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Application of the Dual Parameter Equation to the Correlation Analysis of the Redox Potential Data of Five *para*-Substituted Phenyl Compounds

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Dual-parameter correlation analysis of the redox potential data of five aromatic compounds shows that the transition states of the polarographic processes are affected by the spin-delocalization effect in addition to the polar effect of the substituents.

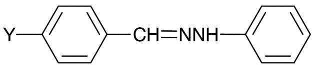
It has been suggested over thirty years ago that transition states (TS) of polarographic potential-determining steps possess free radical character.[1c,2b,2d] However, the dual-parameters [eqn. (1)] have never been successfully applied to the polarographic half-wave potential data. On the basis of the correlation analysis of the measured polarographic reduction potentials of 12 substituted benzyl chlorides by the Hammett-type eqn. (2), Streitwieser proposed that in addition to polar effects, the radical stabilizing effects of substituents must also be taken into consideration to achieve good correlations for the polarographic potentials.[1c] Unfortunately, the relative importance of the spin-delocalization effect and the polar effect of the substituents could not be evaluated for the contributions to their TS of polarographic processes because a reliable $\sigma^\bullet$ scale of spin-delocalization substituent constants was not available at that time.

$$\text{variable} = \rho^x\sigma^x + \rho^\bullet\sigma^\bullet + C \quad (1)$$

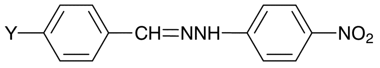
$$\text{variable} = \rho^x\sigma^x + C \quad (2)$$

$$\text{variable} = \rho^\bullet\sigma^\bullet + C \quad (3)$$

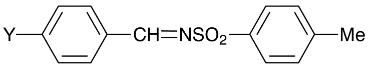
On the basis of our recent work in radical chemistry, we came to realize that there are four possible circumstances (I–IV).[5a] I. When both polar and spin effects are important, the $|\rho_{\text{mb}}/\rho_{\text{JJ}}^\bullet|$ values of the dual-parameter eqn. (1) ($\rho^x = \rho_{\text{mb}}$, $\rho^\bullet = \rho_{\text{JJ}}^\bullet$) might fall in the range of (very) roughly 0.2 to 0.8. Under these circumstances, the necessity of using eqn. (1) can be easily established because it yields much better correlation results than those of single-parameter eqn. (2). II. When polar effects dominate, this ratio might be around or greater than unity. Under these circumstances, the necessity of applying eqn. (1) cannot be established in a definitive manner. However, the existence of the spin effect can still be revealed by careful examination of the individual deviations of the data from the regression lines of eqns. (1) and (2).[5a] III. When the spin-delocalization effect dominates, then eqn. (3) applies, and application of eqn. (1) might yield a $|\rho_{\text{mb}}/\rho_{\text{JJ}}^\bullet|$ ratio of less than 0.2. IV. When there are other complicating and interacting factors or effects, then none of the three equations can be successfully applied.



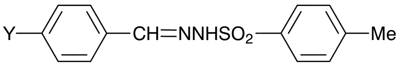
1-Y



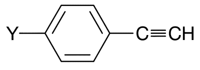
2-Y



3-Y



4-Y



5-Y

The present work is an attempt to perform the correlation analyses of the polarographic potentials by eqn. (1), with peak redox potentials [$E_{\text{p(ox)}}$] or [$E_{\text{p(red)}}$] as the variable, and with $\rho^x\sigma^x$ and $\rho^\bullet\sigma^\bullet$ representing the polar and spin-delocalization contributions of the substituents respectively. The oxidation potentials of **1-Y** and **2-Y** are listed in Table 1, and the reduction potentials of **3-Y**, **4-Y** and **5-Y** are listed in Table 2. It should be noted that all the oxidation potentials [$E_{\text{p(ox)}}$] are positive, thus a larger $E_{\text{p(ox)}}$

Table 1 Oxidation potentials of **1-Y** and **2-Y**

	$E_{\text{p(ox)}}$/V[a]	
Y	**1-Y**	**2-Y**
H	0.87	1.27
Me_2N	0.43	0.54
MeO	0.75	0.95
Me	0.75	1.22
MeS	0.71	1.05
F	0.78	1.23
Cl	0.78	1.30
Br	0.79	1.30
CN	0.86	1.21
CF_3	0.88	1.34
NO_2	0.87	1.33
CO_2Me	0.82	

[a]Relative to the Ag/AgCl electrode in saturated KCl solution; uncertainty ± 0.02 V.

Table 2 Reduction potentials of **3-Y**, **4-Y** and **5-Y**

	$E_{\text{p(red)}}$/V[a]		
Y	**3-Y**	**4-Y**	**5-Y**
F	–1.74	–2.06	–2.32
Cl	–1.61	–1.91	–2.18
Br	–1.62	–1.87	–2.17
Me	–1.69	–2.07	–2.36
COMe			–1.75
CN	–1.48	–1.55	–1.88
MeSO			–2.04
H	–1.68	–2.04	–2.31
CF_3	–1.53	–1.83	–2.10
CO_2Me			–2.03
MeO	–1.80	–2.10	–2.35
Bu^t			–2.34
NO_2	–1.38	–1.52	–1.70
$SiMe_3$			–2.28
Me_2N	–1.77	–2.09	–2.32
SMe	–1.59	–1.88	–2.14

[a]Relative to SCE; uncertainty ± 0.02 V.

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Table 3 Value of ρ^x and $\rho^\bullet$ of eqns. (1) and (2) and corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of $E_{p(ox)}$ values of n **1-Y** with σ^x and $\sigma^\bullet$ [a]

σ^x or $(\sigma^x + \sigma^\bullet)$	ρ^x	$\rho^\bullet$	r or R	ψ	s	F^b
σ_p	0.23		0.852	0.573	0.067	26.5
σ^+	0.16		0.910	0.455	0.053	48.1
$\sigma_p+\sigma_{JJ}^\bullet$	0.17	–0.21	0.968	0.290	0.034	66.7
$\sigma^++\sigma_{JJ}^\bullet$	0.12	–0.16	0.960	0.323	0.038	53.1
$\sigma_{mb}+\sigma_{JJ}^\bullet$	0.13	–0.25	0.964	0.309	0.036	58.3

[a] $n = 12$, Y = H, Me_2N, MeO, Me, MeS, F, Cl, Br, CN, CF_3, NO_2, CO_2Me; [b] Critical F values:[15] $F_{0.001}$ (1, 10) = 21.04; $F_{0.001}$(2,9) = 16.39.

value indicates a greater difficulty for the oxidation, and that all the reduction potentials [$E_{p(red)}$] values are negative, thus a larger $E_{p(red)}$ value indicates an easier reduction process.

The single-parameter correlation results for the oxidation potentials of **1-Y** (Table 3) by eqn. (2) show that σ_p and σ^+ yield results with confidence levels (CLs) greater than 99.9%, *e.g.* for σ^+: $r = 0.910$, $\psi = 0.455$, $n = 12$. Both ρ^x values are positive, while σ^+ gives a better correlation than σ_p, as expected, because the transition states of voltammetric oxidations of organic compounds resemble radical cations.[2d] However, correlations by the dual parameter eqn. (1) yield clearly improved results. All the $(\sigma^x+\sigma_{JJ}^\bullet)$ combinations yield very good correlations, *e.g.* for $(\sigma_{mb}+\sigma_{JJ}^\bullet)$: $R = 0.964$, $\psi = 0.309$, $n = 12$, CL > 99.9%. Therefore, judging by the $|\rho_{mb}/\rho_{JJ}^\bullet|$ value of 0.52 and by the fact that the dual-parameter correlation is clearly better than the single-parameter correlation is, the oxidation process for **1-Y** may be classified as category-I.[5a]

The structures of **2-Y** and **1-Y** all possess a unit (CH=NNH) in conjugation with the *p*-Y-substituted benzene ring, thus similar voltammetric spectral behaviour might be expected. Except for the fact that oxidation potentials of **2-Y** are much larger than those of **1-Y**, which was fully in accordance with the positive values of ρ^x derived from the correlation results of the oxidation potentials for **1-Y**, the correlation results for **2-Y** summarized in Table 4 are in harmony with the aforesaid expectation. The $|\rho_{mb}/\rho_{JJ}^\bullet|$ value is 0.48. Therefore, the voltammetric oxidation for **2-Y** may also be classified as category-I.[5a] The above two voltammetric oxidation systems confirm that the oxidations potentials are affected by both the polar effects and the spin-delocalization effects of the substituents. The fact that all ρ^x values are positive shows that donors will facilitate the oxidations while acceptors will destabilise the TS of oxidations. On the other hand, the fact that all $\rho^\bullet$ values are negative demonstrates that spin-delocalization effects will always facilitate the voltammetric oxidations of these compounds.

At this juncture we ask a second question: 'How the transition states of the voltammetric reductions are affected by the polar and spin-delocalization effects?' The single parameter correlation results for the reduction potentials of **3-Y** by eqn. (2) summarized in Table 5 show that σ_p, σ_{mb} and σ^- all yield results with CLs greater than 99.9%, *e.g.* for σ^-: $r = 0.968$, $\psi = 0.280$, $n = 11$. All the ρ^x values are positive, and σ^- gives the best correlation among the three σ^x values, as expected, because the TS of voltammetric reductions of organic compounds resemble radical anions.[1c,2b] Although the correlation results were not much improved by the dual parameter eqn. (1), the existence of the spin-delocalization effects can still be revealed by examination of the individual and total deviations of the experimental data from the regression lines.[5a] D-1 stands for the deviations from the regression line of [$E_{p(red)}$ *vs.* σ^-], and D-2 represents the deviations from the regression line of [$E_{p(red)}$ *vs.* $(0.22\sigma_{mb}+0.12\sigma_{JJ}^\bullet)$] (see full text for all the D-1 and D-2 values). The total deviation $\Sigma|D\text{-}2|$ is 0.25 V and the total deviation $\Sigma|D\text{-}1|$ is 0.38 V for **3-Y**. Therefore, judging by the $|\rho_{mb}/\rho_{JJ}^\bullet|$ value of 1.83 and the fact that the correlations were not much improved by the dual-parameter eqn. (1), while the existence of the spin-delocalization effects is revealed by the examination of the total deviations from the regression lines, the voltammetric reduction behavior of **3-Y** may be classified as category-II.[5a]

The correlation results of the reduction potentials for **4-Y** and **5-Y** summarized in Tables 6 and 7 are very similar to those of **3-Y**. The $|\rho_{mb}/\rho_{JJ}^\bullet|$ value of 1.12 for **5-Y** and 1.33 for **4-Y** are larger than 1.0. Furthermore, examination of the $\Sigma|D\text{-}1|$ and $\Sigma|D\text{-}2|$ values again suggests the existence of the spin-delocalization effect. Therefore, the voltammetric reduction behaviours of **4-Y** and **5-Y** can also be classified as category-II.[5a] All the above three correlations of the reduction potentials of **3-Y**, **4-Y** and **5-Y** by the dual-parameter eqn. (1) and single-parameter eqn. (2) yield positive values of both ρ^x and $\rho^\bullet$. The fact that all ρ^x values are positive shows that acceptors will facilitate the reductions while donors will destabilize the TS of the reductions. On the other hand, the fact that all $\rho^\bullet$ values are positive demonstrates that spin-delocalization effects will always facilitate the voltammetric reductions of these compounds.

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Techniques used: ^1H and ^{19}F NMR, MS, IR, UV, cyclic voltammetry

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Fig. 1: Plot of $E_{p(ox)}$ *vs.* σ^+ for **1-Y**

Fig. 2: Plot of $E_{p(ox)}$ *vs.* $(0.17\sigma_p–0.21\sigma_{JJ}^\bullet)$ for **1-Y**

Fig. 3: Plot of $E_{p(red)}$ *vs.* σ^- for **3-Y**

Fig. 4: Plot of $E_{p(red)}$ *vs.* $(0.22\sigma_{mb}+0.12\sigma_{JJ}^\bullet)$ for **3-Y**

Table 4: Values of ρ^x and $\rho^\bullet$ of eqns. (1) and (2), and corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of $E_{p(ox)}$ values of n **2-Y** with σ^x and $\sigma^\bullet$

Table 5: Values of ρ^x and $\rho^\bullet$ of eqns. (1) and (2), and corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of $E_{p(red)}$ values of n **3-Y** with σ^x and $\sigma^\bullet$

Table 6: Values of ρ^x and $\rho^\bullet$ of eqns. (1) and (2), and corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of $E_{p(red)}$ values of n **4-Y** with σ^x and $\sigma^\bullet$

Table 7: Values of ρ^x and $\rho^\bullet$ of eqns. (1) and (2), and corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of $E_{p(red)}$ values of n **5-Y** with σ^x and $\sigma^\bullet$

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