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# Time resolved resonance Raman observation of the extreme protonation forms of a radical zwitterion in water

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The reactions of the aqueous proton with the zwitterionic *p*-aminophenoxyl radical in strongly basic to extremely acidic aqueous solutions have been investigated using time-resolved resonance Raman spectroscopy. The dynamic stability of the different protonation forms of the radical, observed on the microsecond time scale in this work, has been achieved by controlling the proton exchange rate in water. In strongly acidic solutions we observe a rare ring-H<sup>+</sup> bonded dication species, a key intermediate in the amine hydrolysis. The neutral *p*-aminophenoxyl radical undergoes NH<sub>2</sub>-deprotonation in strongly basic aqueous solutions, which has no analogues in closed-shell amines. © 2005 American Institute of Physics. [DOI: 10.1063/1.1860311]

## INTRODUCTION

Proton interactions are fundamental chemical interactions in aqueous systems that can drastically alter the physicochemical properties of a chemical species.<sup>1</sup> They provide a natural probe for the charge distribution in solvated molecules and radicals.<sup>1–5</sup> We have examined in this work the reactions of protons with the *p*-aminophenoxyl radical, a reaction intermediate of considerable chemical and biochemical importance,<sup>6–8</sup> which acquires a strongly zwitterionic electronic structure in water.<sup>8,9</sup>

The *p*-aminophenoxyl radical  $(H_2N\phi O^{\bullet})$  is isoelectronic with the biologically important *p*-benzosemiquinone radical anion  $(\phi O_2^{-})$  and *p*-phenylenediamine radical cation  $[\phi(\mathrm{NH}_2)_2^{+\bullet}]$ , the semiquinone models.<sup>1</sup> The *p*-aminophenoxyl radical can mimic many of the functions of the latter radicals in an aqueous environment.<sup>7,8</sup> It is a prototype of the active site free radical intermediates in enzymes, such as ceruloplasmin and copper amine oxidases, and in metabolic utilization of human health related chemicals, such as serotonin. The semiquinone properties of the *p*-aminophenoxyl radical  $(H_2N\phi O^{\bullet})$  arise due to the effects of hydrogen bonding and the solvent reaction field in water that induce a positive charge on the amine-N and a negative charge on the O site of the radical.<sup>8</sup> The zwitterionic character of the radical is further enhanced on incorporation of ions into the hydration shell.<sup>9</sup> Because of its unusual charge distribution this radical displays interesting protonation behavior in aqueous solution that is not seen in closed shell amines.

The reactions of the aqueous proton with *p*-aminophenoxyl radical were examined in extremely acidic to very strong basic solutions by time-resolved resonance Raman spectroscopy. Here we present a rare observation of proton addition to the cation form of the radical in extreme acid solutions. In strongly basic solutions, the radical exists in its amine-deprotonated anionic form. The spectral changes that occur on successive proton additions establish the most acidic form of the radical as a  $\pi$ -H<sup>+</sup> bonded dication.

#### **EXPERIMENTAL METHODS**

One-electron oxidation of p-aminophenol in oxygen-free water was accomplished by reactions of  ${}^{\bullet}OH$ , HSO<sub>4</sub>, and N<sub>3</sub> radicals produced by pulse radiolysis.<sup>10–12</sup> The proton concentration in solution was varied with H<sub>2</sub>SO<sub>4</sub> and KOH. On electron pulse irradiation of oxygen-free water, 'OH and  $e_{aq}^{-}$ are the main reactive species present in solution on the 100 ns time scale. In mildly acidic to basic solutions,  $e_{aq}^{-}$  was converted into 'OH by its reaction with N2O-saturated water. Secondary oxidants, such as N<sub>3</sub>, were prepared in basic solutions by the reaction of 'OH (pK<sub>a</sub> 11.9) or O<sup>-•</sup> with an excess of  $N_3^-$ . In  $H_2SO_4$  solution, the  $HSO_4^{\bullet}$  radical is produced by the 'OH oxidation of the acid and also by direct action of the radiation. The pulse radiolysis-time resolved resonance Raman techniques used in this work have been previously described. The specific experiments use 2 MeV, 100 ns electron pulses, delivered by a Van de Graaff accelerator at dose rates that produced about  $10^{-4}-10^{-5}$  M radical concentration. The Raman scattering was probed by an excimer-pumped dye laser pulse tuned in resonance with the optical absorption of the radicals. The spectra were recorded using an optical multichannel analyzer, accompanied by an intensified gated diode array detector, with the gate pulse synchronized with the Raman signal pulse. Extensive signal averaging was performed to improve the signal-to-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 carbon tetrachloride. They are accurate to within  $\pm 2 \text{ cm}^{-1}$  for sharp bands and  $\pm 5 \text{ cm}^{-1}$  for broad and shoulder bands.

### **RESULTS AND DISCUSSION**

The absorption spectra of the *p*-aminophenoxyl radicals show only a small variation in strongly acidic to moderately strong basic aqueous solutions, with absorption maxima in

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FIG. 1. Transient Raman spectra observed 1  $\mu$ s after electron pulse irradiation of oxygen-free aqueous solutions containing 2 mM *p*-aminophenol and: (A) 0.1 M NaN<sub>3</sub>, 8 M KOH; (B) 0.1 M NaN<sub>3</sub>, *p*H 11; (C) *p*H 1.8; and (D) spectrum with 16 M H<sub>2</sub>SO<sub>4</sub> in solution–spectrum in (C) (see text). Excitation was at 470 nm for the spectrum in A and 441 nm for B, C, and D.

the 435–445 nm region.<sup>8,13</sup> However, with 8 M KOH in solution, the absorption shifts to the red by  $\sim$ 30 nm.<sup>3</sup> The Raman spectra were recorded 1  $\mu$ s after the electron pulse from which solvent background was subtracted. At very high acid concentration, this subtraction procedure leads to considerable noise in the difference Raman spectra, specifically in the frequency region of strong acid bands. In this frequency region very weak signals cannot be unambiguously attributed to the transients formed. Fortunately, the structure sensitive bands in *p*-aminophenoxyl radicals appear in the >1200 cm<sup>-1</sup> region and are fairly prominent, so they can be readily distinguished from the solvent bands and can be positively identified with the species.

Figure 1 depicts transient Raman spectra in the  $1300-1800 \text{ cm}^{-1}$  region, excited in resonance with radical absorption maxima. Four protonation forms of the radical are evident. All four forms show bands at  $1622\pm30 \text{ cm}^{-1}$ ,  $1505\pm25 \text{ cm}^{-1}$ , and  $1409\pm25 \text{ cm}^{-1}$  (we will use these average frequencies for general discussion) with relative intensities changing with the state of protonation. The nature of the vibrational modes responsible for these bands, their relative enhancement in the spectra and frequency shifts, provide insight into the protonation sites and their structural effects.

The neutral *p*-aminophenoxyl radical ( $H_2N\phi O^{\bullet}$ ), seen in moderately acidic to basic solutions in  $H_2O$  and  $D_2O$ , has been a subject of numerous experimental and theoretical investigations, with and without incorporation of solvent interactions in calculations.<sup>3,8,13,14</sup> Convergence has occurred recently in the spectroscopic and theoretical interpretations of the structure of the radical in water.<sup>8</sup> In brief, the most intense band at 1632 cm<sup>-1</sup> in the spectrum [Fig. 1(b)] is assigned to the 8a mode (Wilson notation) which primarily involves the stretching motion of the central ring CC bonds.<sup>15</sup> The NH<sub>2</sub> scissors is mechanically coupled to the 8a mode, derives intensity from this coupling, and appears as a shoulder band on its higher frequency side ( $\sim 1666 \text{ cm}^{-1}$ ). The NH<sub>2</sub> scissors is not enhanced in other protonation forms of the radical, apparently because the frequency is not in proximity of the 8a mode or the ring and the amine moieties are non-coplanar.<sup>8,9</sup> A high Raman enhancement of the 8a mode occurs due to elongation of the ring along this mode in the excited state of the resonant  $\pi^* \leftarrow \pi \ ({}^2B_2 \leftarrow {}^2B_2)$  electronic transition. The moderately enhanced 1432 cm<sup>-1</sup> mode represents in-phase C-NH<sub>2</sub> and C-O stretching motions (Wilson mode 7a) with a small ring stretching component similar to the Wilson mode 19a. On the other hand, the very weakly enhanced 1516 cm<sup>-1</sup> mode represents out-of-phase C-NH<sub>2</sub> and C-O stretching motions coupled with the 19a ring vibration. The CO and CN bonds in the aqueous radical are typical of the three electron bonds, with bond lengths estimated as 1.284 and 1.34 Å, respectively. This recent study on the neutral p-aminophenoxyl radical<sup>8</sup> provides valuable guidelines for the spectra-structure correlations presented in this work for the different protonation states of the radical.

In the semiquinone state, exchange between the unpaired electron and electron pair on two equivalent atomic sites of a conjugated system leads to formation of two three-electron bonds.<sup>1</sup> Therefore, the bond properties in the semiguinone radicals are intermediate between completely oxidized (quinone-like) and reduced (hydroquinone-like) states. A loss in the unpaired  $\pi$ -electron density from the ring sites of the radical increases its quinoid character and, as a consequence, the 8aCC frequency.<sup>2</sup> In the centrosymmetric  $(D_{2h})$ *p*-benzosemiquinone anion and *p*-phenylenediamine cation radicals, the 19a ring vibration is symmetry forbidden in Raman. It couples with the asymmetric stretching motions of the substituent groups and produces a Raman inactive vibration in the  $\sim 1505 \text{ cm}^{-1}$  region. On the other hand, the symmetric stretching motion of the substituent groups (Wilson mode 7a) in *p*-benzosemiquinone anion and *p*-phenylenediamine cation radicals produces a vibration in the  $\sim 1409 \text{ cm}^{-1}$  region which is quite prominent in the resonance Raman spectra of these radicals. A slight nonequivalence of the substituent groups (CO/CN) in the *p*-aminophenoxyl radical is the reason why the 1516  $\rm cm^{-1}$ mode is seen with a very low intensity in the spectrum [Fig. 1(b)], i.e., it is not strictly forbidden. In essence, the intensity of the  $\sim 1505 \text{ cm}^{-1}$  mode is an indicator of the nonequivalence of the ring-substituent bonds.<sup>8</sup> It represents the most intense band in the 400-430 nm resonance Raman spectra of aqueous phenoxyl ( $\phi O^{\bullet}$ ) and aniline cation  $(\phi NH_2^{+\bullet})$  radicals, attributed to predominantly the CO and CN stretching motions (+small 19a component), respectively.<sup>11</sup> These CO and CN bonds are close to a double bond ( $\pi$ -bond order >0.5). The strengthening of the ringsubstituent bonds weakens the adjacent ring CC bonds involved in the 19a mode. Therefore, the  $\sim 1409 \text{ cm}^{-1}$  mode in phenoxyl ( $\phi O^{\bullet}$ ) and aniline cation ( $\phi NH_2^{+\bullet}$ ) radicals is predominantly a 19a mode which contains a small CO or CN stretching component, and is very weakly enhanced in the resonance Raman spectra. As the CO or CN bonds become weaker in *para*-substituted radicals (e.g.,  $X\phi O^{\bullet}$ ), the relative contribution of the CO or CN stretch decreases in the  $\sim 1505 \text{ cm}^{-1}$  mode, and increases in the  $\sim 1409 \text{ cm}^{-1}$  mode.

On the other hand, the stretching motion of the CX bond which is strengthened and acquires a partial double bond character ( $\pi$ -character) at the cost of the CO or CN bonds also contributes towards the  $\sim 1409 \text{ cm}^{-1}$  mode, particularly when X=O or N. The resonant electronic transitions in these radicals are  $\pi^* \leftarrow \pi$  transitions. It is the  $\pi$ -component of the bonds that can possibly change on electronic excitation. Therefore, the  $\pi$ -bond order of the CO or CN bonds qualitatively correlates with the relative intensities of the  $\sim 1505$ and  $\sim 1409 \text{ cm}^{-1}$  modes. To summarize, the simple qualitative description of the complex  $\sim 1505$  and  $\sim 1409$  cm<sup>-1</sup> modes presented here, which was established on the basis of the systematic experimental studies of closely related systems, explains why the strength of the ring-substituent bonds has only a small effect on the vibrational frequencies, but a drastic effect on their relative enhancement in the resonance Raman spectra.<sup>11</sup> In *p*-aminophenoxyl radical, the contributions of the CO and CN stretches to the 1432 cm<sup>-1</sup> mode are comparable. In the following discussion we will use the neutral *p*-aminophenoxyl radical as reference for interpreting the observed spectral trends that occur on addition or loss of a proton from the radical.

In very basic solutions (e.g., 8 M KOH), the NH<sub>2</sub>-deprotonated anion form of the radical is observed [Fig. 1(a)]. The chemical species that are seen in this strongly basic solution are very short-lived ( $<10^{-9}$  s) in pure water from which they abstract a proton and disappear by protonation. However, in the presence of very high base concentration (>1 M) in solution, their formation rate from the neutral radical can exceed their rate of decay, facilitating observation of the equilibrium concentration on a much longer time scale, as in the present case.<sup>16</sup> NH and O largely share the negative charge on the radical, forming three-electron  $\pi$ -bonds through the ring.<sup>17</sup> Because of the higher electronegativity of O, a slightly more electronic charge resides on it than on NH, which may be the reason why a slightly lower frequency (1385 cm<sup>-1</sup>) of the CN/CO stretching mode than in the neutral radical is observed. The 1385 cm<sup>-1</sup> band is about three times more intense than the 1482 cm<sup>-1</sup> band, which suggests almost comparable CO and CN  $\pi$ -bond orders. The 8aCC frequency  $(1593 \text{ cm}^{-1})$  in the anion radical is closer to that of a hydroquinone structure.<sup>15</sup> To our knowledge, this is a rare example of deprotonation of a neutral amine observed in water.<sup>18</sup>

The neutral radical protonates on its O [Fig. 1(c)] in mildly acidic solutions (pH < 2.2).<sup>13</sup> The 8aCC frequency (1631 cm<sup>-1</sup>) remains virtually unchanged. However, the C -NH<sub>2</sub> bond becomes significantly stronger than in the neutral species. As a result, the 1519 cm<sup>-1</sup> mode containing the CN stretch becomes more prominent in the spectrum, as compared to the 1406 cm<sup>-1</sup> mode that contains the C-OH stretch. The cationic form of the *p*-aminophenoxyl radical is more appropriately described as the *p*-hydroxy-aniline cation radical, with a major fraction of the positive charge on the amine group. Thus, *p*-aminophenoxyl, a nominal oxy radical, becomes an amine radical on proton addition. The O-protonation of the *p*-aminophenoxyl radical in moderately acidic solution and -NH<sub>2</sub> deprotonation in very basic solutions are chemical consequences of a zwitterionic structure.

At very high acid concentration in solution, further protonation occurs. In 16 M acid solution, the singly protonated cation radical still persists, but additional signals at slightly different frequencies also appear. On subtraction of the mono-cation radical signals from the spectrum, the difference spectrum that is obtained is shown in Fig. 1(d). This spectrum is not of the hydroquinone cation radical or its  $\pi$ proton-adduct,<sup>2</sup> indicating that hydrolysis of the amine group has not occurred. The 8aCC frequency shifts upwards by  $21 \text{ cm}^{-1}$  to  $1652 \text{ cm}^{-1}$ , a general trend that we observe on formation of radical cations.<sup>2,11</sup> However, the relative Raman intensities of the 1519 cm<sup>-1</sup> and the 1396 cm<sup>-1</sup> modes are not significantly affected and, in that respect, the spectrum remains similar to that of the mono-cation form of the radical. It should be pointed out that the proton adduct of the mono-cation form of the p-aminophenoxyl radical is extremely short-lived which implies that the H<sup>+</sup>-bonding is extremely weak in the dication radical. However, in 16 M  $H_2SO_4$  solution, the dication radical is formed at a rate faster than its decay rate which gives it dynamic stability and allows observation on the microsecond time scale.

The amine-N, hydroxyl-O, and the ring are the sites where proton addition to the mono-cation form of the *p*-aminophenoxyl radical (HO- $\phi$ =NH<sub>2</sub><sup>+•</sup>) may occur. However, protonation of amine-N, where a large fraction of the positive charge on the radical resides, or hydroxyl-O, is not consistent with the observed spectrum. If N or O-protonation occurred, one would essentially observe an H<sub>3</sub>N<sup>+</sup>-substituted phenol cation  $(H_3N^+-\phi=OH^{+\bullet})$  or an  $H_2O^+$ -substituted aniline cation  $(H_2O^+ - \phi = NH_2^{+\bullet})$  radical. The formation of the  $>C=OH^+$  or  $>C=NH_2^+$  double bonds in such species would transfer the unpaired  $\pi$ -electron density from OH<sup>+</sup>/NH<sub>2</sub><sup>+</sup> to the ring. The  $\pi$ -electron density, however, cannot be effectively shared by the substituent groups, such as  $-NH_3^+$  or -OH<sub>2</sub><sup>+</sup>, which lack vacant  $p\pi$  orbitals to accommodate the electron.<sup>19</sup> The sharing requires the capability to form a  $\pi$ bond.<sup>1</sup> Therefore, the spectrum would be closer to that of the aniline cation  $(\phi NH_2^{+\bullet})$  or phenol cation radical  $(\phi OH^{+\bullet})$ , with a significant drop in the 8aCC frequency.<sup>20</sup> The observed spectrum does not display these characteristics.

It can be readily visualized that loss of  $\pi$ -electron from the HO- $\phi$ =NH<sub>2</sub><sup>+•</sup> radical (oxidation) would produce a quinone-like structure and increase the 8aCC frequency. The sharing of the unpaired  $\pi$ -electron on the ring by the proton amounts to a partial loss of electron from the ring, without a change in the oxidation state. Therefore, an increase in the 8aCC frequency should occur. Since the frequency of the 1396 cm<sup>-1</sup> mode containing the CO stretch is lower than in the mono-cation form of the radical, the proton must add to the ring  $\pi$ -system on the side of the -OH group (HO-(H) $\phi$ =NH<sub>2</sub><sup>+•</sup>), thus reducing the  $\pi$ -component of the CO bond and the frequency. A  $\sigma$ -bonding must be ruled out, as the CO bond would become comparable to or weaker than a single bond and a far greater reduction in the CO frequency would be expected. In the cation form of the *p*-benzosemiquinone radical anion  $[(HO = \phi = OH)^{+\bullet}]$ , proton addition occurs to the ring  $\pi$ -system at the center. It is not surprising that in a relatively less symmetric HO- $\phi$ =NH<sup>+•</sup> radical, the proton addition to the ring  $\pi$ -system occurs closer to the OH side, as

it experiences less electrostatic repulsion than from the positive charge on -NH<sub>2</sub>. The most acid form of the *p*-aminophenoxyl radical is essentially a rare  $\pi$ -H<sup>+</sup> bonded carbonium radical species.<sup>21</sup>

The role of proton-induced double bond character of the  $>C=X^+$  bonds in the hydrolysis of closed-shell molecules is well recognized, although transitory existence of such species has precluded direct observation.<sup>18</sup> One and two proton adducts of the *p*-aminophenoxyl radical (X=NH<sub>2</sub>) are essentially the radical analogues of such close-shell intermediates. In hydrolysis mechanisms, the  $>C=X^+$  bond facilitates H<sub>2</sub>O addition at C, by transferring positive charge on X<sup>+</sup> to O of H<sub>2</sub>O, which is followed by XH elimination and replacement of X by OH.18 We did not observe conversion of the protonated *p*-aminophenoxyl radicals into the hydroquinone cation radical presumably because, under experimental conditions used, radical-radical reactions dominate slow hydrolysis. However, in steady-state oxidation of acidic *p*-aminophenol by mild oxidants, such as  $S_2O_8^{-2}$ , hydrolysis was observed to be complete in a few hours.

In summary, we have presented vibrational spectroscopic evidence of unusual protonation forms of a zwitterionic  $\pi$  radical in water that mimics redox-active sites in a variety of biological systems.

### ACKNOWLEDGMENT

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- <sup>1</sup>L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960).
- <sup>2</sup>G. N. R. Tripathi, J. Am. Chem. Soc. **120**, 5134 (1998).
- <sup>3</sup>G. N. R. Tripathi, J. Phys. Chem. **102**, 2388 (1998).
- <sup>4</sup>G. N. R. Tripathi, Y. Su, J. Bentley, R. W. Fessenden, and P.-Y. Jiang, J. Am. Chem. Soc. **118**, 2245 (1996); G. N. R. Tripathi and Y. Su, *ibid.* **118**, 2235 (1996); G. N. R. Tripathi, Y. Su, and J. Bentley, *ibid.* **117**, 5540 (1995); Y. Su and G. N. R. Tripathi, *ibid.* **116**, 4405 (1994).
- <sup>5</sup>R. P. Bell, *The Proton in Chemistry* (Cornell University Press, Ithaca, NY, 1959).
- <sup>6</sup>S. G. Anchell, *The Darkroom Developer* (Butterworth-Heinemann, London, 2000).
- <sup>7</sup>M. Inal and G. Kanbak, Med. Sci. Res. **25**, 323 (1997); R. H. Bisby, S. A. Johnson, and A. W. Parker, J. Phys. Chem. B **104**, 5832 (2000); R. P.

Mason, in *Free Radicals in Biology*, edited by W. A. Pryor (Academic, New York, 1982), Vol. 5; P. D. Josephy, T. E. Eling, and R. P. Mason, Mol. Pharmacol. **23**, 461 (1983), and references cited in these papers.

- <sup>8</sup>G. N. R. Tripathi, J. Chem. Phys. **118**, 1378 (2003).
- <sup>9</sup>G. N. R. Tripathi, J. Phys. Chem. **108**, 5139 (2004).
- <sup>10</sup>C. von Sonntag, *The Chemical Basis of Radiation Biology* (Taylor and Francis, New York, 1987); B. Lesigne, C. Ferradini, and J. Pucheautt, J. Phys. Chem. **77**, 2156 (1973).
- <sup>11</sup>G. N. R. Tripathi, in *Time Resolved Spectroscopy, Vol. 18*, edited by R. J. J. H. Clark and R. E. Hester (Wiley, New York, 1989), pp. 157–218; G. N. R. Tripathi, in *Multichannel Image Detectors II*, edited by Y. Talmi, ACS Symposium Series 236 (Am. Chem. Soc., Washington, D.C., 1983), p. 171;
- <sup>12</sup>B. Lesigne, C. Ferradini, and J. Pucheautt, J. Phys. Chem. **77**, 2156 (1973).
- <sup>13</sup>G. N. R. Tripathi and R. H. Schuler, J. Chem. Phys. **76**, 4289 (1982); J. Phys. Chem. **88**, 1706 (1984); J. Chem. Soc., Faraday Trans. **89**, 4177 (1993); Q. Sun, G. N. R. Tripathi, and R. H. Schuler, J. Phys. Chem. **94**, 6273 (1990).
- <sup>14</sup>R. Liu and X. Zhou, J. Phys. Chem. **97**, 9613 (1993); **97**, 9618 (1993); K.
  S. Raymond and R. A. Wheeler, J. Chem. Soc., Faraday Trans. **89**, 665 (1993); D. M. Chipman, J. Phys. Chem. A **103**, 11181 (1999).
- <sup>15</sup>Wilson notations used for convenience. See F. R. Dollish, W. G. Fateley, and F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds* (Wiley, New York, 1974).
- <sup>16</sup>Assuming a diffusion-controlled rate ( $\sim 10^{10} \text{ s}^{-1}$ ) for the OH<sup>-</sup> reaction in MH+OH<sup>-</sup>  $\leftrightarrow$  M<sup>-</sup>+H<sub>2</sub>O, a pK<sub>a</sub> of >14 for MH would imply a life-time of  $<10^{-10} \text{ s}$  for M<sup>-</sup> to decay by the reaction with water. However, a steady-state concentration of this species can be observed at a much longer time-scale if it is produced at a faster rate ( $>10^{10} \text{ s}^{-1}$ ) using an appropriate concentration of OH<sup>-</sup>.
- <sup>17</sup>The loss of  $p\pi$ -electron from the hydroquinone state,  $-HN-\phi-O^-$ , is largely confined to NH and O. The three-electron bonds formed on exchange of  $(p\pi)^2$  and  $p\pi$  electrons on HN and O in  $(HN-\phi-O)^{-\bullet}$  have a minor effect on the central ring (hydroquinone-like) bonds.
- <sup>18</sup>C. H. Rochester, *Acidity Functions* (Academic, New York, 1970). See, for example, W. M. Shubert and R. H. Quacchia, J. Am. Chem. Soc. **85**, 1278 (1963); **85**, 1284 (1963). Olah and co-workers pioneered the method of detection of such intermediates. See G. A. Olah, A. Molnar, and K. B. Loker, *Hydrocarbon Chemistry* (Wiley-Interscience, New York, 1995).
- <sup>19</sup>The transfer of the electronic charge to -OH<sub>2</sub><sup>+</sup> and -NH<sub>3</sub><sup>+</sup> is possible only at the cost of weakened bonding with the ring and likely dissociation of the radical. Since the cation and dication forms of the radical are interconvertible by changing the acid concentration, the possibility of the radical dissociation was ruled out.
- <sup>20</sup>The 8aCC frequency is lower than 1600 cm<sup>-1</sup> in aniline cation and anisole and *p*-anisole cation radicals (Ref. 11). Also see G. N. R. Tripathi, Chem. Phys. Lett. **199**, 409 (1992); G. N. R. Tripathi and R. H. Schuler, J. Chem. Phys. **86**, 3795 (1987).
- <sup>21</sup>Structural calculations on the radicals in question lack predictive value and a satisfactory calculation of the vibrational frequencies of  $(HO(H)\phi NH_2)^{2+\bullet}$  could not be performed.