Kinetics of Electron-transfer Reactions of *para*-Substituted Phenols *p*-C₆H₄(X)OH with [Fe(phen)₃]³⁺ (phen = 1,10-phenanthroline) and with [IrCl₆]²⁻ in Aqueous Acidic Solutions: Correlation between the Hammett Constant of X and the One-electron Redox Potential of *p*-C₆H₄(X)OH

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Kinetic studies of the electron-transfer reactions of p-C₆H₄(X)OH (X = H, CH₃, OCH₃, OH, NH₂, or NH₃⁺) with tris(1,10-phenanthroline)iron(III), [Fe(phen)₃]³⁺, and with hexachloroiridate(IV), [IrCl₆]²⁻, have been made in aqueous acidic solutions. The second-order rate constants (k_0) follow the rate law $-d[A]/dt = k_0[A][p$-C₆H₄(X)OH], where A is the one-electron acceptor [Fe(phen)₃]³⁺ or [IrCl₆]²⁻, and were determined at an ionic strength of 1.0 mol dm⁻³ and 25 °C. The order of the forward rate constants (k_f) for the one-electron transfer step, which are defined as $k_0 = k_f$ for X = H and CH₃ and as $k_0 = 2k_f$ for the other X, was H < NH₃⁺ < CH₃ < OCH₃ < OH < NH₂ in approximate ratio $1:35:76:7 \times 10^4:1.5 \times 10^5:1.1 \times 10^7$ in the case of [Fe(phen)₃]³⁺ and $1:150:75:4 \times 10^4:7.2 \times 10^4:1.0 \times 10^8$ in the case of the [IrCl₆]²⁻ reactions. By applying Marcus theory to k_f, standard redox potentials for the radical cations p-C₆H₄(X)OH·⁺ were estimated and found to be well correlated with the Hammett constants (σ_p) for the *para* substituents X.

Previously [1-3] we have found that the rates of the electron-transfer reactions of some organic substrates are governed by the energies of the highest occupied molecular orbitals (E_{homo}) of the substrate, and also by the differences in total electronic energies between the substrate and its radical cation (ΔE_T); both E_{homo} and ΔE_T are well correlated with the standard redox potentials of the radical cations of the substrates. The rates of these electron-transfer reactions can thus be considered essentially to be correlated with the electron density on the substrate. Now the electron-releasing or -attracting tendency of a substituent on a benzene ring can be expressed by the Hammett substituent constant, which can thus be employed to predict the extent of the electron density on the benzene ring. Consequently, we would expect the Hammett substituent constants to be correlated with the rates of electron-transfer reactions of derivatives such as *p*-phenols with one-electron oxidants.

In the present paper we demonstrate a correlation between the Hammett constant (σ_p) and the standard redox potential (E°) of the radical cation of *p*-phenol derivatives *p*-C₆H₄(X)OH (X = H, CH₃, OCH₃, OH, NH₂, or NH₃⁺). The values of E° were determined by applying Marcus theory [4] to the rate constants of electron-transfer reactions of *p*-C₆H₄(X)OH with tris(1,10-phenanthroline)iron(III) and with hexachloro-iridate(IV).
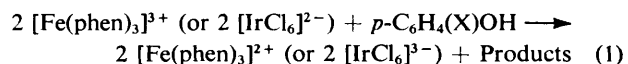
Experimental

Chemicals.—Reagent grade Na₂[IrCl₆], phenol, and *p*-phenol derivatives (Wako Pure Chemical Co.) were used without further purification. The solutions of the reagents were each prepared immediately before use. The salt [Fe(phen)₃]-[ClO₄]₃ (phen = 1,10-phenanthroline) was prepared by oxidizing [Fe(phen)₃]²⁺ with lead(IV) dioxide in dilute sulphuric acid solution; after removal of unchanged lead dioxide and lead(II) sulphate, the perchlorate salt of tris(1,10-phenanthroline)iron(III) was precipitated by addition of Na[ClO₄] and recrystallized from perchlorate solution. A stock solution of [Fe(phen)₃]³⁺ was prepared by dissolving the perchlorate salt in concentrated perchloric acid (70%, v/v). It is quite stable and the concentration does not change for at least 3 months. Sodium perchlorate used for adjusting the ionic strength was recrystallized twice from aqueous solution.

Deionized water was further distilled with and without addition of some permanganate in a glass still.

Kinetic Measurements.—The kinetic experiments were carried out by using a Union RA-401 stopped-flow spectrometer for the reactions of phenol and the *p*-phenol derivatives with [Fe(phen)₃]³⁺, following the increase in absorbance of [Fe(phen)₃]²⁺ at 510 nm, and with [IrCl₆]²⁻, following the decrease in absorbance of the latter at 487 nm. Air dissolved in the reaction solutions and in the cell housing was removed by passage of pure nitrogen gas. Unless otherwise stated, the concentrations of *p*-C₆H₄(X)OH (X = H, CH₃, OCH₃, OH, or NH₂) were kept at least 10 times larger than those of the oxidizing agents in order to ensure pseudo-first-order conditions. Since the rates of reaction of *p*-C₆H₄(OH)₂ and *p*-C₆H₄-(OCH₃)OH with [Fe(phen)₃]³⁺ were extremely fast, second-order conditions were adopted in these cases. The observed rate constants were evaluated from a kinetic curve averaged over 10 runs, the stopped-flow apparatus being equipped with a microcomputer for memorizing and averaging multiple kinetic runs. The acidity was kept constant at 0.11 mol dm⁻³ with perchloric acid, except in the case of reactions of *p*-C₆H₄-(NH₂)OH. For reactions of the latter with [Fe(phen)₃]³⁺ and [IrCl₆]²⁻ the kinetic runs were carried out in solutions of various concentrations of perchloric acid. The ionic strength was adjusted to 1.0 mol dm⁻³ by the addition of sodium perchlorate solution. The temperature (±0.1 °C) of the cell housing was regulated by circulation of thermostatted water.

Results and Discussion

Stoicheiometry.—Titration of [Fe(phen)₃]³⁺ or [IrCl₆]²⁻ with *p*-C₆H₄(X)OH (X = OH, OCH₃, or NH₂), monitoring the absorbance at 510 nm due to [Fe(phen)₃]²⁺ or that at 487 nm due to [IrCl₆]²⁻, gave a stoicheiometry of 2 : 1 for both the ratios [Fe(phen)₃³⁺] : [*p*-C₆H₄(X)OH] and [IrCl₆²⁻] : [*p*-C₆H₄(X)OH]. Thus, the stoicheiometric equation (1) can

$$2 \text{ [Fe(phen)}_3]^{3+} \text{ (or 2 [IrCl}_6]^{2-}) + p\text{-C}_6\text{H}_4(\text{X})\text{OH} \longrightarrow$$
$$2 \text{ [Fe(phen)}_3]^{2+} \text{ (or 2 [IrCl}_6]^{3-}) + \text{Products} \quad (1)$$

be written where the products are probably quinone and hydrogen ions for X = OH; quinone, H⁺, and methanol for

X = OCH₃; and quinone, H⁺, and NH₄⁺ for X = NH₂ (or NH₃⁺). The stoicheiometry for reactions of C_6H_5OH and p-$C_6H_4(CH_3)OH$ with [Fe(phen)₃]³⁺ or [IrCl₆]²⁻ could not be determined, because some complicated and slow reactions occurred subsequently to a fast one-electron transfer; the radical cations which are produced by the electron-transfer reaction cannot be further oxidized to quinone, and may be converted into a peroxide such as $C_6H_5OOC_6H_5$ or $CH_3C_6H_4$-$OOC_6H_4CH_3$ which could react slowly with the oxidants [Fe(phen)₃]³⁺ and [IrCl₆]²⁻. Moreover, the reverse of reaction (2) is apt to occur.

$$[Fe(phen)_3]^{3+} \text{ (or } [IrCl_6]^{2-}) + C_6H_5OH \text{ [or } p\text{-}C_6H_4(CH_3)OH]$$

$$\underset{k_b}{\overset{k_f}{\rightleftharpoons}} C_6H_5OH^{\cdot+} \text{ [or } p\text{-}C_6H_4(CH_3)OH^{\cdot+}] +$$

$$[Fe(phen)_3]^{2+} \text{ (or } [IrCl_6]^{3-}) \quad (2)$$
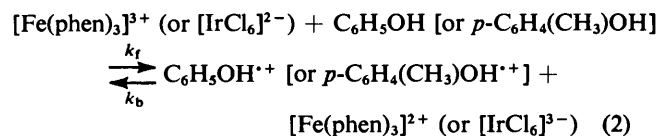
Kinetics of Reaction.—The kinetic runs were carried out at 0.1—1.0 mol dm⁻³ perchloric acid for the p-$C_6H_4(NH_2)OH$ reactions and at 0.1 mol dm⁻³ perchloric acid for the other reactions so that the acid dissociation of phenolic OH could be neglected.⁵ For the reactions of p-$C_6H_4(NH_2)OH$ with [Fe(phen)₃]³⁺, and those of p-$C_6H_4(X)OH$ (X = OH, OCH₃, or NH₂) with [IrCl₆]²⁻, when pseudo-first-order conditions were adopted, plots of ln $(A_\infty - A_t)$ vs. t for the [Fe(phen)₃]³⁺ systems and those of ln $(A_t - A_\infty)$ vs. t for the [IrCl₆]²⁻ systems were linear for at least 80% completion of reaction. For the reactions of p-$C_6H_4(OH)_2$ and p-$C_6H_4(OCH_3)OH$ with [Fe(phen)₃]³⁺, when second-order conditions with [Fe(phen)₃³⁺] = 2[p-$C_6H_4(X)OH$] were adopted, plots of $1/(A_\infty - A_t)$ vs. t were linear for at least 60% completion of reaction. For the reactions of C_6H_5OH and p-$C_6H_4(CH_3)OH$ with [Fe(phen)₃]³⁺ or [IrCl₆]²⁻ a large excess of C_6H_5OH or p-$C_6H_4(CH_3)OH$ over the oxidant was used; plots of ln $(A_\infty - A_t)$ vs. t for the [Fe(phen)₃]³⁺ systems and of ln $(A_t - A_\infty)$ vs. t for the [IrCl₆]²⁻ systems were rectilinear for the initial stages but then deviated from straight lines. The deviation is thought to be due mainly to the reverse of reaction (2). Therefore, for these two cases with C_6H_5OH and p-$C_6H_4(CH_3)OH$ the initial slopes of plots of A_t vs. t were used for determination of the forward rate constants (k_f).

The empirical rate law (3) can be written for all the reaction systems in the present study, where A = [Fe(phen)₃]³⁺ or

$$-d[A]/dt = k_0[A][D] \quad (3)$$

[IrCl₆]²⁻ and D = p-$C_6H_4(X)OH$ (X = H, CH₃, OCH₃, OH, NH₂, or NH₃⁺). Since both the ions [Fe(phen)₃]³⁺ and [IrCl₆]²⁻ are one-electron oxidants, the oxidation of p-$C_6H_4(X)OH$ could occur favourably *via* two successive one-electron-transfer reactions (4) and (5). Assuming steady-state

$$A + D \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A^- + D^+ \quad (4)$$

$$A + D^+ \overset{k_p}{\longrightarrow} A^- + \text{Products} \quad (5)$$
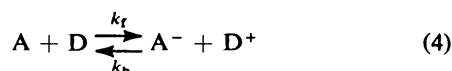
concentrations for D⁺, equation (6) can be derived. Under the condition $k_b[A^-] \ll k_p[A]$, this equation can be written as (7), thus $k_0 = 2k_f$. This was satisfied in the case of p-

$$-\frac{d[A]}{dt} = \left(\frac{2k_p[A]}{k_b[A^-] + k_p[A]}\right)k_f[A][D] \quad (6)$$
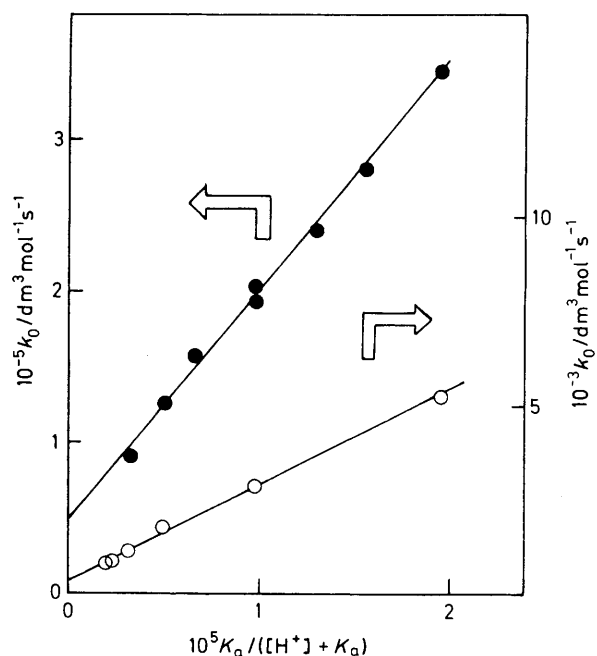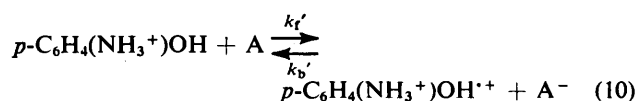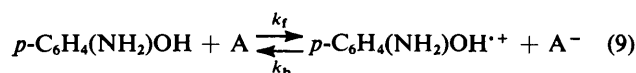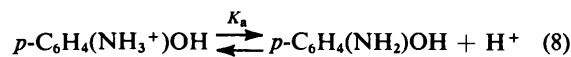
$$-d[A]/dt = 2k_f[A][D] \quad (7)$$

Figure 1. Plots of k_0 vs. $K_a/([H^+] + K_a)$ according to equation (12) for the reaction between p-$C_6H_4(NH_2)OH$ and [Fe(phen)₃]³⁺ (●) and between p-$C_6H_4(NH_2)OH$ and [IrCl₆]²⁻ (O) at 25 °C and ionic strength 1.0 mol dm⁻³. Initial concentrations of reactants: [Fe(phen)₃³⁺] = 5 × 10⁻⁶, [IrCl₆²⁻] = 1 × 10⁻⁴, and [p-C_6H_4(NH₂)OH] = 2 × 10⁻⁴ (●) and 1 × 10⁻³ mol dm⁻³ (O)

$C_6H_4(X)OH$ where X = OH, OCH₃, NH₂, or NH₃⁺. For the reactions of p-$C_6H_4(NH_2)OH$ with [Fe(phen)₃]³⁺ and [IrCl₆]²⁻ the k_0 values decreased with increasing hydrogen-ion concentration and plots of k_0 vs. $K_a/([H^+] + K_a)$ were linear with an intercept (Figure 1).

The mechanism in equations (8)—(11) accounts for the results illustrated in Figure 1, where the radicals are the

$$p\text{-}C_6H_4(NH_3^+)OH \underset{}{\overset{K_a}{\rightleftharpoons}} p\text{-}C_6H_4(NH_2)OH + H^+ \quad (8)$$

$$p\text{-}C_6H_4(NH_2)OH + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} p\text{-}C_6H_4(NH_2)OH^{\cdot+} + A^- \quad (9)$$

$$p\text{-}C_6H_4(NH_3^+)OH + A \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}}$$
$$p\text{-}C_6H_4(NH_3^+)OH^{\cdot+} + A^- \quad (10)$$

$$\text{Radicals} + A \overset{k_p}{\longrightarrow} \text{Products} + A^- \quad (11)$$

radical cations p-$C_6H_4(NH_2)OH^{\cdot+}$ and p-$C_6H_4(NH_3^+)OH^{\cdot+}$ and the products are the same as those in equation (1). Assuming steady-state concentrations for the radicals and that $(k_b + k_b')[A^-] \ll k_p[A]$, equation (12) can be derived which is consistent with the results obtained. The value of K_a was

$$k_0 = 2\left\{k_f' + (k_f - k_f') \cdot \frac{K_a}{K_a + [H^+]}\right\} \quad (12)$$

determined as 2.14 × 10⁻⁶ mol dm⁻³ at an ionic strength of 1.0 mol dm⁻³ and 25 °C, by the pH titration method; a value of 0.77 was used for the activity coefficient of hydrogen ion. The rate constants k_f (and k_f') obtained are in Table 1.

According to Marcus theory,⁴ the variation of the excess free energy of activation for a cross reaction $(\Delta G_{12}^\ddagger)$ with the

Table 1. Forward rate constants (k_f) in equation (4) at 25 °C and at an ionic strength of 1.0 mol dm^{-3}

D	k_f/dm^3 mol^{-1} s^{-1}	
	a	b
p-C$_6$H$_4$(NH$_2$)OH	7.54 × 10^9	1.23 × 10^8
p-C$_6$H$_4$(OH)$_2$	1.10 × 10^8	8.69 × 10^4
p-C$_6$H$_4$(OCH$_3$)OH	5.11 × 10^7	4.56 × 10^4
p-C$_6$H$_4$(CH$_3$)OH	5.5 × 10^4	90
C$_6$H$_5$OH	7.2 × 10^2	1.2
p-C$_6$H$_4$(NH$_3$$^+$)OH	2.5 × 10^4 [c]	180 [c]

[a] A = [Fe(phen)$_3$]$^{3+}$. [b] A = [IrCl$_6$]$^{2-}$. [c] Corresponds to k_f' in equation (10).

Table 2. Standard redox potentials ($E^\ominus$) of the radical cations p-C$_6$H$_4$(X)OH$^{\cdot+}$ and activation parameters *

X in p-C$_6$H$_4$-(X)OH	$\dfrac{\Delta G_{12}^{\ddagger}}{\text{kJ mol}^{-1}}$		$\dfrac{\Delta G_{12}^{\ominus}}{\text{kJ mol}^{-1}}$		$E^\ominus$/V	
NH$_2$	6.23	16.7	−31.5	−24.5	0.73	0.70
OH	16.9	34.6	−3.59	13.3	1.02	1.09
OCH$_3$	18.8	36.2	0.299	16.0	1.06	1.12
CH$_3$	35.7	51.6	28.6	40.6	1.36	1.38
H	46.5	62.3	43.2	55.6	1.51	1.53
NH$_3$$^+$	38.5	50.2	32.6	38.5	1.40	1.36

* The following parameters were used for the estimation of $\Delta G_{12}^{\ominus}$ and $E^\ominus$: $\lambda_{12} = 74.6$ and 110.2 kJ mol^{-1} for the reactions with [Fe(phen)$_3$]$^{3+}$ and with [IrCl$_6$]$^{2-}$, respectively; $E^\ominus\{[\text{Fe(phen)}_3]^{3+/2+}\}$ = 1.06 V [9] and $E^\ominus([\text{IrCl}_6]^{2-/3-})$ = 0.957 V.[10] The first value in each column was evaluated from the [Fe(phen)$_3$]$^{3+}$ system, the second from the [IrCl$_6$]$^{2-}$ system.

standard free-energy change ($\Delta G_{12}^{\ominus}$) for a redox step such as that in equation (4) can be expressed by use of equations (13)—(16). Here Z is the collision frequency in solution

$$k_{12} = Z \exp\left(-\Delta G_{12}^{\ddagger}/RT\right) \tag{13}$$

$$\Delta G_{12}^{\ddagger} = \omega_{12} + \lambda_{12}(1 + \Delta G_{12}^{\ominus\prime}/\lambda_{12})^2/4 \tag{14}$$

$$\Delta G_{12}^{\ominus\prime} = \Delta G_{12}^{\ominus} + \omega_{12} - \omega_{21} \tag{15}$$

$$\lambda_{12} = 2(\Delta G_{11}^{\ddagger} - \omega_{11} + \Delta G_{22}^{\ddagger} - \omega_{22}) \tag{16}$$

(usually taken as 10^{11} dm^3 mol^{-1} s^{-1} at 25 °C), $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$ are the free energies of activation for the self-exchange electron-transfer reactions, ω_{11} and ω_{22} represent the work terms involved in the same reactions, ω_{12} and ω_{21} are the work terms required to bring the reactants or products together in the activated complex, and $\lambda_{12} = \lambda_i + \lambda_o$ where λ_o is the solvent reorientation term and λ_i represents the contribution from the changes in inner-sphere bond lengths and angles in the activated state. If we adopt values for the self-exchange rate constant k_{22} of 3 × 10^8 dm^3 mol^{-1} s^{-1} for [Fe-(phen)$_3$]$^{3+/2+}$,[6] 2.3 × 10^5 dm^3 mol^{-1} s^{-1} for [IrCl$_6$]$^{2-/3-}$,[7] and k_{11} of 1 × 10^7 dm^3 mol^{-1} s^{-1} for p-C$_6$H$_4$(X)OH/p-C$_6$H$_4$(X)-OH$^{\cdot+}$,[8] we obtain $\Delta G_{22}^{\ddagger}$ = 20.0 and 32.2 kJ mol^{-1} for [Fe(phen)$_3$]$^{3+/2+}$ and [IrCl$_6$]$^{2-/3-}$, respectively, and $\Delta G_{11}^{\ddagger}$ = 23 kJ mol^{-1} for p-C$_6$H$_4$(X)OH/p-C$_6$H$_4$(X)OH$^{\cdot+}$. The work terms evaluated by the treatment reported previously [1] are zero for ω_{12}, ω_{21}, and ω_{11} and 0.08 kJ mol^{-1} for ω_{22} at an ionic strength of 1.0 mol dm^{-3} at 25 °C. Consequently, we obtain λ_{12} = 74.6 and 110.2 kJ mol^{-1} for the reactions between [Fe(phen)$_3$]$^{3+}$ and p-C$_6$H$_4$(X)OH and between [IrCl$_6$]$^{2-}$ and p-C$_6$H$_4$(X)OH, respectively. Values of $\Delta G_{12}^{\ddagger}$
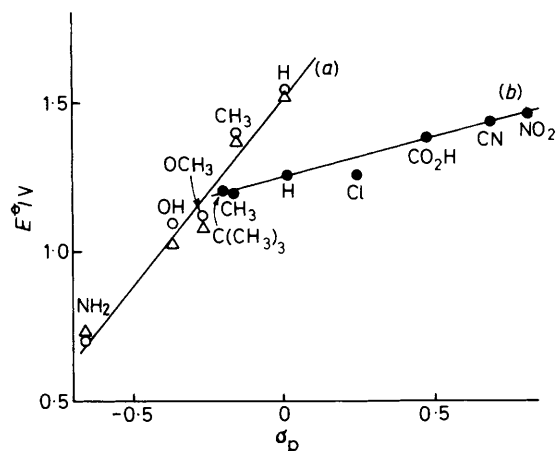
Figure 2. Correlation between Hammett constant (σ_p) of X and the one-electron redox potential ($E^\ominus$) of p-C$_6$H$_4$(X)OH (a) and C$_6$H$_3$(X)(OH)$_2$ (b). Results for p-C$_6$H$_4$(X)OH obtained in the present study pertain to the [Fe(phen)$_3$]$^{3+}$ (△) and [IrCl$_6$]$^{2-}$ (○) reaction systems. The $E^\ominus$ data for 4-substituted benzene-1,2-diols (●) were taken from ref. 11. The Hammett constants were taken from H. C. Brown and Y. Okamoto (*J. Am. Chem. Soc.*, 1958, **80**, 4970). The substituents X are indicated and the correlation lines are drawn arbitrarily

can be obtained from the rate constants (k_f) in Table 1 by use of equation (13). Thus, from λ_{12}, $\Delta G_{12}^{\ddagger}$, and the work terms, $\Delta G_{12}^{\ominus}$ can be estimated. This in turn allows the estimation of the standard redox potential of the radical cations p-C$_6$H$_4$-(X)OH$^{\cdot+}$. By using $E^\ominus$ = 1.06 V [9] for [Fe(phen)$_3$]$^{3+/2+}$ and $E^\ominus$ = 0.957 V [10] for [IrCl$_6$]$^{2-/3-}$, values of the standard redox potentials for the radical cations were estimated and are shown in Table 2 together with values of $\Delta G_{12}^{\ddagger}$ and $\Delta G_{12}^{\ominus}$.

It is of interest to compare the redox potentials between p-C$_6$H$_4$(X)OH and p-C$_6$H$_4$(X)OH$^{\cdot+}$ (Table 2) and the Hammett constant (σ_p) of X for the *para* substituent on the benzene ring. Figure 2 shows the linear plots of $E^\ominus$ vs. σ_p in the cases of p-C$_6$H$_4$(X)OH and 4-substituted benzene-1,2-diols C$_6$H$_3$(X)-(OH)$_2$. The difference in slopes is thought to reflect the difference in total electronic energies of phenol and benzene-1,2-diol. The values of $E^\ominus$ for the benzene-1,2-diols were taken from ref. 11. It should be noted that correlations such as those demonstrated will hold only if the mechanism is unchanged throughout the reaction series.

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