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EXCHANGE OF ORGANOMERCURY COMPOUNDS WITH MERCURY METAL

V*. THE INTERACTION OF DIETHYLTHALLIUM CHLORIDE WITH MERCURY

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Summary

The galvanostatic method has been employed to study the interaction of diethylthallium cation with mercury metal. It has been shown that "organic calomel", Et_2Hg_2, is formed on the mercury surface, probably, via the formation of an intermediate diorganodimetallic cation, $EtHgTl^+Et$.

Introduction

It has been shown recently [2,3] that aryl organometallic compounds in which the metal has an *sp* (R_2Hg, R_2Cd, R_2Zn, R_2Mg, R_2Tl^+) or an sp^2 (R_3Bi) configuration are capable of reacting with mercury metal. The products of the reaction are metal amalgam and diarylmercury [2]:

$$2Ph_nM + Hg \rightleftharpoons n\ Ph_2Hg + 2\ M \qquad (1)$$

When M = Hg, it has been suggested that reaction (1) proceeds via an intermediate dimetallic compound, ArHgHgAr ["organic calomel", $n = 2$ in equation (1)] [1,4]. This assumption stems from studies of organomercury compounds, and particularly $EtHgC_6F_5$, by galvanostatic techniques, which have been described in considerable detail elsewhere [5]. In the present work, the galvanostatic technique has been used to study the interaction of diethylthallium chloride with mercury metal.

Results and discussion

In contrast to organozinc, -cadmium and -magnesium compounds, dialkyl-

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*For Part IV, see ref. 1.

thallium compounds may be investigated in aqueous solutions for they undergo little hydrolysis. Diethylthallium chloride is virtually completely ionized in aqueous solutions and gives rise to solvated cations of the type $EtTl^+Et$, which are isoelectronic with diethylmercury and have a linear structure [6].

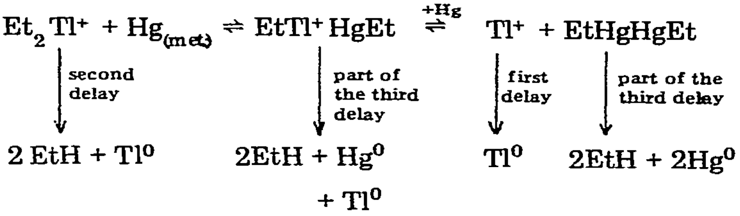
Chronopotentiograms of Et_2TlCl exhibit three delays (Fig. 1) at current densities of 10^{-5} to 2×10^{-3} A·cm^{-2}. The first delay appears at the potentials of ca. −0.5V (sce). It is very short and occurs at potentials corresponding to the reduction of Tl_2SO_4 under the same conditions (water, 1 *M* KOAc). When the system is repeatedly switched from potentiostatic to galvanostatic conditions, with an initial potential of ca. 0 or −0.25 V (sce) at which thallium exists in its oxidized form, Tl^+, this delay smoothly increases in length due to the accumulation of thallium metal on the surface of the electrode. (Zero-valent thallium is formed on the surface of the mercury electrode during the electrolysis of Et_2Tl^+ in galvanostatic experiments.) From the data given, it is possible to conclude that the interfacial interaction of aqueous solutions of diethylthallium chloride with mercury metal results in the formation of small amounts of thallium(I) cations on the mercury surface and that thallium cations undergo electroreduction at potentials corresponding to the first delay.

The second delay occurs at potentials of −1.0 to −1.15 V (sce) and probably corresponds to reduction of the unchanged cation Et_2Tl^+. The range of potentials over which this delay is observed coincides with the potentials for the main wave on a polarogram of Et_2TlCl [$E_{1/2} = -1.1$ V (sce)] in the same solution.

The third delay is observed at −1.45 to −1.6 V (sce) corresponding to the region in which diethyldimercury undergoes electrochemical reduction [4]. Thus, the diethylthallium cation takes part in the following equilibrium on the mercury surface:

$$Et_2Tl^+ + 2Hg \rightleftharpoons EtHgHgEt + Tl^+ \qquad (2)$$

However, if EtHgHgEt alone was reduced during the third delay, the length of this delay would not have been more than twice that of the first delay which corresponds to the reduction of Tl^+ since the concentrations of Tl^+ (one-electron acceptor) and Et_2Hg_2 (two-electron acceptor) are equal [eqn. (2)]. In fact, the third delay is far longer than the first at all current densities (Fig. 1). This indicates that other species besides Et_2Hg_2 are reduced at potentials corresponding to the third delay. It is possible that the length of the third delay increases due to the reduction of some species which precedes the formation of Et_2Hg_2 in reaction (2). These species may include the dimetallic cation $EtHgTl^+Et$ (which is analogous to "organic calomel" EtHgHgEt):



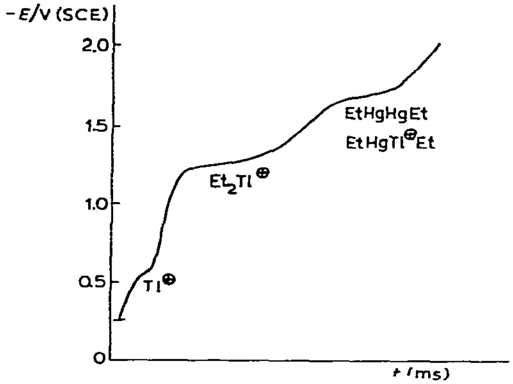


Fig. 1. Chronopotentiogram of Et_2TlCl.

The desorption delay of diethylmercury, which might have been expected in this system [5], is not observed in Fig. 1 since due to the existence of the equilibrium $Et_2Hg_2 \rightleftharpoons Et_2Hg+Hg$ the surface concentration of Et_2Hg is small (smaller than that of Tl^+).

Marshall and Pollard [3] have reported that tetraorganotin and tetraorganolead compounds (in which the metal atoms exist in an sp^3 configuration) do not interact with mercury metal. In a similar manner, our galvanostatic studies of tetramethyltin have shown that in this case no dimethyldimercury Me_2Hg_2 is formed on the mercury drop placed in water-methanol solutions of Me_4Sn at all available current densities.

In summary, diorganodimetallic compounds may be detected by the galvanostatic technique only when reaction (1) occurs. This provides strong evidence in favour of the assumption that species of the type RHgMR act as intermediates in transmetallation reactions.

References

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