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EXCHANGE OF ORGANOMETALLIC COMPOUNDS WITH MERCURY METAL

VI*. SUBSTITUTED DIARYLTHALLIUM CATIONS; EVIDENCE FOR INTERMEDIATE Ar–Tl⁺–Hg–Ar SPECIES

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Summary

Substituted diphenylthallium chlorides, $(XC_6H_4)_2TlCl$ (X = *p*-OCH_3, *p*-CH_3, *m*-CH_3, H, *p*-Cl, *p*-CH_3COO) have been prepared. Polarography and chronopotentiometry were used for study of electrochemical reduction and interaction of these compounds with mercury metal. Intermetallic cations, $ArTl^+HgAr$, were shown to be intermediates in the transmetallation reaction between Ar_2Tl^+ and mercury metal:

$$Ar_2Tl^+ + Hg \rightleftharpoons ArHg\overset{+}{Tl}Ar \rightleftharpoons Ar_2Hg + Tl^+.$$

Introduction

Gilman and Jones [2] were the first to observe exchange between diphenylthallium bromide and mercury metal in pyridine (eqn. 1). This reaction is an

$$Ph_2TlBr + Hg \rightleftharpoons Ph_2Hg + TlBr \qquad (1)$$

example of transmetallation reactions with participation of zero-valent mercury [3, 4], and its mechanism was vague for a long time.

In the previous paper of this series [1] we suggested that bimetallic cations, $EtHgTl^+Et$, are formed in a layer of Et_2TlCl adsorbed on mercury surface, and these cations are the intermediates in the transmetallation reaction 1. In the present paper more evidence is reported for similar intermediate cations from

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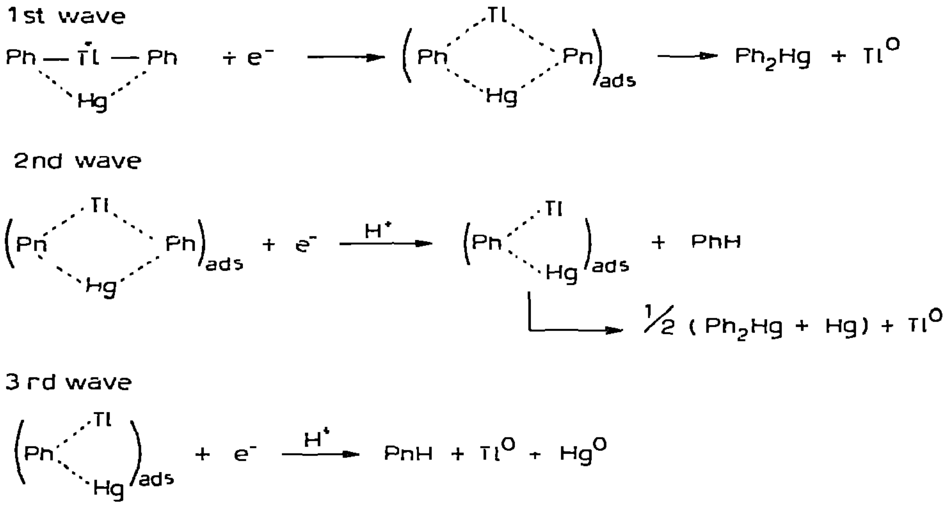
* See ref. 1 for part V.

some substituted diphenylthallium salts. Galvanostatic techniques [5] were used for study of the interaction of diarylthallium salts with mercury.

Electrolysis of aqueous solutions of diphenylthallium halides at a mercury cathode results in diphenylmercury and thallium metal as final products [6]. The mechanism of electroreduction of diaryl- and dialkyl-thallium cations at a mercury electrode has been studied with use of polarography, cyclic voltametry and microcoulometry [6-8].

Digregorio and Morris [6] have observed three waves on polarograms of diphenylthallium bromide, each of them corresponding to one-electron processes. The authors have supposed that the reduction mechanism involves "complexes of depolarizer with electode":



This mechanism was formulated on the basis of the stoichiometry of each electroreduction step (electrolysis at controlled potentials) as well as by analysis of the effects of pH, dropping period, and the depolarizer concentration on heights of the polarographic waves [6].

For dialkylthallium salts, polarograms show only one wave at pH < 7; electrolysis at the potential of the limiting current of the wave yields alkanes and Tl^0 only and no products of mercury alkylation [8].

Different behaviour was observed when electrolysis was carried out in non-aqueous DMF. In this medium polarograms showed two waves, the first at $E_{1/2} = -0.80$ volts (SCE) corresponding to one-electron reduction of Ph_2Tl^+ (eqn. 2) and the second ($E_{1/2} = -2.55$ volts) to two-electron reduction of di-

$$Ph_2Tl^+ + e^- \xrightarrow{Hg} Ph_2Hg + Tl^0 \qquad (2)$$

phenylmercury [8]. The electrolysis of dialkylthallium halides in non-aqueous DMF is complicated by chemical reactions which accompany the electrolysis [8]

Results and discussion

Polarography

Our data on the polarography of diphenylthallium chloride in non-aqueous

DMF are in agreement with those reported previously [8] for Ph_2TlBr. The polarogram of Ph_2TlCl in DMF shows two waves at $E_{1/2}$ −0.79 and −2.58 volts (SCE) (0.05 M Et_4NClO_4 was used as supporting electrolyte). However, we found that when the freshly prepared solution of Ph_2TlCl in DMF was left under a mercury pool overnight the height of the first wave decreased, and the third wave occurred at more anodic potentials. This wave increased progressively in time and had a half-wave potential (−0.46 volts) which coincides with $E_{1/2}$ of the thallous cation, as shown by addition of TlCl to the solution under investigation*. After several days the surface of the mercury pool was covered by a white precipitate which was identified as TlCl. When a 5×10^{-2} M solution of Ph_2TlCl in DMF was heated at 80° with a stirred mercury pool, reaction 1 came to an end after 8 hours and diphenylmercury was isolated from the reaction mixture in 80% yield. Thus in the reduction of diphenylthallium cation on mercury cathode diphenylmercury may be formed both by reaction 2 and by reaction 1.

Substituted diphenylthallium chloride species were studied in aqueous solutions. These compounds are very poorly soluble in water, so saturated solutions (ca. 2 or 3×10^{-5} M) were employed for measurements. Polarograms of all compounds studied show three waves with parameters given in Table 1. Limiting currents, i_l for the first and the second waves are of diffusion nature. This conclusion comes from dependences of the limiting currents on the height of mercury column h ($i_l \propto h^{0.4-0.5}$) and on temperature (0.7-2.2%/°C). For the third wave $i_l = \text{const} \times h^{0.9}$, and the temperature coefficient is 2.8%/°C. These facts testify to the adsorption nature of this wave. The second wave by the factor 1.5-2.0 and the third by the factor 3-4 are higher than the first wave.

TABLE 1

PARAMETERS OF POLAROGRAPHIC WAVES FOR SUBSTITUTED DIPHENYLTHALLIUM CHLORIDE.
Saturated solutions in 1 M aqueous KOAc, 25°

X in $(XC_6H_4)_2TlCl$	$-E_{1/2}$ (volts, SCE)		αn_a [a]		i_l [b] (μA)		$-E_{1/2}$ (volts, SCE) for third waves
	1st wave	2nd wave	1st wave	2nd wave	1st wave	2nd wave	
p-OCH_3	0.57	0.87	0.95	1.00	0.19	0.35	1.10
p-CH_3	0.63	0.87	1.02	1.13	0.13	0.21	1.15
m-CH_3	0.56	0.86	0.74	1.47	0.17	0.31	1.09
H	0.55	0.84	0.79	0.87	0.11	0.20	1.15
p-Cl	0.57	0.84	0.63	1.13	0.12	0.16	1.12
p-$COOCH_3$	0.54	0.82	1.23	0.94	0.08	0.12	1.16

[a] Polarographic transfer coefficient. [b] Limiting current for saturated solutions.

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* Difference between the reduction potentials of Tl^+ and Ph_2Tl^+ cations depends on cathode material. TlCl and Ph_2TlCl give the separate waves on mercury while the waves of $TlNO_3$ and Ph_2TlNO_3 overlap one another on platinum [9].

These data are, in general, in agreement with mechanism of electroreduction of diarylthallium salts proposed by Digregorio and Morris [6]. However, taking into account the data reported in refs. 1 and 10, one may suppose, instead of complexes of organothallium compounds with mercury metal, formation of bimetallic compounds with the covalent Hg—Tl bond taking place. If so, the mechanism of electroreduction of diphenylthallium compounds may be writien as follows:

1st wave

$$\begin{array}{ll} \mathrm{Ph_2Tl^+ + Hg^-} \overset{\text{fast}}{\rightleftharpoons} \mathrm{PhHg\overset{+}{Tl}Ph} \overset{e^-}{\rightleftharpoons} & \mathrm{PhHg\dot{Tl}Ph} \\ & (3)\downarrow \text{fast} \\ & \mathrm{Ph_2Hg + Tl} \end{array}$$

2nd wave

$$\mathrm{PhHg\dot{Tl}Ph + 2e^- \rightarrow 2Ph^- + Tl + Hg}$$

On adsoprtion on the surface of the mercury electrode diphenylthallium cation immediately transforms into PhHgTl$^{\cdot}$Ph and obviously with higher rate than the rates of diffusion and adsorption; this explains the diffusion character of the first polarographic wave. If reaction 3 is fast, the height of the second wave is less than that corresponding to two-electron transfer. Diphenylmercury, the stable product of the first reduction step, blocks the surface of the electrode; this substance desorbs at the potentials of the third wave and thus the third wave corresponds to sum of two processes: (1) three-electron reduction of a portion of Ph_2Tl^+ which could not be reduced on the second wave because of the hindering adsoprtion of Ph_2Hg and (2) desorption of Ph_2Hg.

Galvanostatic measurements

These were carried out at current densities of 1.5×10^{-2} to 5 mA cm^{-2}; the electrode was a hanging mercury drop. At current densities higher than 0.4 mA cm^{-2} chronopotentiograms of all compounds show two Faradaic delays at

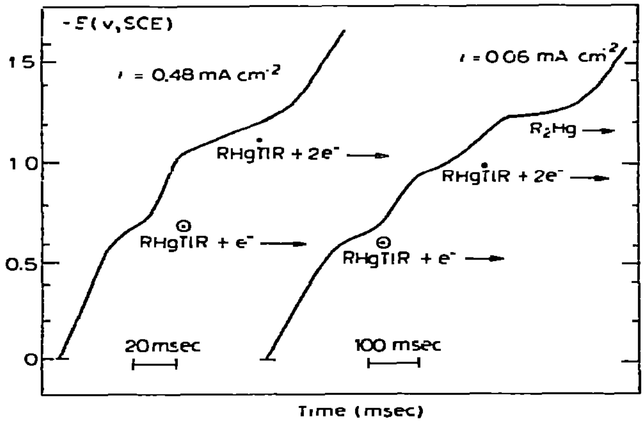

Fig. 1. Schematic representation of charging curves of mercury electrode for galvanostatic reduction of $(m\text{-}CH_3C_6H_4)_2TlCl$ in 1 *M* aqueous KOAc. Adsorption time t = 15 sec (without stirring of the solution), 25°.

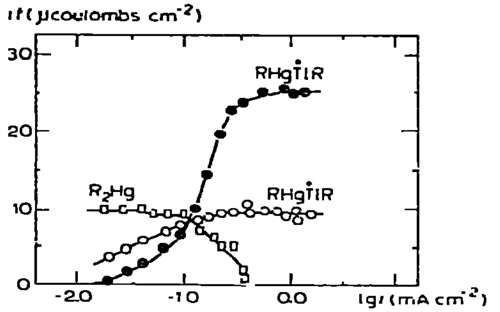

Fig. 2. The relationship between delay lengths and current density for galvanostatic reduction of $(m\text{-}CH_3C_6H_4)_2TlCl$ (2.5×10^{-5} *M*) in 1 *M* aqueous KOAc; E_1 = 0 volts (SCE), *t* = 15 sec (without stirring of the solution), 25°.

the potentials of about —0.6 to —0.7 and —1.0 to —1.2 volts (SCE) (Fig. 1, curve a). With lowering of current density, besides these Faradaic delays, one more delay, of a capacitive nature, appears at potentials of about —1.3 volts (Fig. 1, curve b). Interrelationships between the lengths of the delays and current densities for galvanostatic reduction of di-*meta*-tolylthallium chloride are given in Fig. 2, and similar dependences were obtained for all the other compounds. Figure 2 shows that with increase of current density the lengths of the both Faradaic delays increase, while the length of the capacitive delay becomes shorter and quite disappears at all current densities higher than 0.4 mA cm^{-2}. The capacitive delay corresponds to desorption of diarylmercury off the electrode surface. This follows from the fact that the shape and the reaction potential (appearance potential) E_r of the capacitive delay are the same as for a single delay on the chronopotentiogram of diphenylmercury. Also, $E_r$vs. lg *i* curves for the capacitive delay on the chronopotentiogram of diphenylthallium chloride and for the delay on chronopotentiogram of diphenylmercury which arises due to desoprtion of Ph_2Hg, are practically the same with a slope

$$-\frac{RT}{F}\left(\frac{\partial \lg i}{\partial E}\right) \to \infty.$$

From these data we may suppose that the most anodic delay corresponds to one-electron reduction of the bimetallic cation, ArHgTlAr, and more cathodic Faradic delay to two-electron reduction of ArHg$\dot{T}$lAr. Decrease in the length of the second delay with decreasing current density is due to chemical reaction 3, which becomes more appreciable with long electrolysis times, i.e. at low current densities. With decreasing current density the amount of diarylmercury, formed by reaction 3, increases on the mercury surface (Fig. 2)*. Decrease in length of the first delay with decreasing current density may be explained by several possible reasons, e.g. by desorption of ArHgTlAr for time of pulse (see, for example, ref. 11), by shift of equilibrium 1 to the left side influenced by diarylmercury formed owing to the electrolysis (reaction 3), etc.

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* In a potentiostatic regime, e.g. at potential E_i of about 0 volts (SCE) the formation of diarylmercury on the mercury surface can be observed, the amount increasing in time up to that corresponding to monolayer covering. In this case Ar_2Hg is formed by reaction 1, the rate of which seems to be at least an order of magnitude less than the rate of electrochemical formation of diarylmercury.

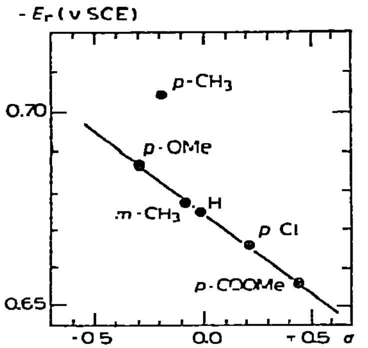

Fig. 3. Correlation of E_r values for galvanostatic reduction of $XC_6H_4HgTlC_6H_4X$ with Hammett σ-constants. Current density 1 mA cm^{-2}.

In the previous paper [1] it has been shown that diethylthallium cation on mercury surface gives various amounts of Tl^+ and Ph_2Hg. With diarylthallium cations the most anodic delay is probably due the reduction of the intermetallic cation, ArHgTlAr, but not of the thallous ion. This is because the first delay is observed at potentials more cathodic than potentials of reversible reduction of Tl^+ (in our experiments $E^0 = -0.46$ volts (SCE) for Tl^+) and furthermore that the reduction potentials E_r of the first delays for substituted diphenylthallium chlorides depend on the nature of the substituent. The plot of E_r vs. Hammett σ-constants is given in Fig. 3. For plotting of this σρ correlation the reduction potentials E_r were measured at high current densities (i = 1 mA cm^{-2}) so that reaction 3 may be neglected (otherwise, as shown above, it influences E_r values). E_r values were measured at the same surface concentrations of all diarylthallium compounds studied. The value for the *p*-tolyl derivative surprisingly fails to correlate (Fig. 3). Also, it should be mentioned that the slope of the Tafel plot for this compound is considerably less (36 mV) than for all the rest (50-60 mV)*.

Thus the first delay on chronopotentiograms of diarylthallium compounds corresponds to reduction of intermetallic cations, $ArHgTl^+Ar$. A small quantity of thallous cations, produced in reaction 1, are apparently reduced on the first delay together with $ArHgTl^+Ar$. Although reduction potentials for $ArHgTl^+Ar$ are by 100-150 mV more cathodic than E^0 for Tl^+, concentrations of Tl^+ on the mercury surface are rather small [1], and therefore a cathodic shift of reduction potential of Tl^+ cation must take place, and delays of $ArHgTl^+Ar$ and Tl^+ can overlap. In case of Et_2Tl^+ cations [1] intermetallic species $EtHgTl^+Et$ are reduced at essentially more negative potentials than Tl^+, so the delay of thallium(I) cations is separate from that of $EtHgTl^+Et$.

To sum up, the data presented in this paper and in ref. 1 show that interaction of organothallium compounds with mercury metal results in formation of intermetallic cations, $RHgTl^+R$ which we think are intermediate in transmetallation reaction 1.

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* Tafel plots were strictly linear for all compounds.

Experimental

Preparation of substituted diphenylthallium chlorides, $(XC_6H_4)_2TlCl$

These were prepared using standard procedures [12], by interaction of the respective substituted arylboronic acids (X = *p*-CH_3, H, *p*-$COOCH_3$) or Grignard reagents (X = *p*-OCH_3, *p*-CH_3, *m*-CH_3, *p*-Cl) with $TlCl_3$. Melting points and data of elemental analysis for compounds studied are given in Table 2.

Dimethylformamide (commercial, grade "Chisti") was shaken with anhydrous K_2CO_3 for 120 h and then distilled in vacuo, b.p. 38°/10 mm.

Reaction of diphenylthallium chloride with mercury in dimethylformamide

1.14 g of Ph_2TlCl dissolved in 60 ml of DMF was stirred with 4 ml of mercury metal (99.999% Hg) at 80° for 8 h. During this time a number of 0.1 ml aliquots were taken from the reaction mixture, and were poured into 25 ml of cool 0.05 *M* soln. of Et_4NClO_4 in DMF and polarograms of the resulting solutions were recorded. After 12 h the polarograms did not show Ph_2TlCl in the reaction mixture therefore the reaction was complete. The organic solution was carefully separated from the mixture of mercury and white precipitate of TlCl and then was diluted by the equal volume of water. The precipitate of diphenylmercury was filtered and dried. Its weight was 0.8 g (80%). After recrystallization from benzene the m.p. was 123° (lit. [14] 123°). The precipitate of TlCl was separated from mercury by multiple shaking with DMF, decantation and filtration. Polarograms of saturated solutions of this precipitate show one clear-cut wave with $E_{1/2}$ = —0.46 volts (SCE).

Polarographic measurements

These were carried out in a thermostatted (25 ± 0.2°) standard electrochemical cell, equipped with a tube for bubbling argon, and an electrolytic key for connection of the cell to the external aqueous saturated calomel electrode. In 1 *M* aqueous solution of KOAc capillary had the following characteristics: for

TABLE 2

ANALYTICAL DATA

X in $(XC_6H_4)_2TlCl$	M.p. (°C)	Found (calcd.) (%)		
		C	H	Cl
p-OCH_3	>310	37.01 (37.05)	2.90 (3.10)	7.85 (7.80)
p-CH_3	>310	39.95 (39.84)	3.29 (3.34)	8.34 (8.40)
m-CH_3	274(235/13/)	39.79 (39.84)	3.18 (3.34)	8.31 (8.40)
H	>310	36.51 (36.58)	2.48 (2.55)	8.91 (8.97)
p-Cl	>310	31.21 (31.13)	1.69 (1.74)	23.08 (22.97)
p-$COOCH_3$	305(dec.)	37.62 (37.67)	2.71 (2.76)	6.85 (6.94)

the broken electric chain: t = 2.8 sec, m = 3.62 mg sec^{-1}. Polarograms were recorded using electronic polarograph LP-7 (Czechoslovakia). Potential of dropping mercury electrode was controlled with help of potentiometer PPTV-I. Oxygen was removed from the cell by bubbling of pure argon.

The procedure for galvanostatic measurements was described in ref. 5. The measurements were carried out at current densities of 1.5 × 10^{-2} to 5 mA cm^{-2}.

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