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ELECTROCHEMICAL REDUCTION OF TRIPHENYLTIN CHLORIDE IN APROTIC MEDIUM

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Summary

The electrochemical reduction of triphenyltin chloride at mercury electrodes in acetonitrile solution has been studied by cyclic voltammetry, polarography and controlled potential coulometry. It has been shown that triphenyltin chloride can be reduced to hexaphenylditin by two different mechanisms, operating in different potential ranges, although only one cathodic wave is detectable in this potential region. At lower cathode potentials, Ph_3SnCl undergoes a one-electron reduction followed by the dimerization of the radical produced; at higher cathode potentials a two electron charge transfer step occurs and subsequently the triphenyltin anion formed reacts with the depolarizer. It is noted that the acid—base reaction:

$$Ph_3Sn^- + Ph_3Sn^+ \rightarrow Ph_3Sn{-}SnPh_3$$

is faster than the radical dimerization.

Introduction

The first polarographic studies on trialkyltin [1—3] and triphenyltin halides [4] were published twenty years ago; subsequently Dessy et al. [5] carried out a comprehensive study on the polarographic and voltammetric behaviour of chlorides of organometallic compounds of Group IVB elements, involving dimethoxyethane as solvent. More recently Fleet et al. [6—9] described a systematic electrochemical investigation of organotin compounds in water/ethanol mixtures. It should be noted that the results reported by Booth and Fleet [6] about the electrochemical behaviour of triphenyltin chloride disagree with those reported by Dessy et al. [5]; the former authors observed two reduction processes corresponding to the formation of the triphenyltin radical and the triphenyltin anion, respectively. They also reported that the $Ph_3Sn\cdot$ radical can dimerize in a side reaction to form the electro-inactive species $Ph_3Sn{-}SnPh_3$, while the anion Ph_3Sn^- undergoes protonation to give the triphenyltin hydride. In contrast, Dessy et al. [5] reported the appearance of two polarographic waves indicating that the mechanism at the first wave is a one electron reduction to give the $Ph_3Sn\cdot$ radical while in the second cathodic process hexaphenylditin is reduced. In view of this disagreement we have studied the voltammetric behaviour of triphenyltin chloride and of hexaphenylditin in acetonitrile.

Experimental

Chemicals and reagents. Reagent grade acetonitrile (Carlo Erba) was purified by repeated distillation from phosphorus pentoxide [10] and stored over molecular sieves (3 Å). Tetrabutylammonium perchlorate was prepared by neutralizing $HClO_4$ with tetrabutylammonium hydroxide (Ega Chemie) and was twice crystallized from methanol, then dried in a vacuum oven at 50°C.

Triphenyltin chloride, triphenyltin hydride, and hexaphenylditin were Reagent Grade Alfa chemicals.

Apparatus and procedure. The experiments were carried out at 20°C; all potentials are relative to an aqueous SCE. The polarizing unit employed both in polarographic and in voltammetric experiments has been described [11]. In the voltammetric experiments a cell of suitable geometry [12] was used and the working stationary microelectrode was a gold sphere freshly coated with a thin mercury layer. An AMEL Model 557/SU potentiostat with an associated AMEL Integrator Model 558 was used in controlled potential electrolyses; in these experiments an H-shaped cell, with anodic and cathodic compartments separated by a sintered glass disk was employed. The working electrode in the coulometric experiments was a mercury pool. Polarograms were obtained with a DME with mechanical control of drop time.

The solutions were prepared by dissolving weighed amounts of the compounds in the degassed 0.1 *M* TBAP acetonitrile.

Results

Fig. 1 shows a typical cyclic voltammetric curve for Ph_3SnCl, 0.1 *M* TBAP, CH_3CN solution with a stationary mercury microelectrode. The anodic peaks "F" and "G", detectable also by scanning in anodic direction from a starting potential of —0.5 V, have been attributed to the mercury oxidation in the presence of free chloride ions by comparison with authentic samples; this indicates that triphenyltin chloride must be dissociated to a significant extent in this solvent.

By scanning in the cathodic direction from the same starting potential (—0.5 V), three cathodic peaks can be observed. The first "A", very small in height and non diffusive in character, located at about —0.75 V, appears to be associated with the anodic peak "E". Its character must be attributed to adsorption of the reduction product, in agreement with the results obtained in ethanol/water by Booth and Fleet [6].

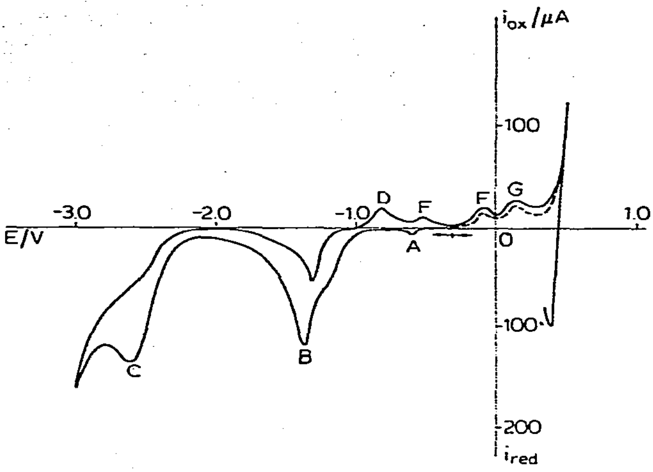


Fig. 1. Voltammetric curves recorded with a mercury microelectrode on a 3×10^{-3} *M* Ph_3SnCl, 0.1 *M* TBAP, CH_3CN soln.; starting potential —0.5 V both in the cathodic direction (———) and in the anodic direction (- - - - -). Scan rate 0.2 V s^{-1}.

The shape of the peak "B", located at about —1.40 V and exhibiting a shoulder at about —1.2 V, is attributable to an adsorption process occurring in this potential region involving the reagent species, as demonstrated by the sharp cathodic peak which appears also in the reverse scan [13] even if the cycle is reversed before traversing peak "C".

Cyclic tests permitted the anodic peak "D" to be associated with the cathodic "B".

Finally, the last cathodic peak "C" appearing in Fig. 1 at an E_p value of —2.60 V occurs at the same potential as that exhibited by hexaphenylditin in the same solvent.

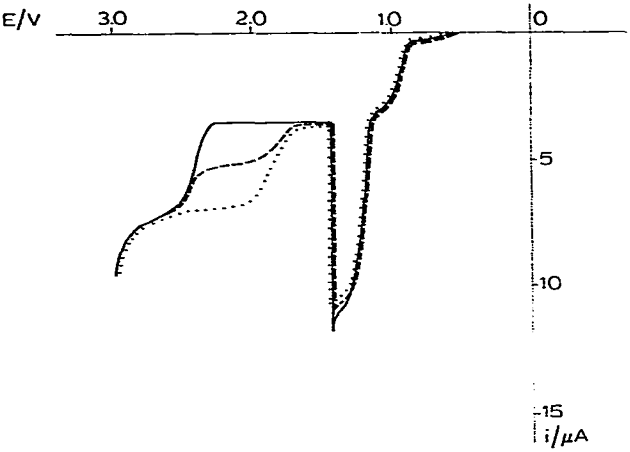


Fig. 2. Polarographic profiles recorded on: (———) 10^{-3} *M* Ph_3SnCl, 0.1 *M* TBAP, CH_3CN soln.; (- - - - -) 10^{-3} *M* Ph_3SnCl, 2×10^{-2} *M* PhOH, 0.1 *M* TBAP, CH_3CN soln.; (· · · · ·) 10^{-3} *M* Ph_3SnCl, 10^{-1} *M* PhOH, 0.1 *M* TBAP, CH_3CN soln.

Three cathodic processes were also observed by recording polarograms on Ph_3SnCl solutions (see Fig. 2, full line) located at potential values corresponding to the E_p reported above; it should be noted that the polarograms exhibit a maximum in the potential range in which the reduction of the adsorbed reagent was observed (peak "B" in Fig. 1).

Controlled potential coulometric experiments carried out at a potential value ranging from —1.0 to —2.0 V, corresponding with the second cathodic process, revealed that one mole of electrons per mole of triphenyltin chloride was always involved. Cyclic voltammetric tests performed at the end of these electrolyses indicated the presence of hexaphenylditin and chloride ions in the solution. In contrast, when the coulometric tests were performed at a potential value of —2.6 V (third cathodic process) a n_{e^-} value of two was obtained. Cyclic voltammetry gave a set of anodic peaks coincident with those exhibited by an electrolyzed hexaphenylditin solution to which chloride ions had been added. Fig. 3 presents a typical cyclic voltammetric curve recorded on a hexaphenylditin solution and shows that three anodic peaks are associated with the single reduction process of hexaphenylditin, "a"; the more anodic peaks "c" and "d" occur at the same potentials as peaks "D" and "E" in Fig. 1, indicating that the same species are involved. To identify the species oxidized at the peak "b" some experiments were carried out in the presence of phenol as proton donor. It was found that on increasing the phenol concentration the height of peak "b" decreased while a sharp anodic peak appeared at about —0.40 V, making the detection of peaks "c" and "d" more difficult. Conversely, the peak "b" was also observed in the presence of a proton donor in high concentration when the scan rate was substantially increased (about 10 V s^{-1}).

The sharp peak at about —0.40 V was identified as due to the oxidation of triphenyltin hydride by comparison with the voltammetric behaviour of a pure sample.

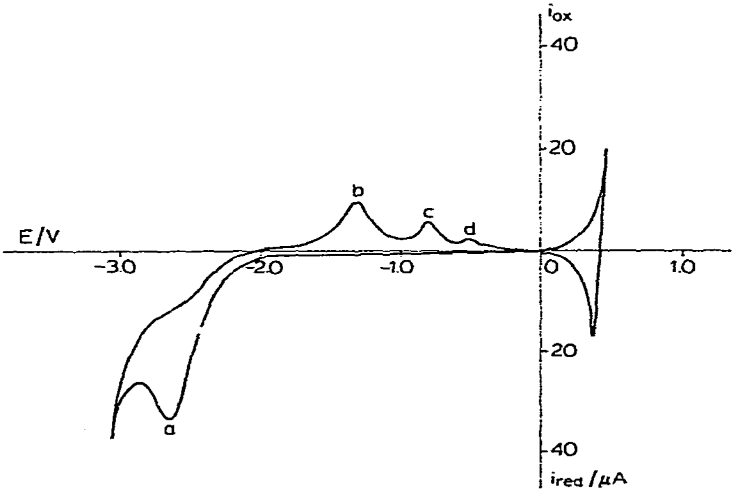


Fig. 3. Cyclic voltammetric curve recorded with a mercury microelectrode on a 8 × 10^{-4} M $Ph_3Sn—SnPh_3$, 0.1 M TBAP, CH_3CN soln. Scan rate 0.2 V s^{-1}.

These findings indicate that peak "b" can be attributed to the oxidation of the triphenyltin anion (Ph_3Sn^-); its lowering observed on addition of a proton donor is a result of Ph_3Sn^- protonation to give triphenyltin hydride (Ph_3SnH). This conclusion is supported by the n_e- value of 2 obtained in controlled potential coulometric experiments carried out under conditions of the Ph_3Sn—$SnPh_3$ reduction (peak "a" in Fig. 3).

In the reduction of triphenyltin chloride, hexaphenylditin can be formed either after a one electron cathodic step followed by dimerization of triphenyltin radical so formed or by an acid—base reaction between the Ph_3Sn^- anion, initially formed in a two electron cathodic step, and the Ph_3Sn^+ cation diffusing from the bulk of the solution towards the electrode surface. In order to clarify what mechanism is operative some experiments were carried out in presence of phenol as proton donor.

Polarograms recorded with Ph_3SnCl solutions to which phenol was progressively added showed the appearance of a new cathodic wave with an $E_{1/2}$ value of about —1.8 V; its height increased with the phenol concentration while the cathodic wave associated with the hexaphenylditin reduction simultaneously decreased to the same extent. When a large excess of phenol was present (ratio phenol/triphenyltinchloride about 100 : 1) the polarograms assumed the shape shown in Fig. 2 (dotted line). In controlled potential coulometric experiments the presence of phenol gave an n_e- value of 1 in the potential range —1 to —1.6 V (first reduction wave in Fig. 2, dotted line). In contrast, in the potential range —1.6 to —2.2 V (second wave in Fig. 2, dotted line) the n_e- value was higher than 1 and increased towards 2 with the phenol concentration. A value of 2 was always obtained by electrolyzing under conditions corresponding to the third wave of Fig. 2 (dotted line).

Table 1 summarizes the coulometric data obtained in presence of various $PhOH/Ph_3SnCl$ ratios.

Voltammetric tests performed after completion of the electrolyses at potentials ranging from —1.6 to —2.2 V revealed the presence of triphenyltin hydride in amounts which increased with the proton donor concentration. Moreover the coulombs used on further electrolyzing these solutions at —2.6 V, when added to those used in the previous electrolyses, always gave a n_e- value of 2 when referred to the moles of Ph_3SnCl used.

TABLE 1

COULOMETRIC DATA AT VARIOUS PHENOL/TRIPHENYLTIN CHLORIDE RATIOS

Phenol/triphenyltin chloride ratios	n_e- (±0.05)		
	$-1.0\ V < E < -1.6\ V$	$-1.6\ V < E < -2.2\ V$	$E = -2.6\ V$
0	1.0	1.0	2.0
10	1.0	1.2	2.0
20	1.0	1.4	2.0
50	1.0	1.6	2.0
100	1.0	1.8	2.0

Discussion

All our experimental results indicate that triphenyltin chloride undergoes, in the aprotic solvent used, two subsequent electrode reductions, leading to triphenyltin radical and triphenyltin anion respectively. However in aprotic media the formation of triphenyltin anion is not detectable owing to a very fast chemical reaction involving the depolarizer Ph_3SnCl following the charge transfer step; consequently the overall reduction process again requires one mole of electrons per mole of triphenyltin chloride. Thus the second cathodic wave, which exhibits a large maximum (see Fig. 2, full line), has to be attributed to an EC mechanism in which the charge transfer involves either a one-electron or a two-electron step, depending on the potential region. At potentials ranging from —1.0 to —1.6 V the electrode reaction leads to the triphenyltin radical, which subsequently dimerizes:

$$2\ Ph_3SnCl + 2\ e^- \rightarrow 2\ Ph_3Sn\cdot + 2\ Cl^- \quad (1)$$

$$2\ Ph_3Sn\cdot \xrightarrow{K_1} Ph_3Sn{-}SnPh_3 \quad (2)$$

$$2\ Ph_3SnCl + 2\ e^- \rightarrow Ph_3Sn{-}SnPh_3 + 2\ Cl^- \quad (3)$$

On the other hand in the potential range between —1.6 and —2.2 V triphenyltin chloride undergoes a two-electron reduction to give triphenyltin anion, which then reacts with the depolarizer as follows:

$$Ph_3SnCl + 2\ e^- \rightarrow Ph_3Sn^- + Cl^- \quad (4)$$

$$Ph_3Sn^- + Ph_3SnCl \xrightarrow{K_2} Ph_3Sn{-}SnPh_3 + Cl^- \quad (5)$$

$$2\ Ph_3SnCl + 2\ e^- \rightarrow Ph_3Sn{-}SnPh_3 + 2\ Cl^- \quad (6)$$

For the overall reactions 3 and 6, it will be seen that pathways 1, 2 and 4, 5 involve the same n_e- value provided that reaction 5 is very fast. A very fast acid—base reaction between Ph_3Sn^- and Ph_3Sn^+ was suggested by Dessy et al. [5] to account for the results obtained in the first cathodic process in their investigation.

The occurrence of two different electrochemical processes in a potential range in which only one cathodic wave can be detected, is confirmed by the results obtained in the experiments carried out in presence of phenol as proton donor. The cathodic wave coming at —1.6 V, which appears in the polarograms recorded under these experimental conditions (see Fig. 2, dashed and dotted line) and which increases with the phenol concentration, has to be attributed to an electrochemical process, involving a number of moles of electrons per mole of Ph_3SnCl greater than one, which become operative as a result of the removal of the triphenyltin anion by reaction with protons instead of with triphenyltin cations. That is, the sequence 4, 5 which operates in aprotic medium must be modified as follows in the presence of proton donors:

$$Ph_3SnCl + 2\ e^- \rightarrow Ph_3Sn^- + Cl^- \quad (7)$$

$$Ph_3Sn^- + PhOH \xrightarrow{K_3} Ph_3SnH + PhO^- \qquad (8)$$

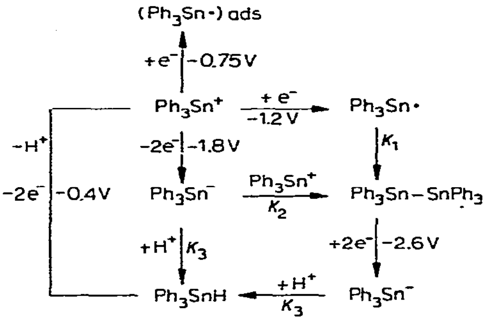
$$Ph_3SnCl + PhOH + 2\,e^- \rightarrow Ph_3SnH + Cl^- + PhO^- \qquad (9)$$

The detection of triphenyltin hydride at the end of the electrolyses performed at —2.0 V, in presence of phenol and also the coulometric data (see Table 1) substantiate our viewpoint. The coulometric data obtained at —2.0 V also indicate that reaction 5 is very fast, because, even when the ratio $PhOH/Ph_3SnCl$ is 100, n_{e^-} is less than 2 and hexaphenylditin is obtained to some extent, indicating that mechanisms 4, 5 and 7, 8 operate simultaneously.

The existence of the third cathodic wave (see Fig. 2, full line) appearing at the same potentials as those at which hexaphenylditin is reduced can be explained by taking into account the chemical reaction 5. Triphenyltin anion is evidently the final product of the overall electrochemical process, leading to a n_{e^-} value of 2, only in the potential range where hexaphenylditin newly formed at the electrode surface can be reduced. This third wave merges progressively into the second on increasing the proton donor concentration. The electro-inactivity of $Ph_3Sn—SnPh_3$ claimed by Booth and Fleet [6] is obviously a consequence of the short cathodic range available in a water/ethanol medium.

In conclusion, all the electrochemical processes occurring in Ph_3SnCl solutions can be summarized as shown in Scheme 1.

SCHEME 1



It should be noted that hexaphenylditin formation via the acid—base reaction is very much faster than via radical dimerization. This conclusion is based on the existence of an anodic peak associated with the cathodic peak corresponding to reaction 1, although no cathodic peak attributable to reduction 4 could be observed in absence of phenol even at very high potential scan rate (10 V s^{-1}).

Acknowledgement

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