Substituent Effect on the Association Equilibria of Free Radical Anions. Electrochemical Reduction of p-Substituted Nitrobenzenes in N,N-Dimethylformamide

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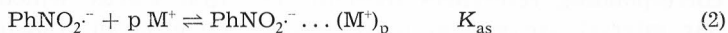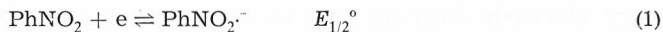*Department of Chemistry, University of Warsaw, 1 Pasteur St. 02-093 Warszawa, Poland*

Association constants between p-substituted nitrobenzene anion radicals, formed by reduction of the parent molecules at a dropping mercury electrode, and tetraethylammonium cation in N,N-dimethylformamide have been determined by studying the variation in the half-wave potential with solution composition. The association constant was observed to depend on the substituent effect; it was shown that the Hammett equation in the form $\log K_{as} = -1.55\sigma + 2.77$ is fulfilled. The dependence of $\log K_{as}$ vs. the hyperfine splitting constant (from ESR spectra) proper for N-nuclei in nitro-group of radical anions is also discussed.

INTRODUCTION

Electrochemical reduction of organic molecules can be profoundly affected by the ions of the supporting electrolyte. It has been found that alkali metal cations are small enough to form ion pairs with free radical anions even in strongly polar solvents as e. g. N,N-dimethylformamide (DMF), dimethylsulfoxide and propylene carbonate. By contrast, salts containing large singly--charged cations, such as tetraethylammonium ions, do not generally show ion pairing interaction with the anionic products of the electrode reaction.

The situation is somewhat different in the case of aromatic nitrocompounds: it is known that nitrobenzene radical anions form polarographically detectable ion pairs even with tetraethylammonium cations in DMF solutions.[1] For the reaction scheme

$$PhNO_2 + e \rightleftharpoons PhNO_2{}^{\cdot-} \qquad E_{1/2}{}^{\circ} \qquad (1)$$

$$PhNO_2{}^{\cdot-} + p\,M^+ \rightleftharpoons PhNO_2{}^{\cdot-}\ldots(M^+)_p \qquad K_{as} \qquad (2)$$

where M^+ denotes the cation of electrolyte, the observed halfwave potential, $\Delta E_{1/2}$, can be expressed by the rearranged Nernst equation[2]

$$\Delta E_{1/2} = (RT/F)\ln(1 + K_{as}\,a_{M^+}{}^p) \qquad (3)$$

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(α_{M^+}p is the activity of M^+ ion). The influence of medium (solvent and electrolyte) effects on the half-wave potentials was considered in terms of empirical relations based on the postulate of linear free energy relationships. In order to ascribe dependence $\Delta E_{1/2} = E_{1/2} - E^{\circ}_{1/2}$ to the nature of cation[3,4] and of solvent[5,6] the following equations have been introduced

$$\Delta E_{1/2} = \mu \times 1/r_{M^+} \tag{4}$$

and

$$\Delta E_{1/2} = \chi\, DN \tag{5}$$

where r_{M^+} stands for crystallographic ion radius of the cation interacting with radical anions, DN is Gutmann's donor number,[7] the quantity approximating Lewis basicity of solvents, whereas μ and χ are simply slopes of regression lines (4) and (5), respectively.

The effect of structural factors on the ion pairing phenomena is considerably less known. Therefore, the purpose of the present investigations was to make a quantitative study of the substituent effect on the association constant value K_{as}. A series of p-X-nitrobenzenes (X denotes -H, -Cl, -Br, -CH$_3$, -OCH$_3$, -COOCH$_3$ and -CN) was selected because the corresponding radical anions and ion pairs are stable under experimental conditions, which facilitates discussion of the problem. Experiments were performed in DMF solutions containing $(C_2H_5)_4NClO_4$ as electrolyte.

<center>EXPERIMENTAL</center>

Polarographic and cyclic voltametric measurements were made by means of a Radelkis OH-105 apparatus (three electrode system). The cell solutions were connected to an aqueous sce; the salt bridge contained 0.10 M tetraethylammonium perchlorate. The working electrode was either a mercury drop electrode characterized by a drop time of 2.0 s (a drop timer was used throughout experiments) or a hanging mercury drop electrode[8] of 0.82 mm diameter.

Nitrobenzene and its p-substituted derivatives were purified before use; the fundamental characteristics of these compounds were identical with literature values. The concentrations of depolarizers were 0.50 mM. Tetraethylammonium perchlorate was recrystallized several times from triply distilled water and dried in vacuo at 60 °C. Commercial DMF was dried first with anhydrous K$_2$CO$_3$, later with CaH$_2$ and then stored over molecular sieves of 4A type. The solvent was distilled at reduced pressure under argon atmosphere. Before each experiment the solvent was passed through a column of active alumina[9] (Woelm neutral, ICN Pharmaceuticals). All solutions were deaerated by argon which was passed through molecular sieves and presaturated by bubbling through the solvent. The measurements were carried on at a temperature of 23 ± 0.1 °C.

<center>RESULTS</center>

Nitrobenzene and its p-substituted derivatives reduce at a dropping mercury electrode forming two cathodic waves (see also the review[10] and the corresponding references therein). The first waves, which are the object of our interest, correspond to reversible one electron transfer. In all cases we have registered the cyclic voltametric curves with equal peak currents in the cathodic and anodic sweeps (scan rate 0.1 V s^{-1}). The differences $E_{pa} - E_{pc}$ were 60 ± 2 mV; semi-logarithmic analysis gives also $\Delta E/\Delta \log [i/(i_d - i)]$ values close to 60 mV/log unit. Moreover, the cathodic peak potentials are independent of the scan rate at least in the range 0.01—10 V s^{-1}. The second waves were strongly dependent upon water concentrations; these waves were

found to be reversible in a very dry DMF — alumina suspension. It should be pointed out that such a behaviour was described for nitrobenzene in ref. 11.

In all cases the half-wave potential of the first reduction step shifted in a positive direction as the concentration of tetraethylammonium perchlorate increased indicating the ion pairing of the anion radicals with $(C_2H_5)_4N^+$ cation (Table I).

TABLE I

The Dependence of the Half-Wave Potential of 0.5 mM Nitrobenzene and its Para-Substituted Derivatives on the Concentration of $(C_2H_5)_4NClO_4$ in N,N-Dimethylformamide

Substituent		Measured values						
—H	c/M	0.010	0.025	0.039	0.052	0.066	0.100	
	$-E_{1/2}$/V	1.158	1.135	1.127	1.120	1.114	1.104	
—Cl	c/M	0.010	0.019	0.029	0.038	0.046	0.054	0.100
	$-E_{1/2}$/V	1.073	1.058	1.052	1.045	1.040	1.035	1.023
—Br	c/M	0.010	0.028	0.042	0.066	0.100		
	$-E_{1/2}$/V	1.080	1.055	1.045	1.035	1.028		
—COOCH$_3$	c/M	0.010	0.031	0.046	0.062	0.100		
	$-E_{1/2}$/V	0.925	0.903	0.895	0.890	0.880		
—CN	c/M	0.010	0.032	0.065	0.072	0.100		
	$-E_{1/2}$/V	0.845	0.825	0.817	0.812	0.808		
—CH$_3$	c/M	0.010	0.032	0.046	0.058	0.069	0.100	
	$-E_{1/2}$/V	1.282	1.249	1.241	1.235	1.232	1.223	
—OCH$_3$	c/M	0.010	0.018	0.030	0.044	0.065	0.100	
	$-E_{1/2}$/V	1.333	1.317	1.300	1.293	1.285	1.273	

To calculate K_{as} from the experimental data it is necessary to know the corresponding $E^\circ_{1/2}$ values. We are not able to determine $E^\circ_{1/2}$ in direct experiments; even in the presence of tetra-n-hexylammonium iodide the half-wave potential of nitrobenzene was found to depend on the concentration of $(C_6H_{13})_4N^+$ ions. Consequently, the ion pair formation constants were estimated by the method proposed by Chauhan et al.[12] for solutions of varying ionic strength.

Transforming eq. (3) for $p = 1$ into exponential form

$$\exp(fE_{1/2}) = \exp(fE_{1/2}^\circ) + \exp(fE_{1/2}^\circ) K_{as} \, a_{(C_2H_5)_4N^+} \qquad (6)$$

where $f = F/RT$, we have analyzed the plots of $\exp(fE_{1/2})$ against $a_{(C_2H_5)_4N^+}$. The tactics of calculation of $a_{(C_2H_5)_4N^+}$ was the same as in paper[12], i. e. any variation in the liquid junction potential between the working and reference electrodes has been estimated by the Henderson equation for different concentrations of $(C_2H_5)_4NClO_4$ in electrolytic cell. According to Prue and Sherington[13] we have assumed that tetraethylammonium perchlorate is not associated in DMF solutions.

On the basis of eq. (3) one may believe that for $p = 1$ and $K_{as} \, a_{(C_2H_5)_4N^+} \gg 1$ the plot of $E_{1/2}$ against $\log a_{(C_2H_5)_4N^+}$ should be linear with a slope of 59 mV/log unit. The slopes determined are presented in Table II. These results are taken as evidence that the coordination number, p, for ion association in all the systems investigated is indeed one. Thus, the resulting values of $E^\circ_{1/2}$ and K_{as} are summarized in Table III.

TABLE II

The Values of $\Delta E_{1/2}/\Delta \log a_{(C_2H_5)_4N^+}$ for Electroreduction of Nitrobenzene and its
Para-Substituted Derivatives in DMF

Substituent	$\Delta E_{1/2}/\Delta \log a_{(C_2H_5)_4N^+}$ mV/log unit
—H	53
—Cl	50
—Br	52
—COOCH₃	45
—CN	41
—CH₃	59
—OCH₃	59

TABLE III

$E^{\circ}_{1/0}$ and K_{as} Values Calculated From The Polarographic Curves
of Para-X-Nitrobenzenes in DMF

Substituent X	$-E^{\circ}/_{21}$/V	K_{as}	r^*	σ	A_N^+	Ref.
—H	1.184	437	0.998	0.00	9.79	17
—Cl	1.089	248	0.997	0.23	9.16	17
—Br	1.093	244	0.992	0.23	9.04	17
—COOCH₃	0.980	123	0.998	0.45	7.1	16, 18
—CN	0.842	60	0.990	0.62	6.60	19
—CH₃	1.327	1180	0.998	—0.17	10.06	20
—OCH₃	1.388	1770	0.992	—0.27	10.9	16, 18

* r = correlation coefficient of linear regression (6). Number of experimental points
as in Table I.
⁺ A_N = hyperfine splitting constant from ESR spectra in gauss (1 G = 10^{-4} T).

This Table also contains appropriate values of the substituent constants, σ,
together with hyperfine splitting constants, A_N, proper for N-nuclei in nitro-
-group, determined by the ESR technique for anion radicals generated in DMF
containing tetraethylammonium salts. It is apparent that ion pairing is visibly
affected by the nature of substituent X. Let us note, however, that considering
the uncertainty in the correction for liquid junction potentials and in the
estimation of activity coefficients, the association constants can be treated
as an order of magnitude estimates.

DISCUSSION

To describe the substituent effect in organic electrochemistry the Ham-
mett-type equations[14,15] are usually used in relation $E_{1/2}$ vs. σ. In the case of
para-substituted nitrobenzenes all the radical anions are involved in the ion
pairing interaction. Since in this series $p = 1$ and the association is sufficiently
strong ($K_{as} a_{(C_2H_5)_4N^+} \gg 1$), it seems to be reasonable to apply the Hammet
expression in the form

$$\log K_{as} = \varrho\, \sigma \tag{7}$$

As it can be seen from Figure 1, $\log K_{as}$ actually displays a correlation with σ,
yielding

$$\log K_{as} = -1.55\, \sigma + 2.77 \tag{8}$$

with a correlation coefficient of $r = 0.993$ for 7 experimental points.
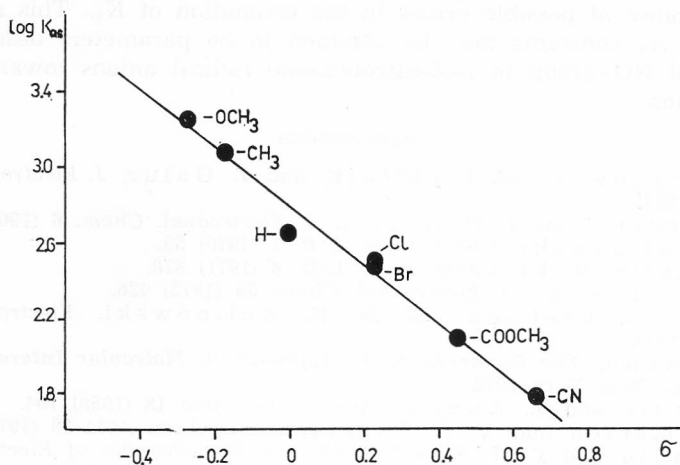

Figure 1. Dependence of $\log K_{as}$ on substituent constant σ for para-substituted nitrobenzene radical anions.

Thus, it is clear that the Hammet equation is attractive for describing substituent effects on the ion pairing phenomenon. However, let us consider the results presented in[16]: the authors have suggested that μ parameter of eq. (4) correlates satisfactorily with A_N. Does A_N value influence also the association constant K_{as}?

The answer is: rather yes. In Figure 2 a plot of $\log K_{as}$ against A_N is presented. Now we obtain

$$\log K_{as} = 0.309 A_N - 0.260 \qquad (9)$$

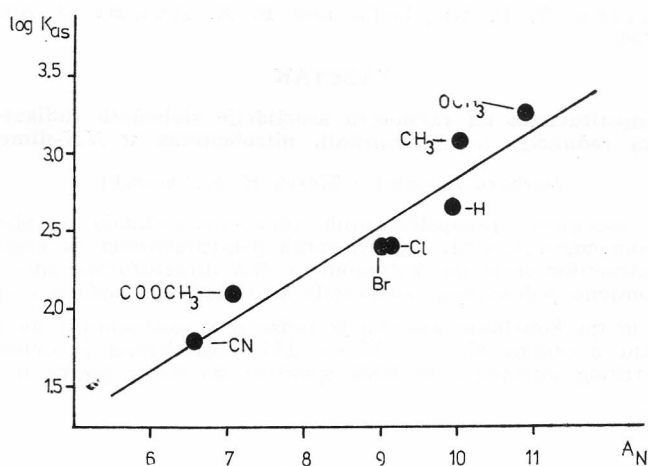with $r = 0.943$ for the same set of $\log K_{as}$ as in relation (8)

Figure 2. Plot of the $\log K_{as}$ against the hyperfine splitting constant, A_N, for para-substituted nitrobenzene radical anions.

Although correlation (8) is far better than (9), the latter should not be rejected because of possible errors in the estimation of K_{as}. This means that both σ and A_N constants may be assumed to be parameters describing the properties of NO_2-group in p-X-nitrobenzene radical anions towards the ion pair formation.

REFERENCES

1. T. M. K r y g o w s k i, M. L i p s z t a j n, and Z. G a l u s, *J. Electroanal. Chem.* **43** (1973) 261.
2. M. E. P e o v e r and J. D. D a v i e s, *J. Electroanal. Chem.* **6** (1963) 46.
3. M. K. K a l i n o w s k i, *Chem. Phys. Lett.* **7** (1970) 55.
4. M. K. K a l i n o w s k i, *Chem. Phys. Lett.* **8** (1971) 378.
5. T. M. K r y g o w s k i, *J. Electroanal. Chem.* **35** (1972) 436.
6. E. L e ś n i e w s k a - Ł a d a and M. K. K a l i n o w s k i, *Electrochim. Acta* **28** (1983) 1415.
7. V. G u t m a n n, *The Donor-Acceptor Approach to Molecular Interactions,* Plenum Press, New York 1978.
8. W. K e m u l a and Z. K u b l i k, *Anal. Chim. Acta* **18** (1958) 104.
9. O. H a m m e r i c h and V. D. P a r k e r, *Electrochim. Acta* **18** (1973) 537.
10. W. K e m u l a and T. M. K r y g o w s k i, in *Encyclopedia of Electrochemistry of the Elements,* A. J. B a r d and H. L u n d eds., vol. 13, chapter 2, Marcel Dekker, New York 1979.
11. B. S. J e n s e n and V. D. P a r k e r, *J. Chem. Soc. Chem. Commun.* (1974) 367.
12. B. G. C h a u h a n, W. R. F a w c e t t, and A. L a s i a, *J. Phys. Chem.* **81** (1977) 1476.
13. J. E. P r u e and P. J. S h e r i n g t o n, *Trans. Faraday Soc.* **57** (1961) 1795.
14. P. Z u m a n, *Substituent Effects in Organic Polarography,* Plenum Press, New York 1967.
15. M. K. K a l i n o w s k i and T. M. K r y g o w s k i, *Croat. Chem. Acta* **58** (1985) 107.
16. M. L i p s z t a j n, T. M. K r y g o w s k i, M. S m o l a r z, and W. S z e l ą - g o w s k a, *Polish J. Chem.* **52** (1978) 1069.
17. T. K i t a g a w a, T. P. L a y l o f f, and R. N. A d a m s, *Anal. Chem.* **35** (1963) 1086.
18. A. H. M a k i and D. H. G e s k e, *J. Am. Chem. Soc.* **83** (1961) 1852.
19. P. L u d w i g, T. P. L a y l o f f, and R. N. A d a m s, *J. Am. Chem. Soc.* **86** (1964) 4568.
20. J. M. F r i t s c h, T. P. L a y l o f f, and R. N. A d a m s, *J. Am. Chem. Soc.* **87** (1965) 1724.

SAŽETAK

Utjecaj supstituenata na ravnotežu asocijacije slobodnih radikal-aniona. Elektrokemijska redukcija *p*-supstituiranih nitrobenzena u *N,N*-dimetilformamidu

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Konstante asocijacije *p*-supstituiranih anionskih radikala nitrobenzena, dobivenih redukcijom odgovarajućih supstituiranih *p*-nitrobenzena na kapajućoj živinoj elektrodi, s tetraetilamonijevim kationom u *N,N*-dimetilformamidu, određene su mjerenjem promjene poluvalnog potencijala kao funkcije sastava otopine.

Utvrđeno je da konstante asocijacije ovise o supstituentu i da slijede Hammettovu relaciju u obliku $K_{as} = -1{,}55\ \sigma + 2{,}77$. Diskutirana je ovisnost $\log K_{as}$ o konstanti hiperfinog cijepanja (iz ESR spektra) dušikove jezgre u nitro-skupini radikal-aniona.