

Amphoteric Redox Nature of *p*-Benzoquinones with Donor- and Acceptor-Substituents

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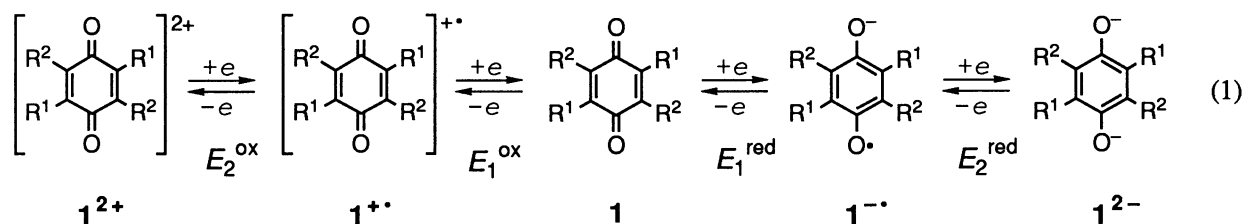
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The redox potentials of sixteen substituted *p*-benzoquinones were measured by cyclic voltammetry. In addition to the first and the second reduction potentials, the first oxidation potential showed linear dependence on  $\Sigma(\sigma_m + \sigma_p)/2$  Hammett constant for a wide range of substituents.

Wurster type acceptors possessing quinoid structures are recognized as important components to explore new charge transfer complexes which show metallic conduction,<sup>1)</sup> neutral-ionic phase transition,<sup>2)</sup> and intermolecular proton transfer.<sup>3)</sup> For the precise control of the electronic properties of such acceptors as well as the crystal packing of the derived complexes, knowledge about the effect of substituents on the electrochemical behavior of quinoid compounds, *e.g.* *p*-benzoquinones, seems essential. Aumüller and Hünig found a linear correlation between first reduction potentials ( $E_1^{\text{red}}$ ) of substituted *p*-benzoquinones and Hammett substituent constants.<sup>4)</sup> Furthermore Bock *et al.* have reported anodic oxidation for tetrakis(dimethylamino)-*p*-benzoquinone,<sup>5)</sup> which indicates its capacity to behave as an amphoteric redox system as shown by Eq. 1.



In the present study, the redox properties of sixteen substituted *p*-benzoquinones (**1a–p**) were measured by cyclic voltammetry (Table 1). Four new *p*-benzoquinones, **1c**, **1d**, **1m**, and **1o**,<sup>6)</sup> were synthesized by stepwise nucleophilic substitution on chloranil or fluoranil as outlined in Scheme 1. Some redox potentials have already been reported in the literature, yet all potentials were redetermined under the same conditions in order to obtain a self-consistent data set.

Despite the presence of bulky substituents  $E_1^{\text{red}}$  showed a good linear correlation with  $\Sigma(\sigma_m + \sigma_p)/2$  (Fig. 1).<sup>7)</sup> Thus the linear relationship was extended to those quinones which are substituted by extremely electron-donating groups up to tetraamino substitution ( $-1.64 < \Sigma(\sigma_m + \sigma_p)/2 < 1.20$ ). Linear relationship was also

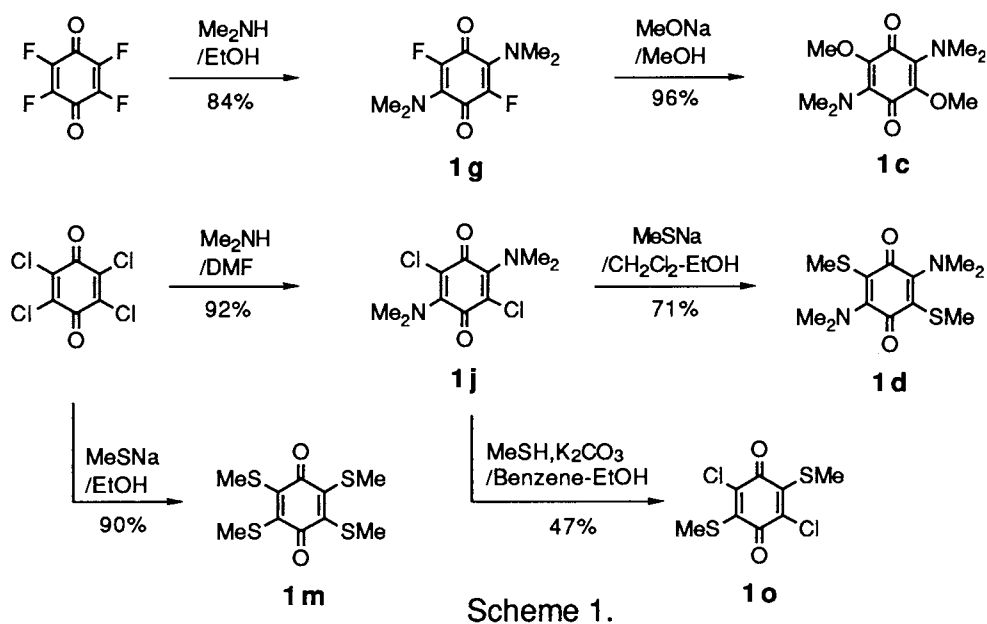


Table 1. Redox potentials,<sup>a)</sup> LUMO and HOMO levels,<sup>b)</sup> and carbonyl stretching frequencies<sup>c)</sup> of substituted *p*-benzoquinones

Compound	R <sup>1</sup>	R <sup>2</sup>	$\frac{\Sigma\sigma_m + \sigma_p}{2}$	$E_2^{\text{red}}$	$E_1^{\text{red}}$	$E_1^{\text{ox}}$	$E_2^{\text{ox}}$	LUMO	HOMO	$\nu_{\text{C=O}}$
1a	NH <sub>2</sub>	NH <sub>2</sub>	-1.64	-1.47	-1.08	0.28	1.35 <sup>d)</sup>	-1.199	-9.162	
1b	NMe <sub>2</sub>	NMe <sub>2</sub>	-1.62		-1.14	0.19			-9.012	1627
1c	NMe <sub>2</sub>	OMe	-0.96		-0.91	0.79 <sup>d)</sup>	1.48	-1.378	-9.170	1633
1d	NMe <sub>2</sub>	SMe	-0.72		-0.89	0.81	1.00	-1.562	-9.432	1630
1e	OH	OH	-0.72			1.00 <sup>d)</sup>	1.30	-1.703	-9.504	
1f	Me	Me	-0.48		-0.76			-1.468	-10.500	
1g	NMe <sub>2</sub>	F	-0.41	-1.24	-0.71	1.16 <sup>d)</sup>		-1.965	-9.760	1651
1h	OMe	OMe	-0.30		-0.71	1.56 <sup>d)</sup>	1.78	-1.338	-9.600	1667
1i	NH <sub>2</sub>	Cl	-0.22	-1.25	-0.72	1.52 <sup>d)</sup>		-1.889	-10.225	
1j	NMe <sub>2</sub>	Cl	-0.21	-1.13	-0.67	1.19 <sup>d)</sup>		-1.888	-9.783	1644
1k	H	H	0.00	-1.14	-0.51			-1.505	-10.952	1655 <sup>e)</sup>
1l	SMe	H	0.09	-1.08	-0.49			-1.582	-9.949	1664
1m	SMe	SMe	0.18	-1.09	-0.50	1.44 <sup>d)</sup>	1.54	-1.676	-9.342	1652
1n	OMe	Cl	0.45	-1.00	-0.30			-1.698	-10.141	1656 <sup>e)</sup>
1o	SMe	Cl	0.69	-0.87	-0.22	2.02 <sup>d)</sup>	2.20	-1.968	-10.106	1661 <sup>e)</sup>
1p	Cl	Cl	1.20	-0.72	0.01			-2.530	-11.290	1685 <sup>e)</sup>

a) Measured by cyclic voltammetry (V vs. SCE). CH<sub>3</sub>CN / Platinum electrode / Et<sub>4</sub>NClO<sub>4</sub> / 100 mV s<sup>-1</sup>.

b) Calculated by MNDO (eV)<sup>8)</sup>. c) KBr disk (cm<sup>-1</sup>). d) Oxidation peak potential. e) Weighted average of some bands.

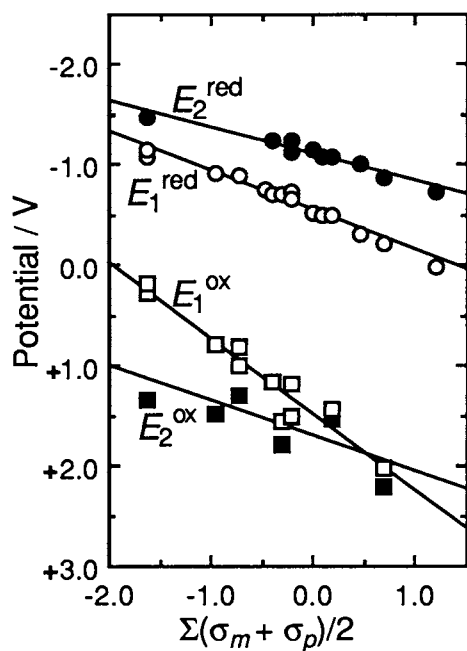


Fig. 1. Plot of redox potential of substituted *p*-benzoquinones vs.  $\Sigma(\sigma_m + \sigma_p)/2$ .

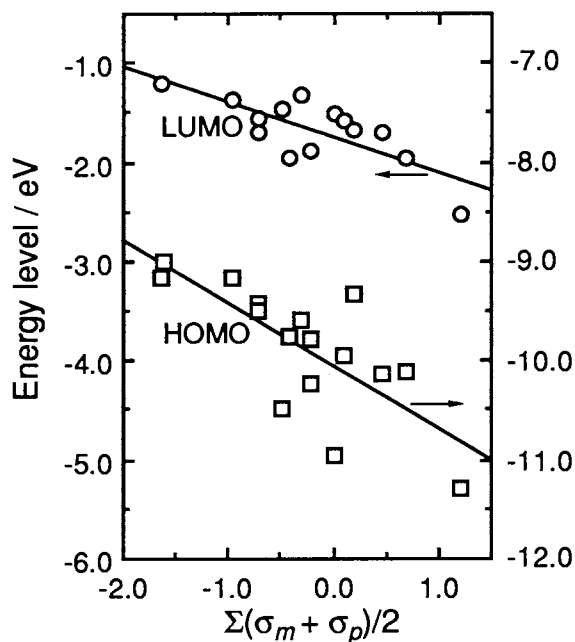


Fig. 2. Plot of LUMO and HOMO levels of substituted *p*-benzoquinones vs.  $\Sigma(\sigma_m + \sigma_p)/2$ .

Table 2. Correlation coefficients for the plots of redox potentials and carbonyl stretching frequencies against Hammett substituent constants

Substituent constant	Correlation coefficient				
	$E_2^{\text{red}}$	$E_1^{\text{red}}$	$E_1^{\text{ox}}$	$E_2^{\text{ox}}$	$\nu_{\text{C=O}}$
$\Sigma(\sigma_m + \sigma_p)/2$	0.969	0.983	0.965	0.709	0.865
$\Sigma\sigma_m$	0.930	0.932	0.990	0.792	0.843
$\Sigma\sigma_p$	0.936	0.960	0.934	0.653	0.834
$\Sigma(\sigma_m^+ + \sigma_p^+)/2$	0.899	0.931	0.972	0.825	0.880
$\Sigma\sigma_m^+$	0.934	0.943	0.959	0.732	0.814
$\Sigma\sigma_p^+$	0.810	0.867	0.966	0.851	0.856

obtained for the potential of the second reduction ( $E_2^{\text{red}}$ ) against  $\Sigma(\sigma_m + \sigma_p)/2$ . The deviation caused by the steric substituent effect, which was observed by Zuman<sup>9)</sup> and Brown,<sup>10)</sup> is negligibly small because of the large change in the reduction potentials observed for this series of compounds. The linearity becomes poor if  $E_1^{\text{red}}$  and  $E_2^{\text{red}}$  are plotted against  $\sigma_m$  or  $\sigma_p$  alone instead of  $\Sigma(\sigma_m + \sigma_p)/2$  (Table 2).

It is noteworthy that most of the quinones in Table 1 showed the oxidation peak potentials ( $E_1^{\text{ox}}$ ). The  $E_1^{\text{ox}}$  data can be also linear to  $\Sigma(\sigma_m + \sigma_p)/2$ . The use of some other Hammett substituent constants gives better

linearity (Table 2). The fact that all the quinones substituted with  $\pi$ -donor groups ( $\text{NH}_2$ ,  $\text{NMe}_2$ ,  $\text{OMe}$ , and  $\text{SMe}$ ) show  $E_1^{\text{ox}}$  suggests that the positive charge of the resulting radical cation is distributed predominantly on the heteroatoms of the substituents rather than on the quinone oxygen atoms. Furthermore, seven quinones including the four newly synthesized ones showed the second oxidation peaks ( $E_2^{\text{ox}}$ ). Among the substituted *p*-quinones, **1a**, **1m**, and **1o** were unique in exhibiting all four of the redox processes shown in Eq. 1.

The observation of good linearity for  $E_1^{\text{red}}$ ,  $E_2^{\text{red}}$ , and  $E_1^{\text{ox}}$  over a wide range of substituents allows us to discuss on the relative sensitivity of these potentials toward the substituent effect. The lower sensitivity of  $E_2^{\text{red}}$  to  $\Sigma(\sigma_m + \sigma_p)/2$  relative to that of  $E_1^{\text{red}}$  indicates that semiquinone radical anion  $1^{\cdot-}$  is destabilized to a larger extent by stronger electron-donating substituents. That is, there exists a linear relationship between the semiquinone formation constant expressed by  $\ln K = (F/RT)(E_1^{\text{red}} - E_2^{\text{red}})$ <sup>12</sup> and  $\Sigma(\sigma_m + \sigma_p)/2$ . In addition, a measure of amphotericity,  $E^{\text{sum}} = E_1^{\text{ox}} - E_1^{\text{red}}$ ,<sup>13</sup> is a linear function of  $\Sigma(\sigma_m + \sigma_p)/2$ . This suggests narrow HOMO – LUMO gaps of quinones with electron-donating substituents. In fact, LUMO and HOMO energy levels calculated by MNDO (Table 1) show roughly linear dependence on  $\Sigma(\sigma_m + \sigma_p)/2$  (Fig. 2) with slopes that are in good agreement (0.35 and 0.63 eV, respectively) with those for  $E_1^{\text{red}}$  and  $E_1^{\text{ox}}$  (0.40 and 0.76 V, respectively).

In accordance with the electrochemical behavior, the carbonyl stretching frequency ( $\nu_{\text{C=O}}$ ) linearly correlates to  $\Sigma(\sigma_m + \sigma_p)/2$ , reflecting the increasing contribution of polarized structure ( $>\text{C}^+ - \text{O}^-$ ) by introduction of electron-donating substituents. This result provides another information for predicting the property of complexes such as quinhydrone in which the carbonyl oxygen of the quinone participates in the hydrogen bonding.

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