

## POLAROGRAPHY OF DIPHENYLTHALLIUM(III) CATION IN AQUEOUS SOLUTION

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Thallium forms ionic organocompounds of the type  $R_2TlX$  where R is an alkyl or aryl group and X is a halide, sulphate, cyanide, nitrate or other anion (1). These compounds are stable and many are water soluble. Dialkyl- and diarylthallium(III) cations are electroreducible at the dropping mercury electrode.

Costa (2) studied the polarographic reduction of dialkylthallium bromides,  $R_2TlBr$ , in aqueous propanol solution where R is an ethyl, propyl or butyl group. He reported that these species are reducible to lower oxidation states of thallium and ultimately to thallium amalgam. He proposed a mechanism involving the formation of a Tl-Tl bond but did not attempt to identify the reaction products. We have examined in detail the mechanism of the polarographic reduction of the diphenylthallium(III) cation and have established the decay schemes for the subvalent organothallium radicals formed at the dropping mercury electrode.

**Experimental.** Diphenylthallium bromide was prepared by the Grignard synthesis (3). Diphenylthallium fluoride was prepared by reaction of commercial diphenylthallium iodide (Metallomer Laboratories, Fitchburg, Mass.) and silver fluoride (4). The electrochemical behavior of diphenylthallium bromide and diphenylthallium fluoride is identical. Triton X-100 (Rohm and Haas) was used as received. The supporting electrolyte (pH = 6.20) was prepared from reagent grade potassium dihydrogen phosphate and sodium hydroxide. All solutions were prepared using distilled water and contained 0.001% Triton X-100 as a maximum suppressor.

Polarograms were made on solutions in a water-jacketed cell maintained at  $25.0 \pm 0.1^\circ C$ . Potentials are reported versus the saturated calomel electrode.

**Results.** The mechanism of the polarographic reduction of aqueous solutions of diphenylthallium(III) cation,  $(C_6H_5)_2Tl^+$ , at the dropping mercury electrode is concentration dependent. At low concentrations,  $0.1 \times 10^{-3} M$  to  $0.5 \times 10^{-3} M$ , three irreversible, diffusion-controlled, one-electron waves are observed. At high concentrations, above  $0.5 \times 10^{-3} M$ , two irreversible, diffusion-controlled, one-electron waves are observed.

A typical low concentration polarogram ( $0.1 \times 10^{-3} M (C_6H_5)_2Tl^+$ ) is shown in Figure 1. On the ascending portion of the first wave, the current, as a function of time, does not increase monotonically, but instead reaches a maximum value during the lifetime of the drop and then decreases as the drop continues to grow. The current on the ascending portion of the second wave is also non-monotonic. The shape of the current-time curve as a function of potential is currently under investigation, and apparently is related to the adsorption of intermediate species at the electrode surface. Controlled potential electrolysis ( $0.1 \times 10^{-3} M (C_6H_5)_2Tl^+$ ) at a mercury pool cathode at a potential corresponding to the first diffusion-current plateau yields diphenylmercury. That the compound formed (M.P.  $125^\circ C$ ) is diphenylmercury was verified by comparison of its infrared spectrum with that of an authentic sample of diphenylmercury. Electrolysis at a potential corresponding to the second diffusion-current plateau was not attempted because of the ill-defined

nature of the wave. No diphenylmercury is formed during electrolysis at a potential on the third diffusion-current plateau.

A typical high concentration polarogram ( $1.0 \times 10^{-3}M (C_6H_5)_2Tl^+$ ) is shown in Figure 2. The first wave is preceded by an adsorption wave. As in the low concentration case, the current, as a function of time, does not increase monotonically. A non diffusion-controlled third wave is observed at potentials more cathodic than  $\tau 1.3$  V. An electrocapillary curve of a solution ( $1.0 \times 10^{-3}M (C_6H_5)_2Tl^+$ ) is shown in Figure 3. Depressions corresponding to adsorption of the parent cation and of both intermediate species at the electrode surface are observed. The more pronounced depressions in the regions of stability of the intermediate species are indicative of the stronger adsorption of these species than of the parent cation. Controlled potential electrolysis at potentials corresponding to both the first and second diffusion-current plateaus yields diphenylmercury.

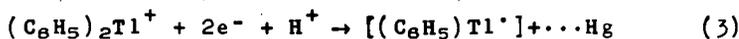
Conclusions. The following reaction scheme is proposed to account for the concentration dependence of the polarographic reduction of diphenylthallium(III) cation. At low concentrations the first electron transfer yields an adsorbed diphenylthallium(II) radical as given by Equation 1.



Transmetalation with the mercury electrode yields diphenylmercury as in Equation 2.



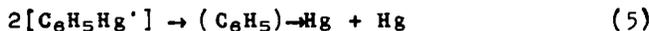
The second electron transfer yields an adsorbed phenylthallium(I) radical as shown in Equation 3.



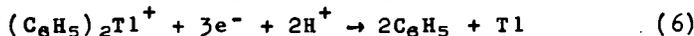
Transmetalation with the mercury electrode yields a phenylmercury radical as in Equation 4.



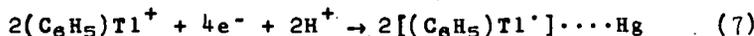
Rapid disproportionation of the mercury radical yields diphenylmercury as in Equation 5.



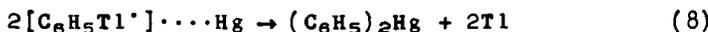
The third electron transfer corresponds to Equation 6.



At high concentrations the first electron transfer proceeds as in Equations 1 and 2. The second electron transfer is given by Equation 7.



Although the stoichiometry is the same in both the low and high concentration cases, the structures of the intermediates are different as shown below. Transmetalation of the phenylthallium radical with the mercury electrode leads directly to diphenylmercury as in Equation 8.



At both low and high concentrations the first reduction proceeds via formation of a radical adsorbed onto the mercury surface followed by transmetalation of the radical. Structure I represents a likely intermediate.



At low concentrations the adsorbed monophenylthallium(I) radicals formed during the second electron transfer are so far apart that each radical reacts with a different mercury atom as shown schematically in structure II.



At high concentrations the adsorbed monophenylthallium(I) radicals are so close together that two radicals can react with the same mercury atom as in structure III.



The third electron transfer at low concentrations (Equation 6) corresponds to reduction of an adsorbed monophenylthallium(I) or phenylmercuric radical to thallium and benzene or mercury and benzene. At high concentrations the direct reaction between two monophenylthallium(I) radicals and a single mercury atom (Equation 8, structure III) removes monophenylthallium(I) radicals so rapidly that further reduction does not occur. If the electroactive species is a phenylmercuric radical, a similar argument applies. Decay of intermediate structure III proceeds directly to diphenylmercury leaving no phenylmercuric radicals available for further reduction.

The transmetalation of diphenylthallium(III) bromide with mercury has been observed in a non-electrochemical system by Gilman and Jones (5). They reported an excellent yield (90%) of diphenylmercury after refluxing eight hours. There have been several reports in the literature of systems involving transmetalations of organometallic compounds with mercury during electrochemical reductions. Morris, McKinney and Woodbury (6) reported arylation of the mercury electrode with aqueous solutions of tetraphenylantimony(V) cation to yield diphenylmercury. Recently Dessy and coworkers (7) studied the electrochemical behavior of triphenyllead acetate and diphenyllead diacetate in dimethoxyethane and reported arylation of the mercury electrode by products of the electroreductions to yield diphenylmercury in both cases.

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CAPTIONS FOR FIGURES

- Figure 1. Polarogram of  $0.10 \times 10^{-3}$  F  $(C_6H_5)_2Tl^+$  in 0.05F  $(H_2PO_4^- + HPO_4^{2-})$ . 0.001% Triton X-100 present as maximum suppressor.
- Figure 2. Polarogram of  $1.00 \times 10^{-3}$  F  $(C_6Y_5)_2Tl^+$  in 0.05F  $(H_2PO_4^- + HPO_4^{2-})$ . 0.001% Triton X-100 present as maximum suppressor.
- Figure 3. Drop time dependence on potential; capillary flow rate = 2.70 mg/sec.
- A. 0.05 F  $(H_2PO_4^- + HPO_4^{2-})$
  - B. 0.05 F  $(H_2PO_4^- + HPO_4^{2-})$  containing 0.001% Triton X-100.
  - C.  $1.00 \times 10^{-3}$  F  $(C_6H_5)_2Tl^+$  in 0.05 F  $(H_2PO_4^- + HPO_4^{2-})$ .
  - D.  $1.00 \times 10^{-3}$  F  $(C_6H_5)_2Tl^+$  in 0.05 F  $(H_2PO_4^- + HPO_4^{2-})$  containing 0.001% Triton X-100.

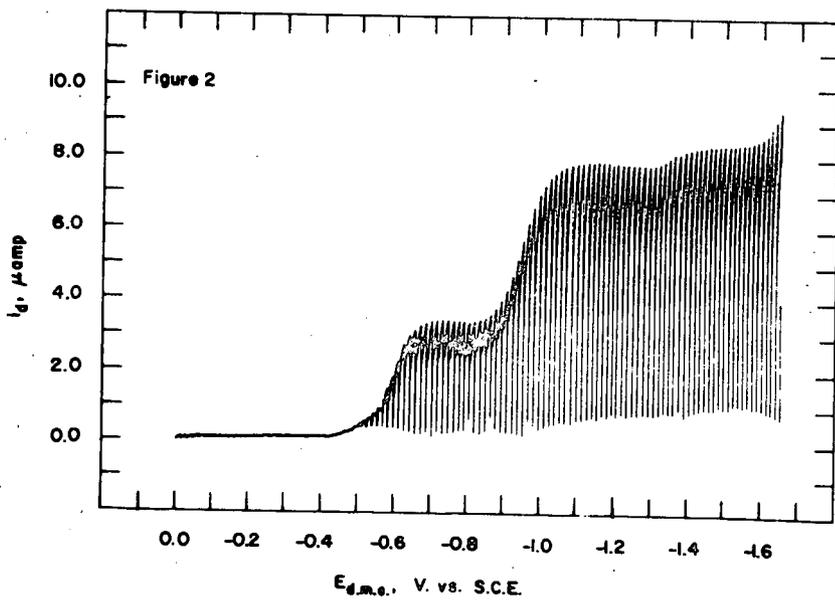
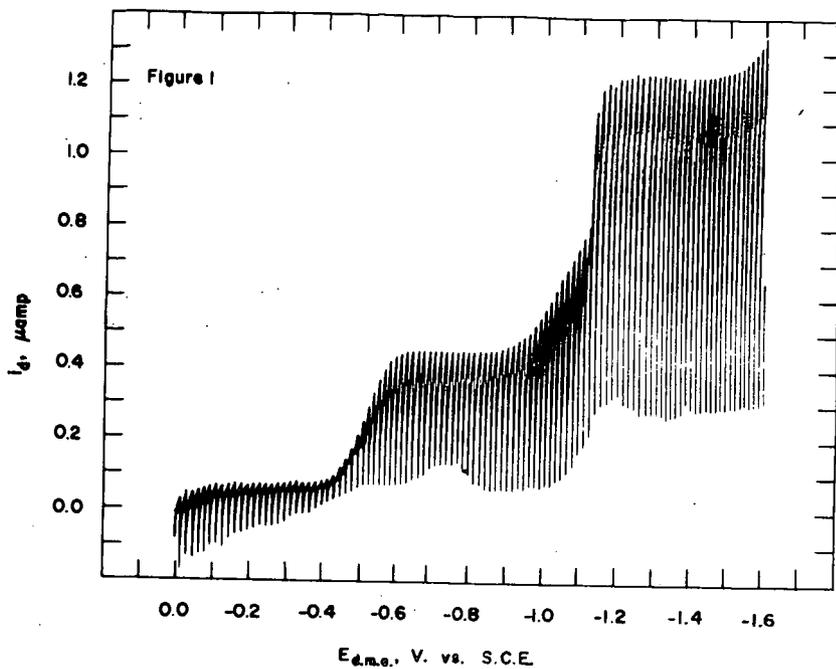


Figure 3

