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ELECTROCHEMICAL PREPARATION OF TRIMETHYLTIN CARBOXYLATES

VALERIO PERUZZO, GUALTIERO PLAZZOGNA AND GIUSEPPE TAGLIAVINI
Institute of Analytical Chemistry, University of Padua (Italy)

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SUMMARY

Trimethyltin carboxylates have been prepared electrochemically. Trimethyltin ions are produced by reaction of tetramethyltin with mercury(I) ions electrolytically generated in methanol containing sodium carboxylate as supporting electrolyte. Trimethyltin formate, acetate, propionate and chloroacetate have been prepared: these compounds are appreciably soluble in solvents such as chloroform and carbon tetrachloride. Molecular weight determinations and IR spectra in solution show a low degree of association in the concentration range 3–30 mg/ml.

INTRODUCTION

We recently described[1] a new method for the preparation of a *soluble* form of trimethyltin acetate, based on the reaction of tetramethyltin and mercury(I) acetate in methanol at room temperature:

$$2\,(CH_3)_4Sn + Hg_2(OOCCH_3)_2 \rightarrow 2\,(CH_3)_3SnOOCCH_3 + Hg + (CH_3)_2Hg$$

Using the same method we also succeeded in preparing other R_3SnOAc compounds[2] (R = Et, Pr, Bu), as well as R_3PbOAc compounds (R = Me, Et). These results suggested to us a general way of preparing trimethyltin carboxylates electrochemically. Mercury(I) ions, electrolytically generated, react with tetramethyltin in methanol containing sodium carboxylate as supporting electrolyte.

Reactions seem to occur according to the following scheme:

$$Hg \rightarrow Hg_2^{2+} + 2e$$

$$Hg_2^{2+} + 2\,Me_4Sn \rightarrow 2\,Me_3Sn^+ + Hg + Me_2Hg$$

$$2\,Me_3Sn^+ + 2\,RCOO^- \rightarrow 2\,Me_3SnOOCR$$

Trimethyltin formate, acetate, chloroacetate and propionate have been prepared in this way.

EXPERIMENTAL

Tetramethyltin, purchased from KK Labs. Inc., New York, was used without further purification. Methanol and sodium carboxylates were reagent grade from

C. Erba (Milan) or Schuchardt (München). IR spectra were run on a Perkin–Elmer Model 621 or 257 equipped with NaCl or KBr optics, using the prepared trimethyltin carboxylates dissolved in chloroform or carbon tetrachloride, or dispersed in Nujol. The melting points were taken with a Büchi apparatus (Switzerland) using sealed capillaries. All melting points are uncorrected. Molecular weights were determined in chloroform or carbon tetrachloride with a Mechrolab Model 301A vapour phase osmometer.

Apparatus and general procedure

A conventional cell equipped with a mercury pool anode (5 cm diameter) and a platinum cathode, has been used. The anodic and cathodic compartments, separated by a sintered-glass disc, were filled with a measured volume of methanolic sodium carboxylate of known concentration. The requisite amount of tetramethyltin was also present in the anodic solution. Mercury(I) ions were generated by connecting the anodic and cathodic leads to an amperostat built by the electronic group of the Chemistry Department of Padua, and an appropriate constant current was passed for a known time. The anodic solution was then evaporated to leave a solid residue containing both trimethyltin and sodium carboxylate, and the trimethyltin carboxylate was isolated by sublimation. Dimethylmercury could be recovered from the distillate.

Preparation of trimethyltin formate, $Me_3SnOOCH$

A current of 25 mA was passed for about 15 h through a methanolic solution (150 ml) containing sodium formate (0.1 *M*) and tetramethyltin (2 ml). After the current was switched off, the anodic solution was distilled. It remained a solid residue, which was sublimed under vacuum to give trimethyltin formate (1.4 g), m.p. 146° with softening between 135–140° (lit.: softening point 135°; m.p. 148° for the *soluble* form[3], 151° for the *insoluble* form[4]). (Found: C, 22.93; H, 4.68. $C_4H_{10}O_2Sn$ calcd.: C, 23.00; H, 4.82%.)

Preparation of other trimethyltin carboxylates

Similarly, from a solution containing sodium acetate (0.1 *M*) but with passage of the current for 12 h, was obtained trimethyltin acetate (1.2 g), m.p. 193° (lit.: m.p. 191–192° for the *soluble* form[3], 196.5–197.5° for the *insoluble* form[5]). (Found: C, 26.85; H, 5.40. $C_5H_{12}O_2Sn$ calcd.: C, 26.96; H, 5.39%.)

From sodium chloroacetate, with passage of current for 16 h, was obtained trimethyltin chloroacetate (1.6 g), m.p. 140–142° (lit.[4] 148°). (Found: C, 23.05; H, 4.24; Cl, 13.85. $C_5H_{11}ClO_2Sn$ calcd.: C, 23.34; H, 4.30; Cl, 13.78%.)

Sodium propionate, with passage of current for 15 h, gave trimethyltin propionate (1.4 g), m.p. 134° (lit.[4], 136°). (Found: C, 30.40; H, 6.06. $C_6H_{14}O_2Sn$ calcd.: C, 30.42; H, 5.95%.)

Solubility and molecular weights in chloroform and carbon tetrachloride

The carboxylates prepared are appreciably soluble in chloroform and less soluble in carbon tetrachloride; the solubilities are sufficient to allow IR spectra measurements of these compounds in solution. Table 1 lists the solubilities at about 20°.

The molecular weights of the compounds were determined in chloroform and

TABLE 1

SOLUBILITIES OF THE TRIMETHYLTIN CARBOXYLATES AT ABOUT 20°

Compound	Solubility (mg/ml) in	
	$CHCl_3$	CCl_4
$Me_3SnOOCH$	320[a]	10
$Me_3SnOOCCH_3$	22[a]	3
$Me_3SnOOCC_2H_5$	100	7
$Me_3SnOOCCH_2Cl$	120	12

[a] From ref. 3: formate solubility 200 mg/ml, acetate solubility 50 mg/ml.

TABLE 2

MOLECULAR WEIGHTS OF TRIMETHYLTIN CARBOXYLATES IN CHLOROFORM AND CARBON TETRACHLORIDE

Compound	Solvent	Concn. (mg/ml)	Mol.wt. found	i[a]
$Me_3SnOOCH$	$CHCl_3$	30.00	322	1.54
		15.00	250	1.20
		7.50	240	1.15
		3.75	237	1.13
	CCl_4	4.60	744	3.60
		2.30	672	3.20
$Me_3SnOOCCH_3$	$CHCl_3$	17.76	280	1.26
		8.88	270	1.21
		4.44	262	1.17
		2.22	257	1.15
	CCl_4	2.80	448	2.01
		1.40	444	1.99
$Me_3SnOOCC_2H_5$	$CHCl_3$	34.24	297	1.25
		17.12	297	1.25
		8.56	295	1.24
		4.28	289	1.22
	CCl_4	10.00	327	1.38
		5.00	325	1.37
$Me_3SnOOCCH_2Cl$	$CHCl_3$	30.80	300	1.16
		15.40	265	1.03
		7.70	260	1.01
		3.85	257	1.00
	CCl_4	6.70	302	1.17
		3.35	289	1.12

[a] i=mol.wt. found/mol.wt. formal.

carbon tetrachloride solutions, and are shown in Table 2. Values of the ratio, i, of the observed molecular weight to the formular weight are also shown.

Infrared spectra

The IR spectra of the examined trimethyltin carboxylates in Nujol agree with

TABLE 3

IR DATA OF TRIMETHYLTIN CARBOXYLATES IN SOLUTION[a]

Compound	Solvent	Concn. (mg/ml)	ν_{as}(COO) (cm^{-1})	Other bands
$Me_3SnOOCH$	CCl_4	5, 10	1655 vs	1360 s
	$CHCl_3$	16	1650 s, 1590 m	1360 vw
		27	1650 s, 1590 s	1360 w
		80	1650 m, 1590 vs	1360 m
$Me_3SnOOCCH_3$	CCl_4	3	1650 s	1365 m, 1300 vs
	$CHCl_3$	20	1640 vs	1315 vs
$Me_3SnOOCC_2H_5$	CCl_4	5, 10	1655 vs, 1645 vs	1460 s, 1420 m, 1380 vs, 1335 s
$Me_3SnOOCCH_2Cl$	CCl_4	3, 7	1685 s, 1655 s	1335 vs

[a] Optics: NaCl, 1 mm in carbon tetrachloride and KBr, 0.1 mm in chloroform.

those previously reported[3-5]. Table 3 lists the IR frequencies of the compounds in carbon tetrachloride and chloroform. Assignments for the only asymmetric stretching vibrations of the carboxylic group have been made.

DISCUSSION

The electrochemical procedure permits the preparation of trimethyltin carboxylates soluble in solvents used in IR spectroscopy. The previous preparative method[4,5], based on the titration of the trimethyltin hydroxide with the appropriate carboxylic acid, gives products insoluble in such solvents. The melting points of the carboxylates prepared by the new procedure are lower than those previously reported[4-6].

From the molecular weight data it appears that the trimethyltin carboxylates are more associated in carbon tetrachloride than in chloroform. In the latter they

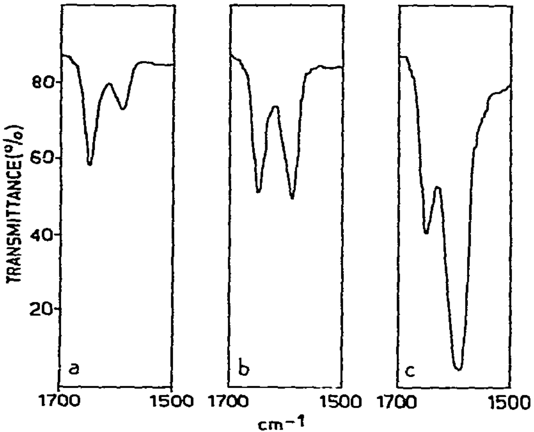

Fig. 1. IR spectra of trimethyltin formate in chloroform. (a) 16 mg/ml, (b) 27 mg/ml and (c) 80 mg/ml. Optics KBr, 0.1 mm.

are virtually monomeric in the concentration range 1–3 × 10^{-2} *M*. Noteworthy is the observation that trimethyltin formate is trimeric or tetrameric in carbon tetrachloride but monomeric or dimeric in chloroform.

From Table 2 it is clear that the degree of association of the formate in chloroform depends upon the concentration, and this is evident also in the IR spectra (*cf.* Fig. 1). This is in agreement with the observations of Simons and Graham[3], who suggested an equilibrium between associated and unassociated forms. We agree with those authors in assigning the absorption at 1650 cm^{-1} to the unassociated form and that at 1590 cm^{-1} to the associated form, but we note that trimethyltin formate in chloroform, at least up to a concentration of 0.15 *M*, is not present as a cyclic trimer, as was suggested[3].

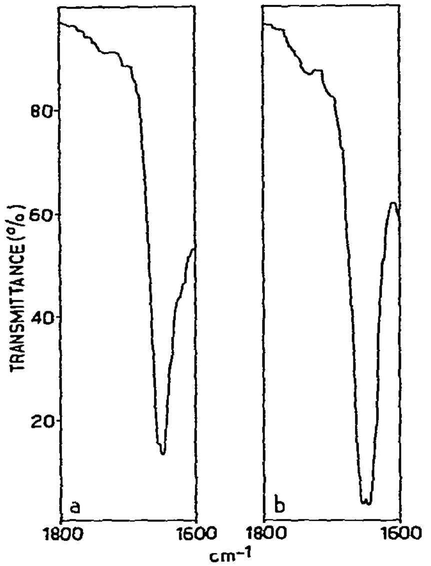

Fig. 2. IR spectra of trimethyltin propionate in carbon tetrachloride. (a) 5 mg/ml and (b) 10 mg/ml. Optics NaCl, 1 mm.

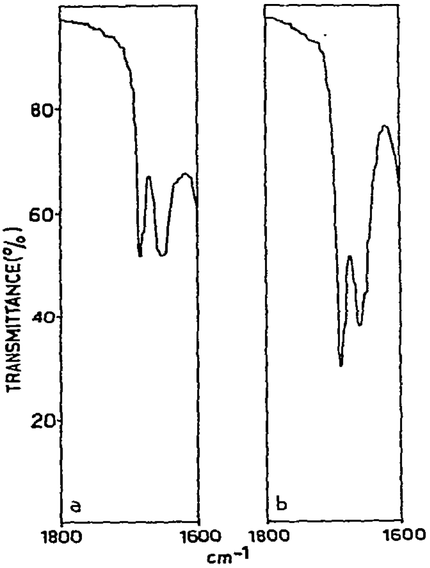

Fig. 3. IR spectra of trimethyltin chloroacetate in carbon tetrachloride. (a) 3 mg/ml and (b) 7 mg/ml. Optics NaCl, 1 mm.

The IR spectra of the propionate and chloroacetate in carbon tetrachloride (*cf.* Fig. 2 and 3 respectively) show two strong bands (those of the propionate are not well resolved) which can be assigned to the asymmetric stretching vibrations of the carboxylic groups in different environment. In these cases also we suggest that the absorption bands at lower frequency refer to associated and those at higher frequency to unassociated forms. Variation of the concentration of these compounds in carbon tetrachloride, within the solubility experimental limits, affects neither the molecular weights (*cf.* Table 2) nor the IR absorption bands (see Fig. 2 and 3), so it seems that equilibria between associated and unassociated forms are concentration independent in these cases. Comparisons of our results with those found by Van der Berghe *et al.*[7] and Van der Kerk and coworkers[8] (*cf.* Table 4), show that the frequency of the absorption band which we attribute to the unassociated form of trimethyltin carboxylates shifts to higher frequencies on increasing the electronegativity of the carboxylate R group.

TABLE 4

IR DATA OF $(CH_3)_3SnOOCR$ IN CCl_4

R[a]	$\nu_{as}(COO)$ (cm^{-1})	Ref.
CF_3	1720	7
CCl_3	1702	7
$CHCl_2$	1700	7
CH_2Cl	1690, 1685	This work
H	1655	This work
CH_3	1648, 1650	This work
C_2H_5	1655	This work
$C_{11}H_{23}$	1642	5

[a] The electronegativity decreases from top to bottom.

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