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HAMMETT REACTION CONSTANTS FOR IRREVERSIBLE ELECTROREDUCTION OF IODOBENZENES IN NON-AQUEOUS SOLVENTS

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Polarographic half-wave potentials for the electrochemical reduction of a series of *para*-substituted iodobenzenes in acetonitrile, acetone, benzonitrile, dimethylformamide, dimethyl sulphoxide and methanol obey Hammett equations and the reaction constant found, $\rho = 0{\cdot}36 \pm 0{\cdot}02$, is independent of the solvent used. The results obtained are discussed on the basis of a mechanism of the electrode process.

INTRODUCTION

Whereas the original Hammett equation and its several extensions have found a number of applications in physical organic chemistry,[1–3] solvent effects on the reaction constant, ρ, have been studied relatively rarely. In some cases the ρ values are linearly dependent on the reciprocal of the solvent electric permittivity, as suggested by Hammett.[1] In particular, such dependences have been observed in mixed solvents, e.g., recently for pK_a values of substituted salicylic acids and pyridinium and anilinium ions in dioxan–water mixtures.[4]

In organic electrochemistry, the above problem has only been discussed for a reversible, one-electron reduction, as recently reviewed.[5] For the reversible process of radical anion formation:

$$R + e \rightleftharpoons R^{-\cdot} \tag{1}$$

the measured half-wave potential has a thermodynamic meaning, i.e it corresponds to the reaction free-energy change. The difference between half-wave potential values for unsubstituted, $E^0_{1/2}$, and substituted compounds, $E_{1/2}$, follows the electrochemical Hammett equation:

$$E_{1/2} - E^0_{1/2} = \rho\sigma \tag{2}$$

Moreover, the half-wave potential can be related to the difference in solvation free energies for a product and a reactant. In dipolar, non-hydrogen-bonded donor solvents with electric permittivities higher than 20 (which are normally used in polarography), the Lewis acid–base interactions contribute decisively to solvation phenomena. The solvation of an ionic product of reaction (1) is stronger than that of a parent neutral molecule. Hence it is not surprising that both the $E_{1/2}$ and ρ values depend on the solvent acidity, e.g. for the polarographic reduction of a series of *p*-quinones a linear dependence of the reaction constant from the Hammett–Streitwieser equation on solvent acceptor number has been found.[6]

On the other hand, if radical anions form 'contact' ion pairs with small, inorganic cations of supporting electrolytes:

$$(R^{-\cdot})_{\text{solv}} + (M^+)_{\text{solv}} \rightleftharpoons (R^{\cdot-} \cdots M^+)_{\text{solv}} \tag{3}$$

the desolvation of cations mainly contributes to changes in solvation energies, and relationships between ρ values and solvent basicity, expressed in terms of Gutmann's donor number, have been established.[7]

For irreversible electroreduction, the Hammett treatment is also valid but the interpretation of equation (2) is more complex. Namely, the irreversible half-wave potential depends on the rate constant of the heterogeneous electron transfer, k_{fh}, and, at 298 K, can be expressed by[8]

$$E_{1/2} = E_0 + (0{\cdot}059/\alpha n)\log(1{\cdot}349 k_{fh} t^{1/2}/D_{ox}^{1/2}) \tag{4}$$

where E_0 is the standard potential, α the cathodic transfer coefficient, n the number of electrons exchanged in a rate-determining step, t the drop time and D_{ox} the diffusion coefficient of the oxidized form of the reactant. It is evident from equation (4) that the polarographic Hammett equation is fulfilled if irreversible $E_{1/2}$ potentials are chiefly determined by only one parameter, the k_{fh} constant.

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On the other hand, a change of the solvent can affect not only the height of the activation barrier but also the frequency factor in the rate constant, the diffusion coefficient, which is proportional to the reciprocal of solvent viscosity, and the position of the reaction plane at the electrode, which can be related to α.[5,9] It should be added that contemporary theories of electron-transfer kinetics (see the discussion and references in Refs 5 and 9) consider only reactions not accompanied by the cleavage of chemical bonds. The Marcus treatment predicts the dependence of the solvent reorganization energy on $(1/\varepsilon_{op} - 1/\varepsilon_s)$, where ε_{op} and ε_s are solvent optical and static electric permittivity, respectively. On the other hand, the frequency of approaching the energy-barrier top has recently been described in terms of the reciprocal of the longitudinal (i.e. 'constant charge') solvent relaxation time τ_L (see references in Refs 5 and 9).

The aim of this paper is the analysis of the reaction constant from the polarographic Hammett equation for the irreversible electroreduction of *para*-substituted iodobenzenes in different solvents. This reaction was chosen because its mechanism in *N*,*N'*-dimethylformamide (DMF) has been investigated[10,11] and a Hammett relationship found.[12]

EXPERIMENTAL

Polarographic measurements. Polarograms were recorded with a Radelkis OH-105 apparatus using a three-electrode system: a dropping mercury electrode ($t = 3{\cdot}15$ s, $m = 2{\cdot}83$ mg s^{-1} in 0·1 M tetraethylammonium perchlorate (TEAP)–DMF, at open circuit), a mercury pool as the auxiliary electrode and an aqueous saturated calomel electrode (SCE) as the reference electrode, which was separated from the measuring solution by a salt bridge. A.c. sinusoidal polarography was performed at a frequency of 60 Hz. The concentrations of the reactants were 0·5 mM; 0·1 M TEAP was used as the supporting electrolyte in all solvents with the exception of methanol, where 0·1 M tetraethylammonium bromide (TEABr) was employed. All solutions were deaerated with pure argon, which was presaturated by bubbling it through the solvent. All measurements were performed at 22 °C.

Materials. Iodobenzene from POCh was used as received. *para*-Substituted iodobenzenes were synthesized by Dr A. Krówczyński: only *p*-acetyl- and *p*-dimethylamino-iodobenzene had to be additionally purified by vacuum sublimation and recrystallization from *n*-hexane, respectively.

Acetonitrile (ACN), dimethyl sulphoxide (DMSO) and DMF were purified and dried as described previously.[13] Benzonitrile (BCN) (from Fluka) was distilled twice under reduced argon pressure after drying over type 4A molecular sieves, acetone (AC) (from POCh) was dried over 4A molecular sieves and methanol (POCh) was used as received. TEAP and TEABr were recrystallized from tripyl distilled water and vacuum dried.

RESULTS

The polarographic behaviour of the series of *para*-substituted derivatives of iodobenzene (Table 1) was examined in six solvents, carefully selected in order to obtain large variations in their dielectric and Lewis acid–base properties. In all cases one irreversible, two-electron wave corresponding to the reduction of the C—I bond was observed (with the exception of *p*-diiodobenzene, which exhibits two, ill-separated waves, indicating the cleavage of both C—I bonds). The results obtained are in full agreement with previous investigations in DMF and ACN.[10-12] In BCN solutions only six compounds with electron-withdrawing substituents could be reduced within an accessible potential range.

The $E_{1/2}$ values obtained are given in Table 1. They were correlated with the original Hammett substituent constants, σ_p, and with the Taft 'normal' σ_p^0 values based on ionization of phenylacetic acids. Much better relationships were obtained with σ_p^0 constants. Such a result is reasonable taking into account that σ_p^0 constants are free from the effects of cross-conjugation which are present in the case of substituted benzoic acids. It may be noted that Sease *et al.*[12] found much better correlations for the electroreduction of substituted chloro- and bromobenzenes with σ^- values, based on aniline systems, than with conventional σ values.

Acceptable Hammett plots are obtained for each solvent, indicating that the same mechanism can be

Table 1. Half-wave potentials for the electroreduction of *para*-substituted iodobenzenes in different solvents

		$-E_{1/2}$(V)					
Substituent	$\sigma_p^{0\,a}$	ACN	BCN	DMSO	DMF	MeOH	AC
$COCH_3$	0·50	1·513	1·570	1·524	1·520	1·420	1·530
Br	0·30	1·611	1·613	1·557	1·579	1·512	1·561
Cl	0·28	1·574	1·623	1·574	1·569	1·514	1·559
I	0·27	1·530	1·599	1·536	1·548	1·484	1·515
NMeCOMe	0·26[b]	1·626	1·658	1·611	1·611	1·545	1·609
NHCOMe	0·03	1·698	1·723	1·673	1·708	1·603	1·730
H	0	1·733	–	1·699	1·696	1·639	1·687
OMe	−0·10	1·739	–	1·725	1·737	1·678	1·742
Me	−0·12	1·732	–	1·713	1·720	1·666	1·732
NH_2	−0·36	1·854	–	1·850	1·853	1·733	1·806
$N(Me)_2$	−0·48	1·834	–	1·813	1·826	1·780	1·810

[a] Substituent constants σ_p^0 from Ref. 14.

[b] Substituent constant σ_p from Ref. 15.

Table 2. Correlation analysis of the Hammett equations for the electroreduction of *p*-iodobenzenes in different solvents

Solvent	No. of points	$-E^0_{1/2}$ (V)[a]	ρ (V/σ unit)[a]	Correlation coefficient (r)
ACN	11	1·70 ± 0·02	0·37 ± 0·08	0·962
BCN	6	1·72 ± 0·02	0·33 ± 0·15	0·926
DMSO	11	1·68 ± 0·02	0·36 ± 0·07	0·970
DMF	11	1·70 ± 0·02	0·36 ± 0·06	0·975
AC	11	1·68 ± 0·03	0·35 ± 0·09	0·947
MeOH	11	1·62 ± 0·01	0·37 ± 0·05	0·986

[a] 95% confidence intervals are indicated.

assumed for all reactants of interest. In order to exclude the possibility of adsorption of some reactants, the a.c. polarograms in DMF were recorded. However, no indication of strong adsorption–desorption processes was found.

The statistical analysis of the Hammett equations for the investigated reactions is given in Table 2. Errors are calculated on the basis of a Student's distribution with a confidence level of 0.95. The correlation coefficients obtained indicate that 90–97% (in AC and MeOH) of the variation in experimental half-wave potentials is explained by the Hammett equation (2). The lowest value of $r = 0{\cdot}926$ found in BCN is caused by a smaller accessible potential range in this solvent: $E_{1/2}$ values are less accurate because corresponding waves are close to the potential limit. High values of the correlation coefficients obtained indicate that $E_{1/2}$ potentials are probably mainly determined by the heterogeneous rate constant, as has been stated previously [equation (4)].

The reaction constant, ρ, has a positive value in each solvent, in agreement with the Hammett behaviour found previously in DMF and ACN.[12] Such a result indicates that the electroreduction process is facilitated by reducing the electron density at the reaction site[2,3] and thus a negative charge at a reaction centre in a transition state for a rate-determining step was suggested.[12] The result obtained is also in accordance with the established mechanism of the electroreduction of aromatic halides,[10] as will be discussed later. Moreover, the data in Table 2 indicate that ρ values are evidently independent of the solvent used. This result will also be discussed on the basis of the reaction mechanism.

DISCUSSION

The general mechanism proposed for the electroreduction of aromatic halides in non-aqueous solvents[10,11] involves the formation of an anion radical [equation (5)] followed by the cleavage of the carbon–halogen bond [equation (6)] and a further reduction of the resulting neutral aryl radical at the electrode [equation (7)] or in the solution [equation (8)], ultimately yielding the hydrocarbon ArH [equation (9)].

$$\mathrm{ArX} + \mathrm{e} \rightleftharpoons \mathrm{ArX}^{-\bullet} \tag{5}$$

$$\mathrm{ArX}^{-\bullet} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^{-} \tag{6}$$

$$\mathrm{Ar}^{\bullet} + \mathrm{e} \rightarrow \mathrm{Ar}^{-} \tag{7}$$

$$\mathrm{Ar}^{\bullet} + \mathrm{ArX}^{-\bullet} \rightarrow \mathrm{Ar}^{-} + \mathrm{ArX} \tag{8}$$

$$\mathrm{Ar}^{-} + \mathrm{H}^{+} \rightarrow \mathrm{ArH} \tag{9}$$

A two-electron irreversible wave is obtained if the lifetime of the anion radical $\mathrm{ArX}^{-\bullet}$ is short with respect to the time scale of the electrochemical method used and the neutral radical, $\mathrm{Ar}^{\bullet}$, has a higher electron affinity than $\mathrm{ArX}^{-\bullet}$.

For the reduction of unsubstituted chlorobenzene and bromobenzene in DMF, it has been established[10] that the kinetics of the overall process are determined by the slow initial electron transfer [equation (5)]. However, for the reduction of iodobenzene, the electrochemical process is probably kinetically controlled[10] by the both steps: charge-transfer [equation (5)] and chemical reaction [equation (6)]. For electroreduction of three halobenzenes in DMF the apparent forward rate constant (which is a function of standard rate constant and standard potential) was determined[10] from the measured change of the peak potential against sweep rates. The values obtained[10] increase in the order chlorobenzene < bromobenzene < iodobenzene. It follows from the above mechanism that for the reaction with the slowest electron-transfer step [equation (5)] the carbon–halogen bond is becoming more negative as the system moves into the transition state. The ρ values found in DMF[12] support this interpretation; they are $\rho = 0{\cdot}35$, $0{\cdot}57$ and $0{\cdot}81$ V/σ unit for *para-* and *meta-*substituted iodobenzenes, bromobenzenes and chlorobenzenes, respectively. The observed dependence between ρ values and rate constants related to a change in transition state can also be discussed in terms of the reactivity–selectivity principle (see, e.g., review in Ref. 3).

The solvent-independent ρ value found for the electroreduction of *para*-substituted iodobenzenes (Table 2) indicates, in our opinion, that the initial electron–transfer [equation (5)] and also the cleavage reaction [equation (6)] are concomitantly rate-determined steps in all the solvents investigated. In other words, both processes (5) and (6) occur simultaneously, as was proposed by Elving.[16] Hence two different possibilities can be considered to explain why the values of rate constants, half-wave potentials and reaction constants are almost independent of the solvent. The first suggestion is that the charge at a carbon atom in a transition state is small (and thus independent of the solvent) and/or there is a compensation of solvent effects in both steps (5) and (6). It follows from this interpretation that in the electroreduction of substituted chlorobenzenes and bromobenzenes, when the initial electron-transfer step [equation (5)] controls the overall kinetics, the values of ρ should be dependent on the solvent used.

On the other hand, the remarkable slowness of the initial electron transfer for the reduction of unsubstituted chlorobenzene and bromobenzene in DMF in comparison with processes not accompanied by bond breaking indicates[10] the significant contribution to the energy barrier of the initial step [equation (5)] of the internal reactant reorganization due to the stretching of the carbon–halogen bond. If this contribution is also responsible for the solvent independence of rate constants and the observed reaction constant, then the ρ values for a series of substituted chloro- and bromobenzenes should also be independent of the solvent.

An experimental verification of the two proposed alternatives is in progress.

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