One-Electron Redox Potentials of Phenols in Aqueous Solution

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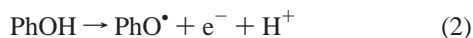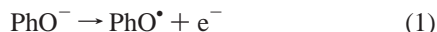*Department of Chemistry, Boston University, Boston, Massachusetts 02215*

Received: September 22, 1998; In Final Form: June 3, 1999

The oxidation peak potentials (E_p) of 31 phenolate, chlorophenolate, and other para-substituted phenolate ions were measured as a function of scan rate, substrate concentration, and pH by cyclic voltammetry in aqueous solution. The one-electron reduction potentials (E_{red}^o) of the phenoxyl radical/phenolate ion couples were evaluated from E_p and the rate constants for dimerization of the phenoxyl radicals. The dependence of E_{red}^o on pH was established, and the relationships that connect E_{red}^o with the Brown σ^+ constant, the pK_a values of the phenols and the protonated phenoxyl radical cations, and the reduction potentials of the protonated radicals were explored.

Introduction

In addition to their being important environmental pollutants in aqueous solution, phenol and its substituted analogues are facile one-electron reducing agents that are often involved in electrochemical, photochemical, and radiation chemical electron-transfer reactions. Phenols are oxidized by one electron to phenoxyl radicals, which generally decay via rapid dimerization,[1] although severely hindered radicals can be long-lived in solution.

To evaluate the energetics of electron-transfer reactions that involve phenols, phenolate ions, and phenoxyl radicals in aqueous solutions, their electrochemical potentials in water must be known. Although the oxidation of phenolate ions (generically PhO$^-$) to their corresponding phenoxyl radicals (PhO$^\bullet$) is straightforward (reaction 1), the oxidation of phenols (PhOH) involves loss of H$^+$ (reaction 2), making the potentials pH dependent. In addition, the instability of phenoxyl radicals toward dimerization in aqueous solution (reaction 3) generally leads to irreversible cyclic voltammetric (CV) waves because the time frame of the CV scan is too long to detect any current from the reduction of the radicals.

$$PhO^- \rightarrow PhO^\bullet + e^- \qquad (1)$$

$$PhOH \rightarrow PhO^\bullet + e^- + H^+ \qquad (2)$$

$$2PhO^\bullet \rightarrow \text{dimerization products} \qquad (3)$$

However, CV can be used to evaluate the standard reduction potential (E_{red}^o) of the oxidized half of a couple that involves reactive radicals through the measurement of the one-electron oxidation peak potential (E_p) as a function of the scan rate (ν) and the application of eq 4,[2−5] where $2k$ is the rate constant of reaction 3 and C^o is the bulk concentration of the oxidized species. This technique was used by Harriman who obtained values of E_{red}^o for the reduction of PhO$^\bullet$ from phenol (pH 7), *p*-cresol (pH 7), and *p*-methoxyphenol (pH 7 and pH 13) of 0.86, 0.77, 0.66, and 0.44 V (vs NHE), respectively;[6] Thanasekaran et al. recently reported a value of 0.35 V (vs SCE) for phenol at pH 12.5 obtained by use of the same technique.[7]

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All in all, there are very few electrochemically determined potentials for the oxidation of phenols and phenolate ions in aqueous solution.[8]

$$E_p = E_{red}^o + 0.902\frac{RT}{F} - \frac{RT}{3F}\ln\left(\frac{2kC^o}{\nu}\frac{2RT}{3F}\right) \qquad (4)$$

On the other hand, pulse radiolysis has been used to obtain values of E_{red}^o for a number of phenoxyl radical/phenolate ion couples in alkaline aqueous solution.[9−19] In this technique, oxidized or reduced species are rapidly generated by the reaction of the substrate with the primary water radicals in the presence of an electron donor or acceptor of known potential. The successful use of this method requires that equilibrium between the phenolate ion and phenoxyl radical be established much faster than the removal of phenoxyl radicals via dimerization reaction 3.

In this cyclic voltammetric study, E_p was determined for 31 deprotonated phenols in aqueous solution at pH 12 as a function of ν, from which were calculated values of E_{red}^o for the phenoxyl radical/phenolate ion couples; comparison with E_{red}^o from pulse radiolysis studies demonstrates the efficacy of the electrochemical technique. Values of E_p were also obtained as a function of pH for phenol and 2-chlorophenol from which were extracted values of E_{red}^o in acidic solution for all the substrates by assuming that they all are similarly behaved. The oxidation potentials (E_{ox}^o) of the phenolate ions and the phenols in generic reactions 1 and 2, respectively, are equal to $-E_{red}^o$.

Experimental Methods

Materials. Phenols[20] were purchased from Aldrich or Lancaster and were purified by sublimation if the stated purity was <99%. Distilled water was further purified by passage through a Millipore purification train. NaOH was Baker Analyzed Reagent; ferrocene and [(C$_2$H$_5$)$_4$N]ClO$_4$ were obtained from Aldrich.

Instrumentation. The one-electron oxidation peak potentials of the phenolate ions were determined by cyclic voltammetry in 0.01 M aqueous NaOH solution; in some experiments, the pH of the solution was varied. Voltammograms were recorded with a computer-controlled potentiostat (EG&G PAR model 273A with M270A software) capable of scan rates of 1−5000
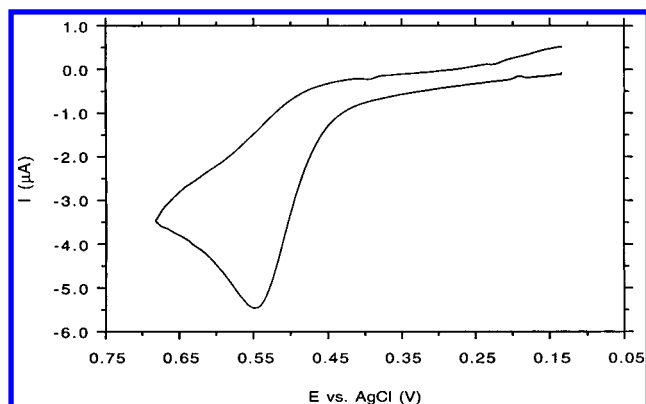
Figure 1. CV scan ($\nu = 0.1$ V s^{-1}) for 0.32 mM PhOH at pH 12 in 0.12 M (C$_2$H$_5$)$_4$NClO$_4$.
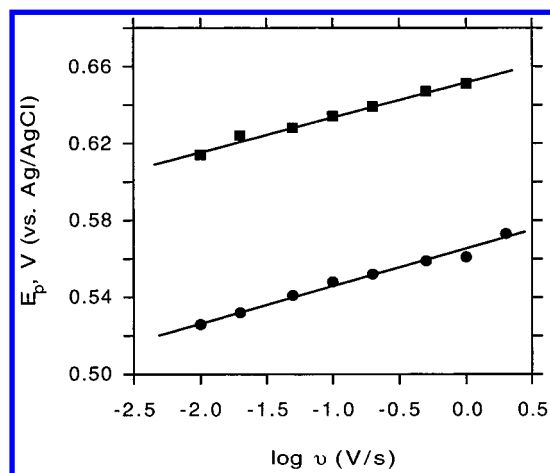

Figure 2. E_p as a function of log ν for PhOH (●) and 2-ClPhOH (■) at pH 12.

mV s^{-1}. The three-electrode system consisted of a glassy carbon (GC) working electrode, an aqueous Ag/AgCl/saturated KCl reference electrode ($E°$ vs NHE = $E°$ vs Ag/AgCl + 0.197),[21] and a Pt counter electrode. Conventional GC disk electrodes (d = 3 mm) or minielectrodes (d = 1 mm) were used. Before each voltammogram, the working electrode was carefully polished with Raybright gem polish (Raytech) and rinsed with CH$_3$CN and H$_2$O. The potential of the reference electrode was checked against the ferrocene/ferrocenium couple. The electrochemical cell was thermostated at 20.0 ($\pm$0.1) °C with a Neslab water bath.

Procedures. Deaerated aqueous solutions of 0.32 mM of the phenol in the presence of 0.12 M [(C$_2$H$_5$)$_4$N]ClO$_4$ at pH 12 were used in the measurement of E_p as a function of the scan rate. The peak potentials for PhOH and 2-ClPhOH were also determined as a function of pH and substrate concentration.

Results

Figure 1 shows a typical CV scan (ν = 100 mV s^{-1}) for PhOH at pH 12; no return peak after the phenoxide ion oxidation was observed. The height of the oxidation peak, compared to the ferrocene system, corresponds to the transfer of 1F mol^{-1}. The cyclic scans were irreversible for all the phenols examined. E_p was determined as a function of ν, pH (for PhOH and 2-ClPhOH), and substrate concentration (for PhOH); the values of E_p are given in the Supporting Information. In accordance with eq 4, plots of E_p vs log ν (Figure 2) and E_p vs log [substrate] (Figure 3) are linear.
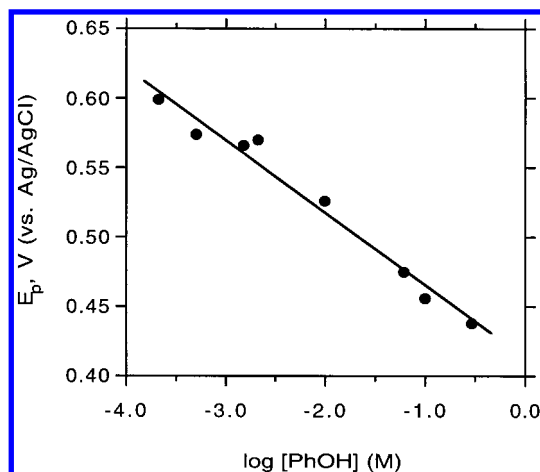

Figure 3. E_p as a function of log[PhOH] at pH 12.

Discussion

$E_{red}°$ for Phenoxyl Radical/Phenolate Ion Couples. To convert E_p to $E_{red}°$ with eq 4, values of 2k must be available. The dimerization rate constant of PhO• in H$_2$O is 2.6 × 10^9 M^{-1} s^{-1};[22−24] inasmuch as 2k varies by approximately a factor of 10 in CH$_3$CN,[25] which would result in a variation of only $\pm$19 mV in $E_{red}°$, the value of 2k of PhO• was assumed to be the same for the other phenolate ion systems as well. The error in $E_{red}°$ is taken as $\pm$19 mV even though E_p can be determined to $\pm$10 mV. Table 1 gives the pK_a values of the phenols from the literature, the values of $E_{red}°$(pH 12) (vs NHE) determined here for the phenoxyl radical/phenolate ion couples at pH 12, and the corresponding values from pulse radiolysis in alkaline solution. The generally good agreement of the values of $E_{red}°$ from the two techniques argues that the assumption is reasonably valid that the phenoxyl radicals in this study have similar values of 2k.

$E_{red}°$ as a Function of pH. As the results for PhOH and 2-ClPhOH show in Figure 4, $E_{red}°$ is constant at pH > pK_a; at pH < pK_a, $E_{red}°$ increases with increasing acidity. This behavior is in accord with the theoretical predictions of Stradins and Hasanli.[26] The dependencies of $E_{red}°$ on pH fit the Nernstian line quite well with a slope of −0.0582 V/pH at 20 °C, indicating that the reduction of the phenoxyl radicals at pH < pK_a involves the concerted gain of an electron and a proton (reverse of reaction 2).

Because of the low solubility of most of the phenols in neutral and acidic solution, values of $E_{red}°$ at pH < pK_a could not be directly obtained. Instead, $E_{red}°$(pH 12) was determined; by assuming that the other phenols follow the pattern shown by PhOH and 2-ClPhOH as expressed by eq 5, values of $E_{red}°$ at 20 °C for the phenoxyl radicals from the phenols at any pH < pK_a ($E_{red}°$(pH)) can be calculated.

$$E_{red}°(\text{pH}) = E_{red}°(\text{pH 12}) + 0.0582(\text{p}K_a - \text{pH}) \quad (5)$$

It should be noted that, in the case of 4-HOPhOH, the pK_a values for the first and second deprotonation steps occur around pH 11.5. Thus, at pH 12, where $E_{red}°$ was determined, the solution is a mixture of the three acid−base conjugates. The discrepancy between the values of $E_{red}°$ obtained here and by pulse radiolysis may reflect differences in the solution compositions, although Figure 4 shows that the potentials of PhOH and 2-ClPhOH do not change very much in the vicinity of the pK_a. The use of eq 5 is not valid for 4-HOPhOH and 4-HO$_2$CPhOH, both of which have two deprotonatable hydrogens.

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TABLE 1: Parameters for Phenols in Aqueous Solution

phenol	$pK_a{}^a$	σ^{+c}	$E_{red}{}^o$(pH 12)^f	$E_{red}{}^{o f,g}$	$pK_a{}'^h$	$E_{red}{}^{o\prime\ f,i}$
PhOH	9.98	0.00	0.86	0.79	−2.00	1.6
2-ClPhOH	8.52	0.086	0.93		−1.27	1.5
3-ClPhOH	8.97	0.40	0.88		−1.75	1.5
4-ClPhOH	9.37	0.11	0.85	0.80	−1.30	1.5
2,3-Cl$_2$PhOH	7.71	0.49	0.92			
2,4-Cl$_2$PhOH	7.90	0.21	0.88			
2,5-Cl$_2$PhOH	7.51	0.49	0.94			
2,6-Cl$_2$PhOH	6.80	0.17	0.90			
3,4-Cl$_2$PhOH	8.62	0.51	0.89			
3,5-Cl$_2$PhOH	8.25	0.80	0.88			
2,3,4-Cl$_3$PhOH	6.97	0.61	0.89			
2,3,5-Cl$_3$PhOH	6.43	0.89	0.94			
2,3,6-Cl$_3$PhOH	5.80	0.57	0.93			
2,4,5-Cl$_3$PhOH	6.72	0.61	0.90			
2,4,6-Cl$_3$PhOH	5.99	0.30	0.90	0.88		
2,3,4,6-Cl$_4$PhOH	5.22	0.70	0.97			
2,3,5,6-Cl$_4$PhOH	5.03	0.97	0.99			
Cl$_5$PhOH	4.74	1.1	0.99			
4-CNPhOH	7.95	0.66	1.14	1.12		
4-CHOPhOH	7.62	0.73	1.14			
4-HO$_2$CPhOH	5 (1),^{b}	−0.02 ^{d}	0.97	0.90		
	9.40 (2)					
4-O$_2$NPhOH	7.16	0.79	1.28	1.22	−1.79	1.8
4-*tert*-butylPhOH	10.39	−0.26	0.70	0.76		
4-FPhOH	9.92	−0.07	0.80	0.76	−1.59	1.5
4-BrPhOH	9.40	0.15	0.84	0.82		
4-IPhOH	9.33	0.14	0.81	0.82		
4-CH$_3$PhOH	10.28	−0.31	0.71	0.68	−1.60	1.4
4-C$_2$H$_5$PhOH	10.00	−0.30	0.71			
4-HOPhOH	11.40 (1),	−2.3 ^{e}	0.17	0.023	−1.33	
	11.65 (2)					
4-CH$_3$OPhOH	10.20	−0.78	0.58	0.54		
4-C$_2$H$_5$OPhOH	10.2 ^{c}	−0.25	0.56			

^{a} From ref 26. ^{b} Estimated value. ^{c} Evaluated as described in the text. ^{d} For (4-O$_2$CPhOH)$^-$. ^{e} For (4-OPhOH)$^-$. ^{f} In volts vs NHE. ^{g} From pulse radiolysis measurements in alkaline solution; refs 13, 16, and 17. ^{h} From refs 32−34. ^{i} Calculated from measured and estimated values of $E_{red}{}^o$(pH 12), pK_a, and $pK_a{}'$.
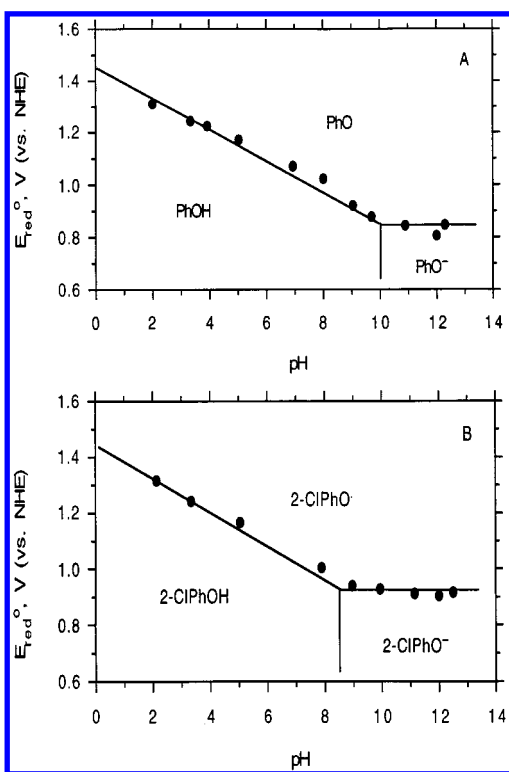

Figure 4. $E_{red}{}^o$ as a function of pH for PhOH (A) and 2-ClPhOH (B). Error bars of ±19 mV are within the points.

Correlation of $E_{red}{}^o$(pH 12) with σ^+. Good correlations of the reduction potentials for phenoxyl radicals with the σ^+ Brown

substituent constants for substituted phenols were found by others from pulse radiolysis,[13] reversible fast scan CV in CH$_3$-CN,[28] and irreversible CV;[29] it is more appropriate to use σ^+ than the Hammett σ constant because of the through-resonance between the electron-deficient phenoxyl radical site and the ring substituent. For the chlorophenols that contain more than one Cl substituent, σ^+ is taken as the sum of the individual contributions of each Cl in the corresponding monochlorophenols,[30] i.e., $\sigma^+ = \sigma_{o2}{}^+ + \sigma_{m3}{}^+ + \sigma_p{}^+ + \sigma_{m5}{}^+ + \sigma_{o6}{}^+$. Values of $\sigma_m{}^+$ and $\sigma_p{}^+$ of 0.40 and 0.11 are taken from the literature;[31] $\sigma_o{}^+$ is calculated from $\sigma_p{}^+$ with the relationship of Jonsson et al. ($\sigma_o{}^+ = 0.66\sigma_p{}^+$; 0.086 for Cl).[30] For the other para-substituted phenols, values of $\sigma_p{}^+$ ($=\sigma^+$) were taken from the literature.[31] The σ^+ values for 4-HOPhOH and 4-HO$_2$CPhOH are for their singly deprotonated forms.

A plot of $E_{red}{}^o$(pH 12) as a function of σ^+ (Table 1) for all 31 phenols is shown in Figure 5; a good linear correlation ($E_{red}{}^o$-(pH 12) = 0.81 + 0.26σ^+; corr. coef. = 0.90) is obtained. The results show, not unexpectedly, that the oxidation of phenolate ions is more facile when electron-donating substituents are present. The slope of the line yields a ρ^+ reaction constant (($\partial E^o/\partial\sigma^+$)/0.0582) of 4.5, indicating that the dipolar phenoxyl radical is stabilized by the partial transfer of negative charge from the substituent to the radical site.[13] The value of ρ^+ is in reasonably good agreement with values obtained for various para-substituted phenols from pulse radiolysis (7.0),[13] fast-scan CV in CH$_3$CN (6.8),[28] and irreversible potentials (9.3).[29]

Of course, the electron-withdrawing and -donating properties of the substituents on the ring affect both the acid−base behavior of the phenols and the reduction of the phenoxyl radicals, which
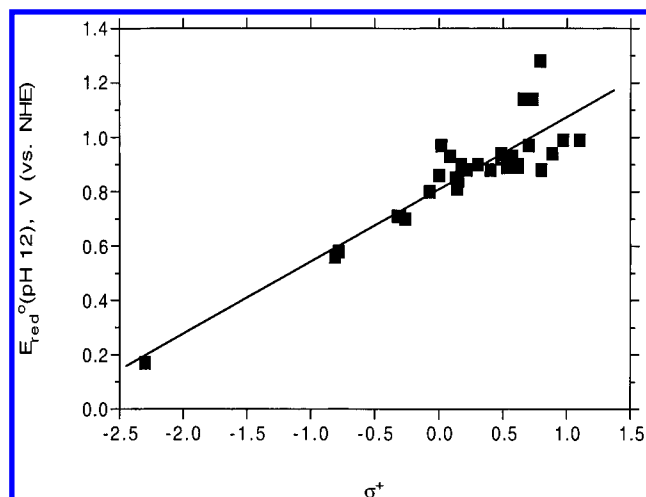
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Figure 5. E_{red}^{o}(pH 12) as a function of σ^+. Error bars of ± 19 mV are within the points.

is more facile as the acidity of the corresponding phenol increases. In other words, the oxidation of the phenols (loss of a negative charge) parallels the basicity of their conjugates (gain of a positive charge).

Dissociation Constants and Reduction Potentials of PhOH$^{\bullet+}$. Values of the acid dissociation constants of a number of protonated phenoxyl radicals (pK_a') have been determined in aqueous solution by EPR techniques;[32-34] the PhOH$^{\bullet+}$ species are very strong acids with negative pK_a' values. From the measured and estimated values of E_{red}^{o}(pH 12), pK_a, and pK_a', an application of a simple thermochemical cycle permits the reduction potentials of the PhOH$^{\bullet+}$ species ($E_{red}^{o'}$) that have only one acidic hydrogen to be estimated; $E_{red}^{o'} = E_{red}^{o}$(pH 12) $+ 0.0582($p$K_a -$ p$K_a')$. These data are given in Table 1 and show that the protonated phenoxyl radicals are stronger oxidizing agents than are their deprotonated conjugates.

Supporting Information Available: Tables of E_p as a function of scan rate, E_p as a function of pH for PhOH and 2-ClPhOH, and E_p as a function of [PhOH]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Abbreviations: phenol (PhOH), 2-chlorophenol (2-ClPhOH), 3-chlorophenol (3-ClPhOH), 4-chlorophenol (4-ClPhOH), 2,3-dichlorophenol (2,3-Cl$_2$PhOH), 2,4-dichlorophenol (2,4-Cl$_2$PhOH), 2,5-dichlorophenol (2,5-Cl$_2$PhOH), 2,6-dichlorophenol (2,6-Cl$_2$PhOH), 3,4-dichlorophenol (3,4-Cl$_2$PhOH), 3,5-dichlorophenol (3,5-Cl$_2$PhOH), 2,3,4-trichlorophenol (2,3,4-Cl$_3$PhOH), 2,3,5-trichlorophenol (2,3,5-Cl$_3$PhOH), 2,3,6-trichlorophenol (2,3,6-Cl$_3$PhOH), 2,4,5-trichlorophenol (2,4,5-Cl$_3$PhOH), 2,4,6-trichlorophenol (2,4,6-Cl$_3$PhOH), 2,3,4,6-tetrachlorophenol (2,3,4,6-Cl$_4$PhOH), 2,3,5,6-tetrachlorophenol (2,3,5,6-Cl$_4$PhOH), pentachlorophenol (Cl$_5$PhOH), 4-cyanophenol (4-CNPhOH), 4-hydroxybenzaldehyde (4-CHOPhOH), 4-hydroxybenzoic acid (4-HO$_2$CPhOH), 4-nitrophenol (4-O$_2$NPhOH), 4−*tert*-butylphenol (4-(CH$_3$)$_3$CPhOH), 4-fluorophenol (4-FPhOH), 4-bromophenol (4-BrPhOH), 4-iodophenol (4-IPhOH), *p*-cresol (4-CH$_3$PhOH), 4-ethylphenol (4-C$_2$H$_5$PhOH), 1,4-hydroquinone (4-HOPhOH), 4-methoxyphenol (4-CH$_3$OPhOH), 4-ethoxyphenol (4-C$_2$H$_5$OPhOH).

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