

QUINONE STUDIES—II*

REDUCTION POTENTIALS OF SOME 3-SUBSTITUTED PHENANTHRENE QUINONES

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Abstract—Polarographic reduction potentials of seven 3-substituted phenanthrenequinones have been determined in aqueous dioxan and aqueous ethanol under different pH conditions. The substituent effects on the reduction potentials could be correlated with the Hammett σ constants (correlation coefficients >0.995). The possibility of using reduction potentials as an accurate measure of resonance energy has been pointed out.

THE great facility with which quinones are reduced to hydroquinones reflects the gain in the resonance energy in the process of gaining two electrons to obtain the stable six electron aromatic system. The reduction potential which is a measure of this tendency may be related to the resonance energy. Although a number of theoretical studies^{1,2} have attempted to find the exact relationship, factors like substituent, field and solvent effects which influence the reduction potential render the pattern complicated and not amenable to simple treatment. In their classical researches³ on quinones, Fieser *et al.* attempted to uncover the relationship between structure and reduction potential. Unfortunately, this detailed investigation which was ahead of the current thinking at that time, did not succeed. In 1950, Evans and de Heer² summarized the position as follows: "The important generalizations which were hoped for were not immediately apparent in terms of classical chemical ideas. In particular, the problem of the influence of substituents appeared to be very complicated and even a comparison of unsubstituted 'parent quinones' did not immediately yield results."

More recently† Zuman reported⁴ that the substituent effects on the reduction potentials of quinones could be correlated with Hammett substituent constants. For this analysis, Zuman⁴ used literature data (and not necessarily from the same source). A least-square treatment of the original set of data used by Zuman has yielded correlation coefficients ranging from 0.707 to 0.989, many of which are below the confidence limits of Jaffé⁵ (Table 1).

We present in this paper our data on the reduction potentials of 3-substituted phenanthrenequinones. The present investigation was started with a view of taking a fresh look at the question of correlation of structure and reduction potentials of quinones. Hopefully, if the component factors which influence the reduction potential could be disentangled and evaluated, it may be possible to use the reduction potential

* Quinone Studies I. M. V. Bhatt, *Tetrahedron* **20**, 803 (1964).

† After our present investigation was started.

TABLE I.

No.	Type of compounds	Substituent constant	Reduction potential	Correlation coefficient
1	Alkyl substituted hydroquinones	$\Sigma\sigma^{*a}$	$(\Delta E_{\frac{1}{2}})_H$	0.966
2	Alkyl substituted pyrocatechol	$(\Delta E_{\frac{1}{2}})_H$ calc. ^b	$(\Delta E_{\frac{1}{2}})_H$ exptl.	0.955
3	Substituted <i>p</i> -benzoquinones	σ^{1c}	ΔE_H^{σ}	0.875
4	Substituted <i>p</i> -benzoquinones	$\Sigma\sigma-p^d$	ΔE_H^{σ}	0.933
5	Substituted <i>p</i> -benzoquinones	$\sigma-p$	ΔE_H^{σ}	0.978
6	Substituted <i>p</i> -benzoquinones	$\Sigma\sigma-p$	$(E_{\frac{1}{2}})^f$	0.975
7	Substituted <i>p</i> -benzoquinones	$\Sigma\sigma-p$	$(\Sigma E_{\frac{1}{2}})^g$	0.978
8	2-Phenyl- <i>p</i> -benzoquinones substituted in the meta or para position of phenyl group	σ	ΔE_H^{σ}	0.808
9	2-Substituted 1,4-naphthaquinones	σ^1	ΔE_H^{σ}	0.808
10	Substituted 1,2-naphthaquinones	σ^*	$\Delta E_{CH_3}^{\sigma}$	0.975
11	Substituted 1,2-naphthaquinones	σ^*	$\Delta E_{CH_3}^{\sigma}$	0.707
12	2-Substituted 1,4-naphthaquinones	$\sigma-p$	$(\Delta E_{\frac{1}{2}})_H$	0.974
13	2- and 2,3-Substituted 1,4-naphthaquinones	$\Sigma\sigma-p$	$E_{\frac{1}{2}}$	0.860
14	2- and 2,3-Substituted 1,4-naphthaquinones	$\Sigma\sigma-p$	$E_{\frac{1}{2}}$	0.734
15	4-Substituted 1,2-naphthaquinones	$\sigma-p$	$(\Delta E_{\frac{1}{2}})_H$	0.972
16	1,4-Naphthaquinones substituted in the benzene ring	$\Sigma\sigma-p$	ΔE_H^{σ}	0.872
17	2'- and 4'-Substituted 2-anilino-3-hydroxy-1,4-naphthaquinones	$\Sigma\sigma-p$	$E_{\frac{1}{2}}$	0.764
18	Substituted anthraquinones	$\Sigma\sigma-p$	$(\Delta E_{\frac{1}{2}})_H$	0.757
19	Substituted anthraquinones	$\Sigma\sigma-m$ and $\Sigma\sigma-o$	$E_{\frac{1}{2}}$	0.989

^a Taft polar substituent constant

^b Relation of the shifts in measured half-wave potential $(\Delta E_{\frac{1}{2}})_H$ to $(\Delta E_{\frac{1}{2}})_H$ calc.

^c Inductive substituent constant

^d Hammett substituent constant

^e Shifts in reduction potential

^f Half-wave potential for first wave

^g Half-wave potential for second wave

as an accurate measure of the resonance energy of an aromatic system. Reliability of thermochemical measure of resonance energy of an aromatic system is rarely better than 3 Kcals. Theoretical computations have much larger uncertainties.* If the relationship of the reduction potential and resonance energy could be discovered, electro-analytical methods, which are used for the measurements of reduction potentials, hold promise of being able to measure resonance energy to an accuracy of the order of 0.05 Kcal (1 mv = 46 cal).

When Fieser's values⁹ of reduction potentials of substituted phenanthrene quinones were plotted against Hammett σ p-constants, two lines were obtained—one for electron-donating groups and other for electron-withdrawing groups (Fig 1). In the case of 1- and 4-substituted phenanthrenequinones, ortho and steric effects may be expected to operate. In 2-substituted compounds, the conjugation of diphenyl framework comes into play. We argued that if a linear free-energy relationship could be established for 3-substituted phenanthrenequinones, it could form a good basis for

* Recent theoretical computations^{6,7} of resonance energy of azulene give figures of 3.9 Kcals and 13.3 Kcals compared to the thermochemical figure of 28.3 Kcals.⁸

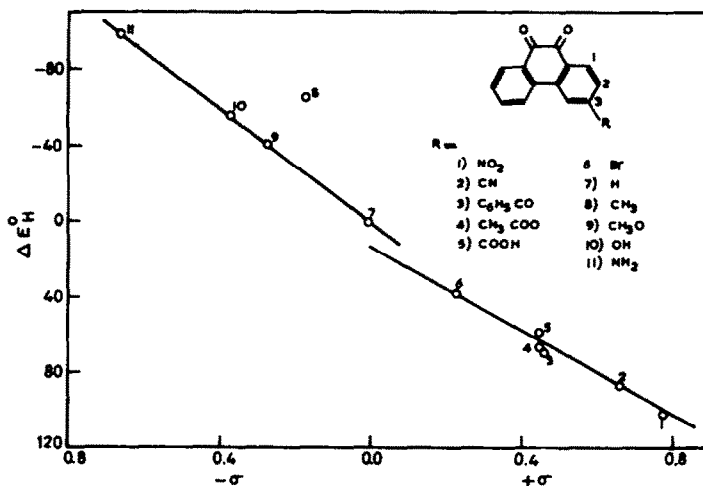


FIG. 1. Fieser's values of oxidation-reduction potentials vs Hammett σ_p -constants.

a more extensive study of the substituent effects and a general treatment of reduction potentials.

RESULTS AND DISCUSSION

To ensure that all compounds are studied under identical conditions and the electrode process has same or similar courses, it would be desirable to measure the half-wave potentials in a pH range where both oxidized and reduced forms are completely dissociated so that $dE_{1/2}/dpH = 0$. As it is very difficult to work in these pH ranges because under the alkaline conditions, quinones decompose, we measured half-wave potentials in a number of well buffered solutions and confirmed that $dE_{1/2}/dpH$ is identical for all compounds studied. The water content of the solvent could not be further increased owing to the difficulty of keeping the organic compound in solution. The half-wave potentials, $E_{1/2}$, and diffusion current constants, I_d , are given in Tables 2–5. I_d values obtained are in close agreement with those of similar

TABLE 2. $E_{1/2}$ VALUES OF 3-SUBSTITUTED PHENANTHRENEQUINONES (pH 4.13)
 I—Phenanthrenequinone; II—3-Ethylphenanthrenequinone; III—3-Isopropylphenanthrenequinone; IV—3-*t*-butylphenanthrenequinone; V—3-Cyanophenanthrenequinone; VI—3-Acetylphenanthrenequinone; VII—3-Bromophenanthrenequinone; VIII—3-Methylphenanthrenequinone.

Compound	$E_{1/2}$ v vs SCE	I_d	Slope of log plot, mv	Slope of Hammett plot, ρ , mv	Correlation coefficient, γ
I	-0.040	2.022	34		
II	-0.053	1.954	32		
III	-0.052	1.950	33		
IV	-0.056	1.950	33	0.087	0.999
V	+0.018	1.901	34		
VI	+0.005	2.000	32		

0.5N Citric acid, 0.1N NaOH and 0.1N NaClO₄ in 50% dioxan; pH = 4.13; temp 30°.

TABLE 3. E_3 VALUES OF 3-SUBSTITUTED PHENANTHRENEQUINONES (pH 4.75)

Compound	E_3 v vs SCE	I_d	Slope of log plot, mv	Slope of Hammett plot, ρ , mv	Correlation coefficient γ
I	-0.086	2.109	34		
II	-0.104	2.009	34		
III	-0.103	1.960	34		
IV	-0.105	2.080	33	0.101	0.999
V	-0.019	1.950	33		
VI	-0.038	2.050	33		

0.25N Citric acid, 0.1N NaOH and 0.1N NaClO₄ in 50% dioxan: pH = 4.75; temp 30°

TABLE 4. E_3 VALUES OF 3-SUBSTITUTED PHENANTHRENEQUINONES (pH 5.21)

Compound	E_3 v vs SCE	I_d	Slope of log plot, mv	Slope of Hammett plot, ρ , mv	Correlation coefficient, γ
I	-0.112	2.143	33		
II	-0.124	2.009	34		
III	-0.126	2.130	34		
IV	-0.124	2.090	34	0.096	0.997
V	-0.045	1.958	33		
VI	-0.060	2.090	34		

0.17N Citric acid, 0.1N NaOH and 0.1N NaClO₄ in 50% dioxan; pH = 5.21; temp 30°

TABLE 5. E_3 VALUES OF 3-SUBSTITUTED PHENANTHRENEQUINONES (pH 7.2)

Compound	E_3 v vs SCE	I_d	Slope of log plot, mv	Slope of Hammett plot, ρ , mv	Correlation coefficient, γ
I	-0.236	2.144	34		
II	-0.250	2.002	34		
III	-0.250	2.130	34		
IV	-0.246	2.104	34	0.100	0.995
V	-0.165	2.010	34		
VI	-0.182	2.109	34		

0.2N CH₃COONH₄ and 0.1N NaClO₄ in 50% dioxan: pH = 7.2; temp 30°

compounds. The E_3 values were plotted against measured pH values and yielded parallel straight lines. The change in E_3 values per unit pH is about 60 mv. For a diffusion controlled reaction in which both oxidized and reduced forms are soluble and in which the electrode reaction is reversible, the dependence of $\log(i_d - i)/i$ on potential is expected to be linear.¹⁰ At 30° for a two-electron reduction, the slope of the lines is around 30 mv¹⁰ (Tables 2-5). As the observed E_3 values are independent

TABLE 6.
E_{1/2} VALUES PER pH UNIT

Compound	E _{1/2} /pH unit, mv
I	62
II	61
III	61
IV	61
V	61
VI	60

TABLE 7. E_{1/2} VALUES OF 3-SUBSTITUTED PHENANTHRENEQUINONES (pH 6.2)

Compound	E _{1/2} vs SCE	Slope of Hammett plot, ρ, mv	Correlation coefficient, γ
I	-0.150		
II	-0.170		
III	-0.168		
IV	-0.168	0.118	0.997
V	-0.070		
VI	-0.092		
VII	-0.125		
VIII	-0.175		

0.05N CH₃COOH and 0.05N CH₃COONa in 75% Ethanol :
0.01% gelatin; pH = 6.2; temp 30°

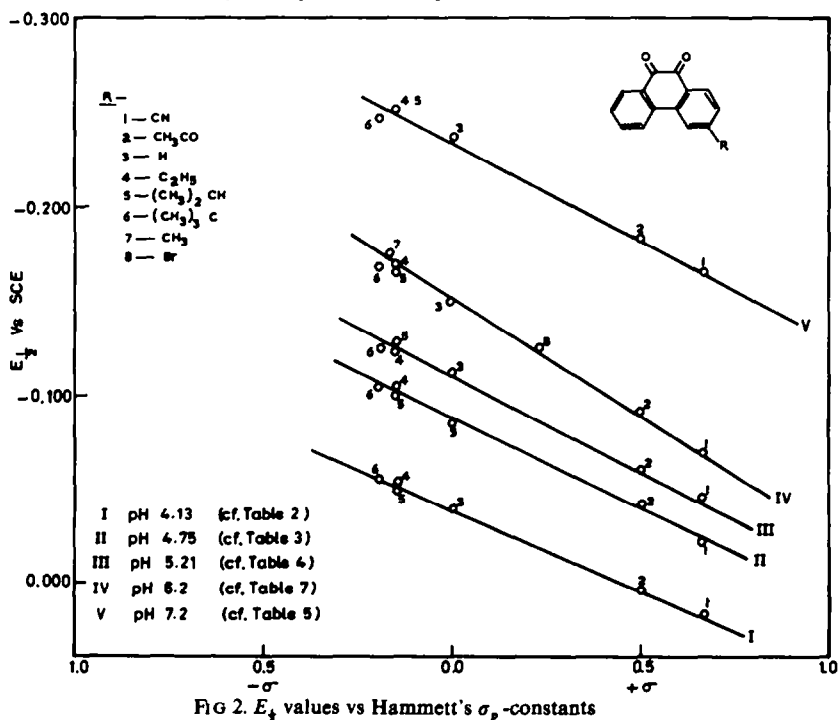


FIG 2. E_{1/2} values vs Hammett's σ_p-constants

of concentration, it can be concluded that the reduction is reversible and involves two electrons. In the case of 3-methoxyphenanthrenequinone, a split wave was obtained under the experimental conditions tried and hence it is not included in further discussion. Half-wave potentials were also determined in 75% ethanol containing 0.05M acetic acid and 0.05 M sodium acetate at pH 6.2. The results are summarized in Table 7. I_d values are not given because of uncertainties in the concentrations.

It was observed that electron-donating groups shifted the half-wave potentials to more negative values and electron-withdrawing groups had the opposite effect. When the $E_{1/2}$ values were plotted against Hammett σ p -constants, good straight lines were obtained (Fig 2). This is the first linear free-energy relationship, as far as we are aware, correlating polarographic reduction potentials of phenanthrenequinones with substituent effects. This finding encourages us to look for correlation of reduction potentials with other structural factors.

EXPERIMENTAL

A programme to calculate the standard deviation (s), correlation coefficient (γ) and slope (ρ) was written for the digital computer IBM 360/44.

All polarograms were taken on a manual set-up. The capillary used had the following characteristics: $m = 0.9$ mg/sec and $t = 4$ sec in 0.1N KCl in an open circuit at the mercury column height of 45 cms. The electrolysis cell was of usual type. A saturated Calomel electrode was used as the reference electrode and was connected to the electrolysis cell by means of a saturated NaNO_3 -Agar bridge. Deaeration was carried out by hydrogen previously passed through base solution. Dioxan used was purified by the literature method.¹¹ All solns were kept out of direct sunlight and determinations were made as soon as the solns were made to prevent any possible decomposition. The temp was maintained at $30 \pm 0.1^\circ$ during the determinations. Half-wave potentials were measured with increasing cathodic voltage and IR drop corrections were applied whenever necessary. Values of pH quoted are simply meter readings and hence no significance should be attached to these values in terms of hydrogen ion activity.

3-Substituted phenanthrenequinones were synthesized specially for the purpose of this investigation. Their synthesis is reported in a separate paper.

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