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ELECTROCHEMICAL STUDIES OF ORGANOMETALLIC COMPOUNDS

III*. THE POLAROGRAPHIC DETERMINATION OF THE C–H ACIDITY OF METALLOCENES

L. I. DENISOVICH and S. P. GUBIN
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)
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SUMMARY

The polarographic reduction of the three sets of compounds, *i.e.* organomercury salts, symmetrical organomercury compounds and σ-derivatives of π-cyclopentadienyliron dicarbonyl, have been investigated. The polarographic parameters obtained have been correlated with the pK_a values of RH. A least squares treatment of the results and a comparison of the accuracy of the determination for the new pK_a values of RH obtained for the three sets of reactions investigated show that the best correlation is obtained for a plot of the half-wave reduction potentials $E_{\frac{1}{2}}$ of π-$C_5H_5Fe(CO)_2$-σ-R and the pK_a values of RH. The pK_a values for ferrocene, cyclopentadienylmanganese and rhenium tricarbonyls as C–H acids have been determined.

INTRODUCTION

Streitwieser and Perrin[1] were the first to compare the polarographic reduction potentials of C–X bonds with their respective C–H acidities. They found a satisfactory linear dependence between the half-wave potentials for the polarographic reduction of arylmethyl chlorides and the acidities of the respective hydrocarbons. A similar relationship has not been observed, however, for the substituted benzyl chlorides. This has been explained in terms of the specific requirements of the transition state formed during the reduction of the substituted benzyl chlorides. Dessy *et al.*[2] have studied the polarographic reduction of organomercury salts in dimethoxyethane and found that the $E_{\frac{1}{2}}$ values for the second reduction step of RHgX, *i.e.*

$$RHg\cdot + e \longrightarrow R^- + Hg \tag{1}$$

correlate with the thermodynamic acidities of the respective hydrocarbons RH. The authors have suggested that the reduction of RHg· at the mercury electrode may provide a convenient model for estimating the stability of the carbanion generated. A comparison of the $E_{\frac{1}{2}}$ value for the second wave of RHgX obtained by Husch and

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* For parts I and II see ref. 18.

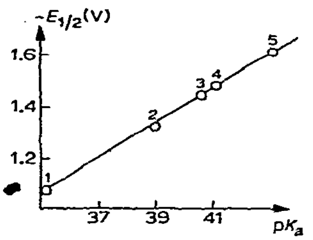

Fig. 1. A plot of the $E_{\frac{1}{2}}$ value for the second reduction wave of RHgX *versus* the pK_a values for RH (from the data of ref. 3). 1, $R=C_6H_5CH_2$; 2, $R=CH_3$; 3, $R=C_2H_5$; 4, $R=n\text{-}C_3H_7$; 5, $i\text{-}C_3H_7$.

Oldham[3] (in aqueous ethanol) with the respective pK_a values for RH again shows a linear dependence (Fig. 1).

Butin *et al.*[4-8] have studied symmetrical mercury compounds and have also observed a linear relationship between the polarographic reduction parameters for

$$R_2Hg + 2e \rightarrow 2R^- + Hg \qquad (2)$$

the process shown in eqn. 2 and the thermodynamic acidities of the respective hydrocarbons RH. They, however, employed the product $\alpha E_{\frac{1}{2}}$ (where α is the transition coefficient) instead of $E_{\frac{1}{2}}$ in deducing their relationship with the pK_a values.

In addition, we have shown[9] that on polarographic reduction of transition metal π-complexes with metal–carbon σ-bonds, a satisfactory linear relationship is observed between the $E_{\frac{1}{2}}$ values for the process shown in eqn. 3 and the pK_a values of the corresponding hydrocarbons RH.

$$\pi\text{-}C_5H_5Fe(CO)_2\text{-}\sigma\text{-}R + 2e \rightarrow [\pi\text{-}C_5H_5Fe(CO)_2]^- + R^- \qquad (3)$$

Thus in a number of cases it has been demonstrated that a linear relationship exists between the reduction potential of the M–C bond and the stability of the carbanion generated. For this reason it should be possible to use the observed linear dependences to determine unknown pK_a values for new hydrocarbons, thus providing a valuable alternative method since the "classical" methods are rather troublesome and do not always give reliable results. The first polarographic determination of the C–H acidity was performed by Butin *et al.*[4-8]. Unfortunately the statistical treatment of the results was included with these studies so that the confidence limits for the new pK_a values could not be obtained. Hence, although a dependence between the $E_{\frac{1}{2}}$ and pK_a values was established, it is not possible to evaluate data for pK_a determinations from these relations in the absence of such statistical treatment.

In the present work an attempt has been made to determine the pK_a values for π-cyclopentadienyl transition metal complexes *i.e.* ferrocene and π-cyclopentadienylmanganese and -rhenium tricarbonyls. Thus the polarographic reduction of three series of compounds containing the above mentioned organometallic radicals has been studied *i.e.* organomercury salts, symmetrical organomercury compounds and σ derivatives of π-cyclopentadienyliron dicarbonyl, and the polarographic parameters obtained correlated with the pK_a values for the hydrocarbons RH. Statistical treatment of the results has been accomplished through the use of the least squares technique and the calculated accuracies of the new pK_a values compared for the three above mentioned series of compounds. The possibility of correlating the pK_a values with $\alpha E_{\frac{1}{2}}$ instead of $E_{\frac{1}{2}}$ has also been studied. The polarographic technique used was similar to that described in Part I of this series.

RESULTS

I. Organomercury salts

In Table 1 are listed the parameters for the second reduction wave of RHgCl obtained in 90% dioxane with 0.1 *N* $(C_2H_5)_4NClO_4$ as the supporting electrolyte. In Part II[18b] of this series it was shown that only under these experimental conditions was it possible to obtain polarographic waves for RHgCl free from distorting maxima and prewaves*. Thus all the compounds listed in Table 1 reduce via a common scheme (eqn. 1) and hence a correct determination of $E_{\frac{1}{2}}$ is possible. The value of the transition coefficient α changes over a relatively wide range of values from 0.40 to 0.67.

TABLE 1

POLAROGRAPHIC CHARACTERISTICS FOR THE SECOND WAVE OF ORGANOMERCURY SALTS RHgX (90% DIOXANE, 0.1 *N* Et_4NClO_4, 25°, SCE, $c = 1 \times 10^{-3}$ $mol \cdot l^{-1}$)

Compound	$-E_{\frac{1}{2}}(V)$	$i_d(\mu A)$	α	α_{mean}	$pK_a(RH)^{2,10}$
C_2H_5HgCl	2.14	1.40	0.40	0.54±0.08	42
CH_3HgCl	1.96	1.70	0.53		40
C_6H_5HgCl	1.78	1.40	0.63		37
$CH_2{=}CH{-}HgCl$	1.62	1.40	0.54		36.5
$C_6H_5CH_2HgCl$	1.34	1.20	0.67		35
$CH_2{=}CH{-}CH_2HgCl$	1.62	1.60	0.40		35.5
$C_6H_5C{\equiv}CHgCl$	0.86	1.40	0.59		18.5
C_5H_5HgCl	0.75	1.50			15
$C_5H_5FeC_5H_4HgCl$	1.84	1.40	0.67		
$C_5H_4Re(CO)_3HgCl$	1.38	1.30	0.50		
$C_5H_4Mn(CO)_3HgCl$	1.42	1.40	0.60		

In order to cover the largest possible range of $E_{\frac{1}{2}}$ changes and hence of pK_a values it is necessary to carefully choose the compounds to be studied. The MSAD scale was used[2,10] to correlate the $E_{\frac{1}{2}}$ values in this and all other cases. As seen from Fig. 2, a linear dependence is obtained for the $E_{\frac{1}{2}}$ values for the reduction of RHgCl compounds and the pK_a values for the respective hydrocarbon RH. The equations of the lines, the correlation coefficient (r) and the mean square error (S) in the ordinate ($E_{\frac{1}{2}}$) and abscissa (pK_a) axes are shown in Table 2. The computed pK_a values for ferrocene and cyclopentadienylmetal tricarbonyls (M = Mn, Re) are also listed in Table 2.

Use of the product $\alpha E_{\frac{1}{2}}$ instead of $E_{\frac{1}{2}}$ for correlating with the pK_a values leads to a considerable scatter in the points and a breakdown in the correlation: the respective parameters are presented in Table 2.

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* C_5H_5HgCl provides an exception: it shows a small maximum in the initial part of the reduction wave.

TABLE 2

THE PARAMETERS FOR THE CORRELATIONAL EQUATIONS AND THE CALCULATED pK_a VALUES FOR π-CYCLOPENTADIENYL COMPLEXES

Reaction series	*Correlated values*	*Number of base points n*	*Equation of line* $y=ax+b$	*r*	*S* pK_a	*S* $E_{\frac{1}{2}}$ *or* *S* $\alpha E_{\frac{1}{2}}$	*Calculated* pK_a *values for* π*-complexes*
$RHg^{\cdot}+e \rightarrow R^{-}+Hg$	$E_{\frac{1}{2}}$–pK_a	8	$E_{\frac{1}{2}}=(-0.05\ pK_a+0.03)$	0.958	3.1	0.15	ferrocene 39 π-$C_5H_5Re(CO)_3$ 30 π-$C_5H_5Mn(CO)_3$ 31
	$\alpha E_{\frac{1}{2}}$–pK_a	8	$E_{\frac{1}{2}}=(-0.59\ pK_a-0.14)$	0.73	5.7	0.16	
$R_2Hg+2e \rightarrow 2R^{-}+Hg$	$E_{\frac{1}{2}}$–pK_a	6	$E_{\frac{1}{2}}=(-0.07\ pK_a+0.16)$	0.966	3.4	0.24	ferrocene 40
	$\alpha E_{\frac{1}{2}}$–pK_a	6	$E_{\frac{1}{2}}=(-0.02\ pK_a+0.11)$	0.961	3.6	0.08	
π-$C_5H_5Fe(CO)_2$-σ-R $+2e \rightarrow [\pi\text{-}C_5H_5Fe(CO)_2]^{-}+R^{-}$	$E_{\frac{1}{2}}$–pK_a	8	$E_{\frac{1}{2}}=(-0.03\ pK_a-0.81)$	0.994	1	0.03	ferrocene 38

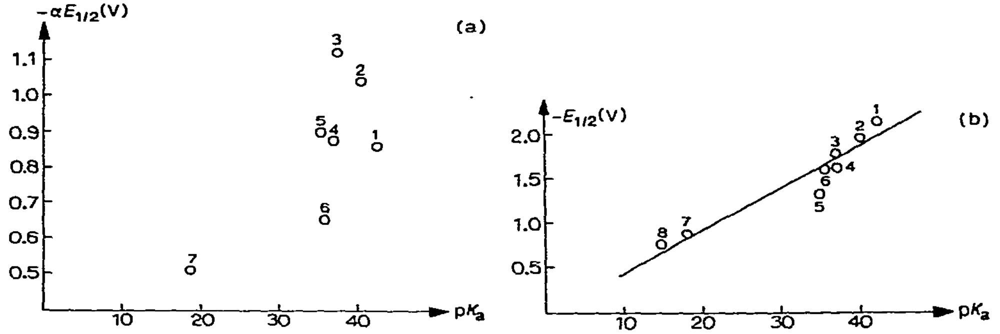

Fig. 2. Plots of $E_{\frac{1}{2}}$ (a), and $\alpha E_{\frac{1}{2}}$ (b), for the second wave of RHgX (in 90% dioxane, 0.1 *N* Et_4NClO_4) *versus* the pK_a values of RH. 1, R=C_2H_5; 2, CH_3; 3, C_6H_5; 4, CH_2=CH; 5, $C_6H_5CH_2$; 6, CH_2=CH–CH_2; 7, $C_6H_5C{\equiv}C$; 8, C_5H_5.

II. Symmetrical organomercury compounds

The parameters obtained for the polarographic reduction of a series of symmetrical mercury compounds in absolute DMF with 0.1 *N* $(C_2H_5)_4NClO_4$ as the supporting electrolyte are listed in Table 3. As shown experimentally, some compounds, for example $(CH_2{=}CH{-}CH)_2Hg$ and $(C_5H_5)_2Hg$, are unstable in aqueous DMF solutions, and for this reason and unlike previous studies[6] we have studied them in the anhydrous solvent. All compounds investigated reduce via a common scheme (eqn. 2), the extent to which the $E_{\frac{1}{2}}$ values change (and thus the pK_a values) being quite large (–1.86 V). The corresponding values of the transition coefficients α changes from 0.17 to 0.29. It should be noted that although calculations give a value of α=0.26, in the case of $(C_5H_5)_2Hg$, measurements using the Kalousek switch indicate that a reversible reduction of this compound occurs (Fig. 3). This result is in agreement with those quoted elsewhere[11], where it is stated that $(C_5H_5)_2Hg$ is reversibly reduced. We have also noticed that the reduction wave of $(C_5H_5)_2Hg$ becomes irreversible and changes its pattern sharply on changing the medium from absolute DMF to 60% aqueous DMF; this may possibly be due to the hydrolysis of $(C_5H_5)_2Hg$ in the aquous medium.

TABLE 3

POLAROGRAPHIC CHARACTERISTICS OF SYMMETRICAL ORGANOMERCURY COMPOUNDS R_2Hg (ABSOLUTE DMF 0.1 *N* Et_4NClO_4, 25°, SCE, $c=1\times10^{-3}$ mol·l^{-1})

Compound	$-E_{\frac{1}{2}}(V)$	$i_d(\mu A)$	α	α_{mean}	$pK_a^{2,10}$
$(C_6H_5)_2Hg$	2.58	3.10	0.29	0.23±0.03	37
$(CH_2{=}CH{-}CH_2)_2Hg$	2.13	3.60	0.24		35.5
$(C_6H_5CH_2)_2Hg$	2.03	3.60	0.24		35
$(C_6H_5C{\equiv}C)_2Hg$	1.60	3.10	0.17		18.5
$(C_5H_5)_2Hg$	0.72	3.10	0.26		15
$(NC)_2Hg$	0.42	1.80	0.17		9.5
$(C_5H_5FeC_5H_4)_2Hg$	2.68		0.22		

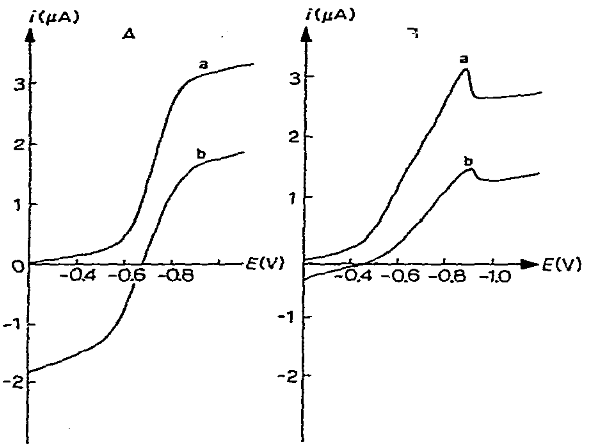

Fig. 3. Polarograms of $(C_5H_5)_2Hg$. A. (a) wave for $(C_5H_5)_2Hg$ (absolute DMF, 0.1 N Et_4NClO_4, $c = 1 \times 10^{-3}$ $mol \cdot l^{-1}$); (b) wave using the Kalousek switch, E_{auxil} −1.2 V, frequency 25 Hz. B. (a) wave for $(C_5H_5)_2Hg$ (60% DMF, 40% H_2O, 0.1 N Et_4NClO_4, $c = 1 \times 10^{-3}$ $mol \cdot l^{-1}$); (b) wave using the Kalousek switch, E_{auxil} −1.2 V, frequency 25 Hz.

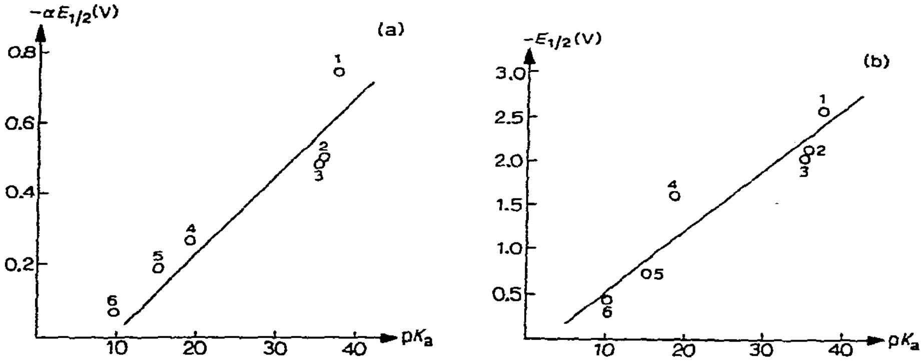

Fig. 4. Plots of $E_{\frac{1}{2}}$ (a) and $\alpha E_{\frac{1}{2}}$ (b) for R_2Hg (DMF, 0.1 N $EtNClO_4$, $c = 1 \times 10^{-3}$ $mol \cdot l^{-1}$) *versus* pK_a values of RH. 1, $R=C_6H_5$; 2, $R=CH_2{=}CH{-}CH_2$; 3, $C_6H_5CH_2$; 4, $C_6H_5C{\equiv}C$; 5, C_5H_5; 6, CN.

This observation suggests that the possibility of determining $E_{\frac{1}{2}}$ for $(C_5H_5)_2Hg$ in 60% aqueous DMF, as reported in ref. 6, is doubtful. Similarly, measurements using the Kalousek switch for $Hg(CN)_2$ indicate that the process is reversible. This is in good agreement with the previous data[12] on the reversible reduction of $Hg(CN)_2$ in the absence of free CN^- ions.

As shown in Fig. 4, a linear relationship exists between the $E_{\frac{1}{2}}$ values for the reduction of R_2Hg and the pK_a values of the respective hydrocarbons RH. The correlation parameters and the calculated pK_a value of ferrocene are given in Table 2*.

In contrast to the data reported in refs. 4–7, use of the product $\alpha E_{\frac{1}{2}}$, instead of $E_{\frac{1}{2}}$, does not improve the dependence; the respective parameters are shown in Table 2.

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* The pK_a values of $C_5H_5M(CO)_3$ (M=Mn, Re) cannot be determined from the equation obtained because of the difference in the mechanism of the reduction of symmetrical mercury derivatives of these π-complexes from that of classical R_2Hg compounds (*cf.* Part I[8a] of this series).

For $(C_5H_5)_2$, the value of α was 0.26, while for $Hg(CN)_2$ α was 0.17, the reduction of both these compounds being reversible. When α was close to unity, the distribution of points was much more scattered and a much poorer interrelationship between the parameters was observed.

III. σ-Derivatives of π-cyclopentadienyliron dicarbonyl

We have previously studied[9] the polarographic reduction of iron σ-complexes, *i.e.* π-$C_5H_5Fe(CO)_2R$ with an Fe–C σ-bond. It was shown that there is a relationship between the half-wave potential for the reduction of this bond (see eqn. 3) and the pK_a values of the respective hydrocarbon RH. In the present work we have extended the list of compounds studied mainly through the inclusion of those with σ-alkyl radicals, and we have also studied the reduction of the σ-ferrocenyl derivative. Measurements were carried out in absolute CH_3CN as the solvent with 0.1 *N* $(C_2H_5)_4NClO_4$ as the supporting electrolyte. The results obtained are given in Table 4. All of the newly investigated compounds display a two-electron wave in the polarogram which corresponds to the irreversible cleavage of the Fe–C σ-bond (see eqn. 3). In addition, there is an anodic one-electron wave in the case of the σ-ferrocenyl compound which may be attributed to the reversible oxidation of the iron in the ferrocene part of the molecule.

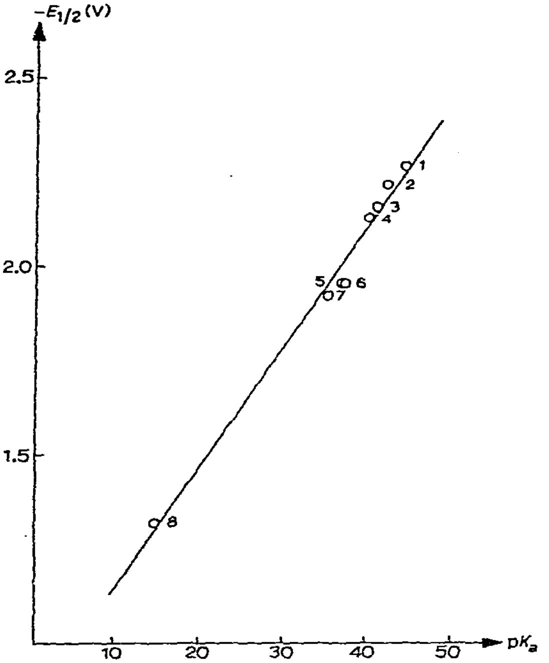
TABLE 4

POLAROGRAPHIC CHARACTERISTICS OF π-$C_5H_4(CO)_2Fe$-σ-R (CH_3CN, 0.1 *N* Et_4NClO_4, 25°, SCE, $c = 1 \times 10^{-3}$ mol·l^{-1})

R	$-E_{\frac{1}{2}}(V)$	$i_d(\mu A)$	α	α_{mean}	$pK_a^{2,10}$
i-C_3H_7	2.27	5.0	0.19	0.24±0.03	44
n-C_3H_7	2.22	4.8	0.21		42
C_2H_5	2.16	4.0	0.25		42
CH_3	2.13	5.1	0.22		40
C_6H_5	1.96	4.6	0.29		37
CH_2=CH–CH_2	1.96	5.10	0.23		35.5
$C_6H_5CH_2$	1.93	5.10	0.29		35
C_5H_5	1.32	4.30	0.27		15
$C_5H_5FeC_5H_4$	2.03	2.7			

As depicted in Fig. 5, all of the compounds studied exhibit a good linear relationship between the $E_{\frac{1}{2}}$ values for the reduction of Fe–R bond and the pK_a values of the respective hydrocarbons. The correlation parameters and the computed value of pK_a for ferrocene are given in Table 2. Correlation of the pK_a values with $\alpha E_{\frac{1}{2}}$ rather than $E_{\frac{1}{2}}$ is of little value for this reaction series, since the values of α are very close, in this case differing by only 0.1. Figure 6 illustrates the good linear relationship observed between the $E_{\frac{1}{2}}$ values for the reduction of compounds with Fe–R bonds and the pK_a values or σ^* inductive constants of the corresponding alkanes. The pK_a values used in this case are on the MSAD scale. If the pK_a values quoted in ref. 6 are used instead of those on the MSAD scale, there is completely random scattering of the points corresponding to the σ-alkyl compounds.

The following reasons appear to account for the complete lack of reliability in the pK_a values determined in ref. 6: (a) The absence of a statistical treatment of the



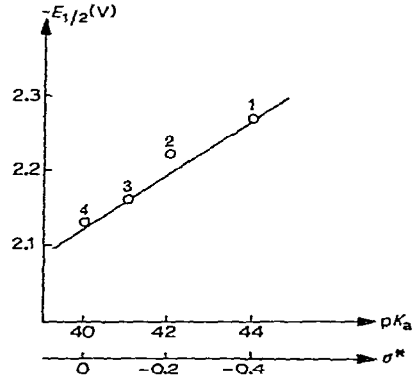


Fig. 5. Plot of the $E_{\frac{1}{2}}$ value for the reduction wave of π-$C_5H_5(CO)_2Fe$-σ-R (CH_3CN, 0.1 *N* Et_4NClO_4, $c=1\times10^{-3}$ mol·l^{-1}) *versus* the pK_a values of RH. 1, R = i-C_3H_7; 2, R = n-C_3H_7; 3, R = C_2H_5; 4, R = CH_3; 5, R = C_6H_5; 6, R = CH_2=CH–CH_2; 7, R = $C_6H_5CH_2$; 8, R = C_5H_5.

Fig. 6. Plot of the $E_{\frac{1}{2}}$ value for the reduction wave of π-$C_5H_5(CO)_2Fe$-σ-Alk (CH_3CN, 0.1 *N* Et_4NClO_4, $c=1\times10^{-3}$ mol·l^{-1}) *versus* the pK_a values for AlkH and the Taft σ^* inductive constants.

data. (b) The results are apparently based on a line drawn through three points. (c) Reduction of dialkylmercury compounds occurs at very negative potentials where the waves are normally distorted and this hinders an accurate determination of the half-wave potentials and of the value of α.

Recently the pK_a values for alkanes have been determined by means of NMR spectroscopy[13]; the values obtained in this case were very similar to those quoted on the MSAD scale.

DISCUSSION

In order to compare parameters for the polarographic reduction and the pK_a values of RH we have studied three series of compounds: organomercury salts, symmetrical organomercury compounds and the σ-derivatives of π-cyclopentadienyliron dicarbonyl. All these compounds reduce via the cleavage of the metal–carbon bond (see eqns. 1–3) and form the carbanion R^- whose thermodynamic stability affects the value of half-wave potential.

It is known that a correlation between the $E_{\frac{1}{2}}$ values and the structure of the compound under study or of its reduction products is valid only when the electrochemical process is strictly reversible. Where irreversible processes occur, in order to correlate the $E_{\frac{1}{2}}$ values for a series of structurally similar compounds it is necessary to determine and to be able to account for the values of the transition coefficients α, correlation being only valid when α is invariable. At present, however, it is only possible to obtain exact information regarding the extent to which α varies by changing the mechanism of the electrochemical reaction. Zuman[14] has, in fact, assumed that α varies over the range ± 0.1, and some cases over a range as large as ± 0.2.

In these experiments the experimental conditions were chosen so that the observed reduction waves of the various compounds were not distorted by maxima and were very close in shape to that which may be described as classical.

Under these conditions we have succeeded in obtaining the following values for the maximum variation in α*: 0.27 for RHgCl, 0.12 for R_2Hg and 0.10 for π-$C_5H_5Fe(CO)_2$-σ-R. Calculations have shown that when $\Delta\alpha = 0.12$ the relationships between pK_a and $E_{\frac{1}{2}}$ or $\alpha E_{\frac{1}{2}}$ for R_2Hg have similar correlation coefficients and mean square deviations along the pK_a(RH) axis ($S = 3.4$ and 3.6 respectively). On the other hand, when the potentials corresponding to the second reduction step of RHgCl are multiplied by α the relationship breaks down and is no longer acceptable for the determination of new pK_a values ($r = 0.958$ and 0.73, $S = 3.1$ and 5.7 respectively).

In order to understand the reasons for these changes in α for various mercury compounds, and specifically for organomercury salts, it is necessary to appreciate that such compounds exhibit an exceptional tendency to undergo coordinative interactions (*i.e.* with the solvent[15], with the supporting electrolyte[16] and of an intramolecular variety[16,17]) because of the unsaturated nature of the mercury atom.

An entirely different pattern is observed during the polarographic reduction of π-$C_5H_5Fe(CO)_2$-σ-R where the metal atom is located in a distorted octahedronal environment being electronically and coordinatively saturated[9]. All these results support the suggestion that the reduction of this series of compounds occurs via a common scheme which leads to the similarity in the observed values of α together with the equality of n and i_d. As seen in Table 2, for such cases the correlation coefficient between $E_{\frac{1}{2}}$ and pK_a is very close to unity and the mean square deviation along the X axis (pK_a) is rather small (± 1.05). The data obtained indicate that this reaction series may be used for the determination of new pK_a values. One disadvantage of this reaction series however is the fact that σ-derivatives other than those listed in Table 4 are difficult to obtain.

The results obtained thus provide a basis for the assumption that polarographic reduction of organomercury salts and symmetrical mercury compounds when carried out under the conditions described in this study should enable the determination of the pK_a values for the respective hydrocarbons (when the latter are considered as C–H acids) to an accuracy of not greater than ± 3 pK_a units**.

If a greater accuracy is required, reduction of the corresponding derivatives of the cyclopentadienyliron dicarbonyl radical should be considered. It is probable that in the near future similar sets of reactions will be established for the octahedral complexes of other transition metals.

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* It is probable that the value $\Delta\alpha = \pm 0.10$ corresponds to an experimental error, for in repeat measurements of waves for the same substance the values of α changed inside these limits under our conditions.

** It should be pointed out that the accuracy of the pK_a values on the MSAD scale has never been reported, although apparently it is not better than ± 3 pK_a units.

The results of this work clearly indicate that there is little merit in employing the product $\alpha E_{\frac{1}{2}}$ for the correlation of pK_a data for the following reasons: (a) The accuracy with which α may be determined especially for the badly formed waves is rather low. Furthermore, a similar deviation in the value of α may result in entirely different deviations in the product $\alpha E_{\frac{1}{2}}$ depending on the absolute value of $\alpha E_{\frac{1}{2}}$. (b) With identical values of α, multiplication by $E_{\frac{1}{2}}$ may either result in no change or in some cases even lead to a complete loss of correlation. (c) When the values of α in a series of compounds are very different ($\Delta\alpha > 0.3$), this may be due to a difference in the mechanism of the electrode reaction. Under such circumstances the relationship loses its meaning.

The pK$_a$ values of metallocenes as C–H acids

From the results listed in Tables 1, 3 and 4, it may be seen that compounds containing the ferrocenyl radical are always more difficult to reduce than the respective phenyl derivatives. This observation is in agreement with the well-known fact that ferrocenyl is always a stronger electron donor in comparison to the phenyl radical. At the same time, mercury compounds of cyclopentadienylmanganese and rhenium tricarbonyls are much more readily reduced than phenylmercury chloride indicating that in such cases the respective radicals are stronger acceptors than the phenyl radical. The values of pK_a estimated from the $E_{\frac{1}{2}}$ values show that ferrocene is more acidic (while CTM and CTR have a lower acidity) than benzene.

If these complexes are considered to be derivatives of a coordinated cyclopentadienyl anion, it follows that in the series cyclopentadienyl anion*, ferrocene, CTM and CTR the acidity of the C–H bond increases in a regular manner. The negative inductive effect of the respective radicals increases in the same order (4.04, 4.83, 5.3 ppm for ferrocene, CTM and CTR respectively). The same sequence has been observed for the decrease in the ring proton shielding (−0.22, −0.05, +0.17, +0.26 for ferrocene, CTM and CTR respectively). All these data indicate that the observed sequence of pK_a values for cyclopentadienyl complexes may be related to the change in the effective positive charge of the ring carbon atoms during the course of coordination.

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* Although no direct measurement of the acidity has been made for the cyclopentadienyl anion, it is reasonable to assume that its pK_a value should be about 50.

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