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STRUCTURE AND SOLVENT EFFECTS IN ORGANOMERCURIC ELECTROCHEMISTRY. POLAROGRAPHICAL SCALE OF C–H BOND ACIDITIES

K. P. BUTIN, I. P. BELETSKAYA, A. N. KASHIN AND O. A. REUTOV
Moscow State University, Moscow (U.S.S.R.)

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Organometallic compounds containing carbon–metal σ-bonds can be reduced electrochemically; and under these conditions there is fission of the carbon–metal bond, and the metal is transferred to a lower oxidation level.

$$R_nM^{n+} + e \rightarrow R^- + R_{n-1}M^{(n-1)+}$$

In the electrochemical reduction of organometallic compounds electron changes are likely to localize in a metal atom (because of C^-–M^+ polarity); therefore, electrochemical data may afford the possibility of judging the effect of structure of the organometallic molecule on the state of the metal in it (in terms of an electron affinity).

In the present work, many symmetrical organomercuric compounds, R_2Hg, and organomercuric salts, RHgX (X is an acid radical) are studied using the classical polarographic method for ascertaining the effect of the structure of the organic radical, R, and the nature of solvents, on the ability of these compounds to undergo electrochemical reduction.

I. SYMMETRICAL ORGANOMERCURIC COMPOUNDS

Reduction of symmetrical organomercuric compounds at the dropping mercury electrode takes place in one stage with the addition of two electrons[1-3].

$$R_2Hg + 2\,e \rightarrow Hg + 2\,R^- \xrightarrow{2H^+} 2\,RH$$

In most cases, the electrochemical reduction is irreversible (although some exceptions are known, *e.g.*, $(NC)_2Hg$[4]).

The values of the half-wave potentials ($E_{\frac{1}{2}}$) corresponding to fission of various kinds of C–Hg bonds in organomercuric compounds are listed in Table 1. They were measured *vs.* the saturated calomel electrode (SCE) at 25° in 60% aqueous dimethylformamide (DMF) as solvent, using 0.1 *N* Et_4NClO_4 as supporting electrolyte.

It appears from the data presented that the reduction of compounds with more polar C–Hg bonds is usually easier (*i.e.*, at more positive potentials) than that of more covalent compounds. However, a more detailed consideration shows no conformity along these lines[1]. This can be explained by the fact that the half-wave potentials of the irreversible processes are not the only characteristics of the electrochemical

TABLE 1

THE POLAROGRAPHIC PARAMETERS OF THE SYMMETRICAL ORGANOMERCURIC COMPOUNDS, R_2Hg; 60% DMF–H_2O, 0.1 *N* Et_4NClO_4, 25°

Number	*R in R_2Hg*	*Concn. (mM/l)*[a]	$-E_{\frac{1}{2}}$[b] (*V*)	α	$-\alpha E_{\frac{1}{2}}$ (*V*)
1	$CH_2{=}CH$	1.0	2.301	0.26	0.60
2	C_6H_5	0.5	2.199	0.29	0.64
3	$C_6H_5CH_2$	0.2	1.719	0.34	0.59
4	C_6Cl_5	0.2	1.687	0.30	0.51
5	$ClCH{=}CH$ (*trans.*)	0.05	1.681	0.30	0.50
6	$CH_2{=}CH{-}CH_2$	0.2	1.207	0.43	0.52
7	$C_6H_5C{\equiv}C$	0.01	1.073	0.19	0.20
8	C_6F_5	0.01	0.862	0.40	0.20
9	CH_3OOCCH_2	0.05	0.798	0.43	0.34
10	$CCl_2{=}CCl$	0.05	0.538	0.45	0.24
11	Cyclo-C_5H_5	0.5	0.499	0.38	0.19
12	$C_6H_5CH(COOC_2H_5)$	0.05	0.364	0.55	0.20
13	$CH_3COCH(COOC_2H_5)$	0.05	0.346	0.26	0.09
14	tert-$C_4H_9COCH_2$	0.05	0.344	0.56	0.19
15	NC	0.1	0.291	0.24	0.07

[a] *When the concentration of R_2Hg is increased, the polarographic wave is usually distorted (maxima, pre-waves etc.); the most convenient concentration, therefore, was chosen for measurements.* [b] *vs.* SCE.

reaction rate. It is necessary to take into account the value of the transfer coefficients, α. This coefficient is an index of the electrode potential used in the reduction.

If we assume that electron changes are localized in the mercury atom, the highest rate of reduction must be shown by R_2Hg as an ionic triplet in solution, and the lowest rate—for a covalent structure.

$$R{:}^{-}Hg^{2+}{:}R^{-} + 2\,e \xrightarrow{\text{fast}} 2\,R^{-} + Hg$$

$$R{-}Hg{-}R + 2\,e \xrightarrow{\text{slow}} 2\,R^{-} + Hg$$

The half-wave potential of irreversible processes depends on the rate constant of the electrochemical reaction as follows[5]:

$$E_{\frac{1}{2}} = \frac{RT}{\alpha n_a F} \ln \frac{0.886 k_f^0}{D^{\frac{1}{2}}} + \frac{RT}{2\,\alpha n_a F} \ln t \qquad (1)$$

where n_a is the number of electrons in the potential-determining stage, k_f^0 the rate constant of reduction at the potential $E = 0$, D the diffusion coefficient of R_2Hg, t the drop-time and R, T and F have their usual significance.

This equation shows that the rate constant of the electrochemical reduction, which should characterize the polarity of the C–Hg bond, is connected not only with $E_{\frac{1}{2}}$ but also with α. Therefore a correlation between $E_{\frac{1}{2}}$-values and the structure of R (*e.g.*, by means of Hammett's σ) is to be observed only in those series of organomercuric compounds for which α is a constant or changes in α are rather small. This can occur when structural differences in R for a R_2Hg series are small. For example, in a series of dibenzylmercury derivatives with various substituents in the benzene rings, (XC_6H_4-

$CH_2)_2Hg$, a satisfactory correlation between $E_{\frac{1}{2}}$ and Hammett's σ-constant (according to equation, $E_{\frac{1}{2}} = 2\,\sigma\rho$) can be observed. The coefficient of 2 summarizes the effects of the substituents from both rings. The calculated ρ-value is +0.49 V (Fig. 1). The value of $\Delta\alpha$ in the given R_2Hg series does not exceed 0.02.

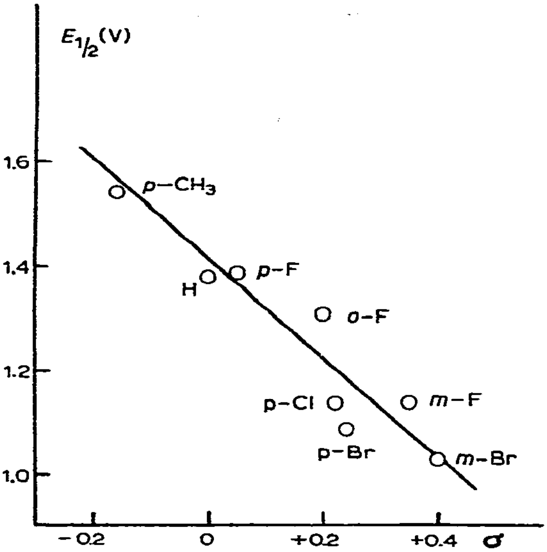

Fig. 1. The effect of substituents in the benzene rings on the half-wave potentials in the $(XC_6H_4CH_2)_2Hg$ series; CH_3CN; 0.1 *N* Et_4NI; 25°; conc. 0.5 mmol.

Such a correlation is impossible if the R's in a R_2Hg series differ from each other more than in the instance given above, as the α-value changes from R to R'.

It is more convenient to rewrite eq. (1) as follows:

$$\alpha E_{\frac{1}{2}} = a \lg k_f^0 + b \tag{2}$$

where k_f^0 depends on activation parameters[6]:

$$\ln k_f^0 = \ln A^* - \frac{Q_0 - \frac{1}{2}Q_D}{RT} \tag{3}$$

where A^* is the apparent frequency factor of the electrode reaction, Q_0 the activation energy of electrode reduction at $E = 0$ and Q_D the activation energy of diffusion.

For two R_2Hg compounds we can write the following equation:

$$\Delta(\alpha E_{\frac{1}{2}}) = a\Delta(\lg k_f^0) \tag{4}$$

since we can neglect for our purposes the differences in the diffusion coefficient values and make the drop-time constant (*e.g.* by applying the positive dropping electrode).

Assuming that in R_2Hg, $\lg k_f^0$ (*i.e.*, Q_0) depends on the polarity of the C–Hg bond, we can say that the meaning of eqn. (4) lies in the fact that when the polarity of the C–Hg bond is lowered the product, $\alpha E_{\frac{1}{2}}$, becomes more negative.

It can be postulated that the $\alpha E_{\frac{1}{2}}$-value depends on the affinity of the carbanion R^- for the Hg^{2+} cation. Unfortunately there are no data for estimating the power of this affinity (except for the NC^- carbanion). However, such data are known for different oxygen and nitrogen bases as well as for halides and sulfur-containing compounds.

Simpson[7] compared the basicities of these bases with their affinities for Hg^{2+} and CH_3Hg^+ cations. He showed that, in general, there was no linear correlation between the basicity of the X particles and their Hg^{2+} affinity. However, it can be seen from the plot drawn in Fig. 2 from Simpson's data that such a correlation is possible in a series of related bases, *i.e.*, those containing the same donor atom (*e.g.*, the nitrogen atom in nitrogen bases)[1].

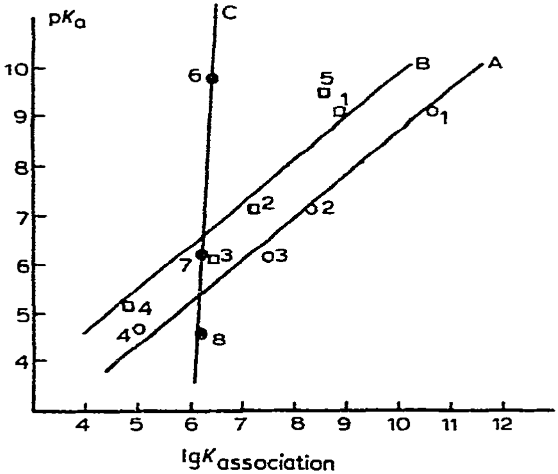

Fig. 2. The dependence between pK_a and the affinities of mercuric cations for different bases. (A), Hg^{2+} $+NR_3$; (B), CH_3Hg^+ $+NR_3$; (C), CH_3Hg^+ $+RO^-$. (1), NH_2(his); (2), Im; (3), Im (his); (4), C_5H_5N; (5), NH_3; (6), $C_6H_5O^-$; (7), HEDTA; (8), CH_3COO^-.

We can assume from this that the affinity of carbanions R^-, *i.e.*, carbon bases, for the mercury atom should also change linearly with the pK_a-values of RH.

On substituting the pK_a-values of RH in place of lg k_f^0 in eqn. (4) we get the following equation:

$$\Delta(\alpha E_{\frac{1}{2}}) = \rho \cdot \Delta pK_a \tag{5}$$

This expresses the dependence of the half-wave potential of R_2Hg upon the basicity of the carbanion, R^-.

The values of the apparent transfer coefficients, α, obtained from the slopes of the logarithmic plots of the polarographic waves [E *vs.* lg $i/(i_d-i)$] together with the calculated $\alpha E_{\frac{1}{2}}$ are given in Table 1. The dependence of $\alpha E_{\frac{1}{2}}$ upon pK_a is shown in Fig. 3. In general, for making this plot, the pK_a-values from the MSAD-scale[8] were used. Attention was paid that the straight line passed through the points corresponding to $(NC)_2Hg$ and $(CH_3COCHCOOEt)_2Hg$, since the pK_a-values for these C–H acids (9.3[9] and 10.7[10] in aqueous solution) are known exactly.

Figure 3 shows that there is good correlation between the values of $\alpha E_{\frac{1}{2}}$ and pK_a, in agreement with eqn. (5), whereas the dependence of $E_{\frac{1}{2}}$ on pK_a is irregular[*].

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[*] The largest deviations from linearity were observed for points in the region of the electrocapillary maximum potentials. In this region, eqn. (1) does not hold because of the large adsorption of R_2Hg on the electrode surface[5].

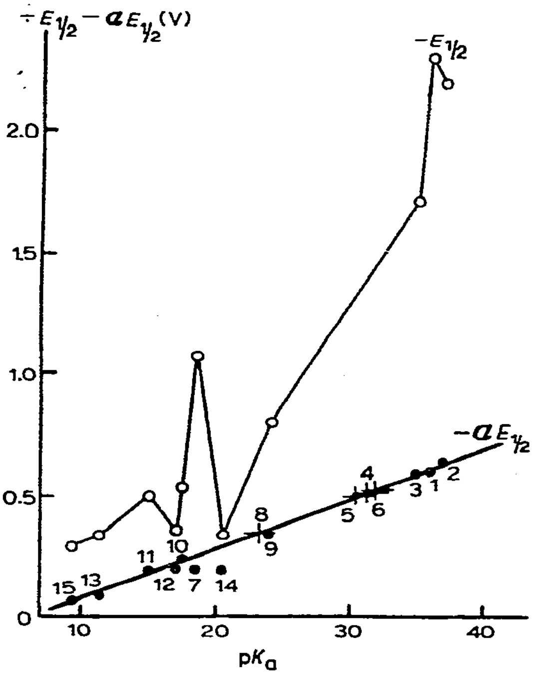


Fig. 3. The plot of $E_{\frac{1}{2}}$ and $\alpha E_{\frac{1}{2}}$ of R_2Hg *vs.* pK_a of RH. The figures correspond to compounds from Table 1.

From the plot of $\alpha E_{\frac{1}{2}}$ *vs.* pK_a new pK_a-values for C–H acids can be found and those already known defined more exactly.

The polarographic scale of C–H acid acidities can thus be constructed; it is shown in Table 2.

In many cases, the pK_a-values found as above agree with those from MSAD-scale, but, for example, the pK_a-value of 32 for propylene (α-H), given by the polaro-

TABLE 2

POLAROGRAPHIC SCALE OF C–H ACID ACIDITIES

RH	*pK_a*	*RH*	*pK_a*
NCH	9.5	CH_2=CH–CH_3(α-pos.)	32
$CH_3COCH_2COOC_2H_5$	11	$HCOOCH_3$[a]	35[b]
Cyclo-C_5H_6	15.5	$C_6H_5CH_3$(α-pos.)	35
$C_6H_5CH_2COOC_2H_5$[a]	17	CH_2=CH_2	36
CCl_2=CClH[a]	18	C_6H_6	37
$C_6H_5C\equiv CH$	18.5[b]	C_2H_6[c]	44
$(CH_3)_3CCOCH_3$[a]	20.5[b]	C_3H_8(pos. 1)[c]	49
C_6F_5H[a]	23	C_4H_{10}(pos. 1)[c]	50
CH_3COOCH_3	24	CH_4[c]	57
C_6Cl_5H[a]	30.5	C_3H_8(pos. 2)[c]	60
ClCH=CH_2[a]	31		

[a] pK_a-values not previously published. [b] see ref. 1. [c] The pK_a-values for the alkanes were determined in absolute DMF with n-tetrahexylammonium perchlorate as supporting electrolyte.

graphic method is less than that from MSAD-scale (36).

Greater differences between the polarographic and MSAD-scales are observed for the saturated hydrocarbons. Unfortunately, under the conditions mentioned above (60% DMF–H_2O, 0.1 *N* Et_4NClO_4) no reduction wave of dialkylmercuric compounds was observed, since the reduction potentials of Alk_2Hg are outside the "window": restricted by the potentials of the dissolution of mercury on the one hand and the reduction of the base electrolyte on the other.

The reduction waves of Alk_2Hg are observable if non-aqueous DMF is used as solvent and tetra-n-hexylammonium perchlorate (Hx_4NClO_4) as supporting electrolyte. This salt reduces in non-aqueous DMF at a potential of about 2.95 V *vs.* S.C.E. The reduction of dialkylmercuric compounds takes place at extremely negative potentials so that the upper part of the wave is distorted by the current of the discharge of the electrolyte. Thus large concentrations of Alk_2Hg ($\sim 10^{-2}$ *M*), are used and that brings about a large drop of the voltage in the cell. The reduction wave parameters for Alk_2Hg were defined after introducing *iR*-corrections and calculating the current of the discharge of the supporting electrolyte. The values of $E_{\frac{1}{2}}$, α and $\alpha E_{\frac{1}{2}}$ obtained in this way for five dialkylmercuric compounds and, for comparison, those for Ph_2Hg, $(PhCH_2)_2Hg$ and $(CH_3OOCCH_2)_2Hg$, are given in Table 3.

TABLE 3

POLAROGRAPHIC PARAMETERS FOR R_2Hg, DMF, 0.1 *N* Hx_4NClO_4, 25°

R in R_2Hg	$-E_{\frac{1}{2}}{}^a$ (*V*)	α	$-\alpha E_{\frac{1}{2}}$ (*V*)	pK_a *MSAD-scale*	*Polaro-graphic scale*
$n\text{-}C_3H_7$	2.976	0.48	1.43	—	49
$n\text{-}C_4H_9$	2.970	0.49	1.45	—	50
CH_3	2.880	0.63	1.81	40	57
$iso\text{-}C_3H_7$	2.861	0.67	1.91	44	60
C_2H_5	2.859	0.43	1.23	42	44
C_6H_5	2.486	0.36	0.90	37	37
$C_6H_5CH_2$	2.053	0.39	0.80	35	35
CH_3OOCCH_2	1.471	0.22	0.33	—	24

[a] *vs.* S.C.E.

The dependence of $\alpha E_{\frac{1}{2}}$ of R_2Hg upon the pK_a of RH (for the three last compounds listed in Table 3, pK_a's are known) is shown in Fig. 4.

It can be seen that the pK_a-values of saturated hydrocarbons determined by the polarographic method differ considerably from those in the MSAD-scale. The difference is especially large for methane and propane (position 2). According to the MSAD-scale, pK_a for methane is 40, but two more pK_a-values for methane have been reported, $pK_a = 48$[11] and $pK_a = 58$[8,12].

In Fig. 5 is given the diagram of the changes in the electrochemical reaction rate constant in the Alk_2Hg series. The rate constant increases from Me_2Hg up to Et_2Hg and then decreases again to iso-Pr_2Hg through n-Pr_2Hg and n-Bu_2Hg. Such an effect of the nature of the alkyl group bonded with mercury on the rate constant can be explained by inductive and hyper-conjugation effects. Both these effects

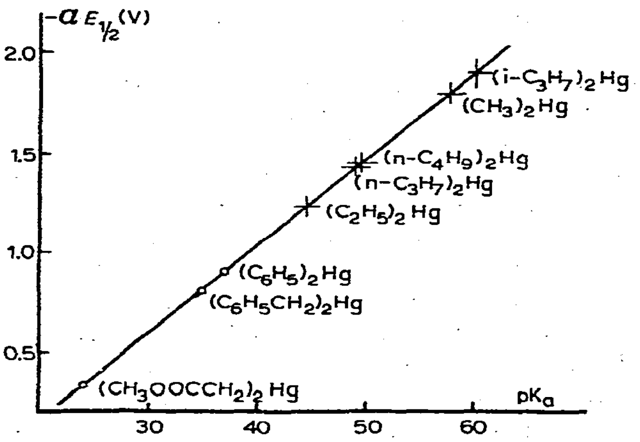


Fig. 4. The plot of $\alpha E_{\frac{1}{2}}$ of R_2Hg *vs.* pK_a of RH; 0.1 *N* Hx_4NClO_4; DMF; 25°.

decrease and effective positive charge on the mercury atom in Alk_2Hg, but as they are not equal, in each case the electron affinity of the mercury in Alk_2Hg depends upon their relative contributions.

The same U-shaped rate constant dependence on the nature of the alkyl radical (Fig. 5b) is observed also in the case of the reduction of organomercuric radicals, $RHg^\bullet$ (the second wave of the reduction of organomercuric perchlorates).

It should be noted that the thermodynamic acidity cannot be determined for some C–H acids in the usual way. In this case, pK_a-values are obtained from the kinetic data of deuterium isotope exchange and a common scale constructed for both. However, a comparison of the C–H bond acidities determined thermodynamically and kinetically shows that there may be a systematic difference between these determined pK_a-values. It is clear that the finding of a common physico-chemical characteristic

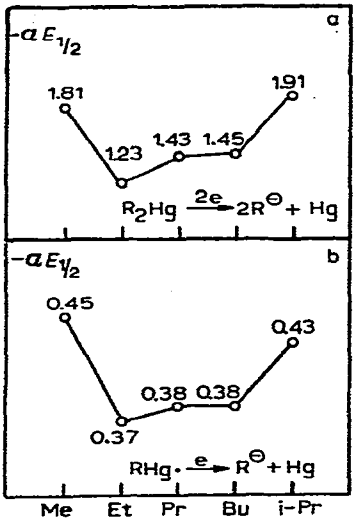


Fig. 5. Diagrams of a change in rate of electrochemical reduction of Alk–Hg species. (a), dialkylmercuric compounds; (b), organomercuric radicals.

for all C–H acids, from HCN to alkanes, that can be related to their acidities, is of value.

As far as the theoretical substantiation of the given correlation is concerned, this is not exhaustive but is based on the postulate that there is a direct proportionality between the carbanion affinities of the proton and the mercury cation.

Coefficient ρ in eqn. (5) changes with experimental conditions (*e.g.*, the nature of the solvent or of the supporting electrolyte) as is easily seen from Figs. 3 and 4. The linear dependence of $\alpha E_{\frac{1}{2}}$ of R_2Hg on the pK_a of RH was examined in five different solvents: dimethylsulfoxide (DMSO), dimethylformamide (DMF), pyridine (Py), methanol (MeOH) and 50% aqueous methanol. In all these solvents, except methanol, Et_4NClO_4 (0.1 *N*) was used as a supporting electrolyte (Hx_4NClO_4, 0.1 *N* was used in methanol, since Et_4NClO_4 is only sparingly soluble).

The comparison of $E_{\frac{1}{2}}$ and $\alpha E_{\frac{1}{2}}$ in different solvents was carried out using Pleskov's method[13], $CsClO_4$ being used as a "standard electrode". The solvation effect for the bulk caesium cation is assumed to be the same in different solvents, so that the electrochemical reduction rate of Cs^+ must be independent of solvent nature. The observed differences in $E_{\frac{1}{2}}$-values for the caesium cation in different solvents can be attributed to a change in the potential jump at the interface of the aqueous saturated calomel electrode and the organic solvent. The half-wave potential of Cs^+ in each solvent can thus be considered as a potential of the "standard electrode" and the half-wave potentials of R_2Hg should be measured *vs.* this electrode.

Polarographic parameters for some symmetrical organomercuric compounds in different solvents are given in Table 4. The apparent transfer coefficients, α, were calculated from the slopes of the polarographic waves in the plot of E *vs.* $\lg \frac{i}{i_d - i}$.

The plots of the electrochemical reaction rate constant ($\alpha E_{\frac{1}{2}}$) *vs.* pK_a-values are given in Fig. 6. For each solvent under investigation, the linear dependence of $\alpha E_{\frac{1}{2}}$ on pK_a was observed. More negative $\alpha E_{\frac{1}{2}}$-values correspond to a decrease of the electrochemical reaction rate constant due to a solvent effect. If one considers that the electrochemical reaction rate constants are affected mainly by a solvation change of the

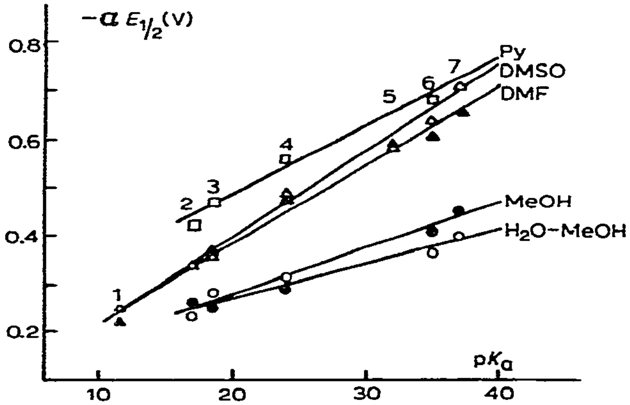


Fig. 6. The plot of $\alpha E_{\frac{1}{2}}$ of R_2Hg *vs.* pK_a of RH in different solvents. The figures correspond to compounds from Table 4. (○), 50% MeOH–H_2O; (●), MeOH; (△), DMSO; (▲), DMF; (□), Py.

TABLE 4

POLAROGRAPHIC PARAMETERS FOR 1 m*M* SOLUTIONS OF SYMMETRICAL ORGANOMERCURIC COMPOUNDS IN DIFFERENT SOLVENTS[a], 0.1 *N* Et_4NClO_4; 25°

Number	*R in R_2Hg*	*Parameters*	*Solvent*				
			50% MeOH–H_2O	*MeOH*[d]	*Py*	*DMF*	*DMSO*
1	$CH_3COCHCOOEt$	$-E_{\frac{1}{2}}$(V)[b]				0.819	0.774
		α				0.24	0.31
		$-\alpha E_{\frac{1}{2}}$				0.22	0.25
2	$C_6H_5CHCOOEt$	$-E_{\frac{1}{2}}$(V)[b]	0.409	0.490	1.000	0.833	0.746
		α	0.56	0.54	0.42	0.43	0.46
		$-\alpha E_{\frac{1}{2}}$	0.23	0.26	0.42	0.36	0.34
3	$C_6H_5C{\equiv}C$	$-E_{\frac{1}{2}}$(V)[b]	0.928	1.626	1.906	1.680	1.664
		α	0.31	0.15	0.25	0.13	0.22
		$-\alpha E_{\frac{1}{2}}$	0.28	0.25	0.47	0.22	0.36
4	CH_3OOCCH_2	$-E_{\frac{1}{2}}$(V)[b]	0.751	1.086	1.581[c]	1.409	1.333
		α	0.41	0.27	0.35	0.34	0.36
		$-\alpha E_{\frac{1}{2}}$	0.31	0.29	0.56	0.48	0.49
5	$CH_2{=}CHCH_2$	$-E_{\frac{1}{2}}$(V)[b]				1.575	1.526
		α				0.37	0.38
		$-\alpha E_{\frac{1}{2}}$				0.59	0.58
6	$C_6H_5CH_2$	$-E_{\frac{1}{2}}$(V)[b]	1.783	2.105	2.301	2.076	2.038
		α	0.20	0.19	0.29	0.29	0.32
		$-\alpha E_{\frac{1}{2}}$	0.36	0.41	0.68	0.61	0.64
7	C_6H_5	$-E_{\frac{1}{2}}$(V)[b]	2.261	2.895		2.741	2.668
		α	0.18	0.16	no wave	0.24	0.26
		$-\alpha E_{\frac{1}{2}}$	0.40	0.45		0.66	0.71
	Cs^+	$-E_{\frac{1}{2}}$(V, *vs.* S.C.E.)	2.120	2.022	1.931	2.031	2.090

[a] A capillary with positive dropping was applied ($t = 0.24$ sec). [b] The potentials were measured *vs.* S.C.E. and zero correction was made according to the $E_{\frac{1}{2}}$ of Cs^+. [c] Two waves were observed. [d] 0.1 *N* Hx_4NClO_4 was used as a phonon.

organomercuric compound, the solvents from Table 4 can be arranged in the following sequence of decreasing ability to solvate the mercury atom in R_2Hg:

$$\text{Py} > \text{DMSO} > \text{DMF} > \text{MeOH} > H_2O.$$

Since coordination of a solvent molecule with the mercury atom transfers it into a lower electron affinity state, the reduction rate constant decreases when the affinity of solvent molecules for the mercury atom in R_2Hg increases (from H_2O to Py, Table 4).

The solvent nature also has an effect on the slope of the plot of $\alpha E_{\frac{1}{2}}$ *vs.* pK_a (ρ in eqn. (5)). The ρ-values expressed as change in $\alpha E_{\frac{1}{2}}$ (in mV)/unit pK_a are as follows: DMSO 18, DMF 16, Py 14, MeOH 10, H_2O–MeOH (50%) 8. These ρ-values could be used for a quantitative estimation of the electrochemical reaction selectivity in different solvents, only if the following law can be proved:

$$pK_a^1 = pK_a^2 + b$$

(the figures "1" and "2" correspond to two different solvents; *b* is a constant). This equation appears to hold approximately for some O–H acids in DMSO, DMF, MeOH and H_2O[14].

It is difficult to explain why the selectivity (ρ) changes with different solvents. It is necessary, first of all, to understand the reason for the changes of both $E_{\frac{1}{2}}$ and α. In connection with this it should be emphasized that a knowledge of $E_{\frac{1}{2}}$-values is insufficient for judging a C–Hg bond strength (or a carbanion, R^-, stability) from polarographic data. The value of an apparent transfer coefficient, α, must be taken into account as well. The product, $\alpha E_{\frac{1}{2}}$, is the relevant criterion.

II. ORGANOMERCURIC CATIONS

Polarograms of organomercuric salts show two reduction waves with the height of the second almost equal to that of the first. According to Benesch[15] these waves correspond to the stepwise reduction:

$$\mathrm{RHgX} + e \rightleftarrows \mathrm{RHg}^{\bullet} + \mathrm{X}^- \qquad \text{(the first wave)}$$

$$\mathrm{RHg}^{\bullet} + e \rightarrow \mathrm{R}^- + \mathrm{Hg} \qquad \text{(the second wave)}$$

$E_{\frac{1}{2}}$ of the first wave is dependent not only on the nature of the R group, but on the nature of the X^- anion as well. There are equilibria in solution[16,17]:

$$\mathrm{RHg}^+ + \mathrm{X}^- \overset{K_1}{\rightleftarrows} \mathrm{RHgX} \qquad K_1 = \frac{[\mathrm{RHgX}]}{[\mathrm{RHg}^+][\mathrm{X}^-]}$$

$$\mathrm{RHgX} + \mathrm{X}^- \overset{K_2}{\rightleftarrows} \mathrm{RHgX}_2^- \qquad K_2 = \frac{[\mathrm{RHgX}_2^-]}{[\mathrm{RHgX}][\mathrm{X}^-]}$$

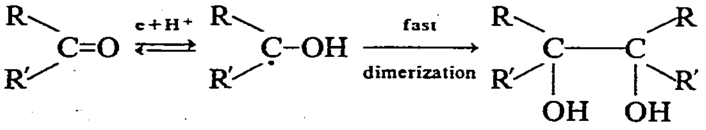
The second part of this work is concerned with the influence of the nature of the organic group on the ability of organomercuric cations to reduce at the dropping mercury electrode. Organomercuric perchlorates were chosen for this investigation because of the very low mercury affinity of the ClO_4^- anion.

In a few cases, the first wave (the reduction of the RHg^+ cation to the $RHg^{\bullet}$ radical) was shown to be reversible[18,19]. The organomercuric radical, $RHg^{\bullet}$, on the first wave generated is an unstable particle and until its reduction potentials are reached it undergoes disproportionation yielding a symmetrical organomercuric compound, R_2Hg[15,20].

For the reversible reduction of RHg^+ followed by a fast dimerization of $RHg^{\bullet}$,

$$\mathrm{RHg}^+ + e \rightleftarrows \mathrm{RHg}^{\bullet} \xrightarrow[k_d]{\text{fast}} \tfrac{1}{2}(\mathrm{R_2Hg} + \mathrm{Hg})$$

if this dimerization occurs in solution, the equation of the current–potential curve must be analogous to that derived by Hanus[21] for the reduction of ketones to pynacones.



This equation is as follows:

$$E = E_0 + \frac{RT}{nF} \ln (nqF)^{\frac{2}{3}} D^{\frac{1}{2}} x^{-1} + \frac{RT}{nF} \ln k_{\mathrm{d}}^{\frac{1}{3}} - \frac{RT}{nF} \ln \frac{i^{\frac{2}{3}}}{i_{\mathrm{d}}-i} \tag{6}$$

where E_0 is the standard equilibrium potential, n the number of electrons, q the average surface of the electrode, D the diffusion coefficient of RHg^+, x the coefficient of proportionality between current and concentrations in the Ilkowic equation, k_d the rate constant of the dimerization. i_d the limiting diffusion-controlled current and i the current at potential E.

Equation (6) suggests that the half-wave potential, $E_{\frac{1}{2}}$, is dependent on the RHg^+ concentration in solution; this parameter is not, therefore, convenient for comparison and we used another parameter E_f, which is independent of the concentration and is given by the following equation:

$$E_f = E_0 + \frac{RT}{nF} \ln (nqF)^{\frac{2}{3}} D^{\frac{1}{2}} x^{-1} + \frac{RT}{nF} \ln k_{\mathrm{d}}^{\frac{1}{3}} \tag{7}$$

where E_f is a potential at which $\ln(i^{\frac{2}{3}}/i_d - i) = 0$

According to eqn. (6) the slope (S) of the logarithmic plot of the first wave (E *vs.* $\ln(i^{\frac{2}{3}}/i_d - i)$) should be equal to 2.3 RT/nF, *i.e.*, 59 mV at 25° C. E_f- and S-values for some organomercuric cations in 60% aqueous and non-aqueous DMF with 0.1 *N* Et_4NClO_4 as a phonon are given in Table 5. In general, the experimental slopes

TABLE 5

POLAROGRAPHIC PARAMETERS OF THE FIRST REDUCTION WAVE OF ORGANOMERCURIC CATIONS RHg^+, 0.1 *N* Et_4NClO_4, 25°C

No.	*R in* $RHg^{\oplus}$	*60% DMF–H₂O*		*DMF*	
		$E_f\ (V)^a$	$S_{exp.}\ (mV)$	$-E_f\ (V)^a$	$S_{exp.}\ (mV)$
1	CH_3	−0.288	113	0.612	107
2	C_2H_5	−0.217	126	0.594	101
3	n-C_3H_7	−0.198	155	0.613	91
4	n-C_4H_9	−0.193	144	0.613	88
5	iso-C_3H_7	−0.183	143	0.592	87
6	n-C_5H_{11}	−0.174	11	0.535	118
7	n-C_7H_{15}	−0.130	95	0.578	118
8	n-C_8H_{17}	−0.118	94	0.596	122
9	Cyclo-C_5H_9	−0.178	127	0.573	112
10	Cyclo-C_6H_{11}[b]	−0.103	70	0.570	80
11	C_6H_5	−0.180	74	0.544	61
12	$C_6H_5CH_2$	+0.023	108	0.370	84
13	$C_6H_5CH_2CH_2$	−0.233	131	0.585	100
14	C_6Cl_5	+0.027	130	—	—
15	$CH_2{=}CH$	−0.090	170	0.862	180
16	*trans*-ClCH=CH[c]	−0.156	176	0.206	93
17	$CH_2{=}CHCH_2$	−0.010	128	0.343	99
18	CH_3OOC	−0.100	100	0.426	88

[a] With reference to S.C.E. [b] Only one wave was found. [c] In contrast with *trans*-β-chlorovinylmercury chloride for which only one wave was observed[20], the polarogram of the cation shows two waves.

(S) exceed the theoretical values by a factor of 1.5–2. However, the lack of accordance with theory may be assumed to be due, not to the irreversibility of the process, but to other effects*, as the $E_{\frac{1}{2}}$-dependence on depolarizer concentration is found, in agreement with eqn. (6). Furthermore, for the reduction of organomercuric halides with Et_4NClO_4 as supporting electrolyte when (because the concentration of halide ions at the electrode surface is a function of a current) the polarographic wave is governed by eqn. (8)[19],

$$E = \text{const.} - \frac{RT}{nF}\ln K_1 - \frac{RT}{nF}\ln\frac{i^{\frac{1}{2}}}{i_d - i} \qquad (8)$$

where $K_1 = \dfrac{[\text{RHgX}]}{[\text{RHg}^+][\text{X}^-]}$ the plot of E *vs.* $\lg\dfrac{i^{\frac{1}{2}}}{i_d - i}$ shows a slope of 60 mV for all systems studied.

Equation (7) suggests that the characteristic potential, E_f, depends on the standard equilibrium potentials, E_0, and on the dimerization rate constant, k_d, of $RHg^{\bullet}$ radicals. These parameters are dependent on the nature of R in RHg^+. If k_d increases 10-fold, E_f becomes more positive by 20 mV. E_0 depends on the Hg^{2+} cation affinity of carbanion R^-; therefore, neglecting changes in k_d and D, we can attempt to find E_f-dependence on the pK_a of RH.

It can be seen from Fig. 7, that although, in general, E_f becomes more positive with decrease in pK_a, there is no direct relationship between these values. E_f of alkylmercuric cations are almost independent of changes in alkyl radicals. For other

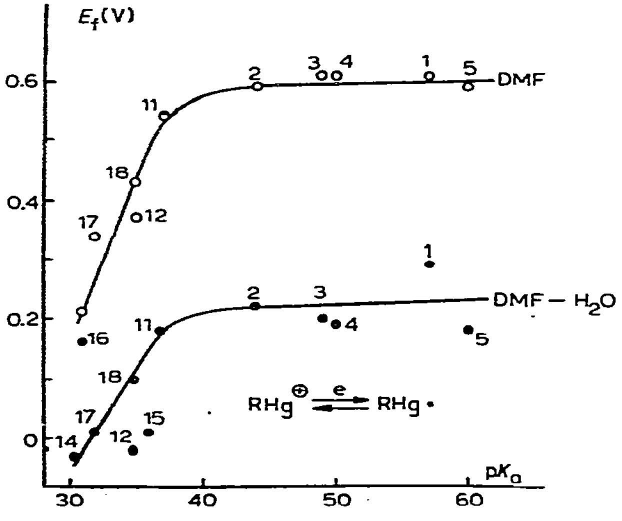


Fig. 7. E_f of RHg^+ dependence on pK_a of RH; 0.1 N Et_4NClO_4; 25°. (●), 60% DMF–H_2O; (○), DMF. The figures correspond to compounds from Table 5.

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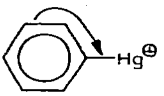
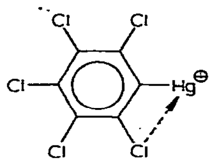
* Equation (6) was derived for dimerization in solution, but for dimerization on the electrode surface another equation can be written.

Dimerizations in a volume and on the electrode surface seem to describe a real situation. Further consideration is being given to this.

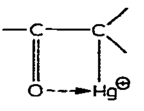
radicals there is a substantial dispersion of points. This is due possibly to the existence in the molecules of a cationic centre, which can conjugate with double bonds.



Intramolecular associations are also a possibility:



or



As a result of these effects, there is a considerable lowering of the positive charge at the mercury atom and the rate constant of the electrochemical reduction decreases.

The ready reduction of organomercuric cations, RHg^+ with the highest alkyl groups (C_7–C_8) in aqueous DMF, is due to their ready adsorption on the electrode surface.

Symmetrical organomercuric compounds are uncharged molecules, and conjugations and intramolecular interactions in them are therefore negligible and their adsorption at such relatively negative potentials is small.

There are thus three main factors that interfere with the use of polarographic data of organomercuric cations for the estimation of C–H acid acidities: the radical, $RHg^{\cdot}$, dimerisation rate constant, intramolecular interactions and conjugations, and adsorption.

III. EXPERIMENTAL

Materials. Most of the organomercurials were prepared by the action of Grignard reagents on mercury (II) halides and some by the action of mercury salts or metallic mercury on organic halides. The symmetrical α-oxoorganomercuric compounds were prepared by symmetrization of the organomercuric bromides with $(C_6H_5)_3P$ in benzene. The purified products were recrystallized before measurements were taken.

Tetra-n-hexylammonium perchlorate was prepared from n-hexylamine and n-hexylbromide[22] and treatment with $Mg(ClO_4)_2$.

Silver perchlorate was prepared according to Hill[23].

Dimethylformamide was distilled *in vacuo* once over CaH_2 and twice over P_2O_5.

Apparatus and experimental techniques. All measurements were carried out in a thermostatted cell, of volume 15 ml, at 25 ± 0.1°C. The capillary had $t = 2.3$ sec and this drop-time was held constant at all potentials by adjustment of the mercury reservoir height. The capillary with positive dropping had a small glass shovel sealed at its outlet and had $t = 0.24$ sec at a potential from 0 to -2.5 V. This drop-time was the same for all solvents.

Polarograms were recorded with a LP-60 Polarograph; the potential of the drop *vs.* the saturated calomel electrode was controlled with Bridge Potentiometer PPTV-1, to within ± 5 mV.

Because of the instability of organomercuric perchlorates in the solid form, they were prepared in solution immediately before measurement by the addition of $AgClO_4$ to a solution of an organomercuric halide in the supporting electrolyte. After a double filtration to remove silver halide, the solution was put into the cell, the air was removed by passing the nitrogen for 30 min, and polarograms were recorded.

SUMMARY

A number of organomercuric compounds, R_2Hg and $RHgClO_4$, with different R groups have been studied by the polarographic method. Both the half-wave potential, $E_{\frac{1}{2}}$, and the transfer coefficient, α, are shown to be necessary for judging the C–Hg bond strength from the polarographic data. These data for R_2Hg were used for the construction of a polarographic scale of C–H bond acidities.

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