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EXCHANGE OF ORGANOMERCURY COMPOUNDS WITH MERCURY METAL

IV*. THE RATE-DETERMINING STEP

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Summary

Rates of mercury exchange between organomercury compounds R_2Hg and mercury metal have been compared with the rates of demercuration of the respective diorganodimercurials (k_{-1}) and with the rates of interaction of R_2Hg with mercury (k_1):

$$R_2Hg + Hg \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RHgHgR$$

The nature of the rate-determining step is discussed.

Introduction

In previous papers [1 - 3] the use of the galvanostatic method, GSM, was described for studies of the exchange of mercury between organomercury compounds and mercury metal. It was shown that on a mercury metal surface organomercury compounds of the type R_2Hg give subvalent species which were suggested as possible intermediates in the exchange.

Organomercury radicals, $RHg^•$, have also been postulated as the products of the one-electron reduction of organomercury salts of the type RHgX [4 - 6]. In a number of studies, however, it has been noted that the structures of the resulting radical species could be somewhat more complex than merely $RHg^•$ [2,7 - 9], and that these species could have the structures $(RHg)_n$, RHg_nR or $RHg_n^•$. For the sake of simplicity, however, in all previous studies the radical species have always been discussed in terms of the simplest structure i.e. the monomeric radical $RHg^•$. However, we have already reported [1,10] the experimental evidence in support of the assumption that the organomercury radicals are not stable species on a mercury surface. It has been shown that there is a

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*For Part III, see ref. 1.

surface equilibrium between R_2Hg and another kind of species which may be readily reduced and oxidized. In such species both organic groups R originally present in the same R_2Hg molecule remain bound to each other through the agency of a few mercury atoms. The most probable structure for such species is that of "organic calomel" [1]:

$$R_2Hg + Hg(met) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RHgHgR(ads) \tag{1}$$

Equilibrium (1) is obviously very similar to equilibrium (2) proposed in refs. 2 and 3, in which the two organomercury radicals are assumed to be kinetically independent:

$$R_2Hg + Hg(met) \rightleftharpoons 2\ RHg^{\cdot}\ (ads) \tag{2}$$

Strong evidence has however been put forward [1] to suggest that the mercuration of R_2Hg to organic calomel, R_2Hg_2, does not proceed via the pre-equilibrium step (2). A mechanism for mercury exchange between an organomercury compound and mercury metal involving organic calomel as an intermediate was first postulated by Kreevoy and Walters [7] for mercury isotopic exchange. Such a mechanism is in good agreement with the fact that the exchange of mercury between p-$NO_2C_6H_4HgC_6H_5$ [11] or p-$CH_3C_6H_4HgC_6H_5$ [12] and mercury metal does not lead to the corresponding symmetrical organomercurials*.

In the present paper the rate-determining steps in the exchange reaction are considered, the discussion being based on data obtained by GSM. In this discussion the intermediates are considered as having the formula R_2Hg_2.

Results and discussion

Exchange of organomercury compounds with mercury metal involves the reaction steps [2, 7, 14] shown in Scheme 1.

The overall rate of the process can be, in principle, controlled by the rate of any of the steps written above. However, other experiments have shown [7,12,14,15] that diffusion is not the rate-determining step. This follows from (i) that the rates of the exchange reactions show little dependence on the rate of stirring of the solution (see, for example ref. 12) and (ii) that the activation enthalpy for the exchange is ca. 5 kcal·mol^{-1} higher than that for the pure diffusion process [7,12]. Both adsorption and desorption of R_2Hg are not rate-determining steps either, since the exchange rate is practically independent of the nature of the solvent [7,11]*. Although adsorption is not a rate-determining step, it can nevertheless affect the reaction rate since the latter depends on the surface concentration, Γ, of reacting species.

From this it may be concluded that the rate-determining step in the

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*It may be supposed that the disproportionation reaction $2ArHgAr \rightarrow Ar_2Hg + Ar'_2Hg$ *on the mercury surface* is followed by a fast back reaction between Ar_2Hg and $Ar'Hg$ *in solution*. However, following the recent data obtained by Pollard and Thompson [13] this is hardly likely.

Scheme 1 (M = Hg)

(i) Diffusion to the mercury surface

$$R_2Hg_{(solv.)} \rightleftharpoons R_2Hg_{(surf.)}$$

(ii) Adsorption on the mercury surface

$$R_2Hg_{(surf.)} + M_{(met)} \rightleftharpoons R_2Hg \cdot M_{(ads.)}$$

(iii) Reversible metal exchange in the adsorpted layer

$$R_2Hg \cdot \dot{M}_{(ads.)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (RHgMR)_{ads} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} R_2M \cdot \dot{Hg}_{(ads)}$$

(iv) Desorption off the mercury surface

$$R_2M \cdot \dot{Hg}_{(ads)} \rightleftharpoons R_2M_{(surf.)} + Hg_{(met)}$$

(v) Diffusion away from the mercury surface

$$R_2M_{(surf.)} \rightleftharpoons R_2M_{(solv.)}$$

exchange process is a chemical reaction involving R_2Hg on the mercury surface. GSM appears to be a very convenient method for elucidating the nature of this rate-determining step. If the reaction path proceeds via the intermediate organic calomel, its rate may be limited either by step k_1 or by step k_{-1} in stage (iii) of the above scheme.

Previous data [3] enable an estimation of the rates of demercuration of diorganodimercurials on mercury surfaces to be made and when these are compared with the corresponding mercury isotopic exchange rates some estimate may be made of the rate of the slowest reaction step. Unfortunately, however, most rate constants quoted for isotopic exchange processes are given without any reference to the surface concentrations of reagents, and they have therefore, rather limited applicability. Only the rates of exchange per unit area of mercury surface may be used in a comparison of the rates of exchange with the rates of formation or demercuration of RHgHgR. In addition, the rates of exchange for different organomercury compounds may be compared with each other only if the surface concentrations, Γ, of all the compounds under comparison are the same. Fortunately, at the concentrations of organomercury comounds generally employed this requirement is apparently satisfied: thus, according to Marshall and Pollard [12], when the concentrations of organomercury compounds in benzene and other organic solvents are higher than 0.1 *M* the rate of exchange is practically independent of the volume concentration of R_2Hg (resulting in a plateau in the corresponding adsorption isotherm). If R_2Hg is adsorbed from aqueous solutions, the plateau in the corresponding adsorption isotherm is achieved at volume concentrations of the solutes of about 10^{-5} to 10^{-6} mol l^{-1} [16].

The following kinetic equation may be written for the rate of reaction (iii) (Scheme 1):

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*This enables discussion of the effect of structure on the rates of the reactions, when carried out in different solvents, to be undertaken without consideration of the difference in the nature of the solvent.

$$\text{Rate} = \frac{1}{\Gamma_{\mathrm{Hg}}} \cdot \frac{\mathrm{d}(\Gamma_{\mathrm{R_2Hg}})}{\mathrm{d}t} = k_1 \Gamma_{\mathrm{R_2M}} - k_{-1} \Gamma_{\mathrm{R_2Hg}} \cdot \frac{\Gamma_{\mathrm{M}}}{\Gamma_{\mathrm{Hg}}}$$

where Γ_{Hg}, $\Gamma_{\mathrm{R_2M}}$, Γ_{M} and $\Gamma_{\mathrm{R_2Hg}}$ are the surface concentrations of Hg, R_2M, M and R_2Hg, respectively.

In the initial stages of the exchange when $\Gamma_{\mathrm{M}} \ll \Gamma_{\mathrm{Hg}}$, i.e. when Γ_{Hg} = constant.

$$\text{Rate} = k_1 \Gamma_{\mathrm{R_2M}}$$

Under stationary conditions, when

$$\frac{\mathrm{d}(\Gamma_{\mathrm{RHgMR}})}{\mathrm{d}t} = 0 \tag{3}$$

the rate of exchange $= k_1 \Gamma_{\mathrm{R_2M}} = k_{-1} \Gamma_{\mathrm{RHgMR}}$

To date, no direct quantitative data exist concerning the value of the rate constant k_1, but data from another report [3] may be used to provide a semi-quantitative estimate of the rate k_{-1}.

Thus, we have previously reported [3] experimental data which were interpreted in terms of a competitive process between the dismutation of RHg· radicals and their electrochemical oxidation. However, more recent studies [1] have shown that the species RHg· are really dimeric, i.e. R_2Hg_2. Hence the data quoted in Table 1 of Ref. 3 are really concerned with competition between the electrochemical oxidation of the diorganodimercurial species R_2Hg_2 and their demercuration via the reaction of rate constant k_{-1}, both processes occurring in the adsorbed monolayer, i.e.

$$2\mathrm{RHg}^{+} \xleftarrow[\text{oxidation}]{} \mathrm{RHgHgR} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{R_2Hg} + \mathrm{Hg}$$

At high current densities demercuration does not occur, the rate of oxidation of R_2Hg_2 being too high for demercuration to occur during oxidation of the monolayer. With low current densities, however, most of the R_2Hg_2 disappeared through the dismutation with rate constant k_{-1}. The highest current density at which such dismutation may be observed is approximately given by the product $k_{-1}\Gamma_{\mathrm{R_2Hg_2}}$ where $\Gamma_{\mathrm{R_2Hg_2}}$ is the surface concentration of R_2Hg_2 in the adsorbed layer during the initial stages of electrolysis. In our previous paper [3] this maximum current density was termed the "break-off current".

At other current densities two processes, the formation of R_2Hg_2 and its demercuration, occur at current densities close to the "break-off current", the surface concentration of R_2Hg being neglected, i.e. the reaction with rate constant k_1 may be neglected. Under such circumstances the rate of demercuration, expressed in electrical units, is equal to the "break-off current", i.e.

$$i_{\text{break-off}} = k_{-1} \Gamma_{\mathrm{R_2Hg_2}} \tag{4}$$

The values [3] of $i_{\text{break-off}}$, (as obtained from experimental data on the lengths of the Faradaic delays [2]), are listed together with the rates of the dismutation reactions in Table 1.

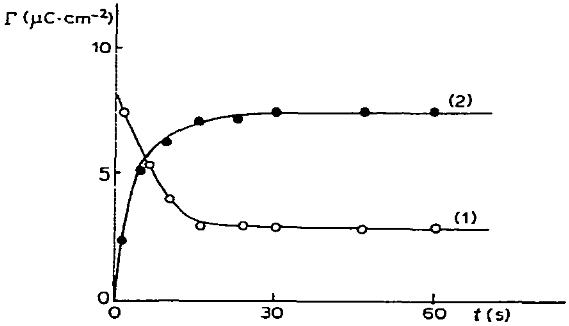

Fig. 1. (1) Oxidation delay lengths for Et_2Hg_2 and (2) anodic delay lengths for the desorption of Et_2Hg as a function of the time for which the mercury electrode was maintained at the pre-setting potential. The Et_2Hg_2 species are formed by the interaction of Et_2Hg with mercury. [Saturated solution of Et_2Hg in $MeOH/H_2O$ (1/9 v/v), using 1 M KOAc as the background electrolyte at 25°C.] $E_i = -0.6$ V (sce), current density 4.5 m A·cm^{-2}.

Under steady-state conditions, the rate of dismutation are equal to the rates of formation of R_2Hg_2. If it is supposed that the rate of formation of organic calomel limits the rate of mercury exchange, then the data given in Table 1 may be considered to be a measure of the relative reactivities of the various R_2Hg_2 species involved in the mercury exchange reaction. The data given in Table 1 show that the rate of demercuration (and therefore the rate of mercury exchange) is much lower for alkylmercury compounds than that for aryl organomercurials. This is in agreement with known experimental data on the rates of mercury exchange [17 - 19].

Heitz [19] has shown that the exchange of diethylmercury with Hg in benzene solutions in the presence of ca. 10^{-1} *M* concentrations of Et_2Hg is slower by a factor of 100 than the exchange of diphenylmercury at the same concentration. It is very interesting that the ratio of the rates of formation (and demercuration) of species of the type Ph_2Hg_2 and Et_2Hg_2 is also ca. 100 (see Table 1). It also follows from Table 1 that dimethylmercury should exchange at a slightly slower rate than diethylmercury, and indeed such behaviour has been observed in experiments with labelled compounds [19].

If the surface concentration of R_2Hg is known, equation (3) may be used

TABLE 1

RATES OF DEMERCURATION OF DIORGANODIMERCURIALS ON A MERCURY SURFACE [$MeOH/H_2O$ (1/9 v/v), 1 M KOAc, 25°C]

R in R_2Hg_2	$\Gamma_{R_2Hg_2}$ [a] (× 10^{10} mol·cm^{-2})	$i_{\text{break-off}}$ [b] (A·cm^{-2})	$\frac{-d[R_2Hg_2]}{dt}$ (Mol·cm^{-2}·s^{-1})
$PhCH_2$	—	$\geqslant 2 \times 10^{-1}$	$\geqslant 2 \times 10^{-6}$
Ph	2.2	1.50×10^{-1}	1.6×10^{-6}
2-Naphtyl	2.9	1.00×10^{-1}	1.0×10^{-6}
Mesityl	1.1	0.64×10^{-1}	0.7×10^{-6}
Me[c]	1.3	1.10×10^{-3}	1.1×10^{-8}
Et	1.2	1.56×10^{-3}	1.6×10^{-8}
n-Pr	2.3	2.04×10^{-3}	2.1×10^{-8}
i-Pr	1.7	1.24×10^{-3}	1.3×10^{-8}
n-Am	1.9	6.60×10^{-3}	6.8×10^{-8}

[a] The values of $\Gamma_{R_2Hg_2}$ were obtained using the method described in ref. 20. [b] See ref. 3. [c] Approximate values.

to estimate the rate constant for the formation of R_2Hg_2 from R_2Hg (k_1)

$$k_1 = \frac{\text{Rate of exchange}}{\Gamma_{R_2Hg}}$$

By using the data on rates of mercury exchange [12,19] and taking Γ_{R_2Hg} for Ph_2Hg and Et_2Hg to be equal to Γ_{R_2Hg} for $(C_6F_5)_2Hg$, i.e. to 10^{-10} mol cm^{-2} [21], it may be shown that k_1 is ca. 60 s^{-1} for diphenylmercury and ca. 0.6 s^{-1} for diethylmercury. It follows from these values that the rates of mercuration are much greater for diarylmercury compounds than for dialkyl organomercurials. Furthermore, the calculations indicate that mercuration of organomercury compounds of the type R_2Hg on a mercury surface, leading to the formation of R_2Hg_2, is a rather fast process.

The data discussed above apparently verify the assumption that diorganodimercurials are the intermediates in transmetallation reactions involving R_2Hg and mercury metal. The amount of R_2Hg_2 on the surface of the mercury, and hence the possibility or impossibility of observing such species on the surface, obviously depends on the position of equilibrium (1). With diarylmercury compounds this equilibrium lies to the left-hand side* but with dialkylmercury compounds it lies more to the side of Alk_2Hg_2. This means that with diaryl organomercurials the step with rate constant k_1 and the adsorption of Ar_2Hg influence the exchange rate most significantly, but with dialkyl organomercurials the step with rate constant k_{-1} plays some part as well. This conclusion is supported by the data plotted in Figure 1 which show that the concentrations of R_2Hg and R_2Hg_2 are comparable when R = Et. The greater rate of exchange of diarylmercury compounds in comparison with dialkyl organomercurials [19] may be explained on the assumption that both k_1 and k_{-1} are high for diaryl organomercurials.

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*For this reason it is difficult to estimate the surface concentration of a given Ar_2Hg_2 species quantitatively. It is only possible to say that, at a certain percentage coverage of the metal surface by molecules of R_2Hg (R = Ar and Alk), the surface concentration of Ar_2Hg_2 is much lower than that of dialkyl calomel.

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