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EXCHANGE OF ORGANOMERCURY COMPOUNDS WITH MERCURY METAL

I. DIETHYLMERCURY AND MERCURY METAL. THE APPLICATION OF THE GALVANOSTATIC TECHNIQUE TO RADICAL REACTIONS ON THE METAL SURFACE

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SUMMARY

By means of a galvanostatic method it has been shown that diethylmercury reacts with mercury metal to form organomercury radicals, a conclusion based on the similarity between the charging curves obtained for solutions of diethylmercury and ethylmercury bromide. RHg· radicals have been suggested as the intermediates in the exchange of organomercury compounds with mercury metal.

INTRODUCTION

It is well known that organometallic, especially organomercury, compounds react with various metals,

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

where M is Li, Na, Be, Zn, Cd, Al, In, Sn, Sb, Bi. The reaction is one of the most important methods of synthesizing organometallic compounds, so that an understanding of its mechanism is a challenging problem. Numerous investigators, especially Razuvayev and Koton[1,2], have found that the C–Hg bond readily undergoes homolytic fission, but although the C–Hg bond is broken homolytically in the activated complex no evidence was obtained for the formation of any free-radical intermediates. Thus, it is still not known whether the reaction proceeds via kinetically independent free radicals or whether the metal exchange is a kryptoradical process[1].

The simplest example of reaction (1) occurs in the interaction of an organomercurial with mercury metal.

$$RHgX + Hg^{*}_{(metal)} \rightleftarrows RHg^{*}X + Hg_{(metal)}$$

$$R_2Hg + Hg^{*}_{(metal)} \rightleftarrows R_2Hg^{*} + Hg_{(metal)}$$

The mechanisms of these reactions were first studied by Reutov *et al.*[3–7], and later by other workers[8–13]

All these investigators started from the premise that the reaction most probably proceeded by a homolytic mechanism, the possible existence of kinetically independent free radicals being excluded[5]. This assumption was based on (*i*) that the configuration at the carbon atom attached to the mercury atom was retained during mercury isotope exchange[3,4,7] and (*ii*) that no R_2Hg or R'_2Hg species were found among the products of the exchange of the unsymmetrical compounds RHgR', despite the existence of an isotope equilibrium in the reaction mixture[5,11]. Other evidence which disagreed with a free-radical mechanism was the fact that isotope exchange of mercury usually proceeded under rather mild conditions (room temperature), such reaction being difficult to visualize as resulting from the dissociation of the organomercurial into RHg· and R· radicals[5].

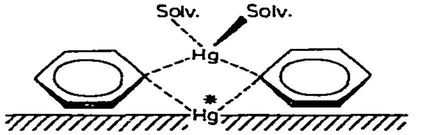
A variant of the kryptoradical mechanism is the formation of an "organic calomel" intermediate,

$$R{-}Hg{-}R' + Hg^* \rightarrow R{-}Hg{-}Hg^*{-}R'$$

$$R{-}Hg{-}Hg^*{-}R' \rightarrow R{-}Hg^*{-}R' + Hg$$

such a mechanism being discussed in a number of papers[3,6,13]. As a rule, however, the existence of such a mechanism was thought to be less probable from the energetic point of view. Kreevoy *et al.*[13] have assumed, however, a modification of such a mechanism in their studies.

The paucity of data in the literature does not allow an assessment of the effect of the structure of the organomercury compound on the exchange rate, since different authors have used different solvents and temperatures. Also the method of stirring the mercury is never specified and so it is possible that different effective surfaces of the reacting mercury were employed. Apart from polar factors, steric hindrance has been suggested as important[3,12]. Electron-donating substituents in the benzene ring of arylmercury compounds accelerate, whilst electron-accepting substituents retard the reaction[5,6,9]. Such effects have led to the assumption that the reaction should be of the S_E type and since from stereochemical considerations retention of the reactant configuration occurs during the reaction it has been suggested that the transition state is "closed", *i.e.* the reaction is of the S_Ei type[6,12]. For diphenylmercury this may be written as follows:



(A)

However, the effect of substituents cannot be taken as clear proof of the S_E mechanism since such an effect could also occur in a possible radical mechanism. It should be emphasised that electron and spatial factors alone cannot account for the effect of the structure of the organic moiety upon the reaction rate. Since the reaction is a heterogeneous process its rate must be significantly influenced by purely physical factors relating to the different degree of adsorption of the various organomercurials on the mercury surface. The entropy of the reaction has been shown to be strongly negative[9-13] suggesting that the reactants are highly ordered in the transition state.

Kreevoy has suggested that an important step in the exchange reaction is the adsorption of organomercurials on to the metal surface. He has assumed that such adsorption is accompanied by an electron transfer from the organomercurial compound to the mercury metal, resulting in the formation of a cation-radical which is then reduced by the metal to give "organic calomel"[13].

$$\mathrm{RHg^{*}X + Hg^{0}} \overset{\text{slow}}{\rightleftharpoons} \mathrm{Hg^{-}\cdot(Hg^{*}RX^{+})_{ads}}$$

$$\mathrm{Hg^{-}\cdot(Hg^{*}RX^{+})_{ads}} \overset{\text{fast}}{\rightleftharpoons} \mathrm{(RHgHg^{*}X)_{ads}}$$

$$\mathrm{(RHgHg^{*}X)_{ads}} \overset{\text{fast}}{\rightleftharpoons} \mathrm{(XRHg^{+})_{ads}\cdot Hg^{*-}}$$

$$\mathrm{(XRHg^{+})_{ads}\cdot Hg^{*-}} \underset{\text{slow}}{\rightleftharpoons} \mathrm{RHgX + Hg^{*0}}$$

According to Kreevoy, the rate-controlling step in the reaction is this process of electron transfer. Such a suggestion agrees with the effect of substituents: electron-donating substituents in RHgX should accelerate the electron-transfer process whilst electron acceptors should slow the process down.

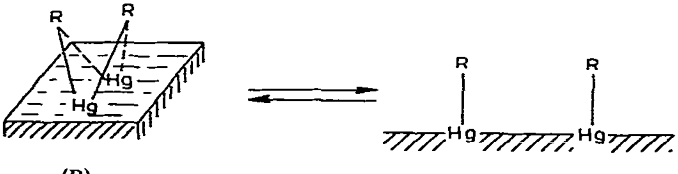
If the Kreevoy mechanism is accepted as correct, *i.e.* if the formation of the cation-radical $(\mathrm{RHgR'})^{\cdot+}$ is the slow step, then symmetrical organomercurials, R_2Hg, should be expected to exchange faster than the respective organomercury salts, RHgX. This follows from a study of the ionisation potentials of organomercury compounds; thus, for example the mass-spectrometric appearance potential for a $(CH_3)_2Hg^{\cdot+}$ molecule ion is 9.1 eV whereas for $(CH_3HgCl)^{\cdot+}$ it is 11.5 eV[14]. However, experimental studies have shown that the rates of exchange[3-13] suggest that the symmetrical species R_2Hg reacts slower than the respective salts, RHgX. This apparent contradiction arises because the exchange rate measurements are concerned merely with the volume concentration of the substrate and not with the *surface* concentration of the adsorbate.

The data discussed above indicate that organomercury compounds have rather high ionisation potentials, a property which should hinder the exchange process. It must be remembered, however, that the exchange reaction occurs at the surface of the mercury metal, electron transfer being facilitated through the work function, F, for an electron, which has a value of -4.52 eV (having been multiplied by -1) for mercury. Accordingly, homogeneous exchange with mercury metal dissolved in benzene is much slower than heterogeneous exchange in the same solvent[13]. This difference in reaction rate is related to an increase in the activation energy for the homogeneous reaction, an increase which is equal to the difference between the electron work function and the affinity of the mercury atom for an electron ($\xi = 1.9$ eV[13]).

R–Hg bonds are presumably partially fissioned in the transition state which is formed on the surface of the metal, and if this is so it might be expected that the reaction rate would depend on the C–metal bond energy. The exchange of mercury metal with phenyl derivatives of various metals (M is Hg, Tl, Cd, Mg, Zn, Bi, Sn, Pb) has

$$2\ \mathrm{Ph}_n\mathrm{M} + n\ \mathrm{Hg^{*}} \rightleftharpoons n\ \mathrm{Ph_2Hg^{*}} + 2\ \mathrm{M}$$

already been studied[12], when the homolytical dissociation energy for the C–metal bonds was found to be related to the reaction rate for the various metallic compounds provided they had the same geometry. When the number of phenyl groups attached to a given metal atom was increased, *i.e.* when *sp*-hybridisation of the metal atom was replaced by sp^3-hybridisation, the rate of exchange decreased noticeably, the rate being zero for tetraphenyltin or tetraphenyllead. Such behaviour cannot be explained by assuming that the transition state belongs to type (A), in other words, involving a metal atom in the metallic mercury lattice with another metal atom positioned somewhat away from the surface (instead of the two solvent molecules in structure (A) one may write, for example, two phenyl radicals). Thus, it must be assumed that in the transition state the metal undergoing exchange is part of the metallic mercury lattice, *e.g.* for mercury:



(B)

Such a transition state would be favoured by the gain in energy arising from the heat of condensation of the metal, some 14.5 kcal/mole for mercury[15]. In order to form such a transition state, the reactant molecule would need to be significantly distorted, and for this reason tetraphenyl derivatives of tin or lead would not exchange. In addition, steric hindrance hampers the electron transfer involved in the formation of the Kreevoy transition state since the probability of transfer depends strongly on the distance between the reacting sites.

If metal insertion into the metallic mercury surface is equivalent to an oxidation of the organometallic compound with the valence electrons of the metal being transferred to the conducting levels of mercury, our mechanism is in agreement with that suggested by Kreevoy[13]. Thus the reaction of organometallic compounds with mercury metal may, ultimately, result in organomercury radicals being inserted into the metal lattice, *i.e.* organic radicals, R, being linked to mercury metal. This is very closely similar to the formation of "organic calomel" postulated by Kreevoy[13]. The retention of optical activity by the radicals during the exchange process may now be explained by assuming that the radicals are firmly linked to the mercury surface. The dissociation energy of such a link is, at present, hard to estimate; probably its value is equal to or greater than 8 kcal/mole, the dissociation energy of an RHg· radical in gas phase[16].

Pollard and Marshall[11], Kreevoy[13], and the present authors have studied the effect of the solvent upon the rate of exchange of organometallic compounds with mercury. The former workers[11,13] have discussed this effect in terms of the specific solvation of the organometallic compounds, this being the traditional approach for the interpretation of homogeneous reactions, and neglected the fact that the effect of the solvent upon a heterogeneous process may be largely due to its influence on the adsorption of the substrate on the interfacial boundary. The reported results indicate that the effect of the solvent is not related to its chemical nature, *i.e.* to its ability to solvate the mercury atom of an organomercury compound. It is probable that most of the effect of the solvent is due to its influence on adsorption phenomena. It should also be noted that conditions exist under which the salt, PhHgCl, exchanges more slowly in benzene than does diphenylmercury. Pollard[11] found that the ratio of the rates of radiochemical exchange for phenylmercury chloride and diphenylmercury depends on the volume concentration of the reactants. At a 0.01 mole/l concentration in benzene, diphenylmercury reacts faster than phenylmercury chloride whereas at a concentration of 0.001 mole/l the organomercury salt exchanges faster than diphenylmercury.

This is probably related to the different rates of adsorption of these substrates from solution on to the mercury surface. Phenylmercury chloride is much less soluble in benzene than diphenylmercury, and hence, at lower solution concentrations of the substrates the *surface* concentration of PhHgCl will be higher than that of diphenylmercury. It has been mentioned already that the rate of exchange is merely dependent on the surface concentration of the substrate, which means that at lower concentrations PhHgCl will exchange faster despite the fact that its inherent reactivity is lower than that of diphenylmercury. On increasing the concentration, the adsorption of diphenylmercury increases faster than that of phenylmercury chloride since the surface concentration of the latter is, even at the lower volume concentrations, close to the limiting value (in comparison with that of diphenylmercury) due to the low solubility of phenylmercury chloride. Thus, at higher concentrations the effective reaction rate is a measure of the inherent reactivity of the compounds, which is presumably related to their ease of oxidation.

From this it follows that the exchange mechanism may be visualised as proceeding in a number of steps. The first step is the adsorption of the organomercurial on to the mercury surface, the adsorption being a function both of the structure and of the concentration of the substrate, as well as of the nature of the solvent and the presence of surface-active compounds. It is probable that the type of adsorption involved in this instance is chemisorption, with the RHgR′ species adhering strongly to the mercury surface. The next step is electron transfer from the organometallic compound to the mercury metal via the transition state (B). This transfer is the rate-controlling step in the process, and since the net effect is the oxidation of the organomercurial the influence of substituents is similar to that observed for S_E reactions. The final step in the process is the insertion of organomercury radicals into the metallic mercury lattice, and since these radicals are firmly attached to the mercury during the course of the reaction retention of configuration occurs. The reaction is terminated by the dismutation of the organomercury radicals and the desorption of the resulting organomercurial from the mercury surface.

In this study we have attempted to verify the formation of organomercury radicals on the mercury surface by the use of pulse electrochemistry techniques, using a galvanostatic method (chronopotentiometry). This allows the identification of both stable and unstable species formed on the electrode surface during the course of adsorption, and allows their surface concentrations to be determined as well as their relative stabilities and adsorption parameters.

METHOD

The use of the galvanostatic method (GSM) with organic depolarisers has already been discussed[17,18]. The method essentially involves the study of various plateaux formed on the double-layer charging curves obtained after the system has been potentiostated at some desired pre-set initial potential, E_i. The electrode is maintained at this potential for sufficent time for the adsorbed film to accumulate on the surface. The potentiostat is then switched off to allow the galvanostatic part of the system (which involves the flow of a pre-set current through the cell) to be switched on. The electrode potential is recorded as a function of time by means of an oscillograph and this allows an E, t curve, *i.e.* a double-layer charging curve (E= potential, t=time) to be obtained (see Fig. 1). At those potentials at which the rate of the electrochemical reaction is low the major process occurring is the charging of the electric double layer. If the double-layer capacity is independent of the potential the charging curve will be rectilinear, the slope being inversely proportional to the capacity (AB region in Fig. 1). The plateau, E_rE_f, which corresponds to a fast reduction of the depolariser or to an increase in the double-layer capacity at a narrow potential interval, is termed the delay. When the delay corresponds to the reduction of the depolariser it is termed the Faraday delay. After the sample has been completely reduced, the subsequent increase in the potential (region CD) corresponds to the charging of the electric double-layer up to the discharge potentials of the cations of the supporting electrolyte.

The use of a special unit in conjunction with the apparatus allows the reversal, if necessary, of the direction of the polarising current at any potential associated with the charging curve. Thus, the variation in both the cathode and anode currents, or in only one of these, may be obtained, allowing the direct identification of short-lived intermediates formed during the course of a chemical reaction on the mercury surface (or during the course of an electrochemical reduction or oxidation) and enables the study of their properties.

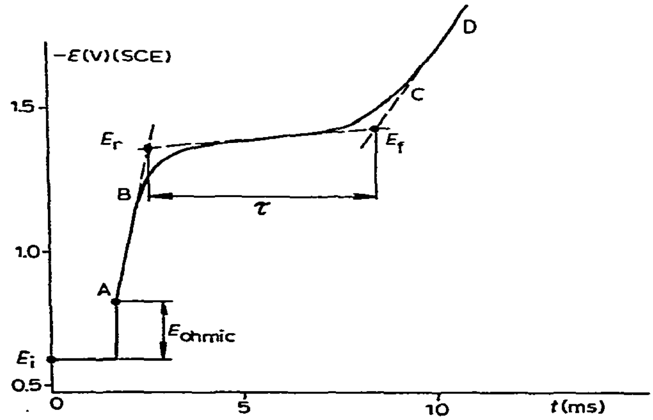


Fig. 1. An example of the mercury charging curve obtained for an electrochemically active compound at high overvoltage. E_i is the initial potential at which the electrode was maintained, E_{ohmic} the ohmic potential drop in the solution, E_r the potential at which the reaction starts, E_f the potential at which the reaction terminates and τ the transition time for the Faraday delay.

The length of the Faraday delay, which is equal to i multiplied by τ, may be expressed in terms of the quantity of depolariser, m, which is reduced during time τ on 1 cm^2 of the electrode surface, *i.e.*:

$$m = \frac{i \cdot \tau}{n \cdot F} \tag{2}$$

where n is the number of electrons involved in the reduction, F = Faraday number.

If the concentration of the depolariser is less than 8×10^{-5} mole/l, or if the current density is above 10^{-2} A/cm^2, then the Faraday delay will, to all intents and purposes, correspond only to the reduction of the adsorbed species[18] (the adsorption delay). At such concentrations and current densities, adsorption delays can only be observed for compounds which are fairly easily adsorbed on to mercury. In these cases, the quantity m is equal to the surface concentration of the depolariser (Γ), which can be therefore be determined from eqn. (2).

Above 8×10^{-5} mole/l or below 10^{-2} A/cm^2, the Faraday delay corresponds to the reduction not only of the adsorbed molecules but also of molecules whose diffusion has brought them into contact with the electrode surface during the time τ. If the depolariser is poorly adsorbed on mercury, then only those molecules which diffuse to the electrode surface will be reduced; the Faraday delay is now termed the diffusion delay. If however, the depolariser is fairly well adsorbed on mercury, then both the adsorbed species and those which have just come into contact with the electrode surface will be reduced and the delay will be due to both adsorption and diffusion. For this composite delay, the length of the plateau as a function of current density will give the surface concentration of the adsorbed species, the quantity Γ (ref. 18),

$$\sqrt{i \cdot \tau} = \frac{\sqrt{a}}{\sqrt{\pi}} + \frac{2\sqrt{b}}{\pi \cdot \sqrt{i}} \tag{3}$$

where

$$a = n \cdot F \cdot \pi \cdot \Gamma\,, \quad b = (n \cdot F \cdot \sqrt{\pi} \cdot C_0 \cdot \sqrt{D})/2$$

with C_0 being volume concentration, D diffusion coefficient for the depolariser, other symbols being conventional. Eqn. (3) holds when

$$\frac{a \cdot i}{b} \gg 1 \tag{4}$$

This criterion was satisfied throughout this work.

RESULTS AND DISCUSSION

This paper deals with the results obtained for diethylmercury by the use of GSM. To apply the method to the species located on the mercury metal surface, it is necessary that both the sample be fairly well adsorbed on mercury and that diffusion from the solution to the electrode be at a minimum value. To achieve these conditions a poor solvent for the organomercurial should be used. In addition for an electrochemical study it is necessary that the solvent be polar, and it was found that water met these two conditions best. The charging curves for solutions of diethylmercury in 10% aqueous methanol with 1 *M* potassium acetate as supporting electrolyte

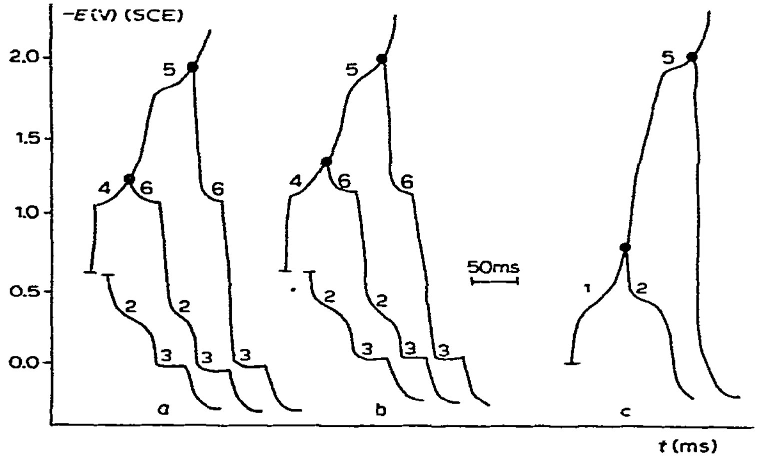


Fig. 2. Schematic representation of the charging curves for Et_2Hg (curves a) and EtHgBr (curves b, c). The branches indicate the instants at which the direction of the polarising current was reversed. The left-hand branches correspond to cathodic processes while the right-hand branches correspond to anodic processes. Delay 1 corresponds to the reduction of EtHgBr, delay 2 to the oxidation of $EtHg^{\cdot}$ radical, delays 3 and 4 to the desorption of Et_2Hg, delay 5 to the reduction of $EtHg^{\cdot}$ and delay 6 to the adsorption of Et_2Hg.

have been studied. Methanol was added in order to raise the solubility of diethyl mercury which is practically insoluble in water, the concentration of a saturated solution of diethylmercury in 10% aqueous methanol still being below 10^{-5} mole/l; for ethylmercury bromide the operating concentration is 10^{-5} mole/l.

The charging curves for the solution of Et_2Hg (cathode polarisation) exhibit two plateaux, at −1.2 V [saturated calomel electrode (SCE), delay 4] and −1.8 V (SCE, delay 5, Fig. 2a). Delay 5 corresponds to the Faraday delay, *i.e.* to the reduction of an electrochemically active species. Plateau 4 corresponds to the capacity effects, *i.e.* to the desorption of diethylmercury from the electrode surface. The delays have been assigned on the basis of the relationship between their reaction potentials (E_r, Fig. 1) and the current density: thus, the potential at which delay 5 starts is dependent on the current density while that for delay 4 is virtually independent. (The charging curves obtained for this system will be analysed in greater detail elsewhere.) With anodic polarisation at the same initial potential ($E_i = -0.6$ V, SCE), both capacity and Faraday delays have been observed (positions 2 and 3, respectively, in Fig. 2a). It should be noted that diethylmercury itself is inactive electrochemically[19] over the potential range studied.

Ethylmercury bromide reveals a similar state of affairs (Figs. 2b, 2c). Thus, diethyl mercury and ethylmercury bromide may be assumed to produce the same electrochemically active species. From the vast electrochemistry of organomercury salts[20–23] it is probable that reduction of these compounds proceeds via two one-electron steps.

$$\begin{array}{l} RHgX + e^- \rightleftarrows RHg\cdot + X^- \\ \qquad\qquad \downarrow k_d \\ \qquad\quad \tfrac{1}{2}(R_2Hg + Hg) \end{array} \qquad (5)$$

$$\mathrm{RHg}\cdot + e^- \xrightarrow[\text{negative potentials}]{\mathrm{H}^+,\ \text{more}} \mathrm{RH} + \mathrm{Hg}$$

This suggests that organomercury radicals, RHg·, should be generated from RHgX on the electrode surface at a definite potential. It follows, therefore, that the Faraday delay 5 present in the charging curves obtained with ethylmercury bromide solutions corresponds to the reduction of the ethylmercury radical. Since the Faraday delays coincide with respect to both their potentials and their shapes for Et_2Hg and EtHgBr, it may be deduced that the organomercury radical EtHg· is the electrochemically active species formed from diethylmercury and that it is produced by the interaction of the symmetrical organomercurial with the metallic mercury surface during the potential pre-setting without any electrolysis occurring in the system:

$$\mathrm{Et_2Hg} + \mathrm{Hg_{(metal)}} \rightleftarrows 2\ \mathrm{EtHg}\cdot$$

The charging curves obtained for EtHgBr solutions at various pre-set potentials and various reverse current potentials have been analysed to give the assignments for each of the delays. Fig. 2b shows the cathodic and anodic charging curves obtained at an initial potential of -0.6 V which generates EtHg· radicals on the electrode surface according to eqn. (5). Since the radicals are partially transformed to Et_2Hg, the cathode pulse reveals two delays: diethylmercury desorption (delay 4) and EtHg· reduction (delay 5). The anodic pulse also reveals two delays: oxidation of EtHg· to $EtHg^+$ (delay 2) and desorption of diethylmercury (delay 3). When the current was reversed, similar delays were observed at potentials lying between delays 4 and 5. Delay 6 corresponds to the adsorption of the diethylmercury desorbed earlier at the cathodic pulse (delay 4). If the current is reversed at potentials more negative than those associated with the reduction of the radicals (delay 5), the delay corresponding to the oxidation of EtHg· (delay 2) will be absent since the reduction of the radicals is irreversible. Delays obtained for solutions of diethylmercury were found to behave in a similar fashion. (Fig. 2a).

In summary, therefore, diethylmercury interacts with metallic mercury to form the same species as those formed when ethylmercury bromide is subjected to a one-electron reduction. It has been suggested[20-23] that the latter process results in the formation of ethylmercury radicals. It is possible that isotopic exchange of mercury between organomercury compounds and mercury metal occurs via the intermediate formation of such radicals. It is probable that the radicals formed on the mercury surface are complex species (*e.g.*, RHgHgR, $\mathrm{RHg(Hg)}_n\cdot$ and others, all of them being equivalent to the organomercury radical inserted into the metallic mercury lattice) rather than simple RHg· particles, but to date there is no data to enable us to distinguish between these two possibilities.

EXPERIMENTAL

Diethylmercury and ethylmercury bromide were synthesised using previously reported methods[24]. Their constants coincided with those reported earlier. Methanol ("chemically pure" grade) was purified by distillation after refluxing with magnesium methoxide[25]. Commercial potassium acetate ("special purity" grade) was used as the background electrolyte. Galvanostatic measurements were carried out using an apparatus designed by the Institute of Electrochemistry, Academy of Sciences of the

USSR. The parameters of the device, as well as the procedure, have been described in detail[17,18]. Their essential features are summarised briefly below.

The device consists of a cell, a potentiostat/galvanostat unit and oscillographs. The unit was supplied with a combination of standard equipment which allowed the reversal of the direction of the polarising current at any potential.

The cell was a glass vessel kept at a constant temperature. It was fitted with a mercury capillary, which produced mercury drops of practically equal mass and surface area, (3.6×10^{-2} to 4.0×10^{-2} cm^2), an amalgamated platinum hook upon which the mercury drop was suspended, with a special trowel to catch the drop and hang it on the hook. The potential of the working electrode (the mercury drop on the platinum hook, *i.e.* the cathode) was set by means of a potentiostat to which the auxiliary electrode (anode) and the reference electrode were connected. The reference electrode (external) was SCE. Its potential was tested twice daily (before and after a series of experiments) against the standard SCE. Its drift was less than 3 mV per 24 h.

During measurements, the reference electrode (SCE) was connected to the solution under investigation by means of an electrolytical key whose cock was shunted with a capacity empirically adjusted so as to minimise any errors due to fast potential variation.

The working electrode potential was set accurately to ±2 mV, and the system could be switched continuously from the potentiostatic to the galvanostatic stage in ca. 3 ms. The galvanostat operating current could be varied over the range 0.5 μA to 5 mA for the cell.

The charging curves were recorded simultaneously on two differently scaled oscillographs. The transition time τ was measured on a C-1-15 oscillograph at a sensitivity of 100, 200, or 300 mV/cm. The reaction potentials E_r (Fig. 1) were measured on the other machine (ENO-1) at a sensitivity of 30 mV/cm. E_r could be measured to within 0 to -1.5 V through the use of a special condenser for the initial component of the potential[18]. The drift of the condenser potential was less than 2 mV per 12 h.

The charging curves were photographed and the negatives used to measure τ and E_r.

The experimental procedure was briefly as follows. A sample of diethylmercury or ethylmercury bromide was dissolved in 2.5 ml methanol and the solution of potassium acetate in doubly-distilled water was added so as to give 25 ml of sample 1 *M* in potassium acetate. The resulting solution was placed in the cell and hydrogen bubbled through for an hour. A mercury drop was suspended on the platinum hook, the drop surface area being calculated on the basis of the rate of mercury flow from the dosing capillary and the time of drop growth (found by means of a timer for each drop). The working electrode (the mercury drop) was maintained for some time at the potential E_i and then the galvanostatic stage was switched on and the charging curves photographed. Each experiment was repeated twice at the same current. All the galvanostatic measurements were carried out at 25±0.2° in a thermostat.

The photographs were projected on to a screen and processed to give the E_r values. These values, which are relative to the SCE, include the ohmic potential drop between the electrode surface and the Luggin capillary (the submerged section of the electrolytic key).

The ohmic potential drop was determined by means of the relationship $\Delta E_{\text{ohmic}} = I \cdot R_{\text{ohmic}}$ where I is the current and R_{ohmic} is the resistance of the electrolyte. For potassium acetate dissolved (1 mole/l) in 10% aqueous methanol R_{ohmic} was 31.7 ohm, as found from the experimental plots of ΔE_{ohmic} *vs.* current which gave a straight line of zero intercept whose slope is equal to R_{ohmic}. The values of ΔE_{ohmic} for a given current I were found from the instantaneous potential jump which occurred immediately after the galvanostatic stage had been switched on. This jump could be observed on the oscillograph before the charging of the electrical double-layer depicted in Fig. 1 commenced.

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