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STRUCTURE AND SOLVENT EFFECTS IN ORGANOMETALLIC ELECTROCHEMISTRY
CORRELATION OF C–H-ACID ACIDITY WITH PARAMETERS OF POLAROGRAPHICAL REDUCTION OF ORGANOMERCURY COMPOUNDS

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SUMMARY

The possibilities for a correlation of the polarographical reduction parameters of organometallic compounds with the pK_a-values of C–H-acids are discussed. It is concluded that the correlation is possible if the electron transfer coefficients for all organometallic compounds of the given series at the same potential are of equal value and if the value of the transfer coefficient depends only upon electrode potential and not on the structure of the organometallic compound.

A method proposed recently[1-3] for the estimation of C–H-acid acidities from the polarographical reduction data of organomercury compounds is based on an assumption that the three following processes are related:
(1) protolytic dissociation of C–H-acids

$$\text{R–H} + \text{B} \overset{K_a}{\rightleftharpoons} \text{R}^- + \text{BH}^+ \qquad (1)$$

(2) association of carbanion, R^-, with the mercury cation

$$2\,\text{R}^- + \text{Hg}^{2+} \underset{K_m}{\rightleftharpoons} \text{R}_2\text{Hg} \qquad (2)$$

(3) electrochemical fission of the C–Hg-bond in symmetrical organomercury compounds

$$\text{R}_2\text{Hg} + 2\,e^- \overset{k_e}{\rightleftharpoons} 2\,\text{R}^- + \text{Hg} \qquad (3)$$

We have proposed an equation relating the changes of pK_a-values of C–H-acids with change in the polarographical reduction parameters of organomercurials, R_2Hg:

$$\Delta(\alpha E_{\frac{1}{2}}) = \rho \Delta \text{p}K_a \,, \qquad (4)$$

where α is the electron transfer coefficient, $E_{\frac{1}{2}}$ the half-wave potential and ρ a constant depending on the nature of the carbon–metal bond and of the solvent.

In this paper a detailed consideration of eqn. (4) shows that its use is limited.

The three processes given above can be expressed by the following equations:

$$\mathrm{p}K_\mathrm{m} = a\mathrm{p}K_\mathrm{a} + \text{const.} \tag{5}$$

$$\mathrm{p}K_\mathrm{e} = b\mathrm{p}K_\mathrm{m} + \text{const.} \tag{6}$$

where

$$\mathrm{p}K_\mathrm{m} = -\log K_\mathrm{m}\,,\ \mathrm{p}K_\mathrm{e} = -\log K_\mathrm{e}$$

Equation (5) relates the affinity of the carbanion for the mercury cation ($\mathrm{p}K_\mathrm{m}$) with carbanion basicity ($\mathrm{p}K_\mathrm{a}$), and eqn. (6) $\mathrm{p}K_\mathrm{m}$ with the equilibrium constant ($\mathrm{p}K_\mathrm{e}$) of the *reversible* electrochemical reduction.

From eqns. (5) and (6) we get:

$$\mathrm{p}K_\mathrm{e} = ab\mathrm{p}K_\mathrm{a} + \text{const.} \tag{7}$$

where the constants, a and b, depend on the nature of the organometallic substrate and the medium.

Further we can express, by means of a Brönsted-type relation, the constant of the electrochemical equilibrium *via* the rate constant of the irreversible electrochemical reaction (k_e).

$$\ln k_\mathrm{e}^0 = -\alpha^0\mathrm{p}K_\mathrm{e} + \text{const.} \tag{8}$$

where α^0 is the transfer coefficient at an arbitrarily chosen electrode potential (E^0) and k_e^0 the rate constant of the electrochemical reduction at that potential.

Substituting $\ln k_\mathrm{e}^0$ for $\mathrm{p}K_\mathrm{e}$ in eqn. (7) we get:

$$\ln k_\mathrm{e}^0 = -\alpha^0 ab\mathrm{p}K_\mathrm{a} + \text{const.} \tag{9}$$

If we postulate that the transfer coefficient, α^0, is a constant for all organomercury compounds at the same electrode potential and that α depends only on electrode potential, and not on the nature of the organomercury compound (*i.e.*, the electrochemical reaction follows the Brönsted principle), the following equation will hold for an organomercury series:

$$\Delta \ln k_\mathrm{e}^0 = \gamma^0 \Delta\mathrm{p}K_\mathrm{a} \tag{10}$$

where γ^0 depends on the same factors as a, b and α^0.

Thus, for a correlation of the electrochemical parameters of R_2Hg with the $\mathrm{p}K_\mathrm{a}$-values of C–H-acids, the rate constants, k_e^0, for all members of the organomercury series must be defined at the same potential. At the present time, however, such a definition is not available for the whole series of organomercury compounds, because the interval of the half-wave potential change in this series is above 2 V. Therefore, for an approximate evaluation of $\ln k_\mathrm{e}^0$ we used the Koutecky–Delahay equation:

$$\frac{\alpha n F}{RT} E_{\frac{1}{2}} = \ln k_\mathrm{e}^0 + \text{const.} \tag{11}$$

which suggests that the transfer coefficient is independent of electrode potential. It can easily be shown that, if α does not depend on the electrode potential, $\mathrm{p}K_\mathrm{a}$-values will correlate *simply* with $E_{\frac{1}{2}}$. However, in practice there is no correlation between the $\mathrm{p}K_\mathrm{a}$-values of RH and the $E_{\frac{1}{2}}$-values of R_2Hg and it must be assumed that the transfer coefficient depends on electrode potential*.

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* Non-linearity of Tafel plots was demonstrated for some compounds[4,5].

When the value of the transfer coefficient at the half-wave potential is similar to that at the potential, E_0, the product, $\alpha E_{\frac{1}{2}}$, obtained from polarographical data, can be used for an estimation of ln k_e^0.

A combination of eqns. (10) and (11) leads to eqn. (4) but because of the limitation mentioned above, the correlation expressed is only approximate.

According to Kryshtalik[4], the transfer coefficient changes from 1 to 0, going from positive to negative potentials, and seems to be a principle for any electrode process. At anodic potentials, $\alpha = 1$ (non-barrieric discharge: the structure at the transition state coincides with the structure of the reaction product). At cathodic potentials, $\alpha = 0$ (non-activationary discharge; the structure of the transition and the initial states are the same). In the intermediate region of potentials, α changes from 1 to 0.

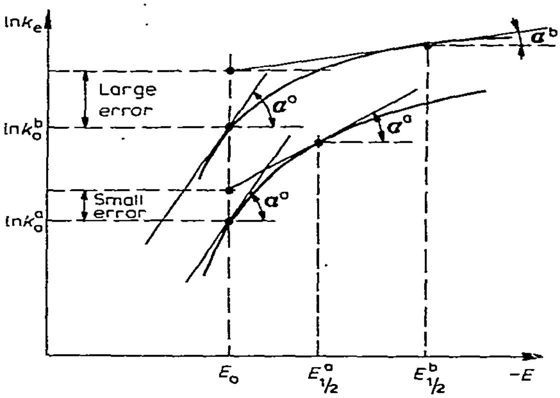

Fig. 1. Dependence of ln k_e upon electrode potential for two different compounds.

The dependence of ln k_e upon the electrode potential is shown in Fig. 1; two curves for two different organomercury compounds are shown, and these curves must be parallel because it is assumed that the transfer coefficients are equal at the same potentials for all organomercury compounds. It can be seen from the figure that an error in the definition of a real ln k_e^0-value depends on the choice of the potential E^0, and that a smaller value of the transfer coefficient corresponds to a substance that has more negative half-wave potential which is true of experimental data obtained for a great number of organomercury compounds[2,3].

Thus, the value of $\alpha nF/RT$ $(E_{\frac{1}{2}} - E_0)$, which is obtained by a linear extrapolation of the tangent in the point $E_{\frac{1}{2}}$ to E_0 (see Fig. 1), will not be the true value of ln k_e^0, and the deviation will be more when the compound reduces at more negative potentials.

Nevertheless, as we have shown recently[2,3], eqn. (4) is fulfilled for a large series of organomercury compounds in which the range of change in pK_a-values is more than 30 pK units*. The correlation should be considered satisfactory because the accuracy in definition of the transfer coefficient from the Heyrovsky plot is about 10 %.

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* It should be noted that $\alpha E_{\frac{1}{2}}$-values previously reported by us[2] for diallylmercury and mercury-bis-α-(ethyl acetoacetate) must be attributed, apparently, to other structures, because diallylmercury decomposes rapidly in 60 % aqueous dimethylformamide[6], and the mercury derivative of acetoacetic ester described previously[7] as the α-mercurated product is in reality the γ-isomer[8].

Similar dependencies of pK_a on $\alpha E_{\frac{1}{2}}$ for the acetylacetonate complexes of palladium and ammonia complexes of cobalt are shown in Figs. 2 and 3. The values of α and $E_{\frac{1}{2}}$ are literature values[9,11]. Figures 2 and 3 show that there is a fairly good correlation between $\alpha E_{\frac{1}{2}}$ and pK_a but not between pK_a and $E_{\frac{1}{2}}$. It is interesting to note that the relation is observed for ligands of different nature (F^-, NH_3 and a number of oxygen ligands; Fig. 3).

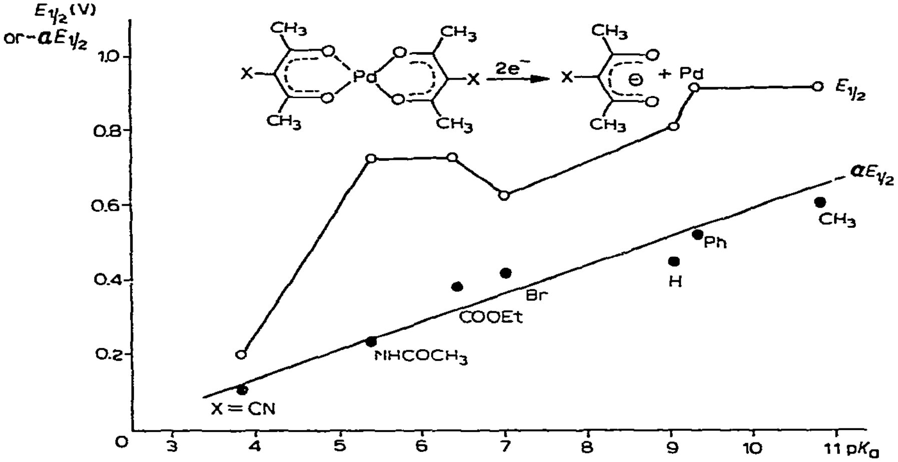

Fig. 2. Dependence of $\alpha E_{\frac{1}{2}}$ upon pK_a for acetylacetonate complexes of palladium.

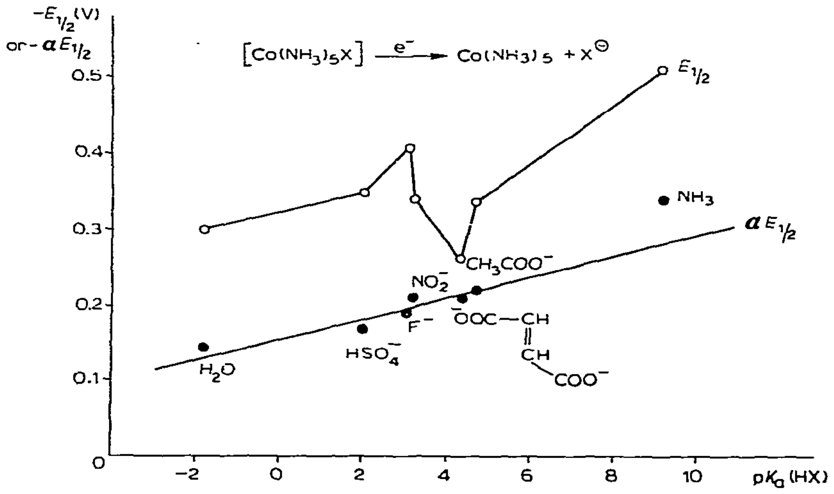

Fig. 3. Dependence of $\alpha E_{\frac{1}{2}}$ upon pK_a of HX for $[Co(NH_3)_5X]^{n+}$.

Besides the purely electrochemical limitations of the quality of correlation (4) there are also some limitations arising from inaccuracies in the hydrocarbon acidities scales which are known at the present time. We have used pK_a-values from the MSAD scale[10] which is known not to take into account the solvent effect; acidities of the C–H-acids in different solvents are at present not available.

In conclusion the following should be noted:

(1) If a linear relation exists between the logarithms of the rate constants of the electrochemical reduction of organometallic compounds ($\ln k_e^0$) at the same electrode potential and the pK_a-values of acids conjugated with anions bonded with a metal, the transfer coefficient at the same electrode potential (α^0) must be the same for all compounds of the given series and must depend only upon electrode potential and not upon any change in structure of organometallic compounds in the given series.

(2) The product, $\alpha E_{\frac{1}{2}}$, which is easily obtained from polarographical data can be used for an approximate definition of pK_a but this may introduce some errors because of a non-linear change of $\ln k_e$ with electrode potential. Apparently, the greater the difference between the half-wave potential of the compound in question and the potential E^0 (at which potential a comparison of $\ln k_e^0$ is made) the more will pK_a deviate from the true value.

(3) The impossibility of constructing a universal scale of relative acidities for all C–H-acids (the solvent effect on one C–H-acid can be far more than that on another) must be taken into account.

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