
INFLUENCE OF SUBSTITUENTS ON ELECTROCHEMICAL REDUCTION POTENTIALS OF BENZENEDIAZONIUM SALTS

Pavel JANDERKA and Igor CEJPEK

*Department of Theoretical and Physical Chemistry,
J. E. Purkyně University, 611 37 Brno*

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TAST polarography, differential pulse polarography, and cyclic voltammetry on a hanging mercury drop and on a platinum disc were employed to measure the electrochemical reduction potentials of nine *para* substituted benzenediazonium salts in dimethylformamide. A satisfactory linear correlation was obtained between the potentials of the adsorption prewave and the substituent constants σ_p^+ . The influence of substituents on some structural parameters was studied by using the CNDO/2 method for both a closed and an opened shell.

Aromatic diazonium salts (DAS) represent a class of organic compounds suitable for studies of substituent effects on the electrochemical reduction potentials. The first reduction step proceeds in both aqueous and nonaqueous media at relatively positive potentials above -0.3 V – according to the solvent – and it can be considered as a one-electron process; its potential is independent of pH in aqueous solutions.

The influence of substituents on the reduction potentials of DAS has not been elucidated in full. Kochi¹ measured the half-wave potentials for polarographic reduction of ten *meta* and *para* substituted benzenediazonium salts in aqueous buffered medium, but he did not obtain the expected linear correlation with the substituent constants. The question about the substituent effects was not cleared even by Zuman², who obtained from Kochi's data an anomalous course of the dependence of $E_{1/2}$ on the σ constants in the form of two linear portions with opposite signs of the slopes (a roof-like form). Elofson³, who first pointed out the existence of adsorption phenomena in electrochemical reduction of DAS, concluded that the stability of the adsorption complex is the principal factor which controls the potential of the adsorption wave. In contrast, a surprisingly good correlation between the half-wave potentials and the substituent constants was obtained later by Elofson⁴ who used sulpholane as a solvent for 18 substituted benzenediazonium salts, similarly to Böttcher⁵ who used nitromethane, and to Kovalchuk et al.⁶ who used acetone as solvent. The aim of the present work is to elucidate the anomalous influence of substituents on the reduction potentials of DAS.

EXPERIMENTAL

The electrochemical methods and apparatus were described in our preceding communication⁷ together with the preparation of chemicals. The results of chemical analyses of the prepared compounds are indicated in Table I.

Quantum-chemical Calculations

Calculations by the CNDO/2 method for both the opened and closed shells were carried out on an EC 1 033 computer using a standard program (Institute of Computer Techniques, J. E. Purkyně University). The geometry of the basic (non-substituted) derivative is shown in Fig. 1 and other structural data are given in Table II based on ref.⁸.

RESULTS AND DISCUSSION

As shown in our preceding work⁷, the acid-base properties of the solvent used have a decisive influence on the mechanism of electrochemical reduction of DAS. In the initial reduction stage in basic solvents (according to the Gutman classification¹⁰), such as dimethylformamide, dimethylsulphoxide, and also water from the point of view of the donor number, adsorption of the reduced form on the Hg electrode surface takes place, whereas in less basic solvents it does not. In less basic solvents (sulpholane, nitromethane, acetone) good linear correlations between the reduction potentials of DAS and the substituent constants σ_p^+ can be obtained, but not when more basic solvents are used.

Nine *para* substituted derivatives of benzenediazoniumtetrafluoroborate prepared by us gave in dimethylformamide (DMF) an adsorption prewave and a wave (or peak) at concentrations higher than $2-3 \cdot 10^{-4} \text{ mol l}^{-1}$; the sum of their heights corresponded to a diffusion-controlled process. In the case of TAST polarography, logarithmic analysis was carried out by plotting $\log [i/(i_{1L} + i_{2L} - i)]$ against E (Fig. 2) at 0°C. In this way we obtained the half-wave potentials $E_{1/2}^{1,2}$ of the prewave and of the wave and the potentials $E_{1,2}^0$ whose meaning is apparent from Fig. 3: E_1^0 would be the half-wave potential of the wave formed by shifting the more negative part to the prewave to form a single wave, and E_2^0 would be the half-wave potential of the wave formed by shifting the prewave to coincide with the more negative wave. These two transformations correspond to two models for the formation of the adsorption prewave:

(i) After attainment of the potential necessary for the electron transfer, part of the depolarizer supplied by diffusion is reduced and the reduced form is adsorbed until the electrode surface is completely covered. Further electron transfer across the interface modified in this manner is only possible after attainment of a sufficiently negative potential.

(ii) Classical model of the formation of the Brdička prewave¹¹: In addition to the potentials E_1^0 and E_2^0 from TAST polarographic measurements, we determined

the peak potentials E_{p1} and E_{p2} in differential pulse polarography, E_{pk1} and E_{pk2} in cyclic voltammetry with a hanging Hg drop, and E_{pk1}^{Pt} and E_{pk2}^{Pt} in cyclic voltammetry with a Pt disc, all these in DMF (Table III). The peak potentials for DAS in cyclic voltammetry with a hanging Hg drop measured in a Britton–Robinson buffer solution of pH 2.21, E_{pk1}^{Aq} and E_{pk2}^{Aq} , and the substituent constants σ_p^+ from ref.¹² are given in the same table for comparison.

TABLE I
Results of elemental analysis of DAS (carbon/hydrogen/nitrogen, %)

No.	Group	Calculated, %	Found, %
I	(CH ₃) ₂ N	40.58/4.29/17.88	38.19/3.99/16.63
II	OH	34.66/2.42/13.47	33.20/2.08/13.76
III	CH ₃ O	37.88/3.18/12.62	37.18/3.20/12.49
IV	CH ₃	40.82/3.43/13.60	39.75/3.62/13.39
V	H	37.55/2.63/14.60	37.95/2.80/14.78
VI	Cl	31.84/1.78/12.38	31.05/1.93/12.15
VII	Br	26.61/1.49/10.34	25.80/1.62/10.21
VIII	COOH	35.64/2.14/11.87	34.28/2.97/11.98
IX	NO ₂	30.42/1.70/17.74	30.50/1.79/17.66

TABLE II
Bond lengths and bonding angles according to ref.⁸

Bond	<i>r</i> , nm	Angle	α , deg
C _{Ar} —N _{nitro}	0.146	C _{Ar} N _{nitro} O	115
N _{nitro} —O	0.122		
C _{Ar} —OH	0.129	C _{Ar} —C—OH	118
C=O	0.124	C _{Ar} =O	122
C—H	0.109	HCH	109.5
C _{Ar} —O	0.142	C _{Ar} OC	128
O—CH ₃	0.142	OCH	109.5
C _{Ar} —Cl	0.169	C _{Ar} C _{Ar} Cl	120
C _{Ar} —Br	0.186	C _{Ar} C _{Ar} Br	120
C _{Ar} —COOH	0.148		
C _{Ar} —N(CH ₃)	0.143	C _{Ar} NC	120
N—CH ₃	0.146		
O—H	0.097	COH	105
N—H	0.101	HNH	108

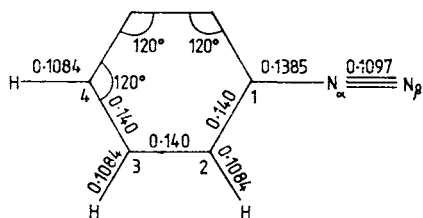


FIG. 1

Geometry of a non-substituted derivative (after ref.⁹); bond lengths are in nm

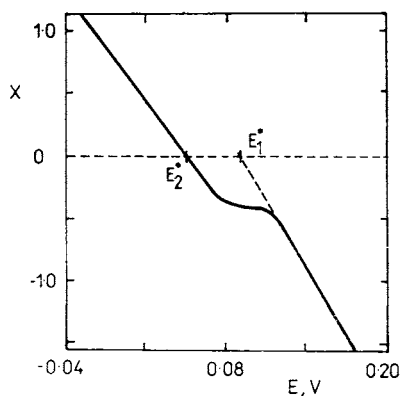


FIG. 2

Plot of logarithmic analysis of the diffusion wave for $\text{CH}_3\text{O-DAS}$ in dimethylformamide ($x = \log [i/(i_{1L} + i_{2L} - i)]$)

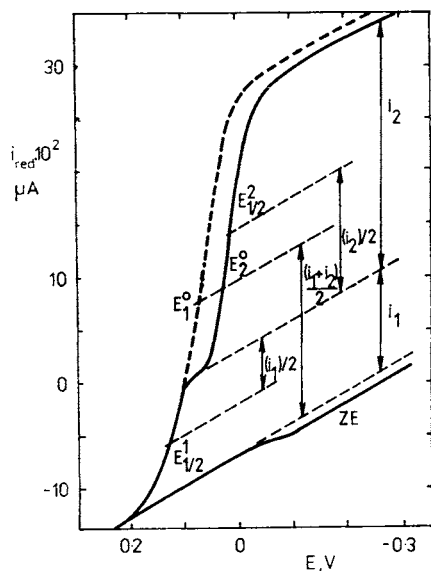


FIG. 3

First reduction wave for $\text{CH}_3\text{O-DAS}$ in DMF with important characteristics ($c = 3 \cdot 10^{-4} \text{ mol l}^{-1}$, $t = 0^\circ\text{C}$, TAST polarography)

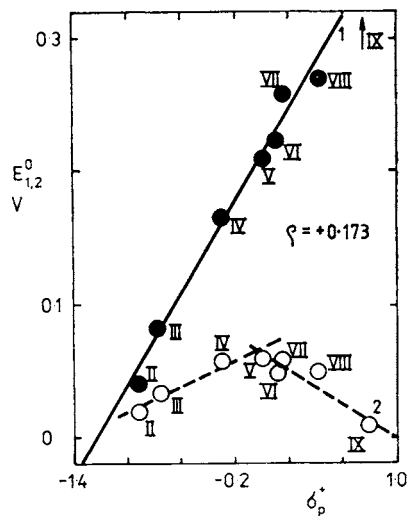


FIG. 4

Dependences of 1 E_1^0 and 2 E_2^0 on σ_p^+ constants

TABLE III
Survey of reduction potentials of *p*-substituted DAS and of the substituent constants σ_p^+ ; potentials are in V against aqueous saturated calomel electrode

X	E_1^0	E_2^0	E_{p1}	E_{p2}	E_{pk1}	E_{pk2}	E_{pk1}^{Pt}	E_{pk2}^{Pt}	E_{pk1}^{Aq}	E_{pk2}^{Aq}	σ_p^+
N(CH ₃) ₂	—	—	—	—	-0.145	-0.185	-0.304	-0.424	-0.220		-1.7
OH	0.040	0.020	0.082	0.020	0.040	-0.045	-0.134	-0.314	-0.030	-0.200	-0.92
OCH ₃	0.082	0.033	0.122	0.032	0.085	-0.015	-0.114	-0.474	-0.010	-0.100	-0.78
CH ₃	0.166	0.057	0.200	0.058	0.175	0.020	0.066	-0.374	0.000	-0.100	-0.31
H	0.209	0.060	0.246	0.050	0.195	-0.015	0.036	-0.434	0.020	-0.160	0
Cl	0.223	0.039	0.264	0.034	0.260	0.005	0.126	-0.364	0.110	0.050	0.11
Br	0.258	0.059	0.300	0.036	0.265	0.000	0.166	-0.424	0.150	0.070	0.15
COOH	0.270	0.050	0.290	-0.006	0.245	-0.135	0.126	-0.454	>0.15	-0.070	0.42
NO ₂	>0.3	0.009	>0.3	-0.007	>0.3	-0.025	0.316	-0.404	>0.15	0.070	0.78

A relation between the potentials E_1^0 and E_2^0 and the substituent constants σ_p^+ is shown in Fig. 4. Similar dependences were found for the potentials determined by the other methods. The linear correlations found by the least squares method are as follows:

$$E_1^0 = 0.173\sigma_p^+ + 0.211, \quad r = 0.990,$$

$$E_{p1} = 0.165\sigma_p^+ + 0.246, \quad r = 0.980,$$

$$E_{pk1} = 0.195\sigma_p^+ + 0.214, \quad r = 0.979,$$

$$E_{pk1}^{Pt} = 0.237\sigma_p^+ + 0.091, \quad r = 0.976.$$

The slope of the linear dependence, corresponding to the reaction constant ρ , is positive in accord with the usual model of nucleophilic reactions, where the depolarizer functions as the electrophilic species and the electron (or electrode surface) as the nucleophilic one. Electron donor substituents, such as OH or CH₃O, which lower the deficiency of the negative charge on the reaction centre, cause a shift of the reduction potential to more negative values. Electron acceptor substituents, such as halogens and especially the nitro group, increase the deficiency of the negative charge on the reaction centre, facilitate the reduction, and shift the potential to more positive values. This is especially marked with the nitro group, so that the prewave of the nitro derivative (on a Hg drop) coincides with anodic dissolution of mercury, but it is observable if a Pt working electrode is used.

The charge distribution in a non-substituted derivative molecule and in a neutral radical (Fig. 5) shows that the main portion of the positive charge is localized on the central N_α atom. This together with the partial positive charges on the C₁ and N_β atoms constitutes about 50% of the charge of the cation. It turns out, however, that the effect of the substituent is manifested by a change of the charge on C₁ and partly on N_β, whereas the charge on the N_α nitrogen atom is only little affected by the substitution (Table IV).

The potentials of the prewaves, E_1^0 , for the studied compounds show a satisfactory correlation with the energies of the first unoccupied molecular orbital (LUMO 1)

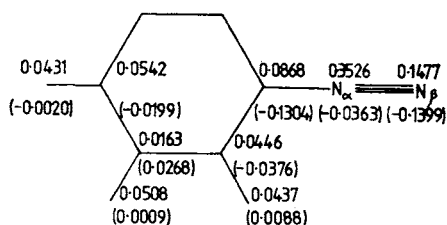


FIG. 5

Charge distribution in a non-substituted derivative and in a neutral radical (in parentheses)

in the form

$$E_1^0 = -0.323E_{\text{LUMO1}} - 1.45, \quad r = 0.825.$$

This orbital has a π symmetry, whereas the second LUMO is combined with the contributions of the atomic orbitals s , p_x , and p_y . Both LUMO's have a nodal plane between the N atoms. This arrangement prefers chemical reactions initiated by electron acceptance in which the C_1-N_α bond is preserved. This applies to the electrochemical reduction mechanism of DAS in aqueous solutions, whereas in aprotic solvents a follow-up reaction was recognized, in which the mentioned bond was disrupted with evolution of nitrogen⁷. Under these conditions, the model of isolated molecules apparently does not satisfactorily describe the chemical reactivity of DAS.

Changes in the electron density distribution (or charge distribution) caused by substitution are manifested mainly on C_1 and N_α atoms, prevailing as changes of the charges in their p_z orbitals (Table IV). These charges are linearly related with E_1^0 as follows:

$$E_1^0 = 6.35q_{N\beta pz} + 0.137, \quad r = 0.848,$$

$$E_1^0 = 3.30q_{C1 pz} + 0.72, \quad r = 0.922, \quad \text{and for the radical}$$

$$E_1^0 = 4.15q_{C1 pz} + 0.21, \quad r = 0.949.$$

Calculations for the radicals (formed by electron transfer to a DAS cation) by the CNDO/2 method for an opened shell and the same geometry gave a similar picture

TABLE IV

Quantum chemical parameters of p -substituted DAS obtained by the CNDO/2 method (closed shell). (Note: derivatives with substituents $N(\text{CH}_3)_2$ and Br were not calculated)

X	q_{C1}^a	$q_{N\alpha}^b$	$q_{N\beta}^c$	$q_{C1 pz}^d$	$q_{N\beta pz}^e$	$-E_{\text{LUMO1}}, \text{eV}^f$	$-E_{\text{LUMO2}}, \text{eV}^g$
OH	0.0649	0.3542	0.1350	-0.1934	-0.0050	4.8406	3.8638
OCH ₃	0.0552	0.3542	0.1330	-0.1929	-0.0064	4.7806	3.7903
CH ₃	0.0679	0.3484	0.1270	-0.1763	-0.0048	4.7562	3.6924
H	0.0868	0.3526	0.1478	-0.1440	0.0176	5.0937	4.0869
Cl	0.0745	0.3542	0.1435	-0.1643	0.0081	5.1100	4.0760
COOH	0.0944	0.3516	0.1494	-0.1348	0.0191	5.3168	4.1196
NO ₂	0.1004	0.3447	0.1707	-0.1223	0.0335	5.8610	4.6148

^a, ^b, and ^c net charges on C_1 , N_α , or N_β atoms, respectively; ^d and ^e net charges in p_z orbitals of C_1 or N_β atoms, respectively; ^f and ^g energies of the first and second lowest unoccupied MO, respectively.

as the preceding treatment (Table V). The energy of a once occupied molecular orbital, SOMO1, is linearly related with E_1^0 as follows:

$$E_1^0 = -0.422E_{\text{SOMO1}} - 3.15, \quad r = 0.851.$$

The molecular orbital has a π symmetry and its distribution is shown in Fig. 6. The calculation of the spin density (Fig. 6) showed that the prevailing part of the

TABLE V

Quantum chemical characteristics obtained by the CNDO/2 method (open shell) for neutral radicals of *p*-substituted DAS

X	$q_{C_1}^a$	$q_{N_\alpha}^b$	$q_{N_\beta}^c$	$q_{C_1}^s d$	$q_{N_\alpha}^s e$	$q_{N_\beta}^s f$	$q_{C_1 p_z}^g$	$-E_{\text{SOMO1}}, \text{eV}^h$
OH	0.1053	0.0345	-0.1451	-0.0697	0.3362	0.5611	-0.0346	7.6950
OCH ₃	0.1083	0.0353	-0.1433	-0.0675	0.3339	0.5620	-0.0301	7.7412
CH ₃	0.1200	0.0380	-0.1329	-0.0720	0.3278	0.5621	-0.0139	7.6868
H	0.1305	0.0363	-0.1390	-0.0604	0.3252	0.5661	-0.0029	7.8855
Cl	0.1228	0.0380	-0.1355	-0.0644	0.3243	0.5646	-0.0087	7.9970
COOH	0.1427	0.0445	-0.1279	-0.0591	0.3063	0.5639	0.0190	8.1195
NO ₂	0.1479	0.0547	-0.1154	-0.0527	0.2957	0.5651	0.0258	8.5657

^a, ^b and ^c net charges on C₁, N_α, or N_β atoms in neutral radicals; ^d, and ^e and ^f spin populations on C₁, N_α or N_β atoms, respectively; ^g net charge in p_z orbital of the C₁ atom; ^h energy of the lowest singly occupied MO.

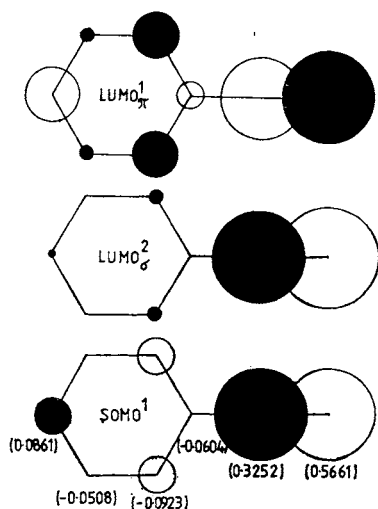


FIG. 6

Scheme of two lowest unoccupied MO of a non-substituted derivative, LUMO¹ and LUMO², and once occupied MO in a neutral radical of the same derivative, SOMO¹. The circle radius equal to the interatomic distance would correspond to a unit magnitude of the expansion coefficient; the spin density distribution is given in parentheses

spin density is localized on the N_α and N_β atoms, namely exclusively in their p_z orbitals, but the effect of substituents is manifested by changes in the spin density on the N_α and C_1 atoms (Table V).

All the mentioned quantum chemical structural parameters and their comparison with the potentials of the prewaves for electroreduction of DAS in DMF indicate a "normal" influence of substituents expressed by linear correlations between the potentials and the substituent constants, LUMO and SOMO energies, and other structural parameters. The anomalous dependence of the polarographic half-wave potentials for DAS in aqueous solutions on the σ_p^+ constants can be attributed to the fact that Kochi¹ disregarded the existence of the adsorption prewaves.

Physical justification of the described correlations is obtained from the model of the inhibition mechanism of the formation of adsorption prewaves (i), which in this case seems more probable than the classical Brdička model.

We consider approximately equal dimensions of all the derivatives, similar values of their diffusion coefficients, similar degrees of coverage, maximum adsorbed amounts, and degrees of electrochemical reversibility or the same mechanism of the electrode reactions. If these conditions are satisfied and the proposed mechanism of the prewave formation is valid, it may be concluded that the reduction potentials determined from the prewaves (or prepeaks) are functions of the polar and mesomeric substituent effects, while steric effects may be neglected.

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