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EXCHANGE OF ORGANOMERCURY COMPOUNDS WITH MERCURY METAL

II*. DISMUTATION OF ORGANOMERCURY RADICALS ON THE SURFACE OF MERCURY

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SUMMARY

The galvanostatic method has been applied to the study of the dismutation of organomercury radicals formed by the electrochemical reduction of organomercury salts on the mercury surface. The relative stabilities of organomercury radicals have been found to follow the series $AlkHg\cdot > ArHg\cdot$, $CH_2{=}CHHg\cdot \gg PhCH_2Hg\cdot$. The lifetimes on the mercury surface have been determined as 10^{-2} to 5×10^{-2} sec for $AlkHg\cdot$, 1×10^{-4} to 2×10^{-4} for $ArHg\cdot$ and $CH_2{=}CHHg\cdot$, and $\leqslant 10^{-4}$ sec for $PhCH_2Hg\cdot$. The C–Hg bond in radicals on the mercury surface is more stable than that in radicals generated under homogeneous conditions. This has been attributed to the stabilising effect of the metal.

INTRODUCTION

In the previous paper[1] we showed that organomercury radicals were produced in the reaction of diethylmercury with mercury metal. This reaction is probably typical for all organomercurials, the radicals being intermediates formed during the exchange of organomercury compounds with mercury. A convenient technique for producing organomercury radicals on mercury surfaces is the electrolysis of organomercury salts,

$$RHgX_{ads}+e^- \rightleftarrows RHg^{\cdot}_{ads}+X^-$$

the radicals produced probably possessing similar properties to the respective radicals formed as intermediates in the mercury isotope exchange. All organomercury radicals are unstable, disproportionating rapidly,

$$2\,RHg\cdot \rightarrow R_2Hg+Hg \qquad (1)$$

so electrolysis of the salts results in the formation of symmetrical organomercury

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* For Part I see ref. 1.

compounds[2,3]. It is possible, however, to identify these radicals by means of pulse electrochemical techniques[1,4,14,15].

RESULTS AND DISCUSSION

We have applied the galvanostatic method (GSM)[1] to organomercury radicals formed on the mercury surface during the electrochemical reduction of various organomercury salts RHgX, *i.e.* EtHgBr, n-PrHgOAc, i-PrHgBr, n-$C_5H_{11}HgBr$, cyclo-C_5H_9HgBr, PhHgOAc, 2-naphthylmercury acetate, mesitylmercury bromide, vinylmercury chloride and $PhCH_2HgCl$. Measurements were carried out in 10% (v/v) aqueous methanol with 1 *N* potassium acetate as a supporting electrolyte at 25°. Concentrations of the organomercury substrates were usually at or below 10^{-4} mole/l, thus allowing the effect of diffusion on the length of the delay to be a minimum. In this way, adsorption delays[1] which are solely attributable to surface concentrations have been measured.

The accumulation of the substrate on the mercury surface was carried out at more positive potentials than those at which the reduction of the organomercury salts occurs, while the potentiostat was pre-set for a time selected so that a sufficient amount of the substrate should accumulate on the electrode surface. The system was then switched over to the galvanostatic system and the charging curves (chronopotentiograms) recorded at various current densities. At a given potential, the direction of the polarising current was reversed and the delays recorded which corresponded to the oxidation of organomercury radicals, *i.e.*

$$RHg\cdot + X^- \rightarrow RHgX + e^- \qquad (1)$$

The charging curves obtained in this study were, in general, similar to those described previously for ethylmercury bromide[1]. The delays studied have been those associated with the reduction of the salts (delay 1) and with the oxidation of the radicals (delay 2) formed through the reduction of the organomercury salts. The corresponding delays related to the reduction of the organomercury radicals were rather more difficult to measure since they sometimes occurred at potentials coincident with those corresponding to the discharge of the supporting electrolyte.

It is possible for the delays associated with the reduction of RHgX and the oxidation of RHg· to have different lengths; at sufficiently low current densities the delay due to oxidation is shorter than that due to reduction. Since the length of the delay associated with the reduction of the salt is related to the initial concentration of organomercury radicals formed on the mercury surface, the decrease in the oxidation delay at low current densities may be related to a decrease in the concentration of the radicals through the occurrence of reaction (1). At higher current densities, when the time of electrolysis (defined as the time interval between the formation and oxidation of the radicals) is low, this reaction may be neglected, so that the length of the delay due to the reduction of the salt becomes equal to that due to oxidation of the radicals. Figure 1 depicts the length of the delay *vs.* current density for delays 1 and 2 as obtained for 2-naphthylmercury acetate. Similar plots have been obtained for the other compounds investigated in this study.

One major, and as yet unresolved, problem concerns the use of GSM to obtain quantitative characteristics of the stability of organomercury radicals on the

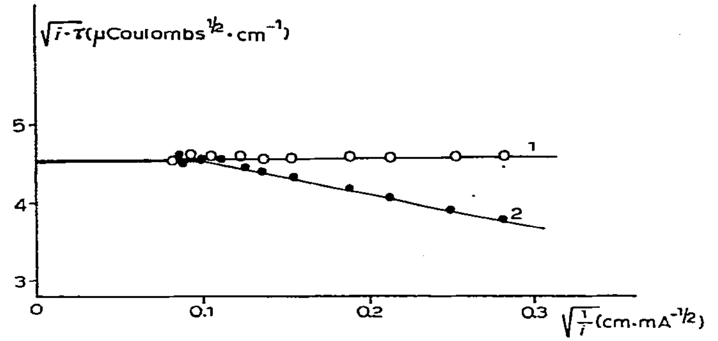

Fig. 1. The dependence of the length of the delay upon the current density for 2-naphthylmercury acetate. Curve 1, the reduction of the organomercury salt; curve 2, the oxidation of the organomercury radical. $c = 6\times10^{-5}$ mole/l, $t = 30$ sec (with stirring of the solution), $E_i = +0.10$ V (*vs.* SCE). The supporting electrolyte was 1 *M* AcOK in MeOH/H_2O (1/9 v/v), the temperature being 25°.

surface of mercury. However, two semi-quantitative approaches may be used in order to obtain the relative reactivity of RHg· towards dismutation, *i.e.* to obtain the relative stability of the radicals. Thus the plot of delay length *vs.* current density, (Fig. 1), demonstrates that at higher current densities delays 1 and 2 are equal in length whereas delay 2 decreases in length as the current density is decreased. The quantity $(\sqrt{1/i})_{\text{break-off}}$, which is related to the instant at which the decrease in the length of delay 2 (with respect to delay 1) starts, is different for the different organomercury radicals, so it may be used as a measure of the relative reactivities of these radicals towards dismutation (the lower the value of $(\sqrt{1/i})_{\text{break-off}}$ the less stable the organomercury radical on the mercury surface, see Table 1).

Apparently, when the lifetime of the radical becomes comparable with the

TABLE 1

THE VALUES OF $(\sqrt{1/i})_{\text{break-off}}$ AND $(1/i_{\max})$ AS CHARACTERISTICS OF THE RELATIVE STABILITIES OF ORGANOMERCURY RADICALS ON THE SURFACE OF MERCURY

R in RHg·	$c\times10^4$ (*mole/l*)	$(\sqrt{1/i})_{\text{break-off}}\times10^2$ (*cm/$\sqrt{mA}$*)	$(1/i)_{\max}\times10^{-3}$ (*cm^2/A*)^a
i-Pr	2	90	26±7
Et	0.1	80	17±4
cyclo-C_5H_9	1	55	16±3
n-Pr	10	ca. 70	13±3
n-C_5H_{11}	0.85	31	7±2
Mesityl	0.17	12.5	0.2±0.04
2-Naphtyl	0.6	10	0.1±0.03
Ph	1		below 0.1
CH_2=CH	1		below 0.01
PhCH_2	1		very low

[a] The error in $(1/i)_{\max}$ was calculated as follows. A perpendicular was dropped from the maximum (Fig. 2) on to the X-axis and a second perpendicular was dropped on to the first. This second perpendicular was positioned at a distance from the maximum of 10% of the entire transition time τ at the maximum (this being equal to the accuracy of the delay length measurements). The distance between the points at which the horizontal straight line intercepted the descending and ascending branches of the curve gave a measure of the error in $(1/i)_{\max}$.

length of the delay the time interval for delay 2 becomes less than that for delay 1. When this occurs the radical lifetime is comparable with the electrolysis time. The charging curves obtained at the current density corresponding to the "break-off" current* allow the lifetimes of the organomercury radicals to be estimated. For example, for the alkylmercury radical the lifetime is 10^{-2} to 5×10^{-2} sec, for the arylmercury radical 1×10^{-4} to 2×10^{-4} sec and for the benzylmercury radical much less than 10^{-4} sec. Similar data have not previously been reported in the literature, although the paper by Laviron[4] who applied cyclic voltammetry to 3-pyridylmercury chloride and obtained 10^{-2} to 10^{-3} sec for the lifetime of the respective organomercury radicals should be noted.

The value of the "break-off current" is always somewhat arbitrary, and for this reason the dependence of the length of delay 2 (τ) on the current density [*i.e.* on $(1/i)$] seems to be a more convenient measure. As shown in Fig. 2, this dependence

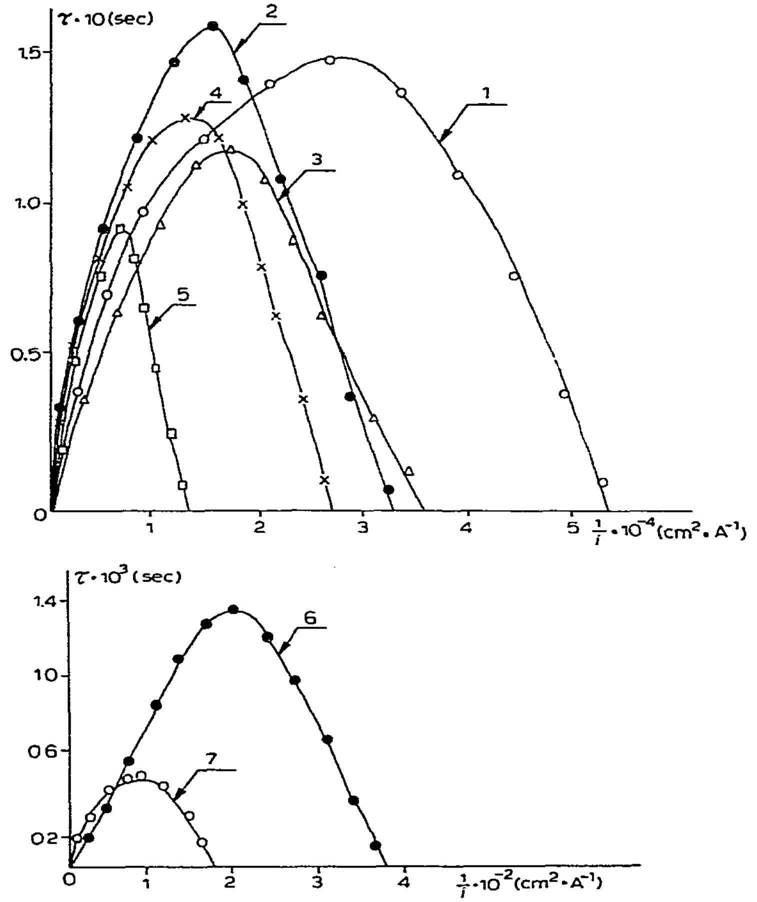

Fig. 2. The dependence of the transition time, τ, on $(1/i)$ for the oxidation delays of organomercury radicals. Curve 1, i-PrHg·; curve 2, EtHg·; curve 3, cyclo-C_5H_9Hg·; curve 4, n-PrHg·; curve 5, n-$C_5H_{11}Hg$·; curve 6, mesitylmercury radical; curve 7, 2-naphthylmercury radical.

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* The "break-off" current is the minimum current at which the lengths of delays 1 and 2 are equal.

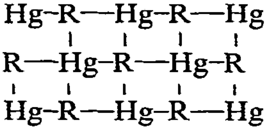
exhibits a maximum value. The number of coulombs which pass through the solution at the potentials associated with the first and second delays are equivalent (at higher current densities) to the amount of RHgX adsorbed and are independent of the current density *i*. For this reason the length of delay 2 and the electrolysis time increase with $(1/i)$.

In addition to electrolysis, dismutation of the radicals also occurs to give R_2Hg and Hg. This process becomes more distinct as the time of electrolysis increases (the value of $(1/i)$ also increases). At lower values of $(1/i)$, radicals disappear mainly through an electrochemical mechanism (oxidation) whilst at higher values of $(1/i)$ they do so through dismutation; in both cases the oxidation delay for residual amounts of RHg· is short. The delay has its greatest length at intermediate values of $(1/i)$ when the oxidation rate is comparable with the dismutation rate. The position of the maximum on the τ vs. $(1/i)_{max}$ curve is a characteristic of the stability of organomercury radicals on the surface of mercury. The greater the value of $(1/i)_{max}$ the more stable the organomercury radical on the mercury surface. This is shown in Table 1. Table 1 also shows that the rate of dismutation increases according to: i-Pr < Et, cyclo-C_5H_9 < n-Pr < n-C_5H_{11} < mesityl < 2-naphthyl < Ph < CH_2=CH $\ll$ $PhCH_2$ for organomercury radicals participating in reaction (1).

The above organomercury radicals may be divided into three groups. The first includes the alkylmercury radicals, the second the aryl- and vinylmercury radicals, while the third consists only of the benzylmercury radical. The lifetimes of the alkylmercury radicals are much greater than those of the arylmercury species, whereas the benzylmercury radical is very short-lived. The high reactivity of the latter towards dismutation may explain the fact that, unlike phenyl- or n-hexylmercury acetates, benzylmercury acetate is electrolysed in the presence of CCl_4 to produce mainly dibenzylmercury rather than benzylmercury chloride, the major product of the reaction of $PhCH_2Hg$· with CCl_4[5].

The above series is the reverse of that related to the stabilities of the respective organic radicals R· in gas phase[6]. It is possible that the stability of the radical R· is directly related to the Hg–R bond strength, *i.e.* the more stable the radical the weaker is its linkage to the metal surface. Thus, alkylmercury radicals are more stable than arylmercury radicals while the benzylmercury radical, probably due to the extremely high stability of benzyl radicals, is much less stable. It should be noted that a similar inverse dependence exists between the stabilities of organic radicals R· and of the respective organosilver compounds RAg[7]. Organomercury radicals on the surface of metallic mercury probably have greater stabilisation energies than the corresponding radicals in the gas phase. The lower the energy of the linkage between an organomercury radical and the mercury surface, the faster should be the rate of dismutation, and for this reason the strength of the radical–mercury surface bond is very important in determining the position of a given radical in the series relating the relative stabilities of organomercury radicals.

At this point it is useful to compare the behaviour of organomercury radicals on the mercury surface with their behaviour in homogeneous media. Previous work[8–10] has demonstrated that in homogeneous media organomercury radicals disappear through demercuration rather than through dismutation. Thus, the radicals formed on the mercury surface may be assumed to be more stable than those in homogeneous media. Probably, the metal surface plays an important role in this stabilisation process possibly through the energy gain due to the transfer of electrons from RHg· to the conducting levels of mercury. Kraus[11], as well as Billinge and Gowenlock[12], has shown that aryl- or alkylmercury chlorides, when electrolysed in liquid ammonia, produce a dark deposit on the cathode, the material deposited having the composition RHg. This substance was not a free radical since it gave no ESR signal and it was found to possess an electro-conducting crystalline structure ("organometal") of the type:



$$\begin{array}{l} \text{Hg-R—Hg-R—Hg} \\ \quad | \quad\; | \quad\; | \quad\; | \\ \text{R—Hg-R—Hg-R} \\ | \quad\; | \quad\; | \quad\; | \quad\; | \\ \text{Hg-R—Hg-R—Hg} \end{array}$$

The unpaired electrons existing in a single RHg unit interact to yield a conducting zone. It is probable that organomercury radicals are stabilised in a similar manner on the surface of mercury metal.

We were also interested in seeing whether the radicals contained in the absorption layer, *i.e.* the radicals in direct contact with the metal surface, differed from those far removed from the metal surface. To investigate this problem we have studied n-propylmercury acetate dissolved in water ($c = 7 \cdot 10^{-3}$ mole/l) containing 1 *N* potassium acetate as a supporting electrolyte at 25°. n-Propylmercury radicals have already been shown to be relatively stable, and thus at higher concentrations (ca. 10^{-2} *M*) of n-PrHgOAc diffusion may be expected to result in a greater number of the radicals (in comparison with those already existing in the monolayer coating the electrode) being generated at the electrode surface. The results obtained through the use of GSM (to be published) demonstrate that in this instance polylayers of propylmercury radicals are formed at the mercury surface, with dismutation, which in this instance yields the symmetrical organomercurial, Pr_2Hg, occurring mainly in those layers which are not directly in contact with the surface.

Polylayers of organomercury radicals probably consist of "organometal" in dynamic equilibrium with the symmetrical organomercurial. This may help to explain the results obtained by Dessy *et al.*[3] who isolated racemic di-sec-butylmercury from the electrolysis of the optically active sec-butylmercury bromide at the mercury electrode. Gowenlock and Billinge[12] have also shown that the "organometal" obtained through the electrolysis of optically active sec-butylmercury chloride in liquid ammonia may be decomposed to produce racemic di-sec-butylmercury. Presumably only the optical activity of the "organometal" is lost, as is implied by the structure of the latter. In contrast, radicals which are chemisorbed on the surface might not lose their optical activity on disproportionation, hence the retention of configuration observed during mercury exchange reactions (see for example, ref. 1 for a survey of this topic).

In summary the metal surface affects not only the relative stabilities of organomercury radicals but also the stereochemistry assumed during dismutation. This conclusion could be significant in the chemistry of organometallic compounds.

EXPERIMENTAL

A description of the electrochemical procedure and the purification of the solvents has already been given[1].

The organomercurials were synthesized through techniques which have been described previously[13]. Their constants coincided with those reported in the literature but as a further check the purity of the samples was tested polarographically. A compound was assumed to be pure if its polarogram exhibited waves at the expected potentials of heights corresponding to the analytical concentration of the organomercurial. All compounds were recrystallised immediately before starting the experiment.

2-*Naphthylmercury acetate*

2-Dinaphthylmercury (1.2 g, 2.8 mmoles) and mercury acetate (0.9 g, 2.8 mmoles) were dissolved in 50 ml n-amyl alcohol and the solution refluxed for 2 h. During this procedure the formation of droplets of metallic mercury was observed. The solution was filtered, cooled and n-amyl alcohol was distilled off to give a crystalline 2-napththylmercury acetate, which was obtained as a white solid after three crystallisations from methanol. The compound decomposed above 200°. A yield of 0.2 g (10% theoretical) was obtained. (Found: C, 38.10, 38.19; H, 2.37, 2.51. $C_{12}H_{10}HgO_2$ calcd.: C, 37.20; H, 2.60%.)

REFERENCES

1 K. P. Butin, A. N. Kashin, A. B. Ershler, V. V. Strelets, I. P. Beletskaya and O. A. Reutov, *J. Organometal. Chem.*, 39 (1972) 39.
2 R. Benesh and R. E. Benesh, *J. Amer. Chem. Soc.*, 73 (1951) 3391.
3 R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen and T. Chivers, *J. Amer. Chem. Soc.*, 88 (1966) 460.
4 C. Degrand and E. Laviron, *Bull. Soc. Chim. Fr.*, (1968) 2228.
5 K. Yosahida and S. Tsutsumi, *J. Org. Chem.*, 32 (1967) 468.
6 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'ev, V. A. Medvedev and Ye. L. Frankevich, *Energiya Razryva Khimicheskikh Svyazei. Potential Ionisatsii i Srodstvo k Elektronu*, the AN SSSR Publishers, Moscow, 1962.
7 F. Glockling and D. Kingston, *J. Chem. Soc.*, (1959) 3001.
8 V. A. M. Chambers, W. R. Jackson and G. W. Young, *Chem. Commun.*, (1970) 1275.
9 Chi-Hua-Wang, *J. Org. Chem.*, 85 (1963) 2339.
10 G. M. Whitesides and J. San Filippo Jr., *J. Amer. Chem. Soc.*, 92 (1970) 6611.
11 G. Kraus, *J. Amer. Chem. Soc.*, 34 (1913) 1732.
12 B. H. M. Billinge and B. G. Gowenlock, *J. Chem. Soc.*, (1962) 1201.
13 L. G. Makarova and A. N. Nesmeyanov, *Metody Elementoorganicheskoi Khimii. Rtut'*, the Nauka Publishers, Moscow, 1965.
14 A. N. Kashin, V. V. Strelets, N. N. Ovsyannikov, K. P. Butin, V. N. Alekseev, I. P. Beletskaya, L. L. Knots, G. A. Tedoradse and A. B. Ershler, *Elektrokhimiya*, 7 (1971) 1586.
15 A. N. Kashin, V. V. Strelets, K. P. Butin, I. P. Beletskaya, L. L. Knots, V. N. Alekseev and A. B. Ershler, *Elektrokhimiya*, 7 (1971) 1587.