

Dual-parameter Correlation Analysis of the Redox Potential Data of 1-Methyl-2-formyl-5-substituted Pyrroles and their Hydrazones

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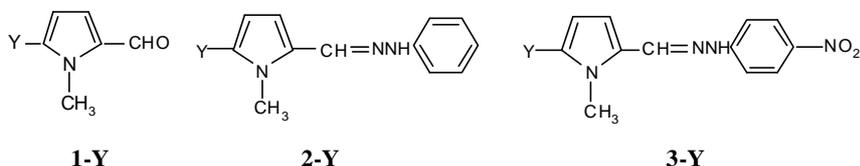
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Abstract: By using 1-methyl-2-formyl-5-substituted pyrroles (**1-Y**), 1-methyl-2-formyl-5-substituted pyrrole phenylhydrazones (**2-Y**) and 1-methyl-2-formyl-5-substituted pyrrole (4-nitro-phenyl)-hydrazones (**3-Y**) as model structures for nitrogen-containing heterocyclic aromatic compounds, correlation analysis of their redox potential data show that the transition states (TS) of the polarographic process are mainly affected by the polar effects, but spin-delocalization effects also exist.

Keywords: Correlation analysis, polar effect, spin-delocalization effect, redox potential.

It has been suggested about forty years ago that the transition states of polarographic potential-determining steps possess free radical character¹. However, the dual-parameter correlation analysis [eqn. (1)] have never been successfully applied to the redox potentials until our recent report on five series of aromatic compounds shows that polarographic processes are affected by the polar effect as well as the spin-delocalization effect². The purpose of this paper is to study the correlation analysis of the redox potentials of heterocyclic aromatic compounds, *e.g.*, pyrrole derivatives **1-Y**, **2-Y** and **3-Y**. We have previously reported their synthesis³, and the correlation analysis of their UV⁴ and fluorescence⁵ spectral data.



Y = H, CH₃, Cl, CN, COCH₃, NO₂, COOH, SCH₃, COOCH₃, Si(CH₃)₃, Br and OCH₃

On the basis of the magnitude of $|\rho_{mb}/\rho_{J^{\bullet}}|$ from Eqn.1, in which $\rho^x\sigma^x$ and $\rho^{\bullet}\sigma^{\bullet}$ represent the polar and spin-delocalization effects respectively, it has been well established that there are four categories of possible circumstances for correlation analysis of radical reactivities and spectral properties⁶. (1) Both polar and spin-

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delocalization effects are important, $0.2 < |\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}| < 0.8$. (II) The polar effects predominate, $|\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}| > 1.0$. (III) The spin-delocalization effects predominate, $|\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}| < 0.2$. (IV) No correlation can be achieved.

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

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

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

Table 1 Redox Potential Data of **1-Y**, **2-Y** and **3-Y** (relative to SCE)

Y	$E_{\text{p(ox)}} \pm 0.02$ (V)			$E_{\text{p(red)}} \pm 0.02$ (V)	
	1-Y	2-Y	3-Y	2-Y	3-Y
H	1.08	0.73	1.14	-1.68	-1.28
CH3	0.96	0.66	0.92	-1.72	-1.34
Cl	1.05	0.71	1.08	-1.66	-1.20
CN	1.59	0.78	1.44	-1.50	-0.88
COCH3	1.55	0.77	1.34	-1.55	-0.98
NO2	1.61	0.80	1.58	-1.45	-0.80
COOH	1.48	0.72	1.24	-1.59	-1.02
SCH3	0.88	0.61	0.84	-1.76	-1.40
COOCH3	1.49	0.74	1.38	-1.60	-0.99
Si(CH3)3	1.20	0.69	1.06	-1.65	-1.08
Br	1.08	0.70	1.12	-1.62	-1.23
OCH3	0.81	0.60	0.72	-1.80	-1.48

The redox potential data of **1-Y**, **2-Y** and **3-Y** are summarized in **Table 1**. A larger $E_{\text{p(ox)}}$ value indicates a greater difficulty for the oxidation, while a larger $E_{\text{p(red)}}$ value indicates an easier reduction process. Single-parameter correlation results for the oxidation potential data of **1-Y** (c.f. **Table 2**) show that correlations with confidence level (CL) greater than 99.9% can be achieved by eqn. (2), *e.g.*, for σ_{p} : $r = 0.9138$, $F = 50.62$; for σ^+ : $r = 0.9463$, $F = 77.15$; for σ_{mb} : $r = 0.9338$, $F = 68.09$. It is noteworthy that σ^+ gives a better correlation than σ_{mb} and σ_{p} , as expected, because the transition states of voltammetric oxidations resemble radical cations^{1b}. However, single-parameter correlation analysis with all the σ^{\bullet} yield meaningless results ($r < 0.60$). By using the dual-parameter eqn. (1), all the six pairings of $(\sigma^{\times} + \sigma^{\bullet})$ yield good correlations with CL > 99.9%, *e.g.*, for $(\sigma^+, \sigma_{\text{JJ}}^{\bullet})$: $R = 0.9626$, $\psi = 0.3177$, $F = 50.50$, $n = 11$; for $(\sigma_{\text{mb}}, \sigma_{\text{JJ}}^{\bullet})$: $R = 0.9342$, $\psi = 0.4120$, $F = 30.84$, $n = 12$. Judging by the $|\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}|$ value of 11.3, the oxidation potential data of **1-Y** are mainly affected by the polar effects of the substituents (category-II).

The correlation analysis results of the redox potential data for **2-Y** and **3-Y** are very similar to those of **1-Y**. As expected, σ^+ gives a better correlation than σ_{mb} and σ_{p} for the oxidations and σ^- gives a better correlation than σ_{mb} and σ_{p} for the reductions, because the TS of voltammetric oxidations and reductions resemble radical cations and radical anions respectively.

Table 2 Correlation results for the oxidation potential data of **1-Y**

σ^x or ($\sigma^x + \sigma^\bullet$)	ρ^x	ρ^\bullet	r or R	s	ψ	F ^a	n ^b
σ_p	0.7953		0.9138	0.1256	0.4449	50.62	12
σ_+	0.5512		0.9463	0.0991	0.3573	77.15	11
σ_{mb}	0.5811		0.9338	0.1107	0.3920	68.09	12
$\sigma_p + \sigma_{JJ^\bullet}$	0.8029	-0.0366	0.9140	0.1323	0.4685	22.84	12
$\sigma_+ + \sigma_{JJ^\bullet}$	0.5423	0.3215	0.9626	0.0881	0.3177	50.50	11
$\sigma_{mb} + \sigma_{JJ^\bullet}$	0.5746	0.0508	0.9342	0.1163	0.4120	30.84	12
$\sigma_p + \sigma_{c^\bullet}$	0.7555	-0.0225	0.9069	0.1389	0.5034	16.23	10
$\sigma_+ + \sigma_{c^\bullet}$	0.4783	0.4016	0.9754	0.0727	0.2634	68.57	10
$\sigma_{mb} + \sigma_{c^\bullet}$	0.5187	0.1483	0.9548	0.0980	0.3552	36.14	10

- a. Critical F values: $F_{0.001}(1, 10) = 21.04$; $F_{0.001}(1, 9) = 22.86$; $F_{0.001}(2, 9) = 16.39$, $F_{0.001}(2, 8) = 18.49$; $F_{0.001}(2, 7) = 21.69$.
- b. N = 12, Y = H, CH₃, Cl, CN, COCH₃, NO₂, COOH, SCH₃, COOCH₃, Si(CH₃)₃, Br, OCH₃; n = 11, all of 12 substituted groups except for COCH₃; n=10, all of 12 substituted groups except for COCH₃ and COOH.

Although application of the dual-parameter eqn.(1) seems to improve the correlation results, this improvement cannot be considered meaningful unless we look into our data more closely. It would be good practice to examine the sum of the deviations $\Sigma |D|$ of the experimental data from the regression lines. $\Sigma |D_{mJ}|$ value stands for the sum of the deviations from the regression line of [eqn. (1); $E_{p(\text{ox or red})}$ vs. $\sigma_{mb} + \sigma_{JJ^\bullet}$], and $\Sigma |D_{mb}|$ value stands for the sum of the deviations from the regression line of [eqn. (2); $E_{p(\text{ox or red})}$ vs. σ_{mb}]. For **2-Y**, the $\Sigma |D_{mJ}|$ value [0.10 V for $E_{p(\text{ox})}$; 0.20 V for $E_{p(\text{red})}$] is smaller than the $\Sigma |D_{mb}|$ value [0.20 V for $E_{p(\text{ox})}$; 0.27 V for $E_{p(\text{red})}$]. For **3-Y**, the $\Sigma |D_{mJ}|$ value [0.42 V for $E_{p(\text{ox})}$; 0.51 V for $E_{p(\text{red})}$] is also smaller than the $\Sigma |D_{mb}|$ value [0.71 V for $E_{p(\text{ox})}$; 0.64 V for $E_{p(\text{red})}$]. Therefore, we believe that the above-mentioned indecisive improvement by application of the dual-parameter equation is genuine and that the spin-delocalization effect is in operation even though it is overshadowed by the polar effect. Judging by the $|\rho_{mb}/\rho_{JJ^\bullet}|$ value (> 1.0) and by careful examination of the total deviations of the experimental data from the regression lines, the behavior of polarographic processes of **2-Y** and **3-Y** can also be classified as category-**II**, *i.e.*, their redox potential is mainly affected by the polar effects of the substituents, but spin-delocalization effects also exist. The fact that all ρ^x values are positive shows that donors facilitate the TS of the oxidations, but destabilize the TS of the reductions; while acceptors facilitate the TS of the reductions, but destabilize the TS of the oxidations. On the other hand, the fact that all ρ^\bullet are negative demonstrates that spin-delocalization effects always facilitate the voltammetric oxidations, but destabilize the TS of the reductions.

Table 3 Correlation results for redox potential data of **2-Y** and **3-Y**

Compd.	E_p	σ^x or ($\sigma^x + \sigma^*$)	ρ^x	ρ^*	r or R	s	F^a	n
2-Y	$E_{p(\text{ox})}$	σ^+	0.1210	-0.1152	0.9666	0.0169	127.9	11 ^b
		$\sigma_{\text{mb}} + \sigma_{\text{JJ}}^*$	0.1377		0.9744	0.0156	84.58	12
	$E_{p(\text{red})}$	σ^-	0.1980	-0.0593	0.9507	0.0352	84.51	11 ^c
		$\sigma_{\text{mb}} + \sigma_{\text{JJ}}^*$	0.2171		0.9711	0.0271	74.41	12
3-Y	$E_{p(\text{ox})}$	σ^+	0.5099	-0.2582	0.9791	0.0558	208.4	11 ^b
		$\sigma_{\text{mb}} + \sigma_{\text{JJ}}^*$	0.5522		0.9787	0.0578	102.2	12
	$E_{p(\text{red})}$	σ^-	0.4240	-0.0332	0.9788	0.0482	205.9	11 ^c
		$\sigma_{\text{mb}} + \sigma_{\text{JJ}}^*$	0.4380		0.9608	0.0656	54.03	12

- a. Same as the footnote a. in **Table 2**.
 b. n = 11, all of 12 substituted groups except for COCH₃.
 c. n = 11, all of 12 substituted groups except for Si(CH₃)₃.

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