Proton Reactivity and Electronic Structure of Phenoxyl Radicals in Water[†]

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Application of proton reactivity in modeling the electronic structure of reactive chemical intermediates, interpreting their resonance Raman spectra in aqueous solution, and testing theoretical procedures has been demonstrated. The case of phenoxyl radicals (p-$XC_6H_4O^•$), for which there has been persistent disagreement between the structural models derived from purely spectroscopic arguments and ab initio MO calculations, is discussed. It has been shown that the neutral p-aminophenoxyl ($X = NH_2$) radical deprotonates in basic aqueous solutions ($pK_a = 14.5$), implying a highly zwitterionic structure with formal positive charge on amine nitrogen, an amide-like CN bond ($\leqslant$1.33 Å), and near planarity of the molecular geometry. The radical protonates at oxygen, rather than nitrogen, the proton dissociation constant ($pK_a = 2.2$) corresponding to ~36% negative electronic charge on the O atom and a CO bond length of ~1.267 Å. This chemical model of the radical structure contrasts with the ab initio UNO-CAS/6-31G* (pyramidal) and ROHF/[32/2] (planar) models which predict CO/CN bond lengths of 1.237/1.395 and 1.367/1.38 Å, respectively. Both ab initio structures relate to radical protonation on the nitrogen position and not the oxygen. In the proton reactivity models of para-substituted phenoxyl radicals, the CO bond length increases in the order $F < H < CH_3 \ll OCH_3 \sim OH \ll NH_2 < O^-$, which is quite different from the UNO-CAS/6-31G* predicted order $NH_2 < OH \sim Cl < H < F \ll O^-$. The near equivalence of the NH_2 and O^- substitutions, observed in spectroscopic and electron-transfer properties of p-aminophenoxyl ($X = NH_2$) and p-benzosemiquinone anion ($X = O^-$) radicals in water, is readily explainable by the structural models derived from proton reactivity but not by the calculated structures. It has been established that solvation is primarily responsible for the observed substituent effects on the spectra, structure, and chemistry of phenoxyl radicals in water.

Introduction

Advances in time-resolved vibrational spectroscopic techniques applicable to dilute solutions have made it possible to investigate the structure and bonding in transient radical intermediates[1] and to provide molecular understanding of their reactive behavior. The observed spectra of solvated intermediates are often not very extensive. Complementary studies on a number of isotopically and structurally related species are required to interpret the spectra and construct a qualitative experimental model of the electronic structure in terms of resonance structures. If the principal resonance structures are correctly identified, they provide considerable physical and chemical insight into the nature of the bonds.[2] However, for a quantitative model of the radical structure, with complete description of the molecular geometry, one has to depend on theory. Recently, there has been a profusion of semiempirical and ab initio structure calculations of prototype organic radicals. It is not uncommon to see the indiscriminate use of drastically different equilibrium molecular geometries and force fields to compute vacuum vibrational frequencies of an intermediate and to interpret solution-phase vibrational spectra on that basis. In a large molecule with numerous vibrational modes, it is often possible to find some calculated frequencies in close proximity to a few experimental frequencies, irrespective of the radical structure and force field approximation used in the computation. In principle, one can measure the *pertinent* frequency shifts on isotopic substitutions, and compare them with the calculated shifts, to verify a computed structure. In practice, such measurements are not always feasible, because of either unavailability of the parent compound with desired isotopic substitutions or the cost involved. More importantly, in the case of a disagreement, it is difficult to determine whether the electronic structure, the force field, or both are responsible. Thus, a definite experimental guideline for developing adequate theoretical procedures cannot be provided. A simple chemical solution to this problem lies in examining the structure−reactivity relationship which, to date, has found little application in experimental and theoretical studies of the molecular spectra and structure of chemical intermediates in solution.

Recently, we have investigated the relationship between the electronic structure and proton reactivity of some reaction intermediates containing oxygen and nitrogen atoms. The procedure that we have evolved involves construction of a qualitative structural model of the hydrated radical from the interpretation of its resonance Raman and ESR spectra based on purely spectroscopic considerations. The experimental qualitative structure is then compared with the ab initio vacuum structure to test the suitability of the latter, and if reasonable agreement is found, both are combined to explain the chemistry. This procedure eliminates the pitfall of using a fictitious agreement between the experimental and calculated vibrational frequencies of the radical as a justification for its calculated electronic structure. We were able to provide a structural explanation for the anomalous protonation behavior of the neutral carboxylic and amide groups when bonded to pyridinyl radical.[3,4] Here we adopt a reverse approach; i.e., we use the

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protonation properties of the radicals capable of exchanging protons with water to elucidate their electronic structure. This approach is extremely valuable when the spectroscopic and computational structural models are in serious disagreement. It will be shown that the protonation site and proton dissociation constant provide insight into the nature of the redox-sensitive bonds in chemical intermediates that can be used to make vibrational assignments for their observed spectra in water, to develop adequate theoretical procedures to calculate electronic structure and vibrational frequencies, and to explain other chemical properties, such as redox potentials.

Theoretical Models of Phenoxyl Radicals

Phenoxyl radicals (p-$XC_6H_4O^\bullet$) provide an illustration of the seriousness of the problem outlined above. These are prototypes of oxygen-containing aromatic radicals that appear as redox intermediates in a variety of chemical and biochemical processes.[5−8] Therefore, they have been the topic of numerous experimental and theoretical investigations for many years.[1,6−25] The calculated CO bond in the unsubstituted phenoxyl ($X = H$) radical has varied in length between that of a double bond (1.216 Å), shorter than in p-benzoquinone, to a single bond (1.40 Å), longer than in phenol.[20] The experimental resonance Raman mode containing the maximum CO stretching component has been assigned at 1505 cm^{-1} based on spectroscopic arguments.[17] This vibrational frequency, which is intermediate between that of a typical $C{=}O$ bond in the $\sim$1700 cm^{-1} region in carboxylic acids ($\sim$1.22 Å)[2] and a $C\overset{\cdots}{-}O$ bond in the $\sim$1400 cm^{-1} region in carboxylate anions[26] ($\sim$1.26 Å),[2] would suggest the CO bond in phenoxyl radical to be of intermediate length, i.e., close to 1.24 Å. Since the spectroscopic interpretation of the radical spectra and structure disagrees with most calculations, the assignment of the 1505 cm^{-1} frequency to the CO stretch has been frequently questioned. A recent ab initio UNO-CAS (unrestricted natural orbital-complete active space)/6-31G* calculation[21] on the phenoxyl radical has produced a vacuum molecular geometry (CO bond length 1.239 Å) that would be consistent with the spectroscopic model of the radical structure in water. However, this computational procedure leads to an erroneous interpretation of the resonance Raman spectra due to “not readily recognizable” force field deficiencies.[19,20] Subsequent calculations with improved force constants have predicted the CO frequency close to 1505 cm^{-1}.[19,20] At this point, we set aside the questions related to frequency calculations and focus on the electronic structure and its consequences to the chemistry. Since the various computational procedures have led to drastically different molecular geometries for phenoxyl radicals, we select the recent UNO-CAS/6-31G* vacuum structures[21] for comparison with the chemical structural models that we develop in this work.

The agreement mentioned above between the vibrational spectroscopic and UNO-CAS electronic structures of the unsubstituted phenoxyl radical does not extend to its para derivatives. In the UNO-CAS/6-31G* models of the para-substituted phenoxyl radicals, the CO bond length is predicted to increase in the order $NH_2 < OH \sim Cl < H < F \ll O^-$.[21] On the other hand, the general spectral features in the 400−445 nm resonance Raman spectra of the radicals change in the order $F \sim H \sim CH_3 < Cl < Br \ll OCH_3 < OH \ll NH_2 < O^-$.[1,12−18] The shortest (1.237 Å) CO bond is predicted for the p-aminophenoxyl ($X = NH_2$) radical and the longest (1.248 Å) for the p-benzosemiquinone anion ($X = O^-$) radical, although the resonance Raman spectra of the two radicals are similar and the ESR hyperfine constants comparable.[10,18] Structure-sensitive physicochemical properties, such as reduction potential which measures the free energy difference ($\Delta G°$) between the parent phenoxide anion and its phenoxyl radical state ($E°(XC_6H_4O^\bullet/XC_6H_4O^-)$), follow the same trend,[7] as seen in the resonance Raman and ESR spectra,[1,10] contrary to the UNO-CAS/6-31G* structural predictions.[21]

TABLE 1: The UNO-CAS Vacuum CO Bond Lengths (in Å) and Physicochemical Properties of Para-Substituted Phenoxyl Radicals in Water

X	bond length[a]	pK[b]	reduction potential[c] (eV)	ESR parameters[d] a_2[e] (G)	ESR parameters[d] a_3[f] (G)
F	1.240	<-2.0	0.76		
H	1.239 1.294[g] 1.231[h]	−2.0	0.80	6.65	−1.85
CH_3		−1.8	0.68	6.1	−1.40
Cl	1.238		0.80		
OCH_3		~-0.75	0.54	5.05	−0.2
OH	1.238	−0.75	0.46	5.1	
NH_2	1.237 1.395[i]	$\sim+2.2$,[j] +14.5[k]	0.217	2.75	1.75
O^-	1.248	+4.0	0.023	2.37	2.37

[a] 6-31G* basis set (ref 21). [b] O−H proton dissociation constant (pK_a) of the conjugate acid of the phenoxyl radicals (ref 10). [c] Data taken from ref 7. [d] Reference 10. [e] Hyperfine constant of the C−H proton, ortho to the O atom in the radical. [f] Hyperfine constant of the C−H proton, ortho to the substituent group (X) in the radical. [g] 3-21G basis set (ref 21). [h] 6-311G(2d,p)basis set (ref 20). [i] CN bond length. 6-31G* basis set (ref 21). [j] O−H proton dissociation constant (pK_a) of the conjugate acid (ref 16). [k] NH_2 proton dissociation constant of the neutral radical, measured in this work.

We will show that the chemical structural models of the para-substituted phenoxyl radicals, conceived from their proton reactivity, predict the CO bond in the p-aminophenoxyl radical to be significantly longer than in the phenoxyl ($X = H$) radical and closer to that of the p-benzosemiquinone anion radical, which would explain the spectral and redox similarities of the two radicals. These purely experimental models, seemingly crude, are far more realistic than the various theoretical models of phenoxyl radicals that are currently being used to interpret the vibrational and electronic spectra of these important radical intermediates in water.

Protonation Properties of Phenoxyl Radicals

The acid−base properties of some para-substituted phenoxyl radicals, available in the literature,[10] are given in Table 1. The pK_a measurements were made by monitoring the changes in the g-factor and ESR hyperfine constants with acid concentration in aqueous solution and by assuming involvement of four water molecules in the proton-exchange process. For p-aminophenoxyl radical (pK_a of the conjugate acid of the radicals has been frequently referred to as the protonation pK_a in this paper), pK_a determination was also done by time-resolved resonance Raman spectroscopy and a slightly higher value than that by ESR was obtained which we consider more reliable.[16] The pK_a values change in the same order, i.e., $F < H < CH_3 \ll OCH_3 \sim OH \ll NH_2 < O^-$, as the ESR hyperfine constants,[10] resonance Raman spectra,[1] and the redox potentials[7] (see Table 1). The NH_2 and O^- substitutions alter the protonation pH much more drastically than the other substituent groups.

In the p-aminophenoxyl radical, where two sites (−O and $-NH_2$) are available for proton attachment, the ESR and Raman studies each identify the oxygen atom as the first protonation site.[10,16] This unexpected result provides insight into the charge distribution in the radical structure. It is well established from numerous chemical and spectroscopic studies that the charge neutral $-NH_2$ generally protonates prior to the charge neutral $-O$. In most aliphatic amino acids $-NH_2$ protonation occurs first, even when there is about 50% negative electronic charge on each of the two O atoms of the carboxylate anion.[26,27] If one assumes a phenoxyl (X = H)-like structure for the *p*-aminophenoxyl radical in water, with the ring$-NH_2$ bond similar to that in aniline, as predicted by the UNO-CAS/6-31G* calculation,[21] the observed protonation form should be *p*-$H_3N^+C_6H_4O^•$, and not *p*-$H_2NC_6H_4OH^{•+}$, contrary to the ESR and Raman evidence. A structural model of the radical resembling the structure of the parent molecule, *p*-aminophenoxide ($H_2NC_6H_4O^-$) anion, with negative charge on the oxygen atom may explain the protonation site. In fact, a low-level ROHF/[32/2] calculation does predict a *p*-aminophenol-like structure for *p*-aminophenoxyl radical (CO bond length 1.367 Å),[22] but with very little extra negative charge on the oxygen atom (spin should not be confused with charge), and therefore, it cannot account for the observed protonation site. Interestingly, the UNO-CAS/6-31G* and ROHF/[32/2] molecular geometries, with drastically different bond lengths and bond angles, have been used to interpret the resonance Raman spectra of the radical in water, with the claim that they support the spectroscopic assignments![21,22]

In closed-shell charge-neutral systems, protonation on $-O$ prior to $-NH_2$ has been observed in aliphatic amides[28] where the vibrational spectroscopic and crystallographic studies suggest a significant amount of formal negative charge on $-O$ and positive charge on $-NH_2$.[2,26] However, the aliphatic amides generally protonate in extremely strong acidic solutions, while the *p*-aminophenoxyl radical protonates in moderately acidic solutions. Therefore, the formal negative charge on the $-O$ atom in the latter species must be much more pronounced. Also, there must be an equal amount of positive charge on the ring, the amine group, or both to make the radical charge neutral. The charge neutral $-NH_2$ does not deprotonate in water, as is evident from the estimated pK_a of ammonia as ~35.[28,29] However, with ~100% positive charge on $-NH_3^+$, deprotonation occurs in weak basic solutions (pK_a ~10) due to enhanced electrostatic repulsion of the proton.[2,29] Whether the formal positive charge is mostly on the $-NH_2$ group or on the ring in the *p*-aminophenoxyl radical structure can be ascertained if the deprotonation pK_a is known. Then, comparison can be made with the isoelectronic *p*-phenylenediamine cation radical ($C_6H_4(NH_2)_2^{•+}$), with obvious positive charge, which deprotonates with a pK_a of 13.2.[30]

We have examined the *p*-aminophenoxyl radical by transient absorption and resonance Raman spectroscopy in mildly to extremely basic aqueous solutions. We present here an unambiguous experimental evidence for the deprotonation of the *p*-aminophenoxyl radical in water. Apparently, this radical represents one of the most acidic neutral amines known to date.

Spectroscopic Evidence of the Deprotonation of the *p*-Aminophenoxyl Radical

Experimental Procedure. The *p*-aminophenoxyl radical was prepared in aqueous solution by pulse radiolysis. On electron pulse irradiation of N_2O-saturated water, the $^•OH$ radical is the main reactive species present in solution on the 100 ns time scale.[31] It can be converted into secondary oxidants, such as $N_3^•$, by the reaction with an excess of N_3^- in solution. The $^•OH$ radical (pK_a 11.9) reacts with N_3^- at a rate constant of 1.2×10^{10} M^{-1} s^{-1} and its conjugate base ($O^{•-}$) at a rate constant of 2×10^8 M^{-1} s^{-1}.[31] With 0.1 M N_3^- in solution the reaction is complete in less than 100 ns in both cases. The $N_3^•$ radical reacts with *p*-aminophenoxide anion at a diffusion-controlled rate, by electron transfer, to produce the *p*-aminophenoxyl radicals.

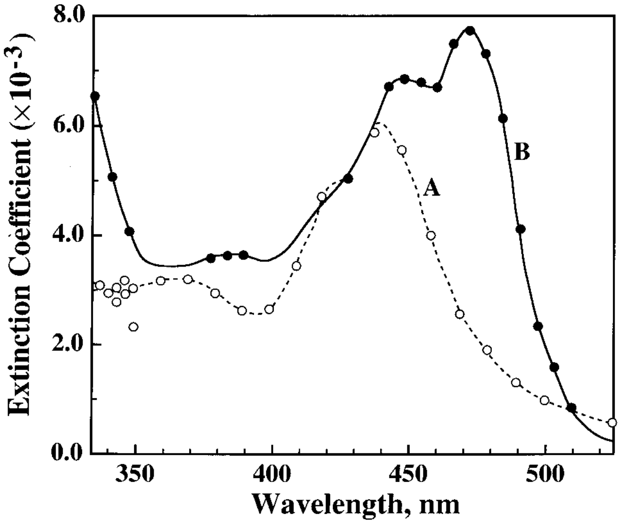


Figure 1. Transient absorption observed 2 μs after electron pulse irradiation of a N_2O-saturated 2 mM *p*-aminophenol aqueous solution containing 0.1 M NaN_3 and (a) 0.1 M KOH and (b) 6 M KOH. The absorption spectrum A is attributed to the *p*-aminophenoxyl radical and B to its deprotonated form.

Pulse radiolysis time-resolved optical absorption and resonance Raman techniques, described in detail in several previous publications from this Laboratory, were used for transient detection.[1,32,33] Radiolysis by ~8 MeV, ~5 ns electron pulses from a linear accelerator facility in the Laboratory, which typically produces a radical concentration of $\sim 3 \times 10^{-6}$ M per pulse, was used in optical absorption measurements. In Raman experiments, 2 MeV, ~100 ns electron pulses, delivered by a Van de Graaff accelerator at dose rates that produced $\sim 10^{-4}$ M radical concentration, were applied. The Raman scattering was probed by an excimer (~100 mJ)-pumped dye laser pulse (~10 ns), tuned in resonance with the optical absorption of the radicals. The spectra were recorded by using an optical multichannel analyzer (OMA), accompanied with an intensified gated diode array detector, with the gate pulse (~20 ns) synchronized with the Raman signal pulse. Extensive signal averaging was performed to improve the signal/noise ratio in the Raman spectra, with the accelerator and laser operated at a repetition rate of 7.5 Hz. In both experiments, a flow system was used to refresh the solution between consecutive electron pulses. Raman band positions were measured with reference to the known Raman bands of common solvents, such as ethanol, and are accurate to within ±2 cm^{-1} for sharp bands and ±5 cm^{-1} for broad and shoulder bands.

Transient Absorption. The transient absorption observed 2 μs after electron pulse irradiation of a N_2O-saturated aqueous solution containing 2 mM *p*-aminophenol (pK_a 3.6 and 10.4)[34] and 0.1 M NaN_3 at pH ~11 is shown in Figure 1A. This absorption spectrum, with a maximum at 444 nm (extinction coefficient $\sim 6.1 \times 10^3$ M^{-1} cm^{-1}) and an unresolved shoulder band on the lower wavelength side, is identical to the spectrum of the *p*-aminophenoxyl radical observed previously in the radiolysis of a similar solution, but without NaN_3, where oxidation is by the $^•OH$ radical.[15] When 6 M KOH was added to the solution, the absorption shifted toward the red, with a maximum at 474 nm (extinction coefficient $\sim 7.5 \times 10^3$ M^{-1} cm^{-1}). The new spectrum obtained is shown in Figure 1B. The

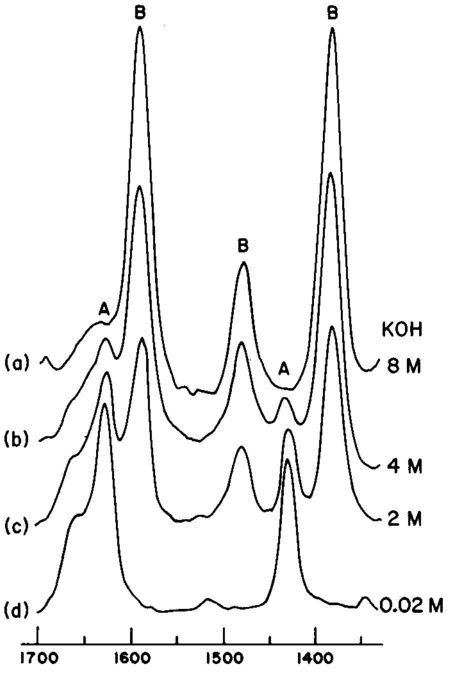


Figure 2. Resonance Raman spectra excited at 470 nm, 1 μs after electron pulse irradiation of N_2O-saturated 4 mM *p*-aminophenol aqueous solution containing 0.1 M NaN_3 at different KOH concentrations. Raman signals marked A represent the *p*-aminophenoxyl radical and B its deprotonated form.

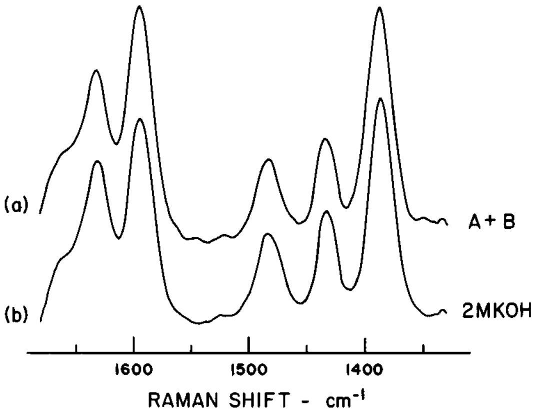


Figure 3. (a) Composite spectrum obtained by digitally combining the Raman spectra in Figure 2a,d. (b) The resonance Raman spectrum excited at 470 nm, 1 μs after electron pulse irradiation of N_2O-saturated 4 mM *p*-aminophenol aqueous solution containing 0.1 M NaN_3 and 2 M KOH. The spectrum in (a) matches the spectrum in (b).

rate constants for the formation of the 444 and 475 nm transients were found to be comparable ($\sim 4.5 \times 10^9$ M^{-1} s^{-1}), within the experimental error. It is clear that the new species is a basic form of the *p*-aminophenoxyl radical, which has its pK_a lower than the pH of the 6 M KOH solution. The deprotonation occurs on a time scale much shorter than the formation period of the radicals under the experimental conditions employed. This is an important chemical observation, as the anionic form of an aromatic amine, whether a stable molecule or a transient radical, is a rare occurrence in aqueous solution.

Resonance Raman Spectra. The transient absorption experiments described above are sufficient to establish that the neutral *p*-aminophenoxyl radical behaves like a species with positive charge mostly on the amino substituent. Additional very strong vibrational spectroscopic evidence was obtained by monitoring the time-resolved resonance Raman spectra at different pH, with KOH concentration in solution ranging between 0.02 and 8 M. The resonance Raman spectra (1300–1750 cm^{-1}) were probed at 445 and 470 nm, 1 μs and 1 ms after electron pulse irradiation of a N_2O-saturated aqueous solution containing 4 mM *p*-aminophenol and 0.1 M NaN_3. No transient Raman signals were seen in the 1 ms spectra, which were subtracted from the 1 μs spectra to obtain the difference spectra that contained only the transient Raman bands. Figure 2 displays the results obtained by 470 nm excitation. With 0.02 M KOH in solution (Figure 2d), the spectrum shows Raman signals of the *p*-aminophenoxyl radical at ~1662, 1632, 1518, and 1434 cm^{-1} (marked A). With increase in KOH concentration in the solution, these signals become weaker, and additional signals due to another species become apparent at 1593, 1482, and 1385 cm^{-1} (marked B). With 8 M KOH in solution, the B signals attain their maximum intensity, and the *p*-aminophenoxyl signals (A signals) disappear completely. An excess of *p*-aminophenol was added to the 8 M KOH solution, which was then diluted with oxygen-free water to attain a pH below 13.5. On radiolysis of this solution the *p*-aminophenoxyl radical signals reappear, with the same intensity as observed for a fresh solution at a comparable pH. It is clear that *p*-aminophenoxide anion is stable under extreme basic conditions, and the changes in the spectral features with pH depicted in Figure 2 are associated with acid–base interconversion. The spectrum obtained with 8 M KOH in solution (Figure 2a) was digitally combined with the spectrum taken with 0.02 M KOH (Figure 2d) to construct a composite spectrum that represents contributions from the equal concentrations of *p*-aminophenoxyl radical and its anion form (Figure 3a). This composite spectrum matches well with the spectrum taken with 2 M KOH in solution (Figure 3b). If activity coefficient is taken into consideration,[29] a 2 M KOH solution corresponds to a pH of 14.5, which is the pK_a of the *p*-aminophenoxyl radical. This pK_a is only ~1.3 units higher than that of the positively charged *p*-phenylenediamine cation radical. The observed resonance Raman frequencies in the anionic form of the *p*-aminophenoxyl radical are 35–50 cm^{-1} lower than in the neutral form and closely resemble those of the *p*-aminoanilino radical (deprotonated form of the *p*-phenylenediamine cation radical).[35]

From the protonation and deprotonation properties of the *p*-aminophenoxyl radical in water emerges a picture of a highly dipolar molecule in which the oxygen atom behaves much like that in *p*-benzosemiquinone anion radical, with substantial negative charge, and the nitrogen atom behaves similar to that in *p*-phenylenediamine cation radical, with significant positive charge.

Proton Reactivity and the CO Bonds

A correlation made between the CO bond properties and the protonation behavior of oxygen atoms in closed-shell molecules can be applied to estimate the bond lengths and bond stretching frequencies in open-shell molecules in water. Our objective is to frame structural models for various phenoxyl radicals, independent of theory, to interpret their resonance Raman spectra and to test the validity of the theoretical procedures.

In the electrostatic model of the acid–base equilibria, the Coulombic interaction energy between the proton and its bonding site is largely responsible for the free energy difference between a molecule and its proton-bound state.[29] At short distances, the Coulombic interaction energy can be taken to be proportional to the effective charge on the molecular site of approach, realizing that this may not be a good approximation when the charge on the atom is small and the charges on the close by atoms also becomes effective. This interaction energy is largely absorbed in the form of the altered covalent bonding and charge distribution in the protonated molecule (resonance stabilization). The pK_a, which depends on the magnitude of the interaction energy, can be directly related to the effective charge on the protonation site in the unprotonated species. This approximation works fairly well when applied to a series of compounds with common protonation site (similar proton-bonding distances).[29] The closed-shell molecules, for which the molecular structures are known from crystallographic data and the vibrational spectra have been properly assigned, provide useful reference systems for relating pK_a to bond properties.

Let us relate the amount of negative charge on the oxygen atom and its protonation behavior, as discussed previously.[3,4] In aliphatic alcohols and water, where the charge is ~100% confined on the oxygen atom in the deprotonated species, protonation occurs at a very high pH, i.e., close to 15. On the other hand, in aliphatic carboxylic acids (e.g., acetic acid), where the charge gets equally distributed between the two oxygen atoms on deprotonation, pK_a drops to ~5.[34] Thus, a decrease of ~0.5 electronic charge on oxygen atom amounts to a decrease of about 10 units in the protonation pK_a.[3,4] Here, we ignore the small statistical effect of the two equivalent oxygen sites. A large molecular species containing CO bond with no extra charge on oxygen atom should protonate below pH ~ −5, i.e., in extremely acidic conditions.[28,29] While the pK_a values are a good indicator of the effective charge on the site where the proton would attach, the effect of this charge on the bonding can be correlated only in closely related systems. The relationship between the CO bond properties and the protonation behavior of the oxygen atoms directly bonded to an aromatic ring can be ascertained by comparing the electronic structures of quinone/hydroquinone (dianionic form) systems. The loss of electrons from the $-\mathrm{CO}^-$ bonds in the completely reduced hydroquinone state produces the CO double bonds (comparable to aliphatic acids) in the completely oxidized quinone state and not a biradical with single CO bonds and the unpaired spins on the two oxygen ends. Therefore, the closed-shell *p*-benzoquinone (CO bond length 1.222 ± 0.008 Å by X-ray diffraction and 1.225 ± 0.003 Å by electron diffraction),[36] to which we attribute a CO bond number of 2 and protonation pK_a of −5, provides a good reference system for developing the structural models of para-substituted phenoxyl ($\mathrm{XC_6H_4O^\bullet}$) radicals. The proton reactivity of phenoxyl radicals can be visualized in terms of fractional electronic charge on the O atom over that in *p*-benzoquinone. In other words, the phenoxyl CO bonds acquire a partial CO^- single-bond character,[2] corresponding to bond number $(n) = 2 - (\Delta \mathrm{p}K_a)/20$, where $\Delta\mathrm{p}K_a$ is an increase in the protonation pK_a over that of the reference C=O bond (see the resonance structures given later on). The question why the electron loss from the ring bonded CO^- should produce a double bond in *p*-benzoquinone, but not in phenoxyl radicals, has to do with the bulk solvent effect that will be discussed later on.

Following Pauling,[2] the potential function (V) for a bond of intermediate character can be given as the sum of two parabolic functions, representing single-bond (force constant k_1) and double-bond (force constant k_2) potential functions, with coefficients $2 - n$ and $n - 1$, respectively:

$$V(R_{\mathrm{CO}}) = {}^1\!/_2(2-n)k_1(R_{\mathrm{CO}} - R_{\mathrm{C-O^-}})^2 + {}^1\!/_2(n-1)k_2(R_{\mathrm{CO}} - R_{\mathrm{C=O}})^2$$

Equating the derivative of $V(R_{\mathrm{CO}})$ with respect to R_{CO} to zero, one obtains

$$R_{\mathrm{CO}} = R_{\mathrm{C-O^-}} - (R_{\mathrm{C-O^-}} - R_{\mathrm{C=O}})\{(k_2/k_1)(n-1)\}/ \times [\{(k_2/k_1) - 1\}n + \{2 - (k_2/k_1)\}]$$

Pauling's suggested value[2] of $(k_2/k_1) = 1.84$ seems reasonable for the CO bonds, in view of the recent literature values used in various frequency calculations (~11 and ~6 mdyn/Å).[19,20] The CO bond length (R_{CO}) can be estimated from the bond number (n) by the equation

$$R_{\mathrm{CO}} = R_{\mathrm{C-O^-}} - (R_{\mathrm{C-O^-}} - R_{\mathrm{C=O}})\{1.84(n-1)\}/ \times (0.84n + 0.16) \quad (1)$$

We assume $R_{\mathrm{C=O}} = 1.222$ Å, and $R_{\mathrm{C-O^-}} = 1.415$ Å, a typical CO single bond length in aliphatic molecules, ignoring specific solvent interactions. The reference bond lengths and $(k_2/k_1) = 1.84$ are also consistent with Badger's relation, $(\text{force constant})\}^{-1/2} \propto (R_{\mathrm{CO}} - 0.68)$.[2,37] While these assumptions are fairly reasonable, a slightly different set of parameters will have only a minor effect (<0.01 Å) on the estimated bond lengths. For hydroquinone dianion ($\mathrm{Q^{2-}}$, protonation pK_a = 11.4),[34] we estimate $R_{\mathrm{CO}} = 1.359$ Å from eq 1, compared to 1.344 Å from MP2/{6-31+ G(d,p)} vacuum calculation.[38] The experimental CO bond length in crystalline hydroquinone ($\mathrm{QH_2}$) is known to be 1.381 Å.[39] The CO bond length in the *p*-hydroxyphenoxide anion ($\mathrm{QH^-}$, protonation pK_a = 9.9)[34] is estimated to be ~0.004 Å shorter (eq 1) and the CO stretching frequency ~8 cm^{-1} higher (Badger's relation) than in $\mathrm{Q^{2-}}$, as observed.[38]

Electronic Structure and Resonance Raman Spectra of Phenoxyl Radicals

While it is possible to calculate the CO force constants by Badger's relation, it is difficult to relate them with the experimental frequencies that rarely represent the stretching motion of a single bond. The phenoxyls and the parent phenoxides have the same number of vibrational modes, but they differ with respect to the nature and the extent of coupling between the ring and the CO vibrations. In general, a significant decrease in the CO bond length would shift the optimum CO stretching component from lower to higher frequency modes, with possible effect on the resonance Raman intensity profile, but not necessarily on the vibrational frequencies. The ring-coupled CO mode is observed at 1639 cm^{-1} in Q and at 1262 cm^{-1} in $\mathrm{Q^{2-}}$ in water.[38] The ratio of these experimental frequencies in water, 1.299, is slightly higher than the ratio, 1.253, expected from Badger's relation for the uncoupled frequencies. Therefore, the frequency estimations that we make for phenoxyl radicals using this relation are of qualitative significance only and may be off by as much as ~4%. They are useful, however, to locate the frequency region where the ring-coupled CO mode should occur. In the following paragraphs, we discuss some representative members of the para-substituted phenoxyl radical series, starting with the radical with net electronic charge.

In purely experimental vibrational spectroscopic assignments of the resonance Raman spectra of radical intermediates, it is fairly common to correlate the observed Raman frequencies with those of the precursor molecule, assuming one-to-one correspondence. However, such a procedure has the same drawback as the theoretical procedure of comparing the calculated frequencies with the experimental frequencies in close proximity. Some of the vibrational modes that are extremely sensitive to the redox reactions have no analogue in the precursor molecules. Their vibrational misassignment would result in an erroneous interpretation of the site and strength of the chemical interactions, operating on the radical in its various chemical and biochemical environments, for which Raman spectroscopy provides a very sensitive probe.[40] In the following discussion we limit ourselves to identifying such modes in the resonance Raman spectra, based on the proton reactivity of the intermediates.

***p*-Benzosemiquinone Anion ($X = O^-$) Radical.** The *p*-benzosemiquinone anion ($Q^{\bullet -}$) radical represents an extreme case of a para-substituted phenoxyl radical. This radical protonates in mildly acidic solutions, with pK_a of its acid form as ~4,[10] suggesting ~0.45 extra electronic charge on each of the two oxygen atoms, corresponding to CO bond number ~1.55. Equation 1 leads to an estimation of the CO bond lengths in the radical as ~1.281 Å. The uncoupled CO stretching frequency in the radical is expected to be ~1.13 times higher than in Q^{2-}, placing the coupled mode in the 1430 cm^{-1} region. Therefore, the resonance Raman band of the radical observed at 1435 cm^{-1} in water[1,12] can be confidently assigned to a vibrational mode comprising largely CO stretching motions. The UNO-CAS/6-31G*,[21] UHF/6-31G*,[21] RHF/3-21G,[23] ROHF/[32/2],[22] and MP2/6-31+G(d,p)[38] calculations predict CO bond lengths of 1.248, 1.245, 1.274, 1.277, and 1.276 Å, respectively, for the vacuum state, compared to our estimated value of ~1.281 Å in water from the proton reactivity. Only the latter three theoretical procedures have been used to calculate the vibrational modes and frequencies and show good agreement with the experimental results in water.

Phenoxyl ($X = H$) Radical. The phenoxyl radical protonates in very strongly acidic solutions. The pK_a of its conjugate acid is −2.0, which would suggest a formal negative charge of ~15% on the oxygen atom and a CO bond number of 1.85. We estimate a CO bond length of ~1.239 Å from eq 1, compared to 1.239 and1.231 Å by the UNO-CAS/6-31G*[21] and UNO-CAS/6-311G(2d,p)[20] vacuum calculations. A relatively small residual electronic charge on the −O atom indicates the CO bond to be far more sensitive to the electron-transfer reactions than the ring bonds of phenoxide anion. Also, the specific solvent interactions, such as hydrogen bonding, should affect the spectra and structure of phenoxyl radical to a lesser extent than those of the *p*-benzosemiquinone anion radical. The uncoupled CO frequency is expected to be ~21% higher than that in Q^{2-}, placing the coupled frequency in the ~1530 cm^{-1} region. The CO bond in phenoxyl radical is significantly shorter (~0.042 Å) than in the *p*-benzosemiquinone anion radical. Therefore, the maximum CO stretching contribution will be made to a vibrational mode at a higher frequency and certainly not lower. The 1505 cm^{-1} Raman mode in phenoxyl radical is 70 cm^{-1} higher in frequency than the 1435 cm^{-1} mode of *p*-benzosemiquinone anion radical. It is clear that the phenoxyl CO mode cannot occur in the 1400−1100 cm^{-1} region, as predicted by most calculations, and the UNO-CAS/6-31G* frequency of ~1400 cm^{-1}[21] is obviously an underestimation. A recent measurement of the $^{16}O/^{18}O$ isotope frequency shifts in the resonance Raman spectrum of phenoxyl radical confirms this point.[19]

***p*-Aminophenoxyl ($X = NH_2$) Radical.** As discussed earlier, the currently available theoretical models of this radical are inconsistent with its resonance Raman spectra and protonation behavior. Let us construct a structural model for the *p*-aminophenoxyl radical based on its proton reactivity. We conclude from the protonation/deprotonation behavior of the radical that its CO and CN bonds are both redox-sensitive bonds; i.e., the oxidation of *p*-aminophenoxide anion involves partial loss of electron from $-O^-$ as well as $-NH_2$ in water. The pK_a of the acid form of the radical, 2.2,[16] suggests about 36% of formal electronic charge on the oxygen atom, corresponding to bond number 1.64. The CO bond length in the radical extrapolates to ~1.267 Å and its stretching frequency to a slightly higher (~34 cm^{-1}) value than in *p*-benzosemiquinone anion radical. In most amides, the CO bond lengths (gas phase) are of the order of ~1.24 Å,[2] which explains why the proton attachment occurs in stronger acidic solutions. On the other hand, the CN bond in the *p*-aminophenoxyl radical must be similar, or somewhat shorter, than in amides, i.e., roughly 1.33 Å in length,[2] in order to explain the observed deprotonation of the radical. In aliphatic amides, the CN stretching mode is generally observed in the 1400 cm^{-1} region.[26] Therefore, a vibrational mode representing a symmetric combination of the CO/CN stretching motions in *p*-aminophenoxyl radical should appear in the 1400−1460 cm^{-1} region, as observed (1434 cm^{-1}).[15] The CO bond in the radical is significantly longer than in phenoxyl (by ~0.028 Å) radical. Therefore, the CO stretching component in the higher frequency ~1500 cm^{-1} modes (1518 cm^{-1})[15] must be small. The 1434 cm^{-1} mode in the *p*-aminophenoxyl radical is analogous to the 1435 cm^{-1} mode (CO) of the isoelectronic *p*-benzosemiquinone anion[12] and the 1424 cm^{-1} mode (CN) of *p*-phenylenediamine cation radicals.[41] There is an inverse isotope shift in the 1424 cm^{-1} vibration of the *p*-phenylenediamine cation radical; i.e., it shifts upward by 27 cm^{-1} on amine deuteration.[41] Since the contribution of the CN stretching motion to the 1434 cm^{-1} mode of the *p*-aminophenoxyl radical is roughly half of that in the *p*-phenylenediamine cation radical, one would expect an upward shift of roughly half on deuteration, as observed (~13 cm^{-1}).[15] The currently available theoretical models of the radical structure cannot explain this shift.[18]

A structural model of *p*-aminophenoxyl radical in water, intermediate between that of phenoxyl and aniline cation radicals, is fairly logical from a chemical perspective. In the UNO-CAS/6-31G* model of the radical structure it is the CO (1.237 Å) bond, and not the CN (~1.39 Å), that is most redox sensitive. On the other hand, in the ROHF/[32/2] model none of the bonds are very sensitive to the redox process. In both computational models, the CN bond is similar to that in closed-shell aromatic amines (~1.40 Å) and not amides (~1.33 Å).[2] Therefore, the observed protonation site and deprotonation pK_a of the radical cannot be explained. If the CO bond in the radical was shorter than that of the phenoxyl radical, as predicted by the UNO-CAS/6-31G* structure, one would expect protonation on the oxygen atom in an aqueous solution of comparable or higher acidity, and not much lower, contrary to the observations.

The proton reactivity model of the radical structure predicts, although indirectly, a nearly planar molecular geometry in water. That is a consequence of the significant double-bond character acquired by the CN bond. In amides, the CN and NH_2 groups are coplanar for the same reason.[2] The NH_2−ring interplanar angle is ~45° in the UNO-CAS structure,[21] as in aniline.[42] A pure NH_2 scissors (bending) vibration cannot affect the π-electron distribution in the radical. Therefore, this mode is not expected to appear with appreciable intensity in the Raman spectrum observed in resonance with a $\pi-\pi$ electronic transition, unless it borrows intensity by coupling with a strongly resonance-enhanced ring vibration. Since the NH_2 scissors mode at ~1662 cm^{-1} is fairly strong in the 445 nm resonance Raman spectrum[15] (also see Figure 2), it clearly shares intensity with the nearby 1632 cm^{-1} mode. The coupling between the NH_2 scissors and planar ring vibrations is most effective when the NH_2 group is coplanar with the ring. Thus, the observed

TABLE 2: Proton Reactivity Model of the CO Bond Length (in Å)[a] and Vibrational Frequencies and Relative Enhancement[b] of the ∼1500 and ∼1400 cm^{-1} Modes in the 400−450 nm Raman Spectra of Para-Substituted Phenoxyl Radicals in Water[c]

X	bond no.	bond length	∼1500 cm^{-1} mode	∼1400 cm^{-1} mode	int ratio
F	>1.85	<1.239	1511 vs	1413 vw	$\gg 1^d$
H	1.85	1.239	1505 vs	1398 vw	$\gg 1^d$
CH_3	1.84	1.240	1517 vs	1407 vw	$\gg 1^d$
OCH_3	∼1.788	∼1.247	1518 vs	1406 vw	$\gg 1^d$
OH	1.788	1.247	1511 s	1432 vw	$\gg 1^d$
NH_2	1.64	1.267	1518 w	1434 m	$\ll 1$
O^-	1.55	1.281	*e*	1435 m	$\ll 1$

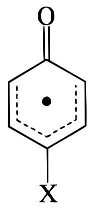
[a] This work. [b] v = very, s = strong, m = medium, w = weak. [c] Data taken from refs 1, 12, 13, and 15. [d] The ∼1400 cm^{-1} mode in the spectrum is too weak to measure the exact ratio. [e] The ∼1500 cm^{-1} mode not enhanced (zero intensity).

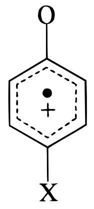
enhancement of the NH_2 scissors mode in the 445 nm Raman spectrum of the radical is explainable by a nearly planar structural model, but not by the pyramidal UNO-CAS/6-31G* model. The ROHF/[32/2] structural model is planar, but it predicts an aniline-like single CN bond, which must be attributed to a sever deficiency in the computational method.

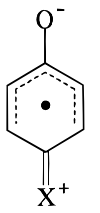
Para-Substituted Phenoxyl Radicals with X = F, CH_3, OH, and OCH_3. In other para-substituted phenoxyl radicals, the protonation properties are known only for X = CH_3, OH, and OCH_3. For X = F, the radical seems to protonate in stronger acidic solutions than for X = H,[10] implying a shorter CO bond (<1.239 Å). On the other hand, for X = CH_3, the protonation pK_a is only 0.2 unit higher, which would suggest a comparable (∼1.240 Å) CO bond. The resonance Raman spectra of *p*-fluoro- and *p*-methylphenoxyl radicals[1,14] are very similar to that of phenoxyl radical,[17] as expected from the model. A significant increase (by ∼1.25 units) in protonation pK_a occurs for X = OH and OCH_3,[10] which extrapolates to CO bond number of 1.79 and bond length ∼1.247 Å. The 400−450 nm resonance Raman spectra of *p*-hydroxy- and *p*-methoxyphenoxyl radicals exhibit spectral characteristics intermediate between those of phenoxyl and *p*-aminophenoxyl radicals, as expected.[1,13,17] The uncoupled CO stretching frequency for X = OH and OCH_3 should be slightly lower (∼20 cm^{-1}) than for X = H but considerably higher (∼53 cm^{-1}) than for X = NH_2. Therefore, the prominent ∼1500 cm^{-1} resonance Raman band is still attributable to the CO stretch, but with diminished contribution to the mode. The validity of this interpretation can be checked by removing the CH bending component from the ∼1500 cm^{-1} modes by ring deuteration, which, of course, is not the only ring component in the mode. The CO stretch in *p*-hydroxyphenoxyl radical at 1511 cm^{-1} shows a downward shift of 22 cm^{-1} on ring deuteration,[13] compared to a shift of 16 cm^{-1} for the 1505 cm^{-1} mode of phenoxyl radical.[17] The CO stretching component in the ∼1500 cm^{-1} phenoxyl modes should decrease in the order F > H > $CH_3 \gg$ OH ∼ $OCH_3 \gg NH_2 \gg O^-$, which is also the order of the relative intensity of the corresponding Raman band in the spectra (Table 2). For X = NH_2 and O^-, the CO stretching component in the ∼1500 cm^{-1} mode becomes smaller than in the lower frequency ∼1400 cm^{-1} mode, and the latter becomes relatively stronger in the spectrum (Table 2). It can be seen that the vibrational frequencies, in themselves, are not very sensitive to the nature of the CO bond which is the reason it has been possible to justify the diverse theoretical models by matching the calculated and resonance Raman frequencies.

ESR Spectra and Redox Potentials of Phenoxyl Radicals

It would be useful to express the proton reactivity of phenoxyl radicals, discussed above, in terms of the following principal resonance structures to be able to establish consistency with the other physicochemical properties.


I


II


III

The resonance structure **I** is well recognized as the main contributor to the electronic structure of phenoxyl radical (X = H).[43] The lack of significant coupling at the oxygen site in radical−radical reactions[6] is a chemical consequence of the predominance of the resonance structure **I**.[44] The resonance structure **II** has been discussed previously, in the context of ESR hyperfine constants, as a minor component in the structure.[43,45] In aqueous solution, about 86% of the spin density resides on the five ring carbon atoms (excluding CO) and ∼14% on CO which is consistent with the ∼85% contribution of the resonance structure **I** and ∼15% of the resonance structure **II** to the radical structure, as determined from proton reactivity. The resonance structure **III** needs to be considered only in para-substituted phenoxyl radicals. In the *p*-benzosemiquinone anion (X = O^-) radical, it is equivalent to the resonance structure **I**. On the other hand, in the *p*-aminophenoxyl (X = NH_2) radical the resonance structure **I** is slightly more important than the resonance structure **III**. In the *p*-hydroxyphenoxyl radical (X = OH), the pK_a of the acid form of the radical is ∼3 units lower than that for the *p*-aminophenoxyl radical. Therefore, the resonance structure **III** is considerably less important than in the *p*-aminophenoxyl radical. The protonation data on para-halogenated phenoxyl radicals are not available. However, it can be argued that the removal of a pπ electron from the highly electronegative −F atom would require much more energy than from −Cl and −Br. The contribution of the resonance structure **III** to the radical structure should increase in the order F < CH_3 < Cl < Br $\ll$ OH ∼ $OCH_3 \ll NH_2 < O^-$. In the following discussion, we consider the resonance structure **II**, which contributes only ∼15% to the electronic structure of the unsubstituted phenoxyl radical, included in the resonance structure **I** or **III**. The resonance structure **II** shows that the unsubstituted phenoxyl radical is significantly zwitterionic in nature.

ESR Hyperfine Constants. By expanding the principal resonance structures, depicting the probable ring sites for the unpaired spin, it can be shown that the spin population on the ring carbon atom, ortho to the CO bond (i.e., C(2) and C(6)), should depend on the CO bond strength. In view of the McConnell relationship,[46] the spin population on these carbon atoms can be taken to be proportional to the hyperfine constant of the hydrogen atoms bonded to them. The H(2)/H(6) ESR hyperfine constants for X = H, CH_3, OH, OCH_3, NH_2, and O^- in water are reported as 6.65, 6.1, 5.1, 5.05, 2.75, and 2.37 G, respectively.[10] It can be seen that these ESR parameters relate extremely well with the proton reactivity of the radicals (Table 1), while no relationship can be found with the UNO-CAS structures. The H(2)/H(6) ESR hyperfine constants in the *p*-aminophenoxyl radical are only ∼0.4 G higher than in the *p*-benzosemiquinone anion radical and the H(3)/H(5) hyperfine constants (1.75 G) ~0.4 G lower than in *p*-phenylenediamine cation radical,[18] in complete accordance with the proton reactivity model of the radical structures.

Redox Potentials. The reduction potentials ($E°$) are important physicochemical parameters in the thermochemistry of electron-transfer reactions. They measure the free energy difference between the radical and its stable precursor. Therefore, to visualize the effect of X on $E°(p\text{-}XC_6H_4O^\bullet/p\text{-}XC_6H_4O^-)$, structural variations in the phenoxyl as well as the phenoxide states need to be considered. The proton reactivity of the phenoxide (X = H) anion (pK_a ~10) corresponds to ~75% of the effective negative electronic charge on the oxygen atom. The phenoxide states for X = NH_2 (pK_a = 10.4)[34] and O^- (pK_a = 11.4)[34] are slightly more reactive and X = Cl (pK_a = 9.5)[34] and Br (pK_a = 9.6)[34] slightly less reactive toward the proton, as compared to X = H. However, the enhanced reactivity amounts to only a small change (~2.5−7%) in the effective negative electronic charge on the O atom, and the CO bonds in most phenoxides can be taken to be of almost identical strength. Therefore, $E°(p\text{-}XC_6H_4O^\bullet/p\text{-}XC_6H_4O^-)$ should largely depend on the electronic structure of $p\text{-}XC_6H_4O^\bullet$. The obvious exceptions are redox couples with strongly electron-withdrawing groups (e.g., X = NO_2). Since pK_a of phenol may be lowered by several units on such substitutions, the CO bond strength in the phenoxide state will change significantly. In that case, an increase in $E°$ does not necessarily relate to a stronger CO bond in the phenoxyl state. In the proton reactivity models, X = F, Cl, Br, and CH_3 exert only minor effect on the phenoxyl radical structure. Consequently, the $E°$ values show only a small variation (0.8 ± 0.1 V).[7] As the effect of OH and OCH_3 substitutions on the phenoxyl structure are predicted to be much more pronounced, the $E°$ values drop to 0.54 and 0.46 V, respectively.[7] The X = NH_2 and O^- substitutions drastically alter the phenoxyl structure, reducing $E°$ to 0.217 and 0.023 V, respectively. Thus, the observed substituent effects on $E°(p\text{-}XC_6H_4O^\bullet/p\text{-}XC_6H_4O^-)$ are readily explainable by the proton reactivity models of the radicals. Alternatively, the $E°$ values can be used to get insight into the relative strength of the CO bonds in various phenoxyl radicals in water.

Solvation Effects

The solvent dependence of the structural properties of phenoxyl radicals have not been experimentally examined, except for X = O^- where the radical is nonzwitterionic.[38] However, the structural models developed in this work for aqueous solution provide insight into the role of the solvent in augmenting the substituent's effect on the electronic structure of phenoxyl radicals. This point can be elaborated by recourse to the principal resonance structures, depicted earlier. The resonance structures **II** and **III** are zwitterionic in nature, and obviously, their contribution to the electronic structure of the radicals would be strongly solvent dependent. A rough estimation of the energy separation ($\Delta E°$) between the resonance structures **I** (+**II**) and **III** (+**II**) in water can be made from the reduction potentials. If the energy corresponding to the zwitterionic resonance structure **III** is much higher than **I**, the bulk solvent effect on the electronic structure would be almost the same as in unsubstituted phenoxyl radical. On the other hand, if the energy separation between the resonance structures **I** and **III** is small or the zwitterionic resonance structure (**III**) has lower energy, the radical structure and chemical properties would be very strongly solvent-dependent. We present here an approximate estimation of $\Delta E°$ (can be taken roughly equal to $\Delta G°$ for large molecules) for some para-substituted phenoxyl radicals in water.

Assuming the ring−X bond in the resonance structure **I** and the ring−O^- bond in the resonance structure **III** to be similar to those in the parent phenoxide anion, the reduction potential for a hypothetical oxidation state I ($E°$(I)) can be taken to be roughly equal to that of the unsubstituted phenoxyl radical, i.e., ~0.8 V (vs SHE), and the oxidation state III to $C_6H_5X^{\bullet+}$ ($E°$(III)).[47] The energy difference, $\Delta E° = E°(\mathbf{III}) - E°(\mathbf{I})$, is the additional energy required to take out an electron from X in the resonance structure **I** (+**II**) and transfer to O, to produce the resonance structure **III** (+**II**) in water. The literature values of $E°(C_6H_5X^{\bullet+}/C_6H_5X)$ are 0.8 V for X = O^-, 1.03 V for X = NH_2, and 1.66 V for X = OCH_3,[47] leading to $\Delta E^0 = 0$ eV for X = O^-, 0.23 eV for X = NH_2, and 0.86 eV for X = OCH_3. Unfortunately, direct experimental measurements of $E°(C_6H_5X^{\bullet+}/C_6H_5X)$ for X = F, CH_3, Cl, and Br are not available, but the trend is obvious. Since the $E°(p\text{-}XC_6H_4O^\bullet/p\text{-}XC_6H_4O^-)$ values for these substituent groups are all within ~10% of X = H,[7] the resonance structure **III** is almost inconsequential. A significant increase in the zwitterionic component in the electronic structure over X = H occurs for X = OH and OCH_3, and it becomes extremely important for X = NH_2. Since the solvent reaction field, the effect of which is already included in these $\Delta E°$ estimations, depends on the dipole moment of the radicals,[48] the theoretical vacuum structures, irrespective of the degree of sophistication, cannot provide a sensible description of the molecular spectra and the chemistry of the −OH, −OCH_3, and −NH_2 substituted para-substituted phenoxyl radicals in water. On the other hand, for the phenoxyl radicals with X = H, F, Cl, Br, and CH_3, which are not as dipolar, the vacuum structures, in principle, can give a rough approximation of the actual molecular geometry. The *p*-benzosemiquinone anion radical is the only phenoxyl radical for which the bulk solvent effect is negligible. For the gas-phase structures, $\Delta E°$ can be roughly estimated from the electron affinity of the oxygen atom bonded to ring (~2 eV)[7,24] and the ionization energy of C_6H_5X (>7 eV), which leads to $\Delta E° > 5$ eV, even for X = NH_2. Therefore, the resonance structures **II** and **III** are unimportant.

The preceding analysis leads to an interesting prediction on the gas-phase structure of the para-substituted phenoxyl radicals. In most phenoxyl radicals, the CO bond lengths should be comparable (resonance structure **I**) and very close to that in *p*-benzoquinone! The UNO-CAS vacuum calculations essentially support this prediction. The size of the basis set shortens the calculated CO bond (Table 1).[21] With the 6-31G* basis set, the CO bond lengths are around 1.240 ± 0.003 Å for X = NH_2 to F [21] and shrink to 1.231 Å with a larger basis set, 6-311G(2d,p) (calculation available only for X = H),[20] approaching the CO bond length of *p*-benzoquinone (1.222 ± 0.008 Å).

Finally, we make some suggestions, from a chemistry perspective, on how to incorporate the solvation effect in the theoretical structure calculations on highly zwitterionic molecules, such as *p*-aminophenoxyl radical in water. The standard procedures for inclusion of the specific solvent interactions, such as hydrogen bonding,[49] by attaching water molecules to different atomic sites seem to be quite adequate and need not be discussed. It is largely the bulk solvent effect involving the interaction between the solute dipole and the solvent reaction field that converts a phenoxyl-like *p*-aminophenoxyl radical in a vacuum, as suggested by the UNO-CAS calculations, to a *p*-benzosemiquinone anion-like radical in water, as evident from the chemical and spectroscopic properties. It can be seen that it would be futile to treat the solvent effect on a gas-phase electronic structure as a perturbation problem, if one is essentially dealing with a low-polarity structure like resonance structure **I**. Instead, we suggest that the effect of the solvent reaction field on the radical structure be incorporated at the level of configuration interaction. If the energy values for the various electronic configurations are evaluated under the influence of the solvent field, the highly dipolar configurations will interact much more strongly with the lowest energy configuration in water than in a vacuum. For instance, the electronic configurations corresponding to $\mathrm{X{-}Ph{-}O}$ and $\mathrm{X^+{-}Ph{-}O^-}$ (or $\mathrm{X{-}Ph^+{-}O^-}$) representations of a phenoxyl radical have the same symmetry and therefore, interaction is possible. If the energies of the $\mathrm{X^+{-}Ph{-}O^-}$ configurations in water remain much higher than that of the $\mathrm{X{-}Ph{-}O}$ configurations, the bulk solvent effect will be small. On the other hand, if the energies become comparable, there should be a profound solvation effect on the calculated spectra and structure. The $\Delta E° \sim 0.23$ eV for $X = NH_2$, estimated from the redox potentials, gives the effective energy separation between the electronic configurations corresponding to $\mathrm{H_2N{-}Ph{-}O}$ and $\mathrm{H_2N^+{-}Ph{-}O^-}$ in water.

Conclusion

The CO bond lengths in the para-substituted phenoxyl radicals (p-$XC_6H_4O^\bullet$) in water are modeled based on the proton reactivity of the radicals. These models are consistent with the redox-sensitive vibrational modes and frequencies in the time-resolved resonance Raman spectra of the radicals and relate well with the ESR hyperfine constants and reduction potentials. In particular, they help to visualize the effect of solvation on the physicochemical properties of the radicals. It has been found that solvation plays a major role in determining the effect of substitution on the phenoxyl structure. Therefore, the ab initio vacuum calculations cannot predict the observed substituent effects on the radical properties in water. While a dependable electronic structure calculation on highly zwitterionic intermediates in water, such as *p*-aminophenoxyl radical, remains a challenging problem, it is not trivial even to identify such species by calculation. Such a determination can be made in a straightforward way by simple chemical properties, such as protonation and deprotonation behavior of the radical, as demonstrated in this work.

References and Notes

(1) Tripathi, G. N. R. In *Advances in Spectroscopy;* Clark, R. J. H, Hester, R. E., Eds.; John Wiley & Sons: New York, 1989; Vol. 18, pp 157−218.

(2) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(3) Tripathi, G. N. R.; Su, Y.; Bentley, J. *J. Am. Chem. Soc.* **1995**, *117*, 5540.

(4) Tripathi, G. N. R.; Su, Y.; Bentley, J.; Fessenden, R. W.; Jiang, P.-Y. *J. Am. Chem. Soc.* **1996**, *118*, 2245.

(5) West, E. S.; Todd, W. R.; Mason, H. S.; Van Bruggen, J. T. *Textbook of Biochemistry*; The Macmillan Company: New York, 1966.

(6) Nonhebel, D. C.; Walton, J. C. *Free-radical Chemistry: Structure and Mechanism;* Cambridge University Press: Cambridge, 1974.

(7) Lind, J.; Shen, X.; Eriksen, T. E.; Mercnyi, G. *J. Am. Chem. Soc.* **1990**, *112*, 2, 479 and references therein.

(8) Nordlund, P.; Sjoberg, B.-M.; Eklund, H. *Nature* **1990**, *345,* 593. Bender, C. J.; Sahlin, M.; Babcock, G. T.; Barry, B. A.; Chandrashekar, T. K.; Salowe, S. P.; Stubbe, J.; Lindstrom, B.; Petersson, L.; Ehrenberg, A.; Sjoberg, B.-M. *J. Am. Chem. Soc.* **1989**, *111*, 2245. Babcock, G. T. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90,* 10893 and references therein.

(9) Kajii, Y.; Obi, K.; Nakashima, N.; Koshihara, K. *J. Chem. Phys.* **1984**, *87,* 5059. Tripathi, G. N. R.; Schuler, R. H. *Chem. Phys. Lett.* **1982**, *88,* 253. Pullin, D.; Andrews, L. *J. Mol. Struct.* **1982**, *95,* 181. Schuler, R. H.; Buzzard, G. K. *Int. J. Radiat. Phys. Chem.* **1984**, *87,* 5059. Bent, D. V.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *97,* 2599. Ward, B. *Spectrochim. Acta* **1968**, *A24,* 813. Roebber, J. L. *J. Chem. Phys.* **1962**, *37,* 1974. Land, E. J.; Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1961**, *57,* 1885.

(10) Dixon, W. T.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72,* 1221.

(11) Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1974**, *78,* 523. Dixon, W. T.; Norman, R. O. C. *J. Chem. Soc.* **1964,** 4857. Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1964,** 213. Dixon, W. T.; Norman, R. O. C. *Proc. Chem. Soc., London* **1963,** 97. Stone, T. J.; Waters, W. A. *Proc. Chem. Soc., London* **1962,** 253.

(12) Tripathi, G. N. R. *J Chem. Phys.* **1981,** *74,* 6044. Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Phys.* **1982,** *76,* 3139. Hester, R. E.; Williams, K. P. J. *J. Chem. Soc., Faraday Trans.* **1982,** *78,* 573. Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104,* 4789. Schuler, R. H.; Tripathi, G. N. R.; Prebenda, M. F.; Chipman, D. M. *J. Phys. Chem.* **1983**, *87,* 3101. Tripathi, G. N. R.; Sun, Q.; Schuler, R. H. *Chem. Phys. Lett.* **1989,** *156,* 51.

(13) Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91,* 5881.

(14) Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1988**, *92,* 5129.

(15) Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Phys.* **1982,** *76,* 4289; *J. Phys. Chem.* **1984**, *88,* 1706.

(16) Sun, Q.; Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1990**, *94,* 6273.

(17) Tripathi, G. N. R.; Schuler, R. H. *Chem. Phys. Lett.* **1983**, *98,* 594; *J. Chem. Phys.* **1984**, *81,* 113. Beck, S. M.; Brus, L. E. *J. Chem. Phys.* **1982**, *76,* 4700. Johnson, C. R.; Ludwig, M.; Asher, S. A. *J. Am. Chem. Soc.* **1986**, *108,* 905.

(18) Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Soc., Faraday Trans.* **1993**, *89,* 4177.

(19) Mukherjee, A.; McGlashen, Z.; Spiro, T. G. *J. Phys. Chem.* **1995**, *99,* 4912.

(20) Chipman, D. M.; Liu, R.; Zhou, X.; Pulay, P. *J. Chem. Phys.* **1994**, *116,* 44 and references therein.

(21) Liu, R.; Zhou, X. *J. Phys. Chem.* **1993**, *97,* 9613, 9618.

(22) Raymond, K. S.; Wheeler, R. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89,* 665. Wheeler, R. A. *J. Phys. Chem.* **1993**, *97,* 1533.

(23) Chipman, D. M.; Prebenda, M. F. *J. Phys. Chem.* **1986**, *90,* 5557.

(24) Gunion, R. F.; Giles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrosc. Ion Processes* **1992**, *117,* 601.

(25) Takahashi, J.; Momose, T.; Shida, T. *Bull. Chem. Soc. Jpn.* **1994**, *67,* 1. Goddard, J. D.; Yu, H. *Theochem. Soc.* **1991**, *233,* 129. Bofill, J. M.; Pulay, P. *J. Chem. Phys.* **1989**, *90,* 3642. Luzkhov, V. B.; Zyubin, A. S. *Theochem. Soc.* **1988**, *170,* 33. Armstrong, D. R.; Cameron, C.; Nonhebel, D.; Perkins, P. G. *J. Chem. Soc., Perkin Trans.* **1983**, *2,* 569. Bishof, P.; Friedrich, G. *J. Comput. Chem.* **1982**, *3,* 486. Shinagawa, Y.; Shinagawa, Y. *J. Am. Chem. Soc.* **1978**, *100,* 67. Bishof, P. *J. Am. Chem. Soc.* **1976**, *98,* 6844. Chang, H. M.; Jaffe, H. H.; Masmanidis, C. A. *J. Phys. Chem.* **1975**, *79,* 1118. Chang, H. M.; Jaffe, H. H. *J. Phys. Chem.* **1975**, *79,* 1118. Lloyd, R. V.; Wood, D. E. *J. Am. Chem. Soc.* **1974**, *96,* 659. Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Am. Chem. Soc.* **1968**, *90,* 4201. Hinchliffe, A,; Steinbank, R. E.; Ali, M. A. *Theor. Chim. Acta* **1966**, *5,* 95.

(26) Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; John Wiley and Sons: New York, 1974.

(27) Garfinkel, D.; Edsall, J. T. *J. Am. Chem. Soc.* **1958**, *80,* 3807, 3818, 3823. Takeda, M.; Iavazzo, R. E. S.; Garfinkel, D.; Scheinberg, I. H.; Edsall, J. T. *J. Am. Chem. Soc.* **1958**, *80,* 2813. Ghazanfar, S. A. S.; Myers, D. V.; Edsall, J. T. *J. Am. Chem. Soc.* **1964**, *86,* 3439 and references therein.

(28) Rochester, C. H. *Acidity Functions*; Academic Press: New York, 1970. Also see: Fraenkel, G.; Franconi, C. *J. Am. Chem. Soc.* **1960**, *82,* 4478. Berger, A.; Loewenstein, A.; Meiboom, S. *J. Am. Chem. Soc.* **1959**, *81,* 62. Fraenkel, G.; Nieman, C. *Proc. Natl. Acad. Sci. U.S.A.* **1958**, *44,* 688. O'Brien, J. L.; Nieman, C. *J. Am. Chem. Soc.* **1957**, *79,* 1386. Goldfarb, A. R.; Mele, A.; Gustein, N. *J. Am. Chem. Soc.* **1955**, *77,* 1955.

(29) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1959.

(30) Jonsson, M.; Lind, J.; Shen, X.; Eriksen, T. E.; Mercnyi, G. *J. Am. Chem. Soc.* **1994**, *116,* 1423.

(31) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17,* 513.

(32) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6,* 129. Janata, E.; Schuler, R. H. *J. Phys. Chem.* **1982**, *86,* 2078.

(33) Tripathi, G. N. R. In *Multichannel Image Detectors II*; Talmi, Y., Ed.; ACS Symposium Series 236; American Chemical Society: Washington, DC, 1983; p 171.

(34) Serjeant, E. P.; Dempsey, P. *Ionization Constants of Organic acids in Aqueous solution*; Pergamon Press: Oxford, 1979.

(35) Unpublished work from the Laboratory.

(36) Hagen, K.; Hedberg, K. *J. Chem. Phys.* **1973**, *59,* 158. Trotter, J. *Acta Crystallogr.* **1960**, *13,* 86.

(37) Badger, R. M. *J. Chem. Phys.* **1934**, *2,* 128; **1935**, *3,* 710.

(38) Zhao, X.; Imahori, H.; Zhan, C.-G.; Sakata, Y.; Suehiro, I.; Kitagawa, T. *J. Phys. Chem. A* **1997**, *101,* 622.

(39) Sakurai, T. *Acta Crystallogr.* **1968**, *B24*, 403.

(40) Su, Y.; Tripathi, G. N. R. *J. Am. Chem. Soc.* **1994**, *116*, 4405.

(41) Chipman, D. M.; Sun Q.; Tripathi, G. N. R. *J. Chem. Phys.* **1992**, *97*, 8073. Ernstbrunner, E. E.; Girling, R. B.; Grossman, W. E. L.; Mayer, E.; Williams, K. P. J.; Hester, R. E. *J. Raman Spectrosc.* **1981**, *10*, 161.

(42) Tripathi, G. N. R. *J. Chem. Phys.* **1980**, *73*, 5591. Kydd, R. A.; Krueger, P. J. *Chem. Phys. Lett.* **1977**, *49*, 539; *J. Chem. Phys.* **1978**, *69*, 827. Kydd, R. A *Sprctrochim. Acta A* 1**979**, *35*, 409. Lister, B. G.; Tyler, J. K.; Hog, J. H.; Larsen, N. W. *J. Mol. Struct.* **1974**, *23*, 253. Quack, M.; Stockburger, M. *J. Mol. Spectrosc.* **1972**, *43*, 87. Brand, J. C. D.; Williams, D. R.; Cook, T. J. *J. Mol. Spectrosc.* **1971**, *39*, 359. Brand, J. C. D.; Jones, V. T.; Forrest, B. J.; Pirkle, R. J. *J. Mol. Spectrosc.* **1971**, *39*, 352. Evans, J. C. *Sprctrochim. Acta* 1**960**, *16*, 628.

(43) Dewar, M. J. S.; David, D. E. *J. Am. Chem. Soc*. **1980**, *102*, 7387.

(44) Tripathi, G. N. R.; Sun, Q.; Armstrong, D. A.; Chipman, D. M.; Schuler, R. H. *J. Phys. Chem.* **1992**, *96*, 5344.

(45) Lloyd, R. V.; Wood, D. E. *J. Am. Chem. Soc*. **1974**, *96*, 659. This paper mentions a minor contribution of the resonance structure **II**. I am grateful to the referee for drawing attention to this reference. The referee also calculates the spin density on five ring carbon atoms (excluding CO carbon) as 86% in water, using ESR parameters similar to those borrowed from ref 10 and the McConnell equation (ref 46) with $Q = 23$.

(46) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972**.** McConnel, H. M. *J. Chem. Phys*. **1956**, *24*, 764. McConnell, H. M.; Chesnut, D. B. *J. Chem. Phys*. **1958**, *28*, 107.

(47) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(48) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4782.

(49) See, for example: Deng, Y.; Illies, J.; James, M. A.; McKee, M. L.; Peschke, M. *J. Am. Chem. Soc.* **1995**, *117*, 420.