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STRUCTURE AND SOLVENT EFFECTS IN ORGANOMETALLIC ELECTROCHEMISTRY
III*. MERCURY(II) CARBOXYLATES

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SUMMARY

Polarographic half-wave potentials have been measured for fifteen different mercury(II) carboxylates in methanol, dimethylformamide and dimethylsulfoxide. Dissociation constants of the corresponding carboxylic acids have been determined in the same solvents. A linear correlation between the half-wave potentials of mercury carboxylates and the pK_a values of the corresponding carboxylic acids was found in all the solvents studied. The effect of the solvents on the acidity of the OH-acids and on the electrochemical reduction of the mercury carboxylates increases in the order: methanol (standard) < dimethylformamide < dimethylsulfoxide. Solvent effects are discussed in terms of the solvation of the carboxylate anions and the mercury atom in the salts.

In previous work[1-4], it was found that the parameters of the polarographic reduction of organomercury compounds, R_2Hg, can be correlated with the acidities (pK_a) of the corresponding CH-acids, RH:

$$\Delta[\alpha E_{\frac{1}{2}}(R_2Hg)] = \rho \cdot \Delta pK_a(RH) \tag{1}$$

where $E_{\frac{1}{2}}(R_2Hg)$ is the half-wave potential of R_2Hg, α the transfer coefficient (determined from Heyrovský plots), and ρ a constant depending on the solvent. CH-acid acidities may be estimated from eqn. (1), using polarographic data obtained for organomercury compounds. This method is especially useful in cases when no conventional method can be used for such an estimation, for example for the determination of CH-acidities in *ortho*-, *meta*- and *para*-barenes[5].

Further[3], it was shown that similar correlations between electrochemical properties and acidity can be applied also to other systems: palladium acetylacetonates and cobalt acidopentamminates. In view of these results it follows that the electrochemical method may be used for the estimation of the acidities of O–H, N–H, S–H, etc., as well as C–H bonds.

Although the correlation of $\alpha E_{\frac{1}{2}}$ with pK_a is successful, its accuracy must

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* Parts I and II, see refs. 2 and 3.

depend on several factors among which are: (i) non-linear dependence of the electrochemical reduction rate constant of R_2Hg on the electrode potential so that the proportionality between $\alpha E_{\frac{1}{2}}$ and $\log k_{\text{electrochem.}}$ becomes disturbed at a potential, $E=0$, thus leading to considerable errors; (ii) lack of data concerning CH-bond acidities in various solvents means that the MSAD-scale of pK_a-values must be used for all solvents thus neglecting the effect of the solvent on the acidity of the CH-acids. It is known, however, that the acidity of hydrocarbons depends strongly on the nature of solvent[6,7]. This problem has recently been reviewed by Shatenstein and Shapiro[8]. Therefore, an acid–salt system was needed to which the correlation between the electrochemical reduction parameters of the salt and the pK_a of the corresponding acid might be applied but which would be free from the defects of the system, R_2Hg–RH, *i.e.*, the electrochemical reduction of the salt would be reversible (net $E_{\frac{1}{2}}$-values correlated with pK_a) and the acids would be sufficiently strong that their pK_a-values could be established by some independent method (titration for instance) in the solvents used for the electrochemical reduction of the salt.

In the present work, we have studied the polarographic behaviour of mercury(II) carboxylates in three solvents: methanol, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) and correlated the electrochemical parameters with the pK_a-values of the corresponding carboxylic acids. In some cases the pK_a-values were known in these solvents but for other acids they were estimated titrimetrically. A comparison of $E_{\frac{1}{2}}[(RCOO)_2Hg]$ with $pK_a(RCOOH)$ enables the effect of the solvent on the acidity of OH-acids and on solvation of mercury(II) carboxylates to be evaluated.

The electrochemical reduction mechanism for mercury carboxylates may be regarded as involving two consecutive steps: dissociation of the salt and reduction of the mercuric cation,

$$(RCOO)_2Hg \overset{K_D}{\rightleftharpoons} 2\,RCOO^- + Hg^{2+}$$

$$Hg^{2+} + 2\,e \rightleftharpoons Hg^0$$

the half-wave potential being described by eqn. (2)[10],

$$E_{\frac{1}{2}} = \text{const.} + \frac{RT}{nF} \ln K_D \tag{2}$$

where K_D is the dissociation constant; n the number of electrons; the const. $= E^0 - (RT/nF) \ln (i_d/2) - (RT/nF) \ln (x_1/x_2)$, E^0 is the standard equilibrium potential, i_d the limiting diffusion current and x_1 and x_2 are proportionality coefficients for the oxidised and reduced forms in the Ilkovic equation.

According to this mechanism, the polarograms of mercury carboxylates show one two-electron wave at a potential depending on carboxylate ion affinity to the mercury cation, *i.e.*, on K_D.

Table 1 shows $E_{\frac{1}{2}}$-values of mercury carboxylates measured in methanol, DMF and DMSO. The figures in brackets refer to the salts reducing at very positive potentials where the wave is not sufficiently pronounced; pK_a-values of the corresponding carboxylic acids taken from literature or estimated in the course of this work are given in the same Table. The plot of $E_{\frac{1}{2}}[(RCOO)_2Hg]$ *vs.* $pK_a(RCOOH)$ is shown in Fig. 1. There is a good linear correlation between these parameters which can be expressed by the equation:

$$\Delta E_{\frac{1}{2}} = \rho \cdot \Delta pK_a \tag{3}$$

where $\Delta E_{\frac{1}{2}}$ is the half-wave potential difference between two mercury salts, ΔpK_a the difference in pK_a-values for the two corresponding carboxylic acids and ρ a constant depending on the nature of the solvent.

Equation (3) is identical with eqn. (1), with the exception of the transfer coefficient, α, present in eqn. (1) but not in eqn. (3), because of the reversibility of the reduction of mercury carboxylates.

TABLE 1

pK_a-VALUES FOR SOME CARBOXYLIC ACIDS AND HALF-WAVE POTENTIALS OF THE CORRESPONDING MERCURY(II) CARBOXYLATES IN METHANOL, DMF AND DMSO

R in RCOOH and in $(RCOO)_2Hg$	MeOH		DMF		DMSO	
	pK_a	$E_{\frac{1}{2}}$ (V)	pK_a	$E_{\frac{1}{2}}$ (V)	pK_a	$E_{\frac{1}{2}}$ (V)
1. Cl_2CH	6.4	(0.57)	7.2	0.33	2.0	0.41
2. $3,5\text{-}(NO_2)_2C_6H_3$	7.4	(0.49)	7.9	0.29	5.4	0.26
3. $ClCH_2$	7.7	(0.47)	9.0	0.25	6.2	0.24
4. $o\text{-}NO_2C_6H_4$	7.9	(0.46)	9.5	0.20	6.2	0.25
5. $p\text{-}NO_2C_6H_4$	8.6	(0.43)	8.5	0.27	7.1	0.23
6. $m\text{-}NO_2C_6H_4$	8.6	(0.41)	8.5	0.25	7.8	0.18
7. $ClCH_2CH_2$	9.0	0.38	9.6	0.18	8.2	0.15
8. C_6H_5	9.1	0.37	10.2	0.17	10.0	0.09
9. CH_3	9.6	0.34	11.1	0.14	11.4	0.03
10. CH_3CH_2	9.3	0.34	11.0	0.11	10.8	0.05
11. $CH_3CH_2CH_2$	9.4	0.34	10.0	0.14	11.0	0.03
12. $CH_3(CH_2)_3$	9.4	0.32	10.9	0.11	12.2	−0.01
13. $CH_3(CH_2)_5$	9.6	0.32	10.9	0.13	11.1	0.02
14. $ClCH_2(CH_2)_9$	9.6	0.32	11.1	0.12	12.0	0.00
15. $(CH_3)_2CH$	9.5	0.34	10.6	0.12	10.5	0.03

[a] vs. SCE.

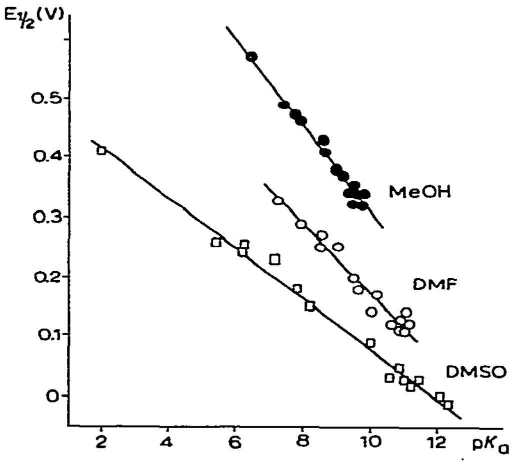

Fig. 1. Plots of $E_{\frac{1}{2}}[(RCOO)_2Hg]$ vs. $pK_a(RCOOH)$ in MeOH, DMF and DMSO.

The above correlation suggests that the affinity of carboxylic anions to the mercury cation and to the proton, changes in the same order. We think this correlation confirms the assumption[1] (taken as the basis of the polarographic method for the estimation of hydrocarbon acidities) that changes in carbanion affinity to the mercury cation and to the proton can be expressed by a linear dependence. Equation (3) allows the pK_a of the carboxylic acid to be defined when $E_{\frac{1}{2}}$ of the corresponding mercury salt is known, and also the $E_{\frac{1}{2}}$-value of $(RCOO)_2Hg$ to be predicted with an accuracy of ±20 mV when the pK_a-value of the corresponding RCOOH is known.

The plots given in Fig. 1 show straight lines with slopes depending on the solvent nature: 80 mV for MeOH, 60 mV for DMF and 40 mV for DMSO. The difference in slope is likely to be due to both difference in solvation of the mercury salts and the different effects of solvents on acid strengths. It is known[9] that acidities of OH-acids change appreciably going from protic to dipolar aprotic solvents. This is illustrated by the plots of pK_a in DMSO and pK_a in DMF *vs.* pK_a in methanol (Fig. 2). The slopes of the straight lines are 0.3 and 0.6, respectively*.

$$pK_a(\text{MeOH}) = 0.3\ pK_a(\text{DMSO}) + C \qquad (4)$$

$$pK_a(\text{MeOH}) = 0.6\ pK_a(\text{DMF}) + C' \qquad (5)$$

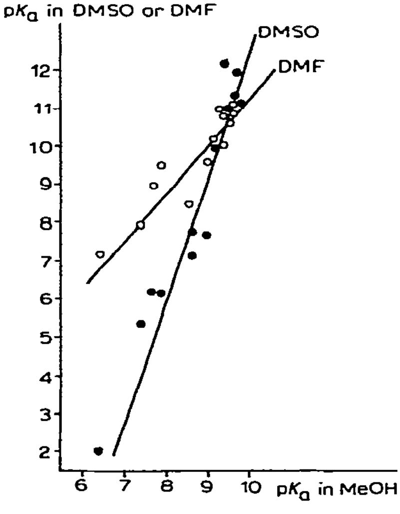

Fig. 2. Plots of pK_a in DMSO or pK_a in DMF *vs.* pK_a in methanol.

It has been shown by Parker[6], that the difference in strengths of uncharged acids in protic and in aprotic solvents (for example in MeOH and in DMSO) is conditioned almost solely by the difference in solvation of the conjugated anions. The levelling effect of methanol on the acidity of carboxylic acids is due to hydrogen bonding to carboxylic anions.

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* According to Ritchie[11], the slope of the plot of pK_a(DMSO) *vs.* pK_a(MeOH) for substituted benzoic acids is equal to 0.6. It appears from the above, that the aprotic dipolar solvents, DMSO and DMF(DMSO being the more effective), have a stronger effect on acidity than the protic solvent (methanol).

The plots of $E_{\frac{1}{2}}$(DMSO) and $E_{\frac{1}{2}}$(DMF) *vs.* $E_{\frac{1}{2}}$(MeOH) (as expected in view of eqn. (3) and of the rough linear dependence between the pK_a-values in different solvents) are approximately straight lines with slopes of 0.6 and 0.9, respectively (Fig. 3).

$$E_{\frac{1}{2}}(\text{MeOH}) = 0.6\ E_{\frac{1}{2}}(\text{DMSO}) + C_1 \qquad (6)$$

$$E_{\frac{1}{2}}(\text{MeOH}) = 0.9\ E_{\frac{1}{2}}(\text{DMF}) + C_2 \qquad (7)$$

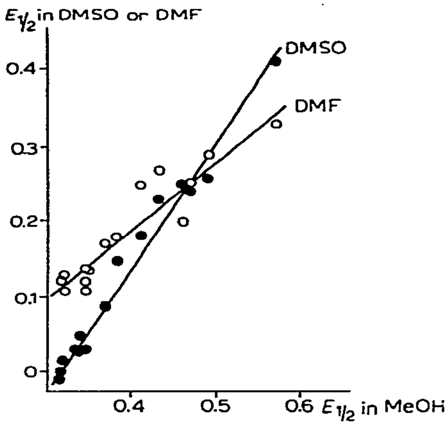

Fig. 3. Plots of $E_{\frac{1}{2}}$ (DMSO) or $E_{\frac{1}{2}}$ (DMF) *vs.* $E_{\frac{1}{2}}$ (MeOH).

It should be noted, that a comparison of pK_a-values in protic MeOH and aprotic DMF or DMSO produces a scatter diagram. The coefficients in eqns. (4) and (6), and (5) and (7) are less than unity and those for DMSO are less than for DMF. This means that the interval in pK_a-values of carboxylic acids and in $E_{\frac{1}{2}}$-values of mercury carboxylates, *i.e.*, the differentiating effect of solvents decreases in the following order: DMSO > DMF > MeOH.

The parallelism in the effect of solvent on carboxylic acid dissociation constants and on half-wave potentials of mercury carboxylates shows that solvation of the carboxylic anion is the main factor for both processes.

However, the plots of $E_{\frac{1}{2}}$ *vs.* pK_a in different solvents are of unequal slope which means probably that the solvation of the metal atom is also important and must be taken into account.

Just as solvation of carboxylic anions by protic solvents leads to a levelling in the strengths of carboxylic acids, solvation of mercury in salts by dipolar aprotic solvents must lead to some levelling in $E_{\frac{1}{2}}$-values. Nevertheless, as stated above, the solvation of carboxylic anions is the main factor determining both electrochemical reactivity of the salts and dissociation constant of the acids.

EXPERIMENTAL

Mercury salts were obtained by reaction of mercury oxide or acetate with the corresponding carboxylic acids. Elemental analysis data and melting points of salts obtained are summarized in Table 2.

TABLE 2

ELEMENTAL ANALYSIS DATA AND MELTING POINTS OF MERCURY(II) CARBOXYLATES

No.	Mercury salt	Found (%)					Calcd. (%)					M.p. (°
		C	H	Hg	Cl	N	C	H	Hg	Cl	N	
1.	Propionate	20.70	3.26	58.19			20.82	3.02	57.61			108–11
		20.94	3.22	58.40								
2.	n-Butyrate	24.76	3.80	55.49			25.62	3.76	53.3			
		24.99	4.00	55.35								
3.	Isobutyrate	25.60	3.90	55.18			25.62	3.76	53.3			96–97
		25.49	4.13	55.26								
4.	n-Valerate	30.52	4.77	50.00			29.20	4.52	49.6			
		30.68	4.96	50.00								
5.	Enantoate	36.07	5.84	43.29			36.62	5.76	43.6			
		36.30	6.07	43.78								
6.	Monochloroacetate	12.86	1.50	51.95	18.88		12.42	1.04	51.6	18.32		142
		13.10	1.54	51.50	18.10							
7.	Dichloroacetate	9.57	0.41	44.22	31.06		10.52	0.26	43.8	31.12		
		9.34	0.49	44.38	29.89							
8.	*β*-Chloropropionate	17.59	2.20	49.65	15.72		17.49	1.94	48.10	17.06		
		17.30	2.25	50.10	16.20							
9.	*ω*-Chloroundecanate	41.80	6.98	31.66	11.3		41.30	6.3	31.2	11.15		96
		42.45	6.75	32.31								
10.	Benzoate	37.58	2.46	46.86			38.00	2.28	45.20			160
		37.88	2.63	46.81								
11.	*o*-Nitrobenzoate	32.10	1.90	39.85		4.99	31.58	1.53	37.6		5.26	
		32.40	1.88	40.35		4.70						
12.	*p*-Nitrobenzoate	31.89	1.73	40.22		5.30	31.58	1.53	37.6		5.26	
		32.00	1.73	40.33		5.03						
13.	*m*-Nitrobenzoate	31.98	2.03	37.73		5.01	31.58	1.53	37.6		5.26	182–18
		31.90	1.87	37.57		4.90						
14.	3,5-Dinitrobenzoate	28.00	1.25	29.77		9.04	27.00	0.97	32.12		9.00	216–21
		27.98	1.23	30.36		9.18						

Dimethylformamide was shaken for 4 days with ignited K_2CO_3 and then distilled *in vacuo* (b.p. 32°/7 mm). Methanol was boiled with magnesium methylate and then distilled. Dimethylsulfoxide was shaken with BaO and then distilled over CaH_2 in an atmosphere of argon (b.p. 36°/1 mm). All the acids were distilled or recrystallized before titration.

Polarographic measurements were carried out at $25 \pm 0.2°$. The polarograms were registered by an LP-60 electronic polarograph; the potential of the dropping mercury electrode was controlled by means of a PPTV-1 potentiometer. Oxygen was removed from the cell by bubbling of purified nitrogen. Polarography in MeOH and DMSO was carried out using 0.02 *M* $LiClO_4$ solutions and in DMF with 0.1 *M* Et_4NClO_4 solution.

Potentiometric titrations were carried out on a TTT-I Radiometer automatic titrator using a glass electrode with 0.1 *N* tetrabutylammonium hydroxide solution in a benzol–methanol mixture (10/1 v/v) as a titrant. Purified nitrogen was bubbled through the solution before titration to remove dissolved CO_2. pK_a-values were determined from the calibration plots of electrode potential *vs.* pK_a for some acids with known pK_a-values in the solvents studied.

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