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Voltammetric Behaviour of Some 1,1,2,2-Tetraphenyl-1,2-diacyloxyditin Compounds in Aprotic Solvent

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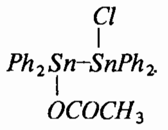
The voltammetric behaviour of hexaphenylditin and of some 1,1,2,2-tetraphenyl-1,2-diacyloxyditin compounds has been investigated in acetonitrile–benzene solution by cyclic voltammetry and controlled potential coulometry.

The results obtained by using platinum microelectrodes point out that hexaphenylditin is oxidized according to a two electron step leading to the formation of triphenyltin cations while the tetraphenyldiacyloxyditin compounds undergo a dissociation equilibrium in this medium with the release of acyloxy groups which can be oxidized according to a Kolbe-type reaction.

This fact suggested to us the electrochemical preparation of the asymmetric compound



$$Ph_2\overset{Cl}{\underset{OCOCH_3}{Sn}}-SnPh_2.$$

The voltammetric behaviour exhibited by 1,1,2,2-tetraphenyl-1,2-diacyloxyditin compounds on mercury microelectrodes was similar to that of Ph_3SnCl acetonitrile solutions; the reduction processes occurring have been discussed and the data confirmed the existence of a dissociation equilibrium.

Introduction

Previous studies on organoditin carboxylates of the general formula $Ph_4Sn_2(OCOR)_2$, R being CH_3, CH_2Cl, $CHCl_2$, CCl_3 and $C_6H_5CH_2$, carried out by IR [1], Raman [2], Mössbauer spectroscopy [3] and X-ray methods [4] have produced a body of evidence indicating that these compounds are monomeric in the solid state as well as in organic solvents, with intramolecular bidentate binding of the carboxylate groups between the two tin atoms.

Spectroscopic data support an increased Sn–Sn bond strength in the carboxylate derivatives compared with the hexaphenylditin, whereas tin-carboxylate bonds seem to be weak [2]. The increased strength of the tin–tin bond may be related to a lower reactivity of these compounds towards oxidizing agents [1, 5–8] in comparison with the analogous R_6Sn_2 compounds.

This state of affairs suggested to us the present investigation of the voltammetric behaviour of some 1,1,2,2-tetraphenyl-1,2-diacyloxyditin compounds in benzene–acetonitrile mixtures, the aim of which is to gain further information about the strength of the tin–tin and tin–carboxylate bonds and also to explore the existence of equilibria in aprotic media. It seems to us that electrochemical data could be useful for analytical determinations of this class of compounds and to establish procedures for electrochemical preparations.

Experimental

Chemicals and Reagents

Reagent grade acetonitrile (C. Erba) was purified by distilling repeatedly from phosphorus pentoxide [9] and stored on molecular sieves (3 Å).

Tetrabutylammonium perchlorate was prepared by neutralizing $HClO_4$ with tetrabutylammonium hydroxide (Fluka); the salt was twice cristallized from methanol and dried in a vacuum oven at 50 °C.

Reagent grade benzene was stored on sodium wire.

Acetonitrile–benzene (60/40 V/V) mixtures were chosen as solvent in view of the low solubility of the investigated compounds in pure acetonitrile. The 1,1,2,2-tetraphenyl-1,2-diacyloxyditin compounds $Ph_4Sn_2(OCOR)_2$, R being CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3 and $C_6H_5CH_2$, were prepared by the reaction of diphenyltin dihydride in ether and the appropriate acid according to the method previously reported [10].

Reagent grade hexaphenylditin (Fluka) was employed without further purification.

Apparatus and Procedure

The experiments were carried out at 20 °C, all potential values are referred to an aqueous SCE. The polarizing unit employed in the voltammetric experiments has been already described [11]. In the voltammetric tests a cell of suitable geometry was used [12].

An Amel mod. 557/SU potentiostat with an associated Amel Integrator mod. 558 was used in controlled potential electrolyses. An H shaped cell with cathodic and anodic compartments separated by a sintered glass disk was employed in large scale electrolyses. The working electrode in the coulometric tests was a mercury pool in cathodic investigations and a platinum gauze in the anodic ones.

In the voltammetric tests the working stationary microelectrode was a gold sphere freshly covered by a thin mercury layer or a platinum sphere.

Conductivity measurements were carried out in an oil thermostat at 20 °C with a LKB 3216 B Conductivity Bridge.

IR spectra were recorded on a Perkin–Elmer Model 457 equipped with CsI optics. The solutions were prepared by dissolving weighed amounts of the compounds in the degassed 0.1 *M* TBAP acetonitrile–benzene (60/40 V/V) mixture.

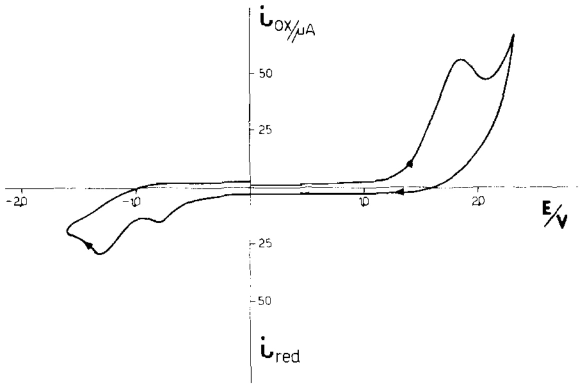


Figure 1. Cyclic voltammetric curve recorded with a platinum microelectrode on a 1.0 × 10^{-3} *M* $Ph_3Sn–SnPh_3$, 0.1 *M* TBAP $CH_3CN–C_6H_6$ soln. Scan rate 0.1 V s^{-1}.

Results

Fig. 1 shows a typical cyclic voltammogram recorded on a hexaphenylditin solution by using a platinum microelectrode.

A rounded anodic peak located at +1.80 V near to the solvent oxidation and two poorly defined associated cathodic peaks at about –0.80 V and –1.30 V respectively can be noted. The tests carried out at various hexaphenylditin concentrations gave peak currents linearly dependent on the concentration while the experiments carried out at various scan rates (20 mV s^{-1}–6 V s^{-1}) showed a slight upward curvature of the plots i_p *vs.* $v^{1/2}$, indicating that a weak adsorption of the reagent is operative.

Controlled potential coulometric tests carried out at +1.90 V on platinum microelectrodes indicated that two mol of electrons per mol of hexaphenylditin were involved. This result agrees with previous reports [1, 5, 8] and is consistent with the oxidative breaking of the tin–tin bond leading to the formation of two Ph_3Sn^+ cations which can be reduced at potential values of –0.80 V and –1.30 V on platinum electrodes. The cyclic voltammograms performed during the coulometric tests showed a progressive lowering of the anodic peak and conversely the increase of the two cathodic ones. The voltammetric behaviour exhibited by all the compounds studied, $Ph_4Sn_2(OCOR)_2$ (R = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3 and $C_6H_5CH_2$) was very similar.

In Fig. 2 is shown a typical cyclic voltammetric curve, relative to a tetraphenylditin diacetate solution, recorded on a platinum microelectrode. At variance with the hexaphenylditin case, the cathodic peaks located at –0.80 V and –1.30 V are both present when scanning directly in the cathodic direction and also after traversing the anodic peak now commencing at +1.0 V and exhibiting a rounded maximum at +1.80 V.

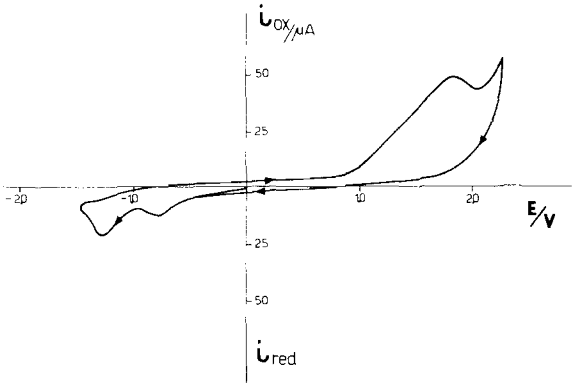


Figure 2. Cyclic voltammetric curve recorded with a platinum microelectrode on a 1.0 × 10^{-3} *M* tetraphenylditin diacetate, 0.1 *M* TBAP $CH_3CN–C_6H_6$ soln. Scan rate 0.1 V s^{-1}.

The voltammetric tests performed at various tetraphenylditin diacetate concentrations and scan rates indicated that also in this case a weak adsorption of the reagent is involved in the anodic process. The controlled potential coulometric tests carried out at +1.90 V on the tetraphenylditin diacetate solutions indicated that at variance with the hexaphenylditin case, only one electron per mol is involved in the anodic process.

The voltammetric tests performed during these electrolyses revealed that the cathodic peaks increased progressively in height while the anodic one disappeared at the end of the electrolysis.

Some electrolyses at +1.90 V have been carried out under a continuous flow of nitrogen. When the gas stream was collected in a trap containing a $Ba(OH)_2$ solution a turbidity appeared, indicating that CO_2 was produced in the anodic process.

The hypothesis that one acetate group is the oxidized species was tested by studying the voltammetric behaviour of a tetrabutylammonium acetate solution. This compound was prepared by reducing the acidic hydrogen of an acetic acid acetonitrile solution at −1.50 V at a platinum electrode. The resulting solution gave a voltammetric anodic picture very similar to that exhibited by a tetraphenylditin diacetate solution.

Controlled potential coulometric experiments carried out on the TBA–Acetate solution indicated that one electron per mol of acetate was used.

To confirm the above results a 5×10^{-3} *M* tetraphenylditin diacetate acetonitrile solution was exhaustively oxidized at +2.0 V with $NaClO_4$ as supporting electrolyte. At the end of the electrolysis a stoichiometric amount of NaCl was added; NaCl slowly dissolved and the solution was evaporated at reduced pressure. The metallorganic product was separated by extraction with chloroform, and the chloroform solution evaporated in its turn. The white solid product so obtained has been examined by IR spectrophotometry: the spectrum clearly indicated the existence of a new band at 330 cm^{-1} which is related to the Sn–Cl stretching frequency while the band of the carboxylic group appears to be shifted from 1530 [1] to 1640 cm^{-1}.

To confirm the presence of the chloride group in the product, this was treated with hot concentrated nitric acid and SnO_2 was filtered off. Qualitative tests clearly indicated again the presence of Cl^- ions.

To ascertain the nature of the acetonitrile solutions of tetraphenyldiacyloxyditin solutions some conductometric measurements have been performed. The data clearly indicated that considerable amounts of ionic species arising from dissociation equilibria were present. The amount of the dissociation was of the same order of magnitude as equimolar Ph_3SnCl acetonitrile solutions. The presence of cationic species in the solutions account for the cathodic peaks arising also by scanning directly in the cathodic direction.

To gain further information about the processes occurring in the cathodic potential range, some cyclic voltammograms have been obtained by using mercury microelectrodes. Fig. 3 shows a typical voltammetric curve relative to a tetraphenylditin diacetate solution. Three cathodic peaks (A, B and C) appear at potential values of −0.75 V, −1.45 V and −2.30 V respectively and two associated anodic ones (D and E).

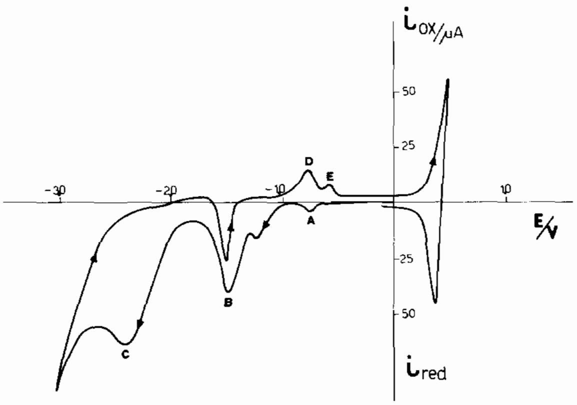


Figure 3. Cyclic voltammetric curve recorded with a mercury microclectrode on a 1.0×10^{-3} *M* tetraphenylditin diacetate, 0.1 *M* TBAP $CH_3CN–C_6H_6$ soln. Scan rate 0.1 V s^{-1}.

The peak A, small in height, is non diffusive in character and appears to be associated with the anodic peak E. Peak B exhibits a shoulder at about −1.30 V and its height appears to be controlled by an adsorption process involving the reagent species as demonstrated by the sharp cathodic peak appearing in the reverse scan. Cyclic voltammetric tests allowed us to associate the anodic peak D with the cathodic B. Finally the presence of the last rounded cathodic peak C conforms with the voltammetric behaviour exhibited by Ph_3SnCl solutions [13–15].

The voltammetric curves recorded using mercury microelectrodes were poorly reproducible and were affected by poisoning processes.

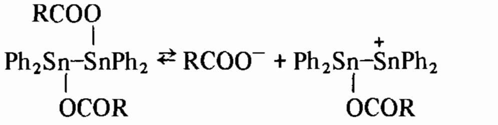
Discussion

The voltammetric and coulometric data indicate that hexaphenylditin is oxidized on platinum electrodes according to the following electrode reaction:

$$Ph_3Sn–SnPh_3 \rightarrow 2Ph_3Sn^+ + 2e^- \qquad (1)$$

The process involves the breaking of the tin–tin bond, in agreement with previous reports [1, 5–8].

The linear sweep voltammetric tests carried out at different scan rates indicated that the oxidation process is complicated by a weak adsorption of the reagent. On the contrary, the results obtained in the oxidation of the tetraphenylditin carboxylates indicate that the anodic process involves one carboxylate group arising from a dissociation equilibrium:



$$\underset{OCOR}{\overset{RCOO}{Ph_2Sn}}–SnPh_2 \rightleftarrows RCOO^- + \underset{OCOR}{Ph_2Sn}–\overset{+}{S}nPh_2 \qquad (2)$$

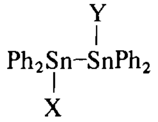
In fact all the voltammetric measurements indicated that ditincarboxylates are oxidized at the same potential value regardless of the changing nature of the carboxylate groups. In addition, the formation of CO_2 as an oxidation product, together with the similar voltammetric behaviour of the tetrabutylammonium acetate indicate that the anodic process occurring on platinum electrodes is a Kolbe-type reaction [16] summarized by the reaction scheme:

$$\begin{aligned} RCOO^- &\rightarrow RCOO\cdot_{ads} + e^- \\ RCOO\cdot_{ads} &\rightarrow R\cdot_{ads} + CO_2 \\ 2R\cdot_{ads} &\rightarrow R{-}R \end{aligned} \qquad (3)$$

The coulometric data, which indicate that only one mol of electrons per mol of ditincarboxylate is used, further support the reaction scheme suggested above.

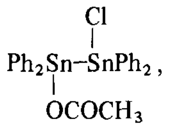
The existence of a dissociation equilibrium involving tetraphenylditin carboxylates in acetonitrile medium has been checked also by conductometric measurements; this finding agrees with previous IR data [2] which suggested an unusual weakness of the tin carboxylate bond in this series of compounds.

The results obtained suggested to us the feasiblity of electrochemical preparations of asymmetric compounds of the type



$$Ph_2\underset{\displaystyle X}{\overset{\displaystyle Y}{Sn}}{-}SnPh_2$$

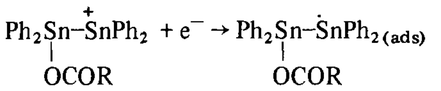
where X is an acyloxy group and Y can be an anionic group. In this connection we have prepared the compound



$$Ph_2\underset{\displaystyle OCOCH_3}{\overset{\displaystyle Cl}{Sn}}{-}SnPh_2,$$

whose IR spectrum showed the presence of a band at 330 cm^{-1} due to the Sn–Cl stretching mode [17] and a marked shift of the $\nu(COO)$ asymmetric stretching frequency of the carboxylic group from 1530 to 1640 cm^{-1}, *i.e.* near to the region of the ester-like vibrations. In our opinion, after the substitution of one acetate group the intramolecular bidentate bond between the two tin atoms no longer exists, due to the change in the molecular symmetry.

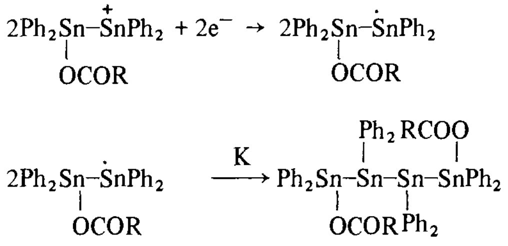
The cyclic voltammetric curves recorded on mercury microelectrodes were very similar to those exhibited by triphenyltin chloride solutions; this result, together with the conductometric data, further demonstrates the existence of dissociation equilibria leading to cationic species. On the basis of previously reported arguments [15], the cathodic voltammetric behaviour observed in the present investigation indicates that tetraphenylditin carboxylates also undergo two subsequent electrode reductions to a radical species and to an anionic form, respectively. By analogy with the voltammetric behaviour of triphenyltin chloride [15] the first reduction peak (A) (Fig. 3) may be attributed to the formation of the adsorbed radical according to:



$$Ph_2\underset{\displaystyle OCOR}{\overset{+}{Sn}}{-}SnPh_2 + e^- \rightarrow Ph_2\underset{\displaystyle OCOR}{Sn}{-}\dot{S}nPh_{2(ads)} \qquad (4)$$

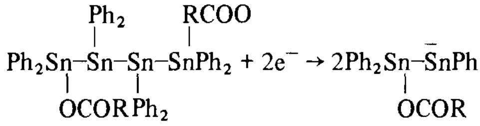
while the associated cathodic peak (E) is attributable to the oxidation of the adsorbed radical to the original cationic species.

At the second cathodic peak (B) the diffusing cations are reduced to the radical by a one electron step, followed by dimerization to an 1,1,2,2,3,3,4,4-octaphenyl-1,4-diacyloxytetratin compound according to the scheme:



$$\begin{aligned} 2Ph_2\underset{\displaystyle OCOR}{\overset{+}{Sn}}{-}SnPh_2 + 2e^- &\rightarrow 2Ph_2\underset{\displaystyle OCOR}{Sn}{-}\dot{S}nPh_2 \\ 2Ph_2\underset{\displaystyle OCOR}{Sn}{-}\dot{S}nPh_2 &\xrightarrow{K} Ph_2\underset{\displaystyle OCOR}{Sn}{-}\underset{\displaystyle Ph_2}{\overset{\displaystyle Ph_2}{Sn}}{-}\overset{\displaystyle RCOO}{Sn}{-}SnPh_2 \end{aligned} \qquad (5)$$

At the last cathodic peak (C) the previously formed tetratin compound is reduced by a two electron step to the anionic form according to the scheme:



$$Ph_2\underset{\displaystyle OCOR}{Sn}{-}\underset{\displaystyle Ph_2}{\overset{\displaystyle Ph_2}{Sn}}{-}\overset{\displaystyle RCOO}{Sn}{-}SnPh_2 + 2e^- \rightarrow 2Ph_2\underset{\displaystyle OCOR}{Sn}{-}\bar{S}nPh_2 \qquad (6)$$

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