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SOLVENT EFFECT ON THE HAMMETT REACTION CONSTANT FOR THE ELECTROREDUCTION OF SUBSTITUTED BENZOPHENONES

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Solvent effects on the Hammett ρ value for the cathodic reduction of substituted benzophenones were determined. The electrochemistry of a series of 11 compounds was studied in acetonitrile, acetone, dimethyl sulphoxide, propylene carbonate, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N,N*-diethylformamide and hexamethylphosphoric triamide. The ρ values for the reversible one-electron transfer are described by the Lewis acid–base model $\rho = -0{\cdot}006AN + 0{\cdot}003DN + 0{\cdot}391$, where AN = solvent acceptor number and DN = solvent donor number.

INTRODUCTION

Structural and medium effects on the redox properties of organic compounds are usually interpreted with linear free energy relationships.[1] One can express the Hammett equation in the form

$$(E_{1/2})_X = (E_{1/2})_H + \rho\sigma \qquad (1)$$

to relate changes in the polarographic half-wave potential for the unsubstituted compound $(E_{1/2})_H$ to that of the *meta*- or *para*-substituted derivatives $(E_{1/2})_X$.

First attempts to correlate electrochemical data with substituent constants σ were published in the early 1950s and were reviewed in Zuman's classical book.[2] Numerous papers deal with applications of equation (1). The dependence of the reaction parameter ρ on the solvent is marked but it is poorly understood; the originally predicted[3] linear relationship with the reciprocal of ε, the dielectric constant, is poor.[1a] Correlations with other functions of ε are not much better.

The donor–acceptor concept[4] is more promising. The dependence of ρ on DN, the solvent donor number,[4] was observed in the one-electron reversible reduction of *meta*-substituted nitrobenzenes and *para*-substituted azobenzenes in aprotic media.[5] However, radical anions formed at the electrode remain paired with the cations of supporting electrolyte; the relationship of ρ with DN thus includes also the solvent effect on the association phenomenon. In the absence of ion pairing, a linear correlation of ρ with AN, the solvent acceptor number[6] was found for a series of quinones.[7] There, the ρ value for *para*-substituted iodobenzenes is independent of the solvent; we have offered an explanation recently.[8]

In this work we studied solvent effects on the Hammett reaction constant for the cathodic reduction of substituted benzophenones. Such a series was chosen because (i) the electroreduction is strongly assisted by the polarization of the carbonyl group in the double layer at the electrode[9,10] and (ii) the attendant radical anions are stable in aprotic media. Our measurements were performed in acetonitrile, acetone, propylene carbonate, dimethyl sulphoxide, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N,N*-diethylformamide and hexamethylphosphoric triamide. These solvents, all 'hard' bases, give a range of Lewis acid–base properties.

EXPERIMENTAL

Tast polarographic curves were obtained using a measuring system consisting of an EP 20B potentiostat, an EG 20B function generator and an EC 20B acquisition and data control unit (all from Elpan, Poland) with an IBM PC AT computer. A Radelkis OH 105 apparatus was used for cyclic voltammetric experiments. Measurements were performed in a three-electrode cell consisting of either a mercury drop electrode (with a drop timer giving $t = 1{\cdot}0$ s) or a hanging mercury drop electrode[11] and an aqueous saturated calomel electrode (SCE).

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Commercially available substituted benzophenones were purified by recrystallization or distillation under vacuum; their physico-chemical characteristics were identical with literature values. Solvents were dried[12] and distilled at reduced pressure under an argon atmosphere. Tetraethylammonium perchlorate was recrystallized from triply distilled water and dried *in vacuo* at 60 °C.

All solutions were deoxygenated with solvent-presaturated argon. The concentrations of reactants and tetraethylammonium perchlorate, the background electrolyte, were usually 0·5 mM and 0·10 M, respectively. Experiments were run at 23 ± 0·5 °C.

RESULTS AND DISCUSSION

Benzophenone and its substituted derivatives are reduced at the dropping mercury electrode, forming two cathodic waves (Ref. 13 and references cited therein) in all the solvents studied. The first, which is the object of our interest, corresponds to the reversible one-electron transfer with the limiting current controlled by diffusion. Such behaviour was confirmed by cyclic voltammograms, which show equal peak currents in the cathodic and anodic sweeps (scan rate $0{\cdot}1\ \mathrm{V\,s^{-1}}$) and differences $E_{pa} - E_{pc}$ equal to 59 ± 3 mV. A semilogarithmic analysis of the polarographic waves gives also $\Delta E/\Delta \log[i_d - i)]$ values close to 60 mV per log unit. Hence it is clear that the first reduction step of benzophenone (and its substituted derivatives) yields the radical anion,[13] which is stable on the time scale of the experiments:

$$Ar_2C{=}O + e \rightleftharpoons Ar_2\dot{C}{-}O^- \qquad (2)$$

The resulting values of $E_{1/2}$ are summarized in Table 1.

For all the members of the reaction series, the $E_{1/2}$ values are independent of the supporting electrolyte concentration, at least over the range 0·01–0·15 M. This indicates convincingly that ion-pair formation in $Ar_2\dot{C}{-}O^-{-}(C_2H_5)_4N^+$ systems an be neglected and that the $E_{1/2}$ values presented in Table 1 can be treated as the formal potentials of $Ar_2C{=}O/Ar_2\dot{C}{-}O^-$ redox couples.

Hence the statistical analysis in terms of the Hammett equation (1) was performed and results obtained are given in Table 2 with values of the solvent *DN* and *AN* characteristics also included. Since the correlation coefficients obtained are acceptable, the solvent effect on the reaction constants can be analysed.

Note that ρ is positive in each solvent: the electroreduction of benzophenones is made easier by a low electron density at the carbonyl group. At the electrode, the reactant, an electron, is the nucleophile. Since ρ refers to the simple electron transfer [process (2)], this parameter should depend mainly on the Lewis acidity of the solvent: solvation of an ionic species $Ar_2\dot{C}{-}O^-$ is stronger than that of the neutral parent molecule. However, only a very poor correlation exists between ρ and *AN* (Table 2):

$$\rho = -0{\cdot}010\ AN + 0{\cdot}520 \qquad (3)$$

Table 1. Substituent effect on the half-wave potential for the first reduction step of benzophenones in aprotic solvents with 0·1 M tetraethylammonium perchlorate

Substituent	$\Sigma\sigma$[a]	$-E^0_{1/2}$ (V)							
		Solvent[c]							
		1	2	3	4	5	6	7	8
4,4′-$(OCH_3)_2$	−0·54	2·031	–	2·050	2·017	2·059	2·003	2·058	2·056
4,4-$(CH_3)_2$	−0·34	1·945	1·978	–	1·928	1·955	1·905	1·947	1·913
4-OCH_3	−0·27	1·933	1·960	1·941	1·944	1·942	1·896	1·951	1·914
4-CH_3	−0·17	1·927	1·930	1·935	1·923	1·938	1·895	–	1·906
3-NH_2	−0·16	1·908	1·922	1·943	1·916	1·944	1·886	1·905	–
3-CH_3	−0·07	1·867	1·890	1·862	1·839	1·861	1·819	1·871	1·832
H	0·00	1·845	1·863	1·857	1·827	1·850	1·803	1·848	1·827
4-F	0·06	1·830	1·860	1·840	1·780	1·826	1·780	–	1·717
4-Cl	0·23	1·759	1·795	1·747	1·712	1·726	1·694	1·734	1·693
3-F	0·34	1·742	1·755	1·736	1·698	1·710	1·677	–	1·643
3-Cl	0·37	1·732	1·750	1·727	1·677	1·703	1·668	1·706	1·639
$E_{Fc^+/Fc}$ (V)[b]		0·381	0·365	0·472	0·485	0·467	0·483	0·474	0·560

[a] $\Sigma\sigma$ is a sum of the appropriate substituent constants for disubstituted derivatives. The values of σ were taken from Ref. 14.

[b] Formal potential (vs SCE) of the ferocenium ion/ferrocene couple.

[c] 1 = Acetonitrile; 2 = propylene carbonate; 3 = acetone; 4 = *N,N*-dimethylformamide; 5 = *N,N*-dimethylacetamide; 6 = dimethyl sulphoxide; 7 = *N,N*-diethylformamide; 8 = hexamethylphosphoric triamide.

Table 2. Hammett's reaction constants for the polarographic reduction of benzophenones under aprotic conditions, with 95% confidence intervals

Solvent	DN^{a}	AN^{b}	ρ (V/σ unit)	r^{c}
Acetonitrile	14·1	18·9	0·33 ± 0·03	0·9938
Propylene carbonate	15·1	18·3	0·33 ± 0·02	0·9983
Acetone	17·0	12·5	0·37 ± 0·04	0·9881
N,N-Dimethylformamide	26·6	16·0	0·39 ± 0·05^{e}	0·9829
N,N-Dimethylacetamide	27·8	13·6	0·40 ± 0·05	0·9865
Dimethyl sulphoxide	29·8	19·3	0·37 ± 0·04	0·9886
N,N-Diethylformamide	30·9	15·9^{d}	0·39 ± 0·05	0·9937
Hexamethylphosphoric triamide	38·8	10·6	0·45 ± 0·07	0·9809

[a] Solvent donor number from Ref. 4.
[b] Solvent acceptor number from Ref. 6.
[c] Correlation coefficient; number of experimental points for calculating ρ as in Table 1.
[d] Estimated from the wavenumber of the long-wavelength absorption band in the electronic spectrum of the $Fe(phen)_2(CN)_2$ complex through the relationship proposed in Ref. 15.
[e] The value of $\rho = 0{\cdot}38$ was reported in Ref. 16.

with a correlation coefficient $r = 0{\cdot}762$, a standard deviation $s = 0{\cdot}025$ and a Fisher–Snedecor test value $F = 2{\cdot}33$. Correlation of ρ with DN is much better:

$$\rho = 0{\cdot}004\,DN + 0{\cdot}276 \qquad (4)$$

with $r = 0{\cdot}906$, $s = 0{\cdot}016$ and $F = 2{\cdot}45$. This means that both AN and DN solvent parameters are important and, hence, the ρ constants should be analysed in terms of the two-parameter model:[17]

$$\rho = \alpha AN + \beta DN + \gamma \qquad (5)$$

where α, β and γ are regression coefficients. Indeed, the weighted planar regression (with experimental errors of ρ) gave the relationship in the form

$$\rho = -0{\cdot}006\,AN + 0{\cdot}003\,DN + 0{\cdot}391 \qquad (6)$$

with $r = 0{\cdot}994$, $s = 0{\cdot}004$ and $F = 11{\cdot}64$. The addition of the second explanatory parameter, AN, to equation (4) is statistically significant with a probability higher than 95% (according to the F_{imp} test of Ref. 18).

Note that DN and AN are co-linear to a small extent and the correlation coefficient between them is 0·473. The partial regression coefficients of equation (6) are equal to 0·674 and 0·488, which indicates[17] that the percentage contributions to the observed solvent effect are 58% and 42% for DN and AN, respectively.

The regression described by equation (6) is graphically presented in Fig. 1. Let us discuss now the physical meaning of this expression.

As can be seen, α in equation (6) is negative, whereas β is positive. Thus, ρ increases with increasing solvent basicity and decreases with increasing solvent acidity. Ion association phenomena are not responsible for this effect of solvent basicity; as indicated above, ion pairs $Ar_2\dot{C}—O^{-}–(C_2H_5)_4N^{+}$ are absent from the systems studied. Equation (6) results rather from polarization of the carbonyl group at the electrode interface. The double-bonded oxygen atom is strongly electrophilic and its fractional negative charge is increased by a donor coordination of a solvent to the carbon atom, whereas the acceptor attack on the oxygen atom leads to an increase in a fractional positive charge at the

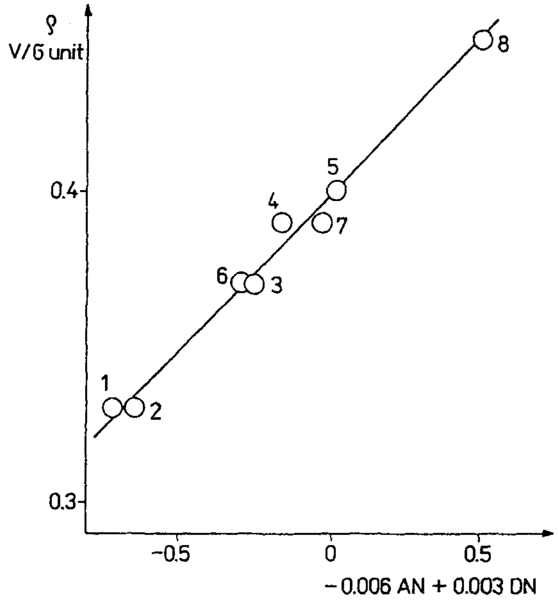

Figure 1. Dependence of Hammett ρ values on solvent donor and acceptor numbers according to equation (6). Solvents: 1 = acetonitrile; 2 = propylene carbonate; 3 = acetone; 4 = *N,N*-dimethylformamide; 5 = *N,N*-dimethylacetamide; 6 = dimethyl suphoxide; 7 = *N,N*-diethylformamide; 8 = hexamethylphosphoric triamide

carbon atom. The regression (6) demonstrates convincingly that the ρ value of substituted benzophenones depends not only on solvation of the ionic species produced in the electrode reaction (2), but also on a solvation of the neutral parent molecule.

A strong influence of the electrical field at the interface on the properties of benzophenone was confirmed[10] in DMF containing benzoic acid. In that case the hydrogen-bonded complex is formed near the electrode, giving a new cathodic pre-wave at more positive potentials than the original wave of benzophenone. Moreover, a large potential gradient in the double layer increases the basicity of the carbonyl group of benzophenone with respect to the value obtained in the bulk of the solution. As a result,[10] a change in the relative basic strengths for a series of ketones at the interface was observed with the basicity of benzophenone higher than that of dinaphtho ketones.

Obviously, the role of solvation of both the neutral molecule and its anion raical is also manifested in the solvent effect on formal potentials, $E_{1/2}$, presented in Table 1. Strictly, a thermodynamic quantity which depends on the solvation is the standard potential of a given redox system. However, taking into account only a minor solvent dependence of activity coefficients,[19] one can consider $E_{1/2}$ values instead of standard potentials.

In order to compare formal potentials in various solvents, they should be expressed against a solvent-independent reference potential. One of the reference redox systems recommended[20] for this purpose, the ferrocenium ion/ferrocene couple (Fc^+/Fc), was applied to our data. It should be stressed, however, that the crucial assumption of the independence of the potential of the variations of the solvent and supporting electrolyte concentration is only approximate for any reference system and it cannot be demonstrated in the strict sense, either experimentally or theoretically (see discussions in Refs. 19 and 21). Nevertheless, for a variety of organic reactants satisfactory explanations of $E_{1/2}$ shifts in different solvents were obtained[1b,19] in terms of a correlation analysis using the ferrocene scale; its practical validity was also recognized in Refs. 4 and 12.

The oxidation potentials of ferrocene (vs SCE) in each solvent are given in Table 1. For the reduction of unsubstituted benzophenone, there are crude linear relationships between formal potentials in the ferrocene scale, $E^{(Fc)}_{1/2}$, and DN or AN:

$$E^{(Fc)}_{1/2} = -0{\cdot}005\ DN - 2{\cdot}180 \qquad (7)$$

with $r = 0{\cdot}793$, $s = 0{\cdot}031$ and $F = 10{\cdot}19$, and

$$E^{(Fc)}_{1/2} = 0{\cdot}015\ AN - 2{\cdot}530 \qquad (8)$$

with $r = 0{\cdot}869$, $s = 0{\cdot}025$ and $F = 18{\cdot}53$.

On the other hand, the following planar regression was found:

$$E^{(Fc)}_{1/2} = 0{\cdot}011\ AN - 0{\cdot}003\ DN - 2{\cdot}394 \qquad (9)$$

with $r = 0{\cdot}971$, $s = 0{\cdot}012$ and $F = 41{\cdot}90$ (Figure 2). The addition of the second parameter, DN, to equation (9) is statistically significant with a probability higher than 99%, as follows from the F_{imp} test.[18]

Only for *p*-fluoro- and *p*-dimethylbenzophenones is the addition of the second parameter statistically unjustified. For all the remaining compounds a planar relationship holds:

$$E^{(Fc)}_{1/2} = E^{i}_{1/2} + aAN - bDN \qquad (10)$$

where $E^{i}_{1/2}$ is the solvent-independent part of the formal potential. As a rule, the coefficient a is positive and b is negative. Then, the physical interpretation of equation (6) may be obtained, taking into account that $E_{1/2}$ values are functions of the substituent constant [equation (1)] and of the solvent parameters [equation (10)]. Assuming further that these functions are differentiable, one can differentiate equation (10):

$$\frac{\partial E_{1/2}}{\partial \sigma} = \frac{\partial E^{i}_{1/2}}{\partial \sigma} + \frac{\partial a}{\partial \sigma} AN - \frac{\partial b}{\partial \sigma} DN \qquad (11)$$

and obtain ρ from differentiation of equation (1). Finally, equation (11) can be expressed as

$$\rho = \rho^0 + (\partial a/\partial \sigma)AN - (\partial b/\partial \sigma)DN \qquad (12)$$

which is analogous to the regression (6). The constant term in equation (6), $0{\cdot}391$, can be interpreted now as the value of ρ^0, i.e. the Hammett reaction constant of

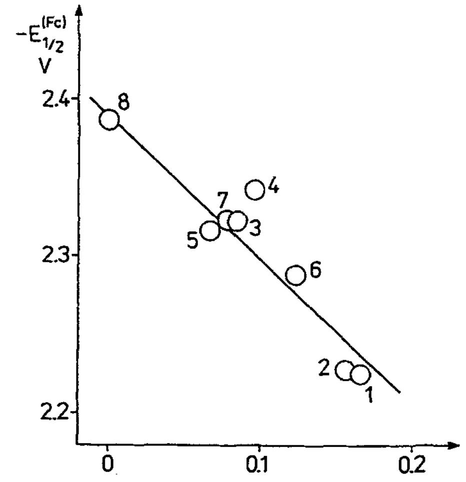

Figure 2. Correlation of $E^{(Fc)}_{1/2}$ values for the reduction of benzophenone with solvent donor and acceptor numbers according to equation (9). Solvents as in Figure 1

substituted benzophenones in a solvent with donor and acceptor numbers equal to zero (e.g. *n*-hexane). On the other hand, the regression coefficients $\partial a/\partial\sigma$ and $\partial b/\partial\sigma$ express how the sensitivity of the system to the solvent effect depends on properties of a substituent. It follows from the comparison of equations (12) and (6) that the coefficients a and b should be linear functions of σ with slopes equal to $\alpha = -0{\cdot}006$ and $\beta = 0{\cdot}003$, respectively. The attendant plots and the lines of the predicted slopes are shown in Figure 3. The great scatter of points is, in our opinion, due mainly to uncertainties in expressing $E_{1/2}$ potentials in terms of the ferrocene scale. Therefore, the analysis of ρ according to equation (6) is more accurate. Nevertheless, the plots shown in Figure 3 are in fair agreement with the proposed interpretation, supporting the practical validity of the ferrocene assumption.

Equation (12) is a consequence of linear dependences of the formal potential on solvent and substituent parameters. It therefore belongs to the family of isoparametric relationships,[22] which are generalizations of LFER postulates. However, to our knowledge, only simple two-parametric cases of such relationships have been observed experimentally (see examples in Refs. 1c and 23), whereas for the reduction of benzophenones three parameters, σ, *AN* and *DN*, are important. According to our interpretation, similar dependences of ρ and $E_{1/2}$ values on both donor and acceptor solvent properties can be expected for other reactants if the local separation of charge in their molecules occurs at the electrode.

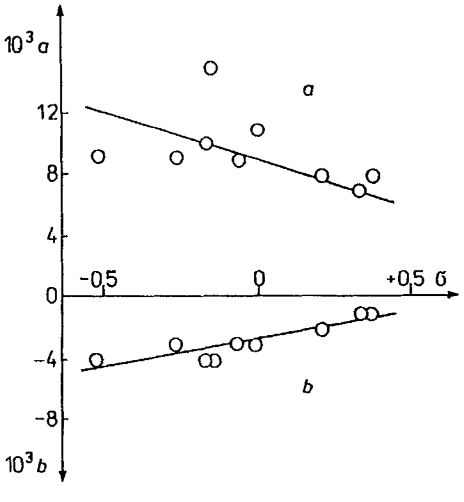

Figure 3. Dependences of coefficients a and b of equation (10) on substituent constants. Lines predicted from equation (6) are shown

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