determinations and infrared spectroscopy in solution indicate the existence of small polymers in which the SnC_3 moiety maintains the same non-planar geometry as in the solid state. The existence of two COO asymmetric stretching vibration bands, which are concentration-dependent, indicates that there is an equilibrium in solution between monomeric and associated forms of trivinyltin formate.

Introduction

Compounds of the general formula $R_3SnOOCR'$ exist as linear polymers having planar SnC_3 moieties bridged by COO groups in the solid state, as small polymers in concentrated solutions, and in the monomeric state in dilute solutions [1 - 4].

Infrared COO and Sn—O stretching absorption data, as well as molecular weight determinations [4 - 9], suggest that in all these compounds the formate group acts as a stronger bridging ligand than the other carboxylates and the associated forms in solution are favoured where R is a methyl group.

Among the trivinyltin carboxylates which have been recently described [10, 11], the formate is unknown. The characteristics of this compound related to those of the known trivinyltin carboxylates are reported here.

Experimental

Trivinyltin formate has been prepared* by treating trivinyltin hydroxide (1.7 g) with formic acid (0.4 g) in diethyl ether (40 ml), as described for triethyltin formate [6].

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* Attempts to prepare the trivinyltin formate by the "electrochemical procedure" have been unsuccessful (see ref. 10).

TABLE 1

MOLECULAR WEIGHTS OF TRIVINYLTIN FORMATE (37°)

Solvent	Concn. (mg/ml)	Mol. wt. found	Mol. wt. calcd.	i^a
Chloroform	23.80	345	244.84	1.41
	14.90	299		1.22
	7.45	289		1.18
	3.73	286		1.17
	1.86	283		1.16
Carbon tetrachloride	20.12	492		2.01
	11.32	428		1.75
	5.66	372		1.52
	1.41	357		1.46

$^a i$ = Mol. wt. found/mol. wt. formal.

The crude product (1.7 g) recrystallized from a mixture of THF/petroleum ether (30 - 70°) gave a solid melting at 80 - 81°. (Found: C, 34.10; H, 4.07; Sn, 48.02 $C_7H_{10}O_2Sn$ calcd.: C, 34.34; H, 4.15; Sn, 48.45%).

IR spectra were recorded on a Perkin—Elmer instrument (Model 457). The samples were analyzed both as Nujol mulls and dissolved in chloroform or carbon tetrachloride. Raman spectra were recorded on a Jarrel—Ash 25—300 Raman spectrometer using an He—Ne laser Spectra Physics 125 A.

Molecular weights were determined in chloroform and carbon tetrachloride with a Mechrolab model 302 B vapour phase osmometer.

Results and discussion

Trivinyltin formate is appreciable soluble in diethyl ether, THF, chloroform and carbon tetrachloride. Apparent molecular weights have been deter-

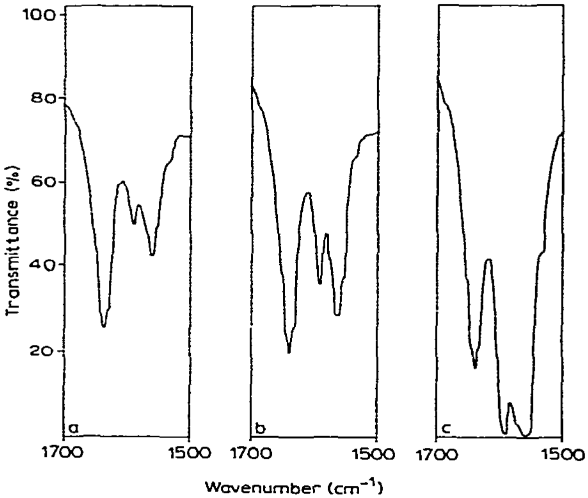


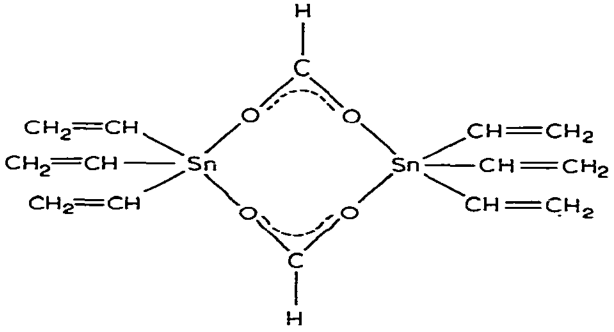
Fig. 1. IR spectra of trivinyltin formate in chloroform. (a) 15 mg/ml, (b) 31 mg/ml and (c) 78 mg/ml.

TABLE 2

IR DATA (cm^{-1}) IN NUJOL MULLS, AND $CHCl_3$ OR CCl_4 SOLUTIONS (OPTICS KBr 0.1 mm).

	ν_{as}(COO)	ν_s(Sn—C)
Nujol mull	1595s 1550s	545s 510(sh) 490s
$CHCl_3$	1640vs 1560s	540s 515(sh) 490s
CCl_4	1650s 1565s	540s 520(sh) 490s

mined and the results are listed in Table 1. These results suggest that an equilibrium between monomeric and dimeric species exists in carbon tetrachloride, and this observation is supported by IR data (cf. Fig. 1a, b, c and Table 2) obtained in solution. The spectra in Fig. 1 show two COO absorption bands clearly over the concentration range 2.1×10^{-3} - 8.6×10^{-3} M. The intensity ratio of the 1640 - 1560 cm^{-1} bands decreases with increase of trivinyltin formate concentration and, in the most concentrated solution, the intensity of the 1560 cm^{-1} band largely dominates that of the 1640 cm^{-1} band. The effect of the concentration of the trivinyltin formate can be evaluated by measuring the intensities of the 1640 and 1560 cm^{-1} bands relative to that of the 995 cm^{-1} band (vinylic absorption). The observed values are summarized in Table 3 and the figures given concur in a semiquantitative way with the above hypothesis. The 1560 cm^{-1} band is typical for OCO groups having C_{2v} symmetry, the higher frequency band (1640 cm^{-1}) being generally attributed to a OCO group in reduced symmetry [6]. The effect of the concentration on the intensity ratio of the 1640 - 1560 cm^{-1} bands, coupled with the molecular weight measurements, leaves little doubt that a monomer—dimer equilibrium occurs in solution and we propose the structure (I) for the dimeric species.



(I)

The IR spectrum of trivinyltin formate mulled in Nujol (cf. Table 2) displays a pattern of bands in the region 450 - 550 cm^{-1} (SnC_3 stretching

TABLE 3

VALUES OF A_1/A_R AND A_2/A_R (A_1 = ABSORBANCE AT 1650 cm^{-1}, A_2 AT 1565 cm^{-1} AND A_R AT 995 cm^{-1})

Solvent	Concn. (mg/ml)	Absorbance ratio	
		A_1/A_R	A_2/A_R
CCl_4	5.3	5.3	5.4
	11.0	2.2	5.8
	21.1	1.4	6.1
$CHCl_3$	15.5	3.9	2.2
	31.0	3.3	2.4
	79.3	1.4	3.6

modes) similar to those observed for other trivinyltin carboxylates [10, 12] and for trivinyltin isothiocyanate and iodide [11]. In the same region, the Raman spectrum shows a strong band at 518 cm^{-1}; similarly for other trivinyltin compounds [10 - 12] strong bands have been observed very close to 520 cm^{-1}. It is reasonable to attribute this band to an SnC_3 symmetric stretching vibration.

We believe that the close similarity between the IR and Raman spectra of trivinyltin formate and the related compounds mentioned is strong evidence that a non-planar configuration of the SnC_3 group also occurs in trivinyltin formate.

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