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**Review**

# "ORGANIC CALOMELS" AND OTHER ORGANOBIMETALLIC COMPOUNDS AS INTERMEDIATES IN TRANSMETALLATION REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH MERCURY METAL

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## Contents

## 1. Introduction

Well known reactions of organometallic compounds with mercury metal, e.g.:

$$2\ R_nM + n\ Hg \rightleftharpoons n\ R_2Hg + 2\ M \qquad (1)$$

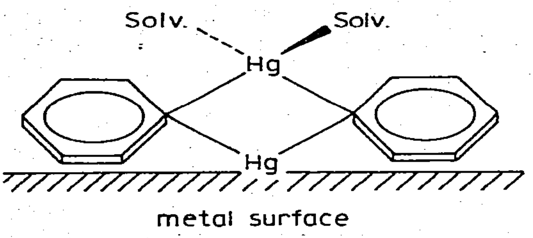
(M = Li, Na, Mg, Be, Zn, Cd, etc.)

are synthetic pathways in organometallic chemistry [1]. Exchange of mercury for mercury is the result of reaction 1 when M = Hg (eqn. 2a) and in eqn. 2b.

$$R_2Hg + Hg^* \rightleftharpoons R_2Hg^* + Hg \qquad (2a)$$

$$RHgX + Hg^* \rightleftharpoons RHg^*X + Hg \qquad (2b)$$

Mechanisms of reactions 2 have been studied by the use of radio isotope techniques [2-14] (see ref. 15 for a review of the papers published up to 1972). As a result of kinetic, stereochemical and structural investigations of reactions 2 two alternative mechanisms were proposed for such processes of transmetallation. According to one [2-12], the transition state is four-centered, i.e. reactions 2 are of the $S_Ei$ type. Marshall and Pollard [12] proposed transition state I for the exchange with diphenylmercury:



(I)

Kreevoy and Walters [13] proposed the two-step transmercuration mechanism. According to these authors adsorption of organomercury compounds on the mercury surface is accompanied by electron transfer from the substrate to mercury metal, and the adsorbed substrate particles are cation radicals which then turn into "organic calomels":

$$\begin{aligned} &\mathrm{RHgX} + {}^{*}\mathrm{Hg} \xrightleftharpoons{\text{slow}} {}^{*}\mathrm{Hg}^{\overline{\cdot}}\,[\mathrm{RHgX}]^{\overset{+}{\cdot}}_{\mathrm{ads.}} \\ &{}^{*}\mathrm{Hg}^{\overline{\cdot}}[\mathrm{RHgX}]^{\overset{+}{\cdot}}_{\mathrm{ads.}} \xrightleftharpoons{\text{fast}} (\mathrm{RHgHg}^{*}\mathrm{R})_{\mathrm{ads.}} \end{aligned} \qquad (3)$$

The rate-determining step, according to eqn. 3, is electron transfer.

To choose between these one and two-step mechanisms, a number of $R_2Hg/Hg$ and RHgX/Hg systems have been studied in our laboratory by pulse galvanostatic techniques. This technique is a variation of chronopotentiometry.

The pulse galvanostatic measurements allow one to detect and identify reducible and oxidizable species of relatively low stabilities, species which might arise during the transmetallation on a mercury surface. The data obtained lead to the conclusion that the mercury exchange occurs via a two-step mechanism with "organic calomels" as metastable intermediates [15-18].

## 2. Evidences for formation of "organic calomels" on a mercury surface

At first, charging curves for a hanging mercury drop placed into solutions of $Et_2Hg$ or EtHgBr in 10% aqueous methanol with 1 *M* concentrations of KOAc were studied. At cathodic polarization chronopotentiograms of diethylmercury show two Faradaic delays at the potential of about —1.2 V (SCE; delay 4 in Fig. 1, curve a) and —1.8 V (delay 5, Fig. 1, cruve a). Delay 5 is a Faradaic one, i.e., it corresponds to the reduction of some electroactive particles. Diethylmercury itself does not reduce at the potentials of delay 5. Consequently, delay 5 is due to reduction of some kind of species arising from diethylmercury on the surface of the mercury drop. Delay 4 is due to capacitive effects; this is probably the desorption of diethylmercury (from the mercury surface*).

Also, two delays, the capacitive (delay 3) and the Faradaic (delay 2; Fig. 1, curve a) are observed at the anodic polarization from the same initial potential ($E_i = -0.6$ V). Diethylmercury itself is not oxidizable at the potential of delays 2 and 3. Therefore delay 2 is due to the oxidation of a species which was formed

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* The appearance potential of delay 4 was practically independent of the current densities: such behavior is a characteristic of adsorption and desorption delays.

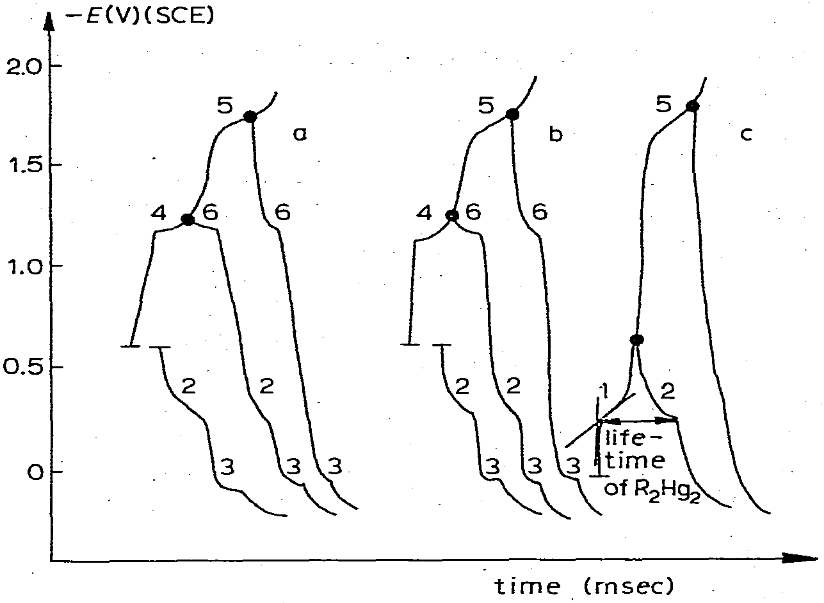

**Fig. 1.** Schematic representation of the charging curves of mercury for $Et_2Hg$ (curve a) and EtHgBr (curves b and c). The full points indicate the instances at which the direction of the polarizing current was reversed The left hand branches correspond to cathodic processes and the right hand branches correspond to anodic processes: 1 *M* KOAc/90% $H_2O$/10% MeOH at 25°C.

by interaction of $Et_2Hg$ with mercury during the time of the potentiostatic regime (ca. 30 sec at —0.6 V without stirring the solution).

The curve for ethylmercuric bromide is very similar to the chronopotentiogram of diethylmercury (Fig. 1, curve b). The potential of —0.6 V corresponds to the diffusion plateau of the first wave on polarograms of EtHgBr. Therefore, during the potentiostatic regime, the one-electron reduction of EtHgBr already has occurred. Thus, the one-electron reduction of EtHgBr and interaction of $Et_2Hg$ with mercury (without current) result in the same electrochemically active species. Let us denote, for the present, this species by the symbols [EtHg] or [RHg].

The charging curves for solutions of EtHgBr at different initial potentials and different potentials of reverse, in the direction of polarizing current, allow one to identify each of the delays. With the current in reverse at a potential between delays 4 and 5 delays 2 and 3 are observed (Fig. 1). Delay 6 is due to adsorption of diethylmercury which had been desorbed before, at the cathodic pulse (delay 4). If the current is reversed at potentials more negative than the reduction potentials of [EtHg], delay 2, which corresponds to the oxidation of [EtHg], is absent (Fig. 1, curve c) because the process of the reduction of [EtHg] is irreversible.

Behaviour similar to that of diethylmercury, is shown by other organomercury compounds, $R_2Hg$. This was shown for R = Me, n-Pr, s-Bu, and PhC≡C [19]. Thus, the interaction of organomercury compounds with mercury metal results in formation of a sub-valent species [RHg] which may be both oxidized and reduced at the appropriate potentials on a mercury electrode:

$$R_2Hg + Hg \rightleftharpoons 2\,[RHg] \qquad (4a)$$

The same species are formed also by one-electron reduction of organomercury salts:

$$RHgX + e^- \rightarrow [RHg] + X^- \qquad (4b)$$

It was shown that the transition of $R_2Hg$ into [RHg] is a reversible process [17]. The galvanostatic method was applied to study the behaviour of the following four systems on a mercury surface [17]: *(i)* $EtHgC_6F_5$
*(ii)* $Et_2Hg + (C_6F_5)_2Hg$
*(iii)* $EtHgCl + (C_6F_5)_2Hg$
*(iv)* $EtHgCl + C_6F_5HgBr$*

The initial potentials were carefully controlled in these experiments and were such that no electrolysis of $EtHgC_6F_5$, $Et_2Hg$ and $(C_6F_5)_2Hg$ took place, but one-electron reduction of the salts EtHgCl and $C_6F_5HgBr$ occurred. If the species [RHg] were the respective organomercury radicals ($EtHg^\bullet$ and $C_6F_5Hg^\bullet$ for the present case), then, because of the cross-dismutation of the radicals, in the galvanostatic regime one could observe the same delays corresponding to the same dismutation products in each of the four systems studied. However, $Et_2Hg$ and $(C_6F_5)_2Hg$ in system *i* and $C_6F_5HgEt$ in systems *ii* and *iii* were not observed.

$$(i)\ 2EtHgC_6F_5 + 2Hg \nrightarrow 2EtHg^\bullet + 2C_6F_5Hg^\bullet \rightarrow Et_2Hg + (C_6F_5)_2Hg + 2Hg$$

$$(ii)\ Et_2Hg + (C_6F_5)_2Hg + 2Hg \nrightarrow 2EtHg^\bullet + 2C_6F_5Hg^\bullet \rightarrow 2C_6F_5HgEt + 2Hg$$

$$(iii)\ (C_6F_5)_2Hg + (2EtHg^+ + 2e^-) + 2Hg \nrightarrow 2C_6F_5Hg^\bullet + 2EtHg^\bullet \rightarrow 2C_6F_5HgEt + 2Hg$$

Cross-dismutation occurred only in system *iv*:

$$(iv)\ 3EtHg^+ + 3C_6F_5Hg^+ + 6e^- \rightarrow 3EtHg^\bullet + 3C_6F_5Hg^\bullet \rightarrow EtHgC_6F_5 + (C_6F_5)_2Hg + Et_2Hg + 3Hg$$

In this case the chronopotentiograms, being recorded after the previous one-electron reduction of a mixture of both organomercury salts in the potentiostatic regime, show four delays which correspond to reduction of $(C_6F_5)_2Hg$, $EtHgC_6F_5$, and [EtHg], and desorption of $Et_2Hg$.

$$EtHg^+ \xrightarrow{\text{electrolysis}} \underset{\text{unstable}}{EtHg^\bullet} \xrightarrow{\text{very fast}} \underset{\text{metastable}}{[RHg]}$$

$$C_6F_5Hg^+ \xrightarrow{\text{electrolysis}} \underset{\text{unstable}}{C_6F_5Hg^\bullet}$$

The data given above show that, at least in the systems studied, the compounds $R_2Hg$ and $RHgR'$ are in equilibrium with species in which both groups,

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* The possible disproportionation of $EtHgC_6F_5$ to $Et_2Hg$ and $(C_6F_5)_2Hg$ does not take place in $H_2O$/MeOH solutions; the back reaction is very slow. Reaction $EtHgCl + (C_6F_5)_2Hg \rightarrow EtHgC_6F_5 + C_6F_5HgCl$ as was shown, may also be neglected. Thus, the redistribution reactions between these organomercury compounds cannot disturb the results of the study of the adsorption layer on mercury surface. However, the system $C_6F_5HgBr + Et_2Hg$ could not be studied because of the fast redistribution in this system leading to $C_6F_5HgEt$ and EtHgBr (the equilibrium constant is ca. 100).

R and R, or R and R′, of the parent molecules do not become kinetically independent. The simplest supposition is that $R_2Hg$ and $RHgR'$ are in equilibria with "organic calomels", RHgHgR and RHgHgR′.

The cross-dismutation is just possible in *iv* in which the simultaneous electrolysis of EtHgCl and $C_6F_5HgBr$ was carried out under conditions of diffusion control. In such conditions deliberately high concentrations of organomercury radicals arise on the mercury surface and cross-dismutation is appreciable.

Thus, the species which were denoted above as [RHg] may be identified now as "organic calomels", and eqn. 4 should be re-written as follows:

$$R_2Hg + Hg \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RHgHgR \qquad (5)$$

The formation of RHgHgR from $R_2Hg$ occurs, obviously, as a result of the direct insertion of mercury atom into the R—Hg bond, but not via the adsorbed radicals, $RHg^{\bullet}$, because in the latter case the products of the cross-dismutation of the radicals $EtHg^{\bullet}$ and $C_6F_5Hg^{\bullet}$ should be observed in runs *i, ii* and *iii**.

## 3. Properties of compounds of univalent mercury

In all inorganic compounds of mercury(I) whose structures are studied nowadays two mercury atoms are directly bonded with each other. Therefore such compounds may be pictured as $Hg_2X_2$ or X—Hg—Hg—X but not as HgX [22-24].

The equilibrium constant for the reaction

$$Hg + Hg^{2+} \rightleftharpoons Hg_2^{2+} \qquad (6)$$

is $1.6 \times 10^2$ [24]; such a high value means that $Hg_2^{2+}$ is a relatively stable cation. Equilibrium 6 is very sensitive to changes in environment, however. If the system $HgX_2/Hg_2X_2$ involves anions X, which are able to give strong complexes with the cation $Hg^{2+}$, equilibrium 6 will be shifted on the left. And because there is a large number of such particles, the number of the mercury(I) compounds is very limited**.

Thus, addition of $OH^-$, $S^{2-}$ or $CN^-$ to solutions of $Hg_2^{2+}$ in water results in the formation of the respective compounds of mercury(II). Concerning the force of the disproportionation action on cations $Hg_2^{2+}$, the anions may be arranged in the following sequence [25,26]:

$$Cl^- < Br^- < I^- < CNS^- < CN^-$$

and this sequence is practically the same as that of the formation constants of the anion—$Hg^{2+}$ complexes:

$$Cl^- < Br^- < CNS^- < I^- < CN^-$$

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* It has been proposed [27] that the system $2RHgX + 2e^- \rightarrow R_2Hg_2 + 2X^-$ is completely reversible and the apparent irreversibility of the one-electron reduction of RHgX is due to the irreversible demercurization of $R_2Hg_2$ to $R_2Hg$. This viewpoint is obviously incorrect because "organic calomels" are in equilibrium with $R_2Hg$. Also, "organic calomels" cannot dissociate to give two organomercury radicals [17] (cf. equilibrium constant for the reaction $Hg_2^{2+} \rightleftharpoons 2Hg^+$, less than $10^{-7}$ [21]).

** Among compounds of mercury(I) only halides, nitrate($x2H_2O$), perchlorate($x4H_2O$), sulfate, chlorate, bromate, iodate and acetate are sufficiently stable at room temperature [24].

TABLE 1

APPROXIMATE LIFETIMES[a] OF "ORGANIC CALOMELS" ON MERCURY SURFACE AT 25°C [16,19]

| R in RHgHgR | Life time (sec) |
|---|---|
| Alkyls | $10^{-2}$ to $5 \times 10^{-2}$ |
| 3-Pyridyl | $10^{-3}$ to $10^{-2}$ [27][b] |
| Aryls, $C_6F_5$, $CH_2{=}CH$ | $10^{-4}$ to $2 \times 10^{-4}$ |
| $C_6H_5CH_2$ | Far less than $10^{-4}$ |

[a] The life times of $R_2Hg_2$ were determined as the time from the beginning of delay 1 to the end of delay 2 (Fig. 1) at current densities at which the lengths of both delays are equal, see ref. 16 for details. [b] Estimated using cyclic voltammetry.

The extremely high affinity of carbanions for the $Hg^{2+}$ cation allows us to propose that equilibrium 5 must be shifted far to the left. This is in agreement with the galvanostatic studies of organomercury compounds on a mercury surface [15-19]. The study of "organic calomels", RHgHgR (R = Me, Et, n-Pr, n-$C_5H_{11}$, cyclo-$C_5H_9$, Ph, $\beta$-naphthyl, mesityl, $CH_2{=}CH$, $C_6F_5$, $PhCH_2$), generated on the mercury surface by one-electron reduction of the respective organomercury salts (eqn. 4b), shows that these compounds of mercury(I) have extremely low stabilities (Table 1), even on the mercury surface where a large excess of Hg is present.

The data of Table 1 show that alkyl derivatives of mercury(I) are more stable than aryl derivatives.

The kinetic data for reaction 5 are given in Table 2. For R = n-Pr and PhC≡C the $k_1$ values were obtained from direct electrochemical measurements [19,28], but for R = Ph and Et these values were estimated indirectly [16,19] from data on mercury exchange of $Ph_2Hg$ and $Et_2Hg$ with mercury [10,14]. It follows from Table 2 that both the mercuration of $R_2Hg$ and the demercuration of $R_2Hg_2$ are the fast processes on the mercury surface, but equilibrium 5 is shifted far on the left (Table 1). For this reason "organic calomels" cannot be isolated as individual substances at room temperature.

TABLE 2

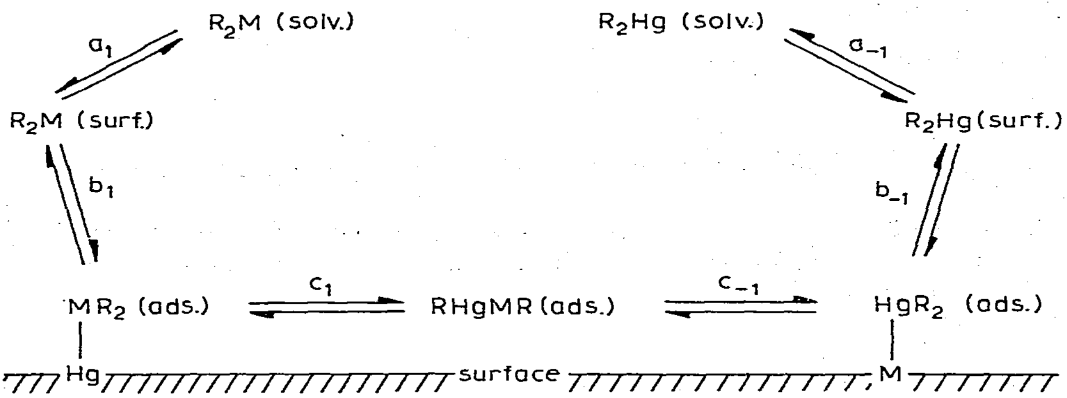
APPROXIMATE KINETIC PARAMETERS FOR EQUILIBRIUM 5 (Interface: mercury/1 *M* aqueous KOAc, 25°C)

| R | $k_1$ ($sec^{-1}$) | $k_{-1}$ ($sec^{-1}$) | $K = \frac{k_1}{k_{-1}}$ | Ref. |
|---|---|---|---|---|
| PhC≡C | ca. 50 | | | 19 |
| Ph | ca. 40 | | | 19 |
| | ca. 60 | | | 18 |
| Et | ca. 0.15 | | | 19 |
| | ca. 0.6 | | | 18 |
| n-Pr | <0.8 | ca. 5-10 | $<4 \times 10^{-2}$ | 28 |
| | | | $10^{-2}$ to $5 \times 10^{-2}$ | 16 |

## 4. The rate-determining step

The short-lived "organic calomels" are apparently the intermediate species which are responsible for the occurrence of mercury isotopic exchange between organomercury compounds and $^{203}Hg$. The exchange involves the kinetic steps (M = Hg) [8,14,18] shown in Scheme 1. In this scheme step $a_1$ and $a_{-1}$ correspond to diffusion of $R_2M$ to and $R_2Hg$ from the mercury surface, steps $b_1$ and $b_{-1}$ to the adsorbtion $R_2M$ and desorbtion of $R_2Hg$, and steps $c_1$ and $c_{-1}$ to formation and demercuration of "organic calomel".

SCHEME 1



In principle, any of these steps may limit the exchange rate. However, under the usual conditions, diffusion, adsorption and desorption are the fast steps [8-10, 14,18,19]. Thus, the rate determining step is the chemical reaction of $R_2Hg$ on the mercury surface which results in "organic calomels":

$$R_2Hg + Hg \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2Hg_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} R_2Hg + Hg \qquad (7)$$

The kinetic equation for reaction 7 may be written as

$$\text{Rate} = k_1 \Gamma_{R_2Hg} - k_{-1} \Gamma_{R_2Hg_2}$$

where $\Gamma_{R_2Hg}$ and $\Gamma_{R_2Hg_2}$ are the surface concentrations of $R_2Hg$ and $R_2Hg_2$.

Under steady-state conditions, when $\frac{d\Gamma_{R_2Hg_2}}{dt} = 0$

$$\text{Rate} = k_1 \Gamma_{R_2Hg} = k_{-1} \Gamma_{R_2Hg_2},$$

i.e., the rate of "organic calomel" formation is equal to the rate of its demercuration. The steady-state conditions may be reached on the quiet surface of mercury rather rapidly (after several seconds) and therefore the rates of mercuration of $R_2Hg$ or demercuration of "organic calomels" may be considered as a measure of the reactivity of different organomercury compounds in the mercury exchange reaction [16,18]. The data of Table 3 show that rates of demercuration of "aryl calomels" are higher than those for "alkyl calomels". Rates of mercury

TABLE 3

ESTIMATION OF DEMERCURATION RATES OF "ORGANIC CALOMELS" [18]

| R in $R_2Hg_2$ | Rate × $10^8$ (mol $cm^{-2}$ $sec^{-1}$) | R in $R_2Hg_2$ | Rate × $10^8$ (mol $cm^{-2}$ $sec^{-1}$) |
|---|---|---|---|
| $PhCH_2$ | (>200) | cyclo-$C_5H_9$ | 3.4 |
| Ph | 160 | i-Pr | 1.3 |
| β-Naphthyl | 100 | n-Pr | 2.1 |
| Mesityl | 70 | Et | 1.6 |
| n-$C_5H_{11}$ | 6.8 | Me | 1.1 |

exchange are also higher for arylmercurials than for alkylmercury compounds [4, 5,14].

The data of Table 3 are in extremely good agreement with Heitz's data [14] on the exchange of organomercury compounds at a radioactive mercury dropping electrode in benzene:

| R | Ph | Et | Me | |
|---|---|---|---|---|
| Relative rate | 112 | 1 | 0.7 | (Ref. 14) |
| | 100 | 1 | 0.7 | (Table 3) |

Thus, it is very possible that "organic calomels" are intermediates in the mercury isotope exchange. The amounts of $R_2Hg_2$ depend on the position of equilibrium 5 on the mercury surface. With diarylmercury compounds this equilibrium is shifted more to the left than with $Alk_2Hg$, i.e. the stability of $R_2Hg_2$, as referred to stability of $R_2Hg$, is higher for R = Alk than for R = Ar.

The mechanism of the mercury exchange via "organic calomel" intermediates has been proposed originally by Kreevoy and Walters [13]. However these authors have postulated a cation-radical, $RHgHgR^{\dot{+}}$ as being an intermediate in the exchange. Kreevoy and Walters considered organomercury compounds acting as cation-radicals to be adsorbed on mercury. But it is hardly possible that the adsorption of organomercury compounds on mercury should be accompanied by an appreciable charge transfer across the interface. According to our galvanostatic measurements, the limiting values of adsorption of $(C_6F_5)_2Hg$ and β-$C_{10}H_7$-HgOAc are 32 and 40 μC $cm^{-2}$, respectively. Assuming that during reduction one electron is consumed per RHgX molecule and two electrons per $R_2Hg$ molecule, by means of the Faraday law one can calculate the limiting values of adsorption of these compounds. We obtained the values $1.6 \times 10^{-10}$ and $2.5 \times 10^{-10}$ mol $cm^{-2}$, respectively, which are in agreement with the model for the plane-parallel orientation of the molecules on the surface (90 and 60 $Å^2$ per molecule, respectively). If, instead, we assume these molecules to be adsorbed as the cation-radicals, it is necessary to increase the electron consumption in the reduction of the molecule to two and three electrons, respectively. Then, according to the Faraday law, the experimental values of the adsorption extent (32 and 40 μC $cm^{-2}$) will correspond to 180 and 90 $Å^2$ of electrode surface per molecule. Such large areas are at variance with the model estimates.

Furthermore, in contrast with ref. 13, we think that organomercury compounds are acceptors while mercury metal is a donor of electrons in the mercury exchange reaction (see Section 7).

## 5. Solvent effect

Solvent effect on rates of the mercury isotope exchange appear mainly to be due to a variation in the extent of adsorption on the mercury/solvent interface. Such a conclusion is inferred from the plot of Fig. 2, which shows that the exchange rate decreases with an increase in the solubility of phenylmercuric bromide. The most rapid exchange was observed in water and i-octane, the solvents with poor solvating ability with respect to PhHgBr. A decrease in solubility leads to an increase of adsorption on the interface, i.e., to an increase in the surface concentration of the substrate. This should lead to an increase of the exchange rate. Also, to provide the high rate of the exchange, the solvent must not compete with the substrate for a place on the mercury surface, or else the surface substrate concentration will be decreased and the observed rate constant (which is the apparent rate constant because it is measured from a kinetic law of the accumulation of radioactivity in the reaction solution) will be lowered. Furthermore, the solvent molecules which give strong complexes with the organomercury substrate will decrease the exchange rate because the substrate adsorption from the solution should be accompanied by desolvation, and this process needs additional energy.

The high adsorption ability of hexamethylphosphortriamide on mercury and its high tendency for specific solvation of organomercury compounds is the probable reason for a low exchange rate in this solvent; the rate constant is lower by an order of ca. ten than that in benzene (Fig. 2), in spite of the same dissolving ability of both solvents with respect to phenylmercuric bromide.

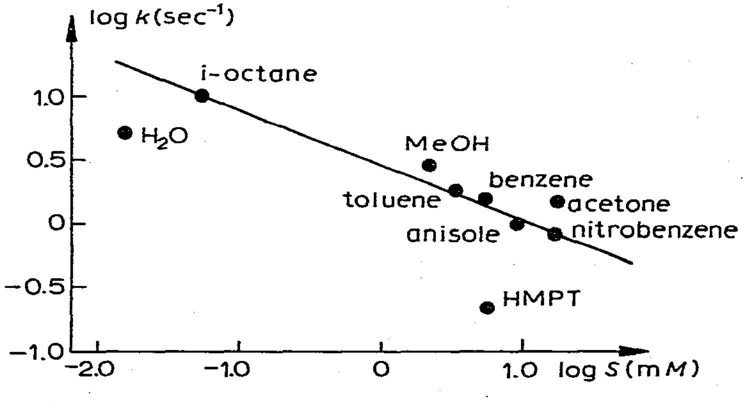


Fig. 2. The dependence between logs of rate constants of the exchange of PhHgBr with mercury-203 and logs of solubilities of this compound in a number of solvents. Data from refs. 12 and 14.

## 6. Exchange of organothallium compounds with mercury

Gilman and Jones [29] were the first to observe exchange between diphenylthallium bromide and mercury metal in pyridine:

$$Ph_2TlBr + Hg \rightleftharpoons Ph_2Hg + TlBr \quad (8)$$

It may be supposed that diorganothallium cations, $R_2Tl^+$, which are isoelectronic with the respective organomercury compounds, $R_2Hg$, will interact with mercury metal via intermediates of the type of $RTl^+HgR$. Evidence for the formation of such organobimetallic cations were obtained from the galvanostatic study of dialkyl- and diaryl thallium halides in 1 *M* aqueous solutions of potassium acetate [30,31].

Chronopotentiograms of $Et_2TlCl$ (Fig. 3) show three Faradaic delays at all current densities studied ($10^{-2}$ to 2 mA cm$^2$). The first delay, which appears at the potential of about —0.5 V (SCE), is rather short; it corresponds to the reduction of thallous ions, $Tl^+$. The second delay at —1.00 to —1.15 V corresponds to the main wave on the polarogram of $Et_2TlCl$; it is the three-electron reduction of diethylthallium cations. The third delay appears at —1.45 to —1.60 V. These are the potentials of reduction of $Et_2Hg_2$ (Fig. 1). Thus, contact of $Et_2Tl^+$ with the mercury surface results in formation of at least three particles on the surface: diethylmercury, and the $Tl^+$ and $Et_2Tl^+$ cations, while the solution contains only diethylthallium cations. This indicates that diethylthallium cations take part in the following equilibrium on the mercury surface:

$$Et_2Tl^+ + 2Hg \rightleftharpoons Tl^+ + Et_2Hg_2 \quad (\rightleftharpoons Et_2Hg + Hg)$$

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) are equal or more than the concentrations of $Et_2Hg_2$ (two-electron acceptor). 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 organobimetallic cation $EtHgTl^+Et$ which is an isoelectronic analogue of the "organic calomel"

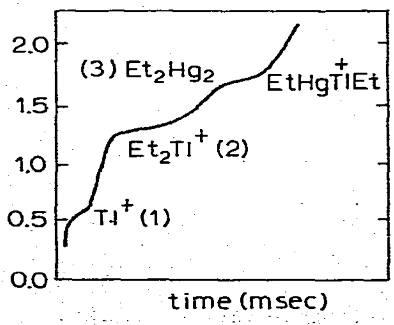


Fig. 3. Chronopotentiogram of $Et_2TlCl$.

EtHgHgEt:

$$Et_2Tl^+ + Hg \rightleftharpoons EtTl^+HgEt \rightleftharpoons Tl^+ + Et_2Hg \xrightarrow{Hg} EtHgHgEt$$

More direct evidence for $ArHgTl^+Ar$ species on a mercury surface was obtained from the study of diarylthallium chlorides by galvanostatic techniques [31]. The substituted diphenylthallium chlorides, $(XC_6H_4)_2TlCl$, where X = *p*-OMe, *p*-Me, *m*-Me, H and *p*-Cl, have been studied in 1 *M* KOAc/90% $H_2O$/10% MeOH solutions. The measurements were carried out at current densities of $1.5 \times 10^{-2}$ 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 potential of about −0.6 to −0.7 and −1.0 to −1.2 V (SCE) (Fig. 4, curve a). With a lowering of current density, besides these Faradaic delays, one more delay of a capacitive nature, appears at potentials of about −1.3 V (Fig. 4, curve b). With increase of current density, the lengths of both Faradaic delays increase while the capacitive delay becomes shorter and disappears at all current densities higher than 0.4 mA $cm^{-2}$. It was shown [31] that the capacitive delay corresponds to desorption of $Ar_2Hg$ from the mercury surface, and the most anodic delay corresponds to simultaneous two-electron reduction of $ArHgTl^+Ar$ and one-electron reduction of thallous cations. The latter occurs because the first delay for substituted diarylthallium chlorides depends on the nature of substituents. The plot of appearance potentials vs. Hammett $\sigma$-constants shows a linear dependence with $\rho = +0.042$ V. We think that intermetallic cations $RHgTl^+R$ are intermediates in transmetallation reaction 8.

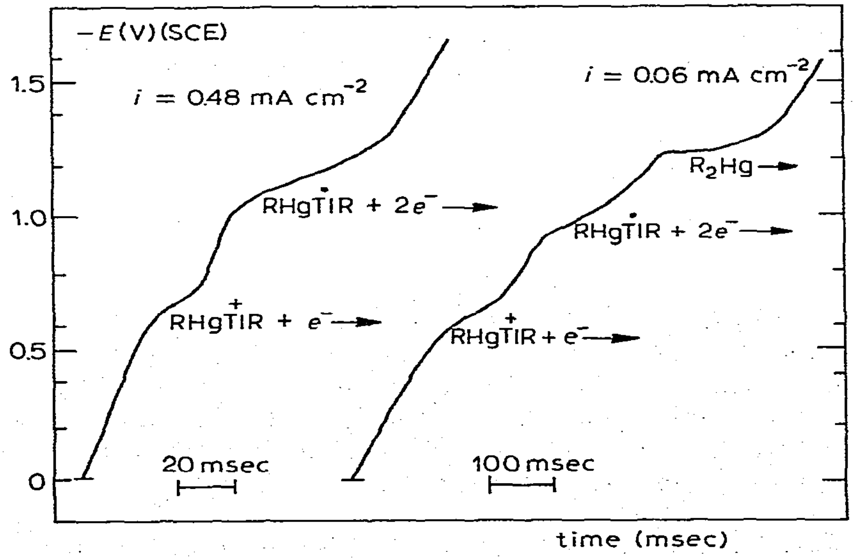
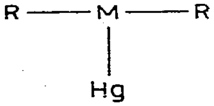


**Fig. 4.** Schematic representation of charging curves of mercury electrode for galvanostatic reduction of $(m\text{-}CH_3C_6H_4)_2TlCl$ in 1 *M* aqueous KOAc at 25°C.

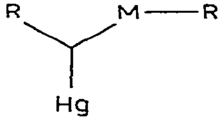
## 7. On the mechanism of the rate-determining step

Marshall and Pollard [12] have reported the data which are of interest for an elucidation of the mechanism of the organometallic compound—mercury exchanges. These authors have investigated the exchange between mercury metal and aryl derivatives of different metals. The data obtained show that only the compounds with *sp*- or *sp*$^2$- hybridization of the bonding orbitals of the metal atom (e.g., $Ph_2Hg$, $Ph_2Cd$, $Ph_2Zn$, $Ph_2Mg \cdot OEt_2$, $Ph_2Tl^+$, $Ph_3Bi$) undergo the exchange. Compounds of *sp*$^3$-type ($Ph_4Sn$, $Ph_4Pb$) did not react with mercury over 3 days. The galvanostatic study of tetramethyltin (10% MeOH/90% $H_2O$; 1 *M* KOAc) carried out in our laboratory, is in agreement with these results. At all current densities ($1.5 \times 10^{-2}$ to 7 mA cm$^{-2}$) chronopotentiograms did not show delays corresponding to $Me_2Hg$, $Me_2Hg_2$, or any other delays which might be ascribed to particles other than $Me_4Sn$.

The rate of the exchange decreases sharply in the sequence: $Ph_2Hg > Ph_2Cd > Ph_2Zn$ [12]. This sequence corresponds to a decrease in electronegativity of the metals (Hg 1.9, Cd 1.7, Zn 1.6), and hence the stability of the respective cation radicals will be increased from mercury to zinc derivatives: $PhHg^{\dot{+}} < Ph_2Cd^{\dot{+}} < Ph_2Zn^{\dot{+}}$. Therefore the mechanism which has been postulated by Kreevoy and Walters (eqn. 3) appears to be invalid. The oxidation level of the metal in $Ph_nM$ molecules should probably decrease in the transition state of the mercurization reaction. We may suppose that formation of organobimetallic compounds occurs via direct insertion of mercury into the carbon—metal bond involving intermediate compounds of the following types:

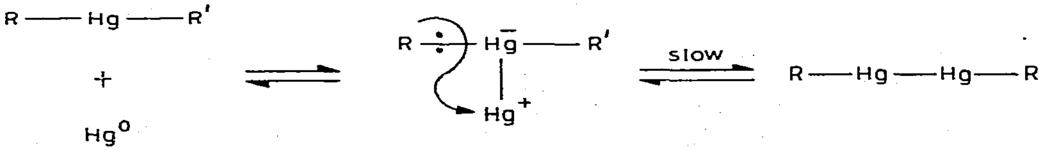


or

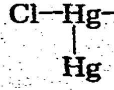


For organomercury compounds the mechanism of mercury—mercury exchange may be schematically written as in Scheme 2. In this scheme the rate

SCHEME 2



determining process is a migration of the anionic group, R, to the positively charged mercury atom. R groups more reactive towards electrophilic agents should migrate with higher rate (as in pinacol—pinacoline and other electrophilic rearrangements). Such a mechanism is in agreement with substituent effects on the mercury exchange rates; it has been shown that electron-releasing substituents increase and electron-withdrawing substituents decrease the reaction rate [7,12].

Nekrasov [23] considers the calomel molecule, $Hg_2Cl_2$, to have a T-shaped structure,  $\underset{\displaystyle Hg}{Cl{-}\underset{|}{Hg}{-}Cl}$, rather than a linear, Cl—Hg—Hg—Cl, structure in gas phase.

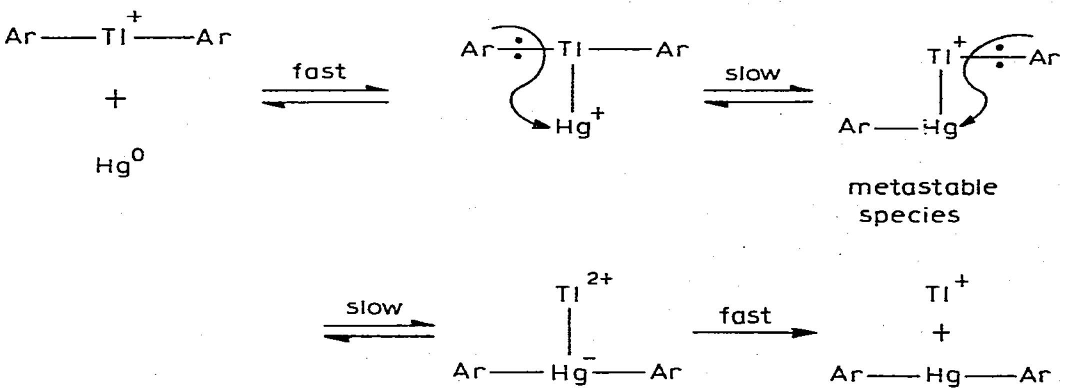
According to this author, calomel is a compound of the complex ion, $Hg(Hg^{2+})$, with two chloride anions. If this is really so, the $R_nM$—Hg species may also be imagined as complexes of organometallic compounds with mercury(0) in which $Hg^0$ plays a role of a donor ligand.

Substituent effects on the diarylthallium chlorides/mercury exchange are the same as those for organomercury compounds: electron-releasing substituents increase and electron-withdrawing substituents decrease the exchange rates. The following data were obtained in our laboratory for the exchange of $(XC_6H_4)_2TlCl$ with mercury in DMF at 60°C [32]:

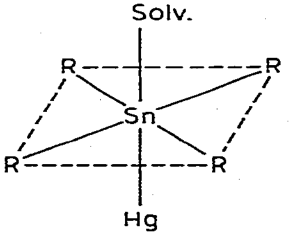
| X in $(XC_6H_4)_2Tl^+$ | *p*-OMe | *p*-Me | *m*-Me | H | *p*-Cl |
|---|---|---|---|---|---|
| $K_{obs.}$ ($\times 10^6$ sec$^{-1}$) | 14.7 | 7.6 | 4.5 | 2.2 | 0.6 |

The Hammett $\sigma\rho$-analysis gives a $\rho$ value of about —2.8. This conforms to the redox mechanism of thallium—mercury exchange shown in Scheme 3.

SCHEME 3

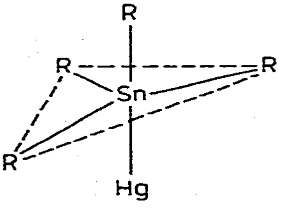


Similar T-shaped or tack-shaped structures for the Group IVb organometallic compounds, e.g.: II and III are, probably, impossible because of significant deformation of the bond angles.



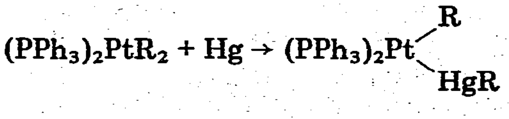
(II)

or



(III)

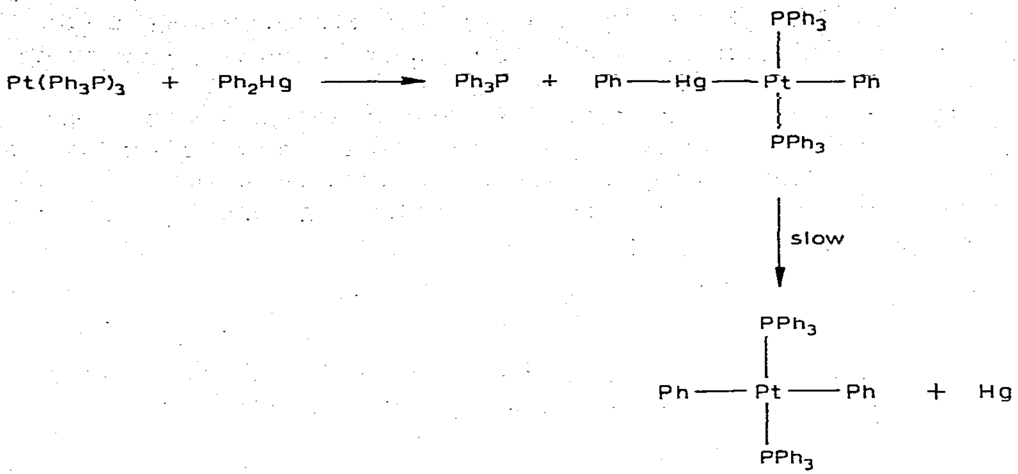
Perhaps, the reaction of platinum(0) triphenylphosphine complexes with organomercury compounds, recently reported from our laboratory [33], occurs via intermediates with Pt—Hg bonds (Scheme 4). The possible reverse reaction:



$$(PPh_3)_2PtR_2 + Hg \rightarrow (PPh_3)_2Pt\begin{array}{l} R \\ HgR \end{array}$$

is not studied nowadays.

SCHEME 4



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