Electrochemical study of triphenyltin piperidyl dithiocarbamate

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Abstract. The reduction of triphenyltin piperidyl dithiocarbamate in acetone has been investigated using d.c. polarography and cyclic voltammetry. Polarographic reduction yielded four well-defined waves, two of which were diffusion-controlled and two of which appear to represent adsorption processes. The cyclic voltammetric study yielded results in close agreement with the polarographic data. Results appear to indicate the release of the dithiocarbamate moiety, followed by reduction to form the triphenyltin radical, which undergoes dimerization, as well as reduction to the triphenyltin anion. For comparison, the polarographic reduction of triphenyltinchloride was investigated. A mechanism similar to that proposed by earlier authors for the polarographic behaviour of tributyltin oxide was found.

Keywords. Electrochemical behaviour; triphenyltin piperidyl dithiocarbamate; polarography; cyclic voltammetry.

1. Introduction

Apart from their importance as fungicides, catalysts and stabilisers, organotin compounds show complex, but interesting electrochemical behaviour. The earliest recorded work appears to be the polarographic reduction of diethyltinchloride by Riccoboni and Peboff (1949). Other early work on trialkyltin halides is that by Costa (1950), Toropova and Saikina (1953) and Saikina (1957).

More recently, Dessy *et al* (1966) reported an electrochemical study of organometallic derivatives of group IV elements, including diphenyltin and triphenyltin chlorides. These authors found that polarographically, Ph_3SnCl in dimethyloxyethane exhibited two well-defined waves at $-1\cdot6$ V and $-2\cdot9$ V versus the $Ag/AgClO_4$ reference electrode. The wave at $-1\cdot6$ V was attributed to the formation of hexaphenylditin ($Ph_3SnSnPh_3$), while that at $-2\cdot9$ V was regarded as due to the formation of Ph_3Sn^- directly without $Ph_3SnSnPh_3$ as an intermediate. More detailed investigations were reported by Fleet and Fouzder (1975) on trialkyl and triaryltin compounds. Booth and Fleet (1970) investigated the electrochemical reduction of triphenyltin acetate and triphenyltin hydroxide in 50% ethanol using a

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† For convenience, the more commonly used terminology of piperidyl dithiocarbamate is used throughout the paper, in place of (piperidine-1-carbodithioato) triphenyltin(1V).
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Hg pool anode and an SCE reference electrode. Three waves were obtained polarographically; however, a large maximum obscured the third wave. The second and third waves were said to be diffusion-controlled. It was claimed that waves I and II corresponded to the same electrode reaction and that wave I is an adsorption wave due to adsorption of the product from wave II onto the electrode surface. The mechanism suggested was the formation first of the triphenyltin radical ($Ph_3Sn\cdot$), which can undergo a further reduction in a 1-electron step to form Ph_3Sn However, it was claimed that the radical formed in the first reduction can undergo a side reaction to produce hexaphenylditin, which is adsorbed onto the electrode surface and corresponded to wave I.

In later work, Fleet and Fouzder (1975) re-investigated the electrochemistry of two organotin compounds – triphenyltin acetate and tributyltin oxide (TBTO). For the latter compound in 50% ethanol, using a three-electrode cell arrangement and an SCE reference electrode, four well-defined waves were found. The first and third waves were said to be typical of an adsorption process, while waves II and IV were ascribed to normal reduction waves. These results were confirmed by cyclic voltammetric studies. The mechanism proposed is that the second wave represents the reduction of the TBTO to yield the tributyltin radical, which is adsorbed onto the electrode surface to give an adsorption prewave (wave I). The fourth wave corresponds to the reduction of the tributyltin radical to give Bu_3Sn^-, while the third wave is thought to be due to adsorption of the electrolysis product onto the Hg surface. These results are not, therefore, in exact agreement with those in the earlier publication by Booth and Fleet (1970). Other workers, Devaud (1966) and Mehner *et al* (1968), as a result of polarographic investigations on triphenyltin halides, proposed different mechanisms.

In the course of work on the use of a series of organotindithiocarbamates as fungicides (Chandra *et al* 1987), the electrochemical behaviour was examined. This paper reports the electrochemical behaviour of one of the series, viz., triphenyltin piperidyl dithiocarbamate, which is representative of the series. As a preliminary, the polarographic behaviour of the triphenyltin chloride was examined and the results are reported in this paper.

2. Experimental

2.1 *Preparation of the organotin compounds*

Triphenyltin chloride was obtained from Alfa Products and used without further purification.

Triphenyltin piperidyl dithiocarbamate: The sodium salt of piperidyl dithiocarbamate was prepared using the method of Gleu and Schwab (1950) and Magee (1973). To synthesise the triphenyltin derivative, 100 ml of A.R. acetone were taken in a reaction vessel and the temperature lowered to $-30°C$. From two separate dropping funnels, an acetone solution of 1·95 g (0·005 mol) of triphenyltrichloride and an acetone solution of an equimolar quantity of sodium piperidyl dithiocarbamate were added to the reaction vessel at the same rate with constant stirring over a period of $1-1\frac{1}{2}$ h. Stirring was continued for a further 2 h at $-30°C$. The mixture was quickly filtered, while still cold (3–5 min). The filtrate was placed

under vacuum ($\approx$ 2 torr) and the acetone removed, while maintaining the temperature between 0 and 10°C. The product remaining was dissolved in sodium-dried diethylether and recrystallised by slow air evaporation. The white crystals obtained were collected and dried in vacuum. Analytical data: C 56·65% (56·58); H 4·73% (4·91); N 2·70% (2·75). Calculated values in parentheses.

2.2 *Apparatus*

All the electrochemical work was carried out on an AMEL 471 Multipolarographic Analyser jacketted to allow thermostatting at $25 \pm 0·2$°C. A three-electrode system was used in the closest and most favourable electrode configuration to minimize uncompensated i.r. potential. For the polarographic work, a dropping mercury electrode (DME) and a 15 cm coiled platinum wire served as the working electrode and the counter electrode, respectively. As reference electrode, the $Ag/AgClO_4$ (0·02 M), $NaClO_4$ (0·40 M) system was chosen. A silver spiral immersed in a solution of 0·02 M $AgClO_4$ and saturated with $NaClO_4$ was separated from a salt bridge (0·40 M $NaClO_4$) by means of a No. 2 sintered glass disc. The salt bridge in turn was separated from the solution under study by means of a No. 2 sintered glass disc.

2.3 *Solvent system*

A number of solvent systems were examined. These included DMSO, propylene carbonate, 50% ethanol and acetone. The latter was found to be the most suitable solvent electrochemically and for compound solubility. All subsequent work was therefore carried out in this solvent. The supporting electrolyte was $NaClO_4$ dissolved in acetone.

3. Results and discussion

3.1 *D.C. polarography*

Triphenyltin chloride (Ph_3SnCl): In acetone, Ph_3SnCl gives five waves, Wave I, a pre-wave, had all the characteristics of an anodic wave. Wave III was obscured by a large maximum, which was difficult to remove with surface active agent, Triton-X-100. Waves II and IV also tended to produce small maxima, which were easily removed by Triton-X-100. Because of the proximity of the anodic prewave 'I and wave I, it was not possible to determine the behaviour of the latter wave with changing concentration etc. Up to a concentration of 5×10^{-4} M, wave II showed dependence on concentration, after which the wave height reached a limiting value. Waves III and IV were also dependent on concentration over a wide range of concentration.

For waves II and IV, limiting current/$h^{\frac{1}{2}}$ was constant indicating diffusion control. Because of the proximity of wave I to wave 'I and the persistent maximum on wave III, it was not possible to determine accurate $i_l/h^{\frac{1}{2}}$ values for these waves. For waves II and IV, half-wave potentials were constant over a range of concentration. The number of electrons transferred in the electrode processes for
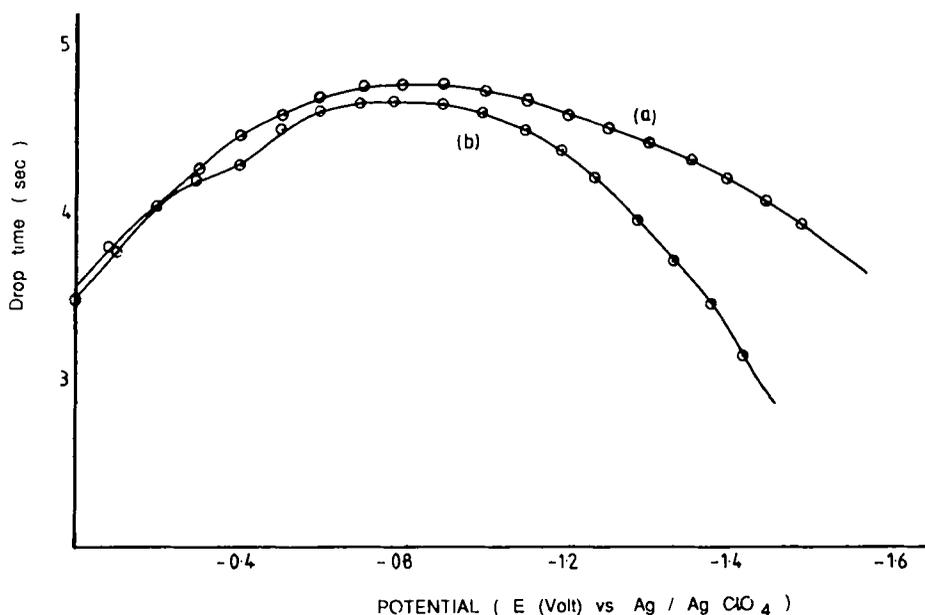
Figure 1. Electrocapillary curve for (a) 0·4 M NaClO$_4$ and (b) Ph$_3$SnCl (1 mM) in

these waves was determined and found to be wave II, $n = 1$, and wave IV, $n = 1$, respectively.

The electrocapillary (drop-time) curves for Ph$_3$SnCl and the solvent-support system are shown in figure 1. The electrocapillary zero occurs at $-0·8$ V. Wave I for Ph$_3$SnCl occurs in the region $-0·3$ to $-0·4$ V: reduction, therefore, takes place at a negatively-charged electrode. Further, the drop-time curve for Ph$_3$SnCl indicates a lowering of surface tension in the potential regions $-0·3$ to $-0·5$ V and $-1·6$ V. It would appear that waves I and III are therefore due to absorption processes. Based on these results, a mechanism similar to that proposed by Fleet and Fouzder (1975), who investigated the polarography and cyclic voltammetry of *bis*(tributyltin)oxide in 50% ethanol, can be assumed. Thus, wave I represents an adsorption wave, wave II, a normal reduction wave corresponding to the reduction of the triphenyltin cation, in a 1-electron transfer process, to the free radical (Ph$_3$Sn·). Combination of the free radicals to form a dimer hexaphenylditin, which is adsorbed on the Hg surface could account for the adsorption wave III. The formation of hexaalkyl/hexaarylditin in the electroreduction of tri-substituted tin compounds has been confirmed (Devaud 1966). Finally, wave IV could represent a further reduction of the free radical (Ph$_3$Sn·), to the anodic species Ph$_3$Sn$^-$.

3.2   *The electrochemical behaviour of triphenyltin piperidyl dithiocarbamate*

3.2a   *D.C. polarography*: The piperidyl derivative of triphenyltin dithiocarbamate is of sufficient solubility in acetone for this solvent to act as a suitable system for the investigation. The same solvent-support system was used for Ph$_3$SnCl and the same reference electrode, viz., Ag/AgClO$_4$. Polarograms showed five well-defined waves labelled 'I, I, II, III, IV (figure 3), where 'I represent an anodic prewave. E values for the various waves were $\approx -0·29$ (wave I), $-0·7$ (wave II), -095 (wave III) and $-1·68$ V (wave IV).
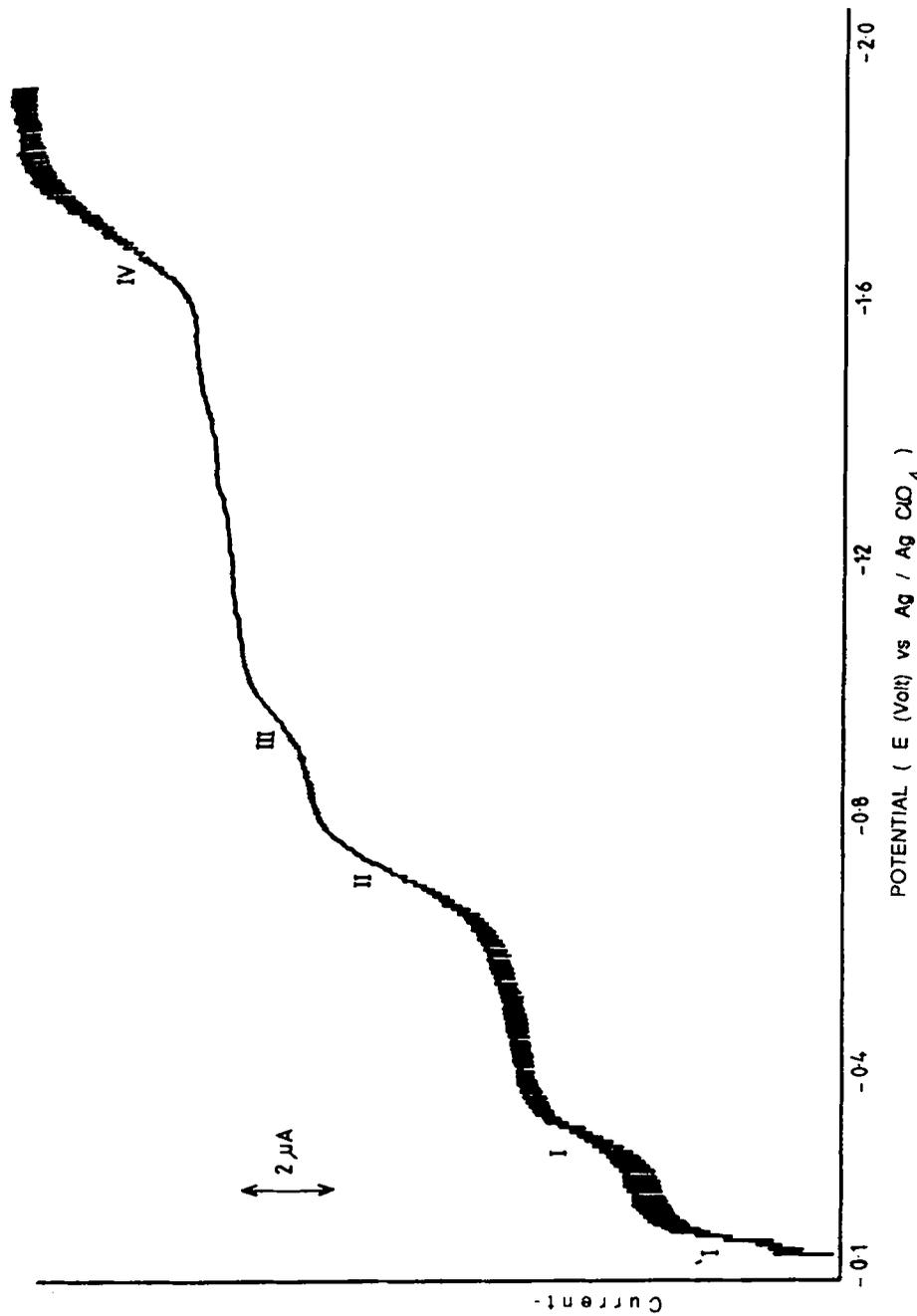
Figure 2. Polarogram of $Ph_3Sn(dtc)(pip)$ (1 mM) in acetone, 0·40 M $NaClO_4$. $T = 25°C$; $h = 68·0$ cm. 0·1% Triton X−100 added.

Up to a concentration of 1 mM, $E_{\frac{1}{2}}$ values for all waves were constant. Further, all waves showed a concentration-wave height dependence. For waves II and IV, limiting current/$h_{\frac{1}{2}}$ was constant, indicating diffusion control. On the other hand, limiting current/$h_{\frac{1}{2}}^{t}$ was not constant for waves I and III indicating departure from diffusion control and suggesting adsorption processes. The number of electrons transferred in the reduction processes producing wave II and wave IV was determined and found to be $n = 1$ and $n = 2$, respectively. The drop-time curve for $Ph_3Sndtc(pip)$ and the solvent-support system are shown in figure 3 and indicates a lowering of surface tension in the potential region $-0\cdot3$ to $-0\cdot5$ and $-0\cdot7$ to $-0\cdot9$ V, which indicates adsorption processes in these regions, thus supporting the polarographic data.

3.2b *Cyclic voltammetry*: The cyclic voltammogram of $Ph_3Sndtc(pip)$ in acetone at a scan rate of 200 mV/sec with $Ag/AgClO_4$ as reference electrode is shown in figure 4. The voltammogram is complex and consists of twelve peaks, seven cathodic and five anodic. The cathodic waves are labelled 'I$_c$, I$_c$, I$_c'$, II$_c$, III$_c$, III$_c'$ and IV$_c$, where waves denoted by superscripts define the position of additional waves with respect to what are considered main waves. Corresponding anodic waves are denoted by a subscript 'a' e.g., I$_a$.

Waves I$_c$ and I$_a$ are due to the adsorption/desorption of a product of the reaction or the compound and appear to correspond to polarographic wave I.

Wave II$_c$: In agreement with the results of polarography, cyclic voltammetry indicates that this wave is a quasi-reversible or reversible, diffusion-controlled
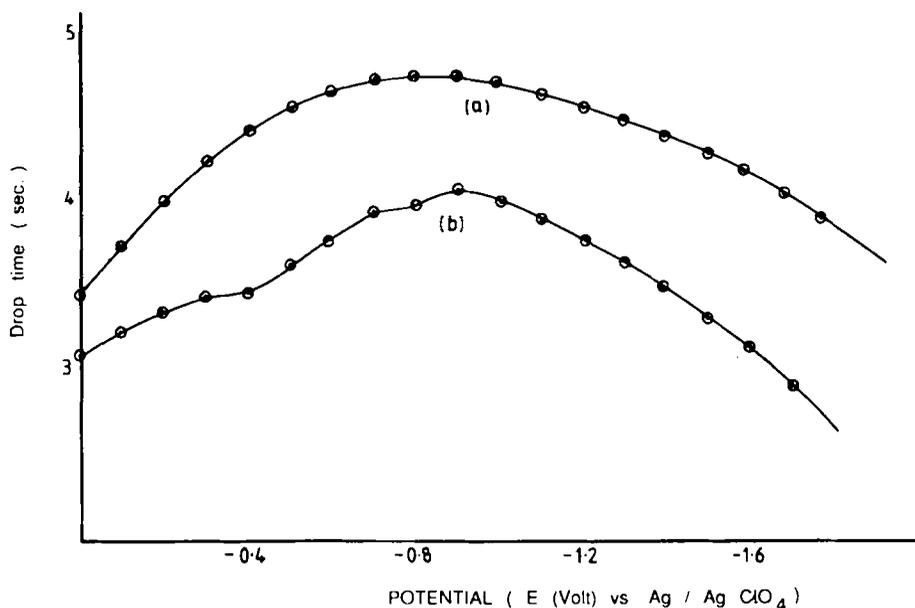

Figure 3. Electrocapillary curve for (a) $0\cdot40$ M $NaClO_4$, (b) $Ph_3Sn(dtc)(pip)$ ($1\cdot00$ mM) in acetone. $T = 25°C$; $h = 68\cdot0$ cm.
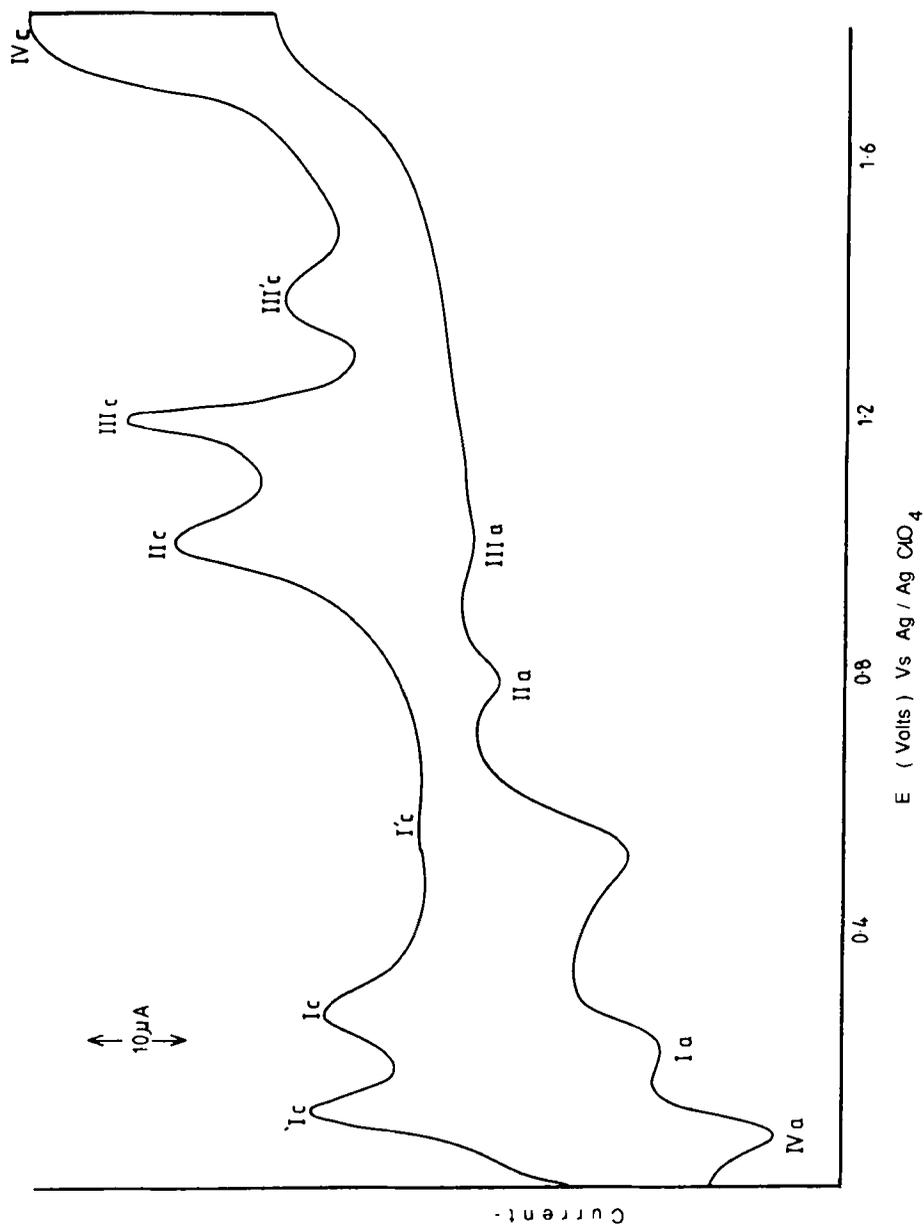
Figure 4. Cyclic voltammogram of **Ph₃Sn(dtc)(pip)** (1·00 mM) in acetone with 0·40 M NaClO₄ and 0·1% Triton X − 100. *T* = 25°C.
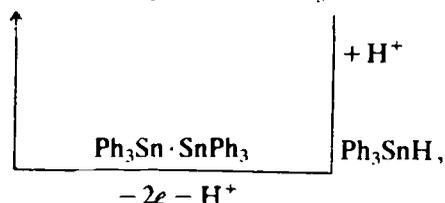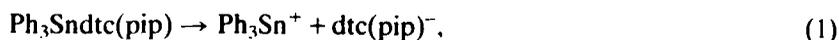
process. This is shown by $\Delta Ep[Ep_a\text{-}Ep_c]$ which is·much greater than expected for a reversible process and increases with increasing scan rate. Diffusion control is indicated by the constancy of ip_c (plane)/$v^{\frac{1}{2}}$ over a wide range of scan rates. An increase of ip_a/ip_c with increasing scan rate also indicates increasing irreversibility. Wave II_a is the corresponding anodic wave.

Wave III_c: This has the characteristics of an adsorption wave. ip_c(plane)$v^{\frac{1}{2}}$ is dependent on scan rate. This adsorption wave is produced by adsorption of the dimer hexaphenylditin resulting from the combination of $Ph_3Sn\cdot$ radicals. Wave III_a is the peak due to the desorption of the species.
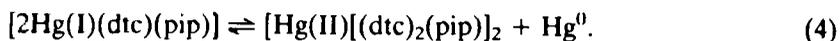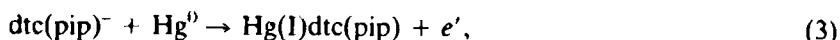
Wave IV_c: This was found to be a normal reduction wave. ip_c(plane)$v^{\frac{1}{2}}$ was constant over a range of scan rates. It represents the reduction of the free radical, $Ph_3Sn\cdot$ to the anion Ph_3Sn^-. It is possible that the wave labelled IV_a represent the oxidation of Ph_3Sn^- back to Ph_3Sn^+

Waves I_c' *and* III_c': In all the voltammograms run, these two peaks were present. I_c' occurs in the region around -0.55 V and III_c' around -1.37 volts. Earlier work in this laboratory by Ahmad & Magee (1979) on the electrochemical behaviour of metal dithiocarbamates showed that waves of this type and in the same regions were due to the release of dithiocarbamate ligand from the metal complex. On this basis, the wave I_c' could be due to the reduction of Hg(I)-[dtc(pip)], Hg(I)[dtc(pip)] + e' → Hg° + dtc(pip), following a chemical reaction Hg(II)[(dtc)$_2$pip]$_2$ + Hg° → 2 Hg(I)[(dtc)(pip)]. Wave III_c' may then be due to the fact that the reaction Hg(II)[(dtgc)pip]$_2$ + Hg° → 2[Hgh(I)(dtc)(pip)] does not go to completion, leaving part of the Hg(II) complex to be reduced at the more negative potential, i.e., -1.37 V. As there is no free ligand present in the original solution, the free ligand must have arisen by release from the $Ph_3Sn(dtc)pip$ complex.

From the results obtained using polarography and cyclic voltammetry, it would appear that the mechanism of reduction might be proposed as follows:

$$Ph_3Sndtc(pip) \rightarrow Ph_3Sn^+ + dtc(pip)^-,\tag{1}$$

$$Ph_3Sn^+ \underset{\rightleftharpoons}{\xrightarrow{+e}} Ph_3Sn\cdot \underset{\rightleftharpoons}{\xrightarrow{+e}} Ph_3Sn^-$$

$$\begin{array}{c} \uparrow \qquad\qquad\qquad\qquad\qquad +H^+ \\ |\qquad\qquad\qquad\qquad\qquad\qquad| \\ |\qquad Ph_3Sn\cdot SnPh_3 \qquad Ph_3SnH, \\ \overline{\qquad -2e - H^+ \qquad} \end{array}$$

$$\tag{2}$$

$$dtc(pip)^- + Hg^0 \rightarrow Hg(I)dtc(pip) + e',\tag{3}$$

$$[2Hg(I)(dtc)(pip)] \rightleftharpoons [Hg(II)[(dtc)_2(pip)]_2 + Hg^0.\tag{4}$$

The presence of the dithiocarbamate moiety as part of the complex makes the reduction of $Ph_3Sndtc(pip)$ more complicated than the reduction of Ph_3SnCl. It

would appear that the difference in the mechanism of reduction of the two species is due to the release of the dithiocarbamate ligand (1), which then is able to react with mercury (3). Following this chemical reacion (4), the resulting product Hg(I)dtc(pip) is reduced. However, it is possible that the chemical reaction does not go to completion leaving the unchanged portion, i.e., Hg(II)[dtcpip]$_2$ to be reduced at the more negative potential.

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