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Time-Resolved Raman Study of the Oxidation Mechanism of Aromatic Diamines by •OH Radical in Water

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The mechanism of the •OH oxidation of aromatic diamines in water has been examined using time-resolved Raman spectroscopy as a diagnostic tool and *p*-phenylenediamine (PDA) as a model system. It has been shown that the initial transient that is formed in the reaction in basic solutions is the cation ($PDA^{\bullet+}$) radical and not the •OH adduct of *p*-phenylenediamine (PDA−OH•), as thought previously. In mildly acidic solutions, where PDA exists in its amine-protonated forms, a fraction of •OH radicals is converted into the *p*-aminophenoxyl radical (APhO•) at the expense of $PDA^{\bullet+}$. The production of $PDA^{\bullet+}$ occurs in two steps: first, simultaneously with the •OH adducts at a diffusion-controlled rate and, second, on decay of the adduct radicals on microsecond times. Thus, transient absorption spectra display a marked pH dependence that was attributed previously to the acid−base conversion of the •OH adduct and cation radicals. It is concluded that direct electron transfer (ET) is the dominant pathway in the •OH oxidation of neutral diamines, which competes with adduct-mediated electron transfer (AMET) path on amine protonation.

Introduction

Because of its wide chemical importance, the reaction of hydroxyl radical (•OH) with aromatic molecules and ions in water has remained a topic of vigorous research for decades.[1−6] Transient absorption spectra and kinetics in the reaction are generally interpreted in terms of initial formation of •OH adducts followed by H^+/water catalyzed loss of OH^-, which results in the loss of an electron from the molecule or ion (adduct-mediated electron transfer; AMET).[1,5] This oxidation mechanism has been revised recently to account for a direct electron transfer (ET) component in the reaction that was not recognized previously.[6] In the new reaction mechanism, the •OH radical displays dual reactive behavior (ET as well as AMET). It reacts primarily by the AMET mechanism when the ionization potential (IP) of a neutral aromatic molecule is greater than 8 eV and by direct electron transfer (ET) when IP is less than 7 eV. In the intermediate IP range, both mechanisms are effective. The aromatic diamines[7] are chemical systems of relatively low IP and, therefore, likely to display the ET mechanism. On the other hand, protonation of the amine should increase IP,[8] which should affect the nature of the reaction intermediates and their formation mechanism. In particular, an increase in the AMET component and a decrease in ET are expected. Thus, the pH dependence of the •OH oxidation of aromatic diamines should provide a test for the new mechanism[6] versus the AMET mechanism.[5,9] With this perspective, we have examined the reaction of •OH with *p*-phenylenediamine (PDA), a prototype of aromatic diamines, in mildly acidic to basic aqueous solutions. Time-resolved resonance Raman spectroscopy was used for transient identification. We report, in this work, the formation of the *p*-phenylenediamine cation ($PDA^{\bullet+}$) and *p*-aminophenoxyl (APhO•) radicals on oxidation of singly protonated *p*-phenylenediamine (H^+PDA). The phenoxyl radical (APhO•) is not produced when neutral PDA is oxidized. The results confirm the dual oxidative behavior (DOB) of the •OH radical in water[6] and explain the pH dependence of the transient absorption spectra in aromatic diamines, observed in earlier studies.[9]

The AMET path in the •OH oxidation of aromatic diamines, including PDA, was first proposed in an early work, which used optical absorption for transient identification and kinetic monitoring.[9] The initial absorption in basic solutions was thought to be due to the •OH adduct radical that acted as a precursor for the cation radical that was presumed to appear several microseconds later. Interestingly, the absorption spectra attributed to the adduct and cation radicals were found to be similar, with few distinguishing features. A marked pH dependence was noted in the transient absorption spectra recorded at different time intervals, which was ascribed to the protonation of the amine group of the •OH adduct and cation radicals. These early spectral and kinetic interpretations have often been used as the standard in the investigations of analogous systems and have never been questioned.

The electronic structure of the aqueous *p*-phenylenediamine cation radical ($PDA^{\bullet+}$) has been studied, in our laboratory, by time-resolved resonance Raman spectroscopy.[10] Substantial double bond character of the radical CN bonds, indicated by the stretching frequency (1422 cm^{-1}), can only be visualized by placing most of the excess positive charge on the radical on two nitrogen atoms.[10,11] Therefore, proton addition to the amine groups of $PDA^{\bullet+}$ is not possible in mildly acidic solutions because of strong electrostatic repulsion.[12,13] We were not able to observe the $H^+PDA^{\bullet+}$ radical even in strongly acidic aqueous solutions (pH < 0). Obviously, protonation of the cation radical is not a plausible explanation for the pH dependence of the transient absorption spectra and kinetics. It is shown here that the previous mechanistic conclusions were based on misidentification of the reaction intermediates.

Experimental Procedure

The hydroxyl (•OH) radical was produced by electron pulse irradiation of N_2O-saturated water. The hydrated electron (e_{aq}^-)

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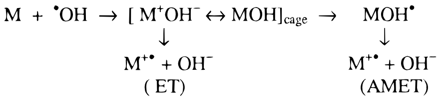
and hydroxyl radical ($^{\bullet}$OH) are the main products of radiolysis of oxygen-free water on the 100 ns time scale.[1,3] In N_2O-saturated water, the e_{aq}^- reacts with N_2O (26 mM) to convert into $^{\bullet}$OH radical in less than 5 ns ($e_{aq}^- + N_2O \rightarrow {}^{\bullet}OH + OH^- + N_2$; rate constant of 9.1×10^9 M^{-1} cm^{-1}). The $H^{\bullet}$ radical is a minor product (~10%) of the radiolysis of water that reacts with aromatic molecules by addition but does not form the cation radical.[1,3] The oxidizing species $N_3^{\bullet}$ was prepared by reaction of $^{\bullet}$OH radical with 0.1 M NaN_3 dissolved in solution ($N_3^- + {}^{\bullet}OH \rightarrow OH^- + N_3^{\bullet}$; rate constant of 1.2×10^{10} M^{-1} cm^{-1}).[3] The yield of $N_3^{\bullet}$ was taken to be equal to that of $^{\bullet}$OH. The $N_3^{\bullet}$ radical generally reacts with organic substrates by electron transfer.[1] Therefore, comparison of the radical cation yield in the $^{\bullet}$OH oxidation with that in $N_3^{\bullet}$ helps to determine the fraction of the $^{\bullet}$OH radical involved in electron transfer.[6,14] The $^{\bullet}$OH oxidation is a complex reaction involving several transients with overlapping absorption spectra. Identification of the reaction intermediates, estimation of their yields, and kinetic determinations are not always possible by the commonly used optical absorption method. Therefore, time-resolved resonance Raman spectroscopy was employed for transient identification.[14,15]

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.[14-16] 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. Absorbance was generally calibrated in terms of extinction coefficient, assuming the yield of radical equal to that of $^{\bullet}$OH. For fractional yields, the actual extinction coefficient can be estimated by dividing the apparent extinction coefficient in the spectra by the fraction. In Raman experiments, 2 MeV, ~100 ns electron pulses, delivered by a Van de Graaff accelerator at dose rates that produced $10^{-4}-10^{-5}$ 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 by 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 *S*/*N* 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.

Results and Discussion

The aqueous *p*-phenylenediamine, like most aromatic diamines, exists in three protonation forms (PDA, H^+PDA, and H^+PDAH^+; pK_as of 3.3 and 6.1) in a narrow pH range.[9,17] Moderately strong PDA solutions (greater than millimolar) act as buffers on electron pulse irradiation. In basic solutions (pH > 8), it is the neutral PDA that is available for reaction, and in very acidic solutions (pH < 2.5) it is H^+PDAH^+. At pH 4.5, the singly protonated form (H^+PDA) should dominate the reaction. If oxidation occurred by the AMET mechanism in all protonation forms, as claimed previously,[9] the $^{\bullet}$OH radical would add initially to different ring sites. The subsequent H^+/H_2O catalyzed[18] OH^- loss from the adduct radicals would produce the cation radical.[1,5] Lifetimes ranging between 3 and 20 μs have been ascribed to the $^{\bullet}$OH adducts of different aromatic amines.[9] The $^{\bullet}$OH addition to the ring sites adjacent to the substituent groups may lead to elimination of the substituent, instead of OH^-, forming an oxy radical.[1,6,14] The latter possibility does not arise if reaction has occurred by direct electron transfer (ET), since only the cation radical would be produced. The observation of an oxy radical is definite evidence of the $^{\bullet}$OH addition. Surprisingly, no oxy radical has been identified previously in the $^{\bullet}$OH oxidation of aromatic diamines.[9]

Dual Oxidative Behavior of $^{\bullet}$OH in Water. In the new oxidation mechanism,[6] the $^{\bullet}$OH radical displays dual oxidative behavior (DOB), as illustrated in the following reaction scheme.



$$\begin{array}{ccccc} M + {}^{\bullet}OH & \rightarrow & [\,M^{+}OH^{-} \leftrightarrow MOH]_{cage} & \rightarrow & MOH^{\bullet} \\ & & \downarrow & & \downarrow \\ & & M^{+\bullet} + OH^{-} & & M^{+\bullet} + OH^{-} \\ & & (\,ET) & & (AMET) \end{array}$$

The adduct and a fraction of cation radicals can appear simultaneously in the reaction, at the rate of $^{\bullet}$OH encounter with M in water. The formation of the cation radical in two steps, first by ET and then by AMET, is an important feature of the DOB mechanism, although these pathways may not be always kinetically distinguishable.

The relative energies of the M^+OH^- and MOH electronic configurations, which are likely to be accessed on $^{\bullet}$OH encounter with M in water, determine the ET and AMET components of the DOB mechanism.[6] A simple description of DOB is possible in terms of IPs for neutral aromatics. Ionization involves a delocalized pπ electron. As pointed out earlier, ET is the dominant oxidation pathway for IP(M) < 7 eV and AMET for IP(M) > 8 eV. In the intermediate IP range, oxidation by both mechanisms is possible. On protonation of aromatic amines (MH^+), an increase in IP is expected.[8] However, complications arise due to large solvation effects on ionic species (e.g., H^+, MH^+) involved in acid−base equilibria, and a description of the reaction in terms of the gas-phase IP is not feasible. Instead, it would be reasonable to consider the standard free energy difference ($\Delta G°$) between MH^+ and M in water, known from pK_a, to visualize the effects of protonation on the reaction. For example, the gas-phase IP in PDA is 7.1 eV.[7] The oxidation of H^+PDA (pK_a = 6.1; ΔG^0 = 0.36 eV) and H^+PDAH^+ (pK_a = 3.3; ΔG^0 = 0.2 eV) is likely to resemble that of neutral molecules with IP ≈ 7.46 and ~7.66 eV, respectively. These IP values are in the range where the ET and AMET components of DOB are expected to be conveniently observed.[6] The loss of a pπ electron from H^+PDA and H^+PDAH^+ would initially produce the $H^+PDA^{\bullet+}$ and $H^+(PDA^{\bullet+})H^+$ radicals. Since these species are unobservable even in extremely strong acidic solutions (pH < 0), they must be extremely short-lived (<10^{-11} s) and must convert instantly into $PDA^{\bullet+}$ in mildly acidic solutions, without a perceptible effect on formation kinetics. We present here spectroscopic and kinetic evidence for the formation of $PDA^{\bullet+}$, first simultaneously with $H^+PDA-OH^{\bullet}$ (ET step) and then on decay of $H^+PDA-OH^{\bullet}$ ($H^+PDA-OH^{\bullet} \rightarrow PDA^{\bullet+} + H_2O$; AMET step), displaying the dual oxidative behavior (DOB) of $^{\bullet}$OH in water.

$^{\bullet}$OH Oxidation of PDA in Basic Solutions. For a proper understanding of the pH effect on oxidation of *p*-phenylenediamine in acidic solutions, comparison with the reaction intermediates and their kinetic behavior in the neutral molecule is required.[19] Figure 1a depicts the absorption spectrum obtained 1 μs after electron pulse irradiation of an N_2O-saturated aqueous solution containing 1 mM PDA at pH 8. The reaction period, as determined by the temporal evolution of optical absorption in Figure 1a, was 120 (±5) ns, which gave a rate constant of 8.3 (±0.5) $\times 10^9$ M^{-1} cm^{-1}. Under the chemical conditions used, this spectrum should mainly contain contributions from

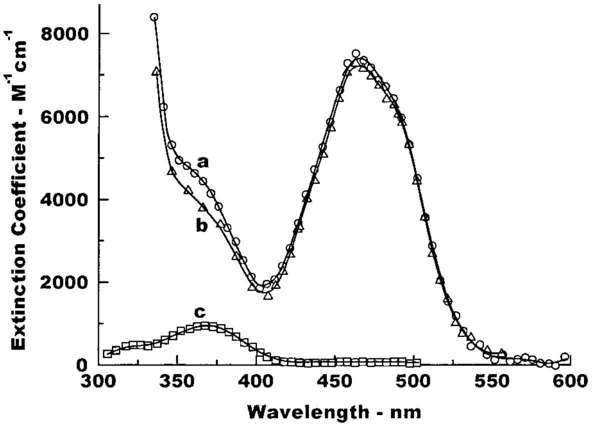


Figure 1. (a) Absorption spectrum obtained 1 μs after electron pulse irradiation of N_2O-saturated aqueous solution containing 1 mM *p*-phenylenediamine at pH 7.8 ($^{\bullet}$OH oxidation, ○). Absorption spectra on addition of (b) 0.1 M NaN_3 ($N_3^{\bullet}$ oxidation, △), and (c) 0.2 M *tert*-butyl alcohol ($^{\bullet}$OH scavenger, □) to the solution of spectrum a. Spectrum in Figure 1c is of H$^{\bullet}$ atom adduct (PDA−H$^{\bullet}$).

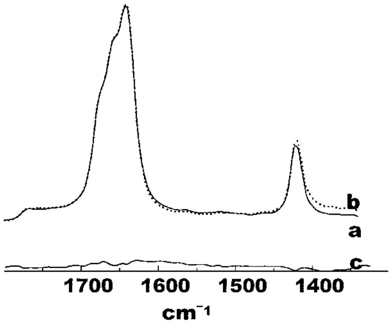


Figure 2. (a) Raman spectrum obtained by excitation at 460 nm, 100 ns after electron pulse irradiation of N_2O-saturated aqueous solution containing 2 mM *p*-phenylenediamine at pH 8 ($^{\bullet}$OH oxidation, solid line). (b) Raman spectrum on addition of 0.1 M NaN_3 to the solution ($N_3^{\bullet}$ oxidation, dotted line). (c) (Spectrum a) − (spectrum b).

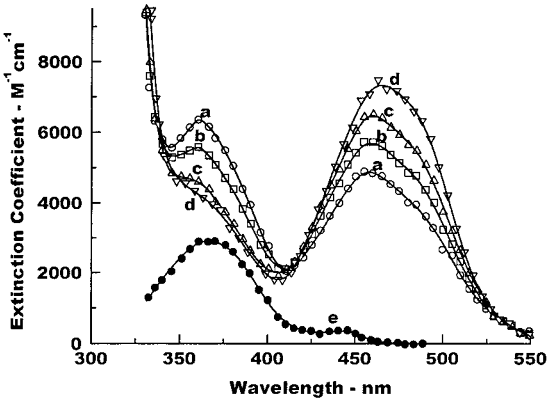


Figure 3. (a) Absorption spectra on electron pulse irradiation of N_2O-saturated aqueous solution containing 1 mM *p*-phenylenediamine at pH 4.5. (a) 1 μs (○), (b) 6.5 μs (□), and (c) 40 μs (△) after the pulse and (d) $N_3^{\bullet}$ oxidation at pH 11 (▽). (e) (Spectrum a) − 0.7(spectrum c) (●).

the transients produced by $^{\bullet}$OH oxidation, with a small contribution from the species produced due to H$^{\bullet}$ reaction. Absorption due to the latter species was ascertained by adding 0.2 M *tert*-butyl alchohol in solution to scavenge $^{\bullet}$OH radicals (Figure 1c). The spectrum in Figure 1c is tentatively attributed to the H$^{\bullet}$ atom adduct (PDA−H$^{\bullet}$), which will not be discussed further. Comparison is made in Figure 1b with the 1 μs absorption spectrum of the species produced when an N_2O-saturated aqueous solution containing 1 mM PDA and 0.1 M NaN_3 at pH 8 was subjected to electron pulse irradiation. Oxidation in this case is by $N_3^{\bullet}$ radical (rate constant of 6×10^9 M^{-1} cm^{-1}), which is believed to produce the cation radical (PDA$^{\bullet+}$) by direct electron transfer. The H$^{\bullet}$ atom is completely scavenged by N_3^- because of its high concentration in solution,[1] and the PDA−H$^{\bullet}$ species is not formed. The absorption spectra in parts a and b of Figure 1 are almost identical (a strong band at ~460 nm with unresolved shoulder at 480 nm) except for the 360 nm region where the H$^{\bullet}$ adduct makes a small contribution to the spectrum in Figure 1a. There is no indication from the absorption spectra in Figure 1 that two distinct species are produced on $^{\bullet}$OH and $N_3^{\bullet}$ oxidation of PDA in basic solutions. It is possible, however, that the $^{\bullet}$OH adduct (PDA−OH$^{\bullet}$) and cation (PDA$^{\bullet+}$) radicals have similar absorption spectra, as claimed previously.[9] Therefore, a definite identification of transients is essential before the previous spectroscopic and kinetic interpretations in terms of AMET can be confidently discarded.

The Raman spectrum excited at 460 nm and recorded 100 ns after the electron pulse irradiation of an N_2O-saturated 2 mM PDA solution at pH 8 ($^{\bullet}$OH oxidation) is shown in Figure 2a. An identical Raman spectrum is obtained on $N_3^{\bullet}$ oxidation of PDA in basic solutions (Figure 2b). A Raman spectrum of PDA$^{\bullet+}$, prepared by alternative methods, is also available in the literature.[11] On comparison, one finds that the Raman spectra in Figure 2, with prominent vibrational features at 1674, 1658, 1642, and 1422 cm^{-1}, are undoubtedly due to the aqueous PDA$^{\bullet+}$. The resonance Raman spectra in parts a and b of Figure 2 have similar spectral intensities (see Figure 1c). Therefore, one must conclude that the yield of PDA$^{\bullet+}$ in the $^{\bullet}$OH oxidation, 100 ns after the electron pulse, is the same as in the $N_3^{\bullet}$ oxidation. The 100 ns Raman spectra excited at 530 nm, where transient absorption is much weaker than at 460 nm, were also no different whether the cation radical was prepared in the reaction of $^{\bullet}$OH or $N_3^{\bullet}$. Thus, a small possibility that PDA$^{\bullet+}$ may form on photolysis of PDA−OH$^{\bullet}$ by the Raman probe laser pulse is ruled out. In another experiment, the PDA concentration in solution was raised to 20 mM, accelerating the reaction period. The formation kinetics of PDA$^{\bullet+}$ was monitored by its 480 nm absorption. About 85% of PDA$^{\bullet+}$ appeared at a diffusion-controlled rate (period of <10 ns) and about 10−15% with a period of 50 ns. However, it was not possible to ascertain the origin of the latter component. We assume it to arise from $^{\bullet}$OH AMET. However, hydrogen abstraction by the $^{\bullet}$OH radical from amine, followed by rapid protonation ($pK_a = 13.2$ for PDA$^{\bullet+}$),[12] can also account for a small amount of PDA$^{\bullet+}$ produced on the nanosecond time scale.

The DOB mechanism predicts the fraction of PDA$^{\bullet+}$ produced via $^{\bullet}$OH adduct of H$^+$PDA (AMET) to be relatively larger, and formation rate relatively smaller, than that in neutral PDA. Therefore, the PDA$^{\bullet+}$component that originates from the $^{\bullet}$OH adduct (H$^+$PDA−OH $^{\bullet}$) can be identified with certainty.

Oxidation of PDA in Acidic Solutions. Electron pulse irradiation was performed on an N_2O-saturated aqueous solution of PDA at pH 4.5 where significant amounts of doubly protonated (H$^+$PDAH$^+$; $pK_a = 3.3$) and unprotonated *p*-phenylenediamine (PDA) are not present in the solution. The reaction rate constant was found to be similar to that in basic solutions, with a reaction period of ~120 ns with 1 mM PDA in solution. Figure 3a−c represents the absorption spectra recorded at different time intervals after the electron pulse. Comparison is made with the 1 μs absorption spectrum when $N_3^{\bullet}$ radical was used as oxidant (Figure 3d). The 40 μs absorption in Figure 3c ($^{\bullet}$OH oxidation) is weaker than the 1 μs absorption in Figure 3d partly because of decay of PDA$^{\bullet+}$

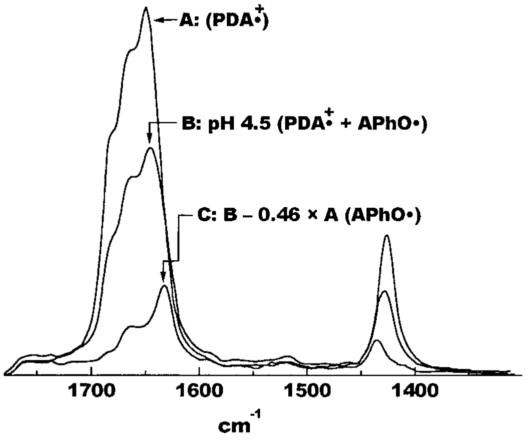


Figure 4. Raman spectrum obtained by 460 nm excitation 100 ns after electron pulse irradiation of N_2O-saturated aqueous solution containing 2 mM *p*-phenylenediamine at (A) pH 8 and (B) pH 4.5. (C) (Spectrum A) − 0.46(spectrum B).

and its precursor by radical−radical reactions (about 10%)[20] and partly because of the formation of another radical, to be identified later, at the expense of $PDA^{\bullet+}$. The absorption at 365 nm (λ_{max}) in Figure 3 decays on microsecond times with concomitant growth of absorption at 460−480 nm. Conversion of the 365 nm species into the 460 nm species occurs at a rate of 1.3×10^5 s^{-1}.[18] However, the 460−480 nm absorption is quite prominent in the 1 μs spectrum (Figure 3a), which cannot be accounted for by the decay of the 365 nm transient.

The absorption spectra in Figures 1 and 3 may suggest that it is the cation radical that is responsible for absorption in the 400−500 nm region in acidic as well as basic solutions. However, there is an overlapping absorption due to another species hidden underneath the spectra of Figure 3a−c that is not readily discernible. The Raman spectra were recorded by excitation at several wavelengths in the 440−530 nm region to identify the species. Figure 4 compares the 440 nm Raman spectra in the 1300−1800 cm^{-1} region, obtained on pulse radiolysis of N_2O-saturated 2 mM PDA solutions at pH 4.5 and 8. The spectrum at pH 4.5 (Figure 4B) is considerably weaker than the spectrum at pH 8 (Figure 4A) and contains vibrational features other than those of $PDA^{\bullet+}$. On digital subtraction of the spectrum in Figure 4B from that in Figure 4A, using a scaling factor of 0.46, one obtains the spectrum in Figure 4C that is readily identifiable as that of the *p*-aminophenoxyl radical ($APhO^{\bullet}$), published in the literature.[21,22] On comparison of the spectrum in Figure 4C with that of *p*-aminophenoxyl radical, prepared by $N_3^{\bullet}$ oxidation of *p*-aminophenol at pH 11, the yield of $APhO^{\bullet}$ in the $^{\bullet}OH$ oxidation of H^+PDA is estimated as 16-($\pm$2)%. The *p*-aminophenoxyl radical ($APhO^{\bullet}$) is not produced on the $^{\bullet}OH$ oxidation of PDA in basic solutions. Presumably, $APhO^{\bullet}$ is formed on $^{\bullet}OH$ addition to the ring carbon site (ipso carbon position) bonded to NH_3^+, followed by very fast NH_4^+ elimination. To our knowledge, spectroscopic evidence of $^{\bullet}OH$-induced deamination in the acid form of an amine has been obtained for the first time. The $PDA^{\bullet+}$ Raman intensity in Figure 4B is about 46% of the intensity in Figure 4A. Thus, 46% of the $^{\bullet}OH$ radicals produced on radiolysis of water react with H^+−PDA to produce $PDA^{\bullet+}$ and 16% to produce $APhO^{\bullet}$ radicals. This accounts for the fate of about 62% of the $^{\bullet}OH$ radicals at 1 μs. The remaining 38% of the $^{\bullet}OH$ radicals are very likely bound to PDA ($H^+PDA{-}OH^{\bullet}$) at 1 μs. Because of the high radical concentration used in Raman experiments, the loss of radicals by bimolecular reactions occurs much more rapidly than in absorption experiments. Therefore, optical absorption is more dependable for monitoring the slow conversion of the adduct radical ($H^+PDA{-}OH^{\bullet}$) into $PDA^{\bullet+}$.

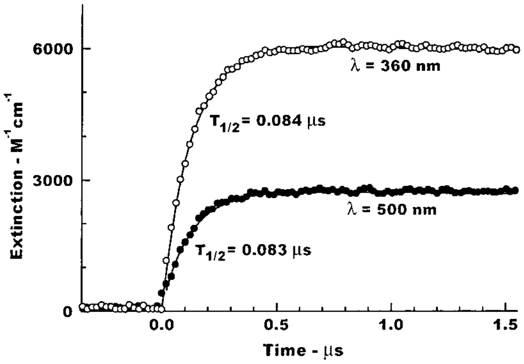


Figure 5. Temporal evolution of transient absorption on electron pulse irradiation of N_2O-saturated aqueous solution containing 1 mM *p*-phenylenediamine at pH 4.5: (○) 360 nm; and (●) 500 nm.

Once it is established by Raman spectroscopy that the 400−500 nm absorption in the spectrum of Figure 3a is largely due to $PDA^{+\bullet}$, its contribution can be subtracted from the spectrum. The difference spectrum is shown in Figure 3e.[23] This spectrum closely resembles the absorption spectra of $^{\bullet}OH$ adducts of benzene derivatives.[1] Unfortunately, we were unable to obtain the resonance Raman spectrum of this species. Formation of the cation radical (460 nm species) via decay of the $^{\bullet}OH$ adduct (365 nm species) is well-documented (AMET mechanism).[1,5] However, that accounts for only 33($\pm$5) % of the adduct precursor of $PDA^{\bullet+}$ (Raman estimation 38%) formed in the reaction at pH 4.5 (see parts a and d of Figure 3). The 460−480 nm absorption in Figure 3a is about 65($\pm$5)% of the absorption in Figure 3d. On excluding the *p*-aminophenoxyl contribution[21,22] to this absorption, one estimates a yield of 55-($\pm$5)% for $PDA^{\bullet+}$ (Raman estimation 46%) at 1 μs. The H^+-$PDA{-}OH^{\bullet}$ and $PDA^{\bullet+}$ transients in Figure 3a appear simultaneously in the reaction, as evident from the formation kinetics on the nanosecond time scale, monitored at 360 and 500 nm (to avoid phenoxyl contribution), respectively (Figure 5). In brief, 55($\pm$5)% of the $^{\bullet}OH$ radicals produced on radiolysis of water oxidize H^+PDA into $PDA^{\bullet+}$ at a diffusion-controlled rate and 33($\pm$5)% at a rate of 1.3×10^5 s^{-1} via initial addition (two-step formation). About 16% of the $^{\bullet}OH$ addition to H^+PDA results in the *p*-aminophenoxyl radical. Thus, the $^{\bullet}OH$ radical adds as well as transfers an electron with almost equal probability on encounter with H^+PDA in water.

Because of molecular asymmetry of H^+PDA, there is a remote possibility that the two-step production of the cation radical, discussed above, may arise because of the loss of OH^- from two distinct $^{\bullet}OH$ adducts, one being too short-lived to be observed. If that were the case, the two steps should merge into one in the $^{\bullet}OH$ oxidation of doubly protonated PDA (H^+-$PDAH^+$) where only one adduct precursor of the cation radical is possible. The $^{\bullet}OH$ adduct at the ipso position produces the *p*-aminophenoxyl radical (protonation pK_a of 2.2).[22] However, the formation kinetics of $PDA^{\bullet+}$ still has two components, as shown in Figure 6. At pH < 4, the hydrated electron reacts with H^+ to convert into $H^{\bullet}$ atom (rate constant of 3×10^{10} M^{-1} cm^{-1}) and the yield of the $^{\bullet}OH$ radical becomes pH-dependent in N_2O-saturated solutions. Therefore, pulse radiolysis was performed on an N_2-saturated aqueous solution containing 2 mM PDA at pH 2.5. At this pH, there is a large contribution to the 360 nm absorption by the $H^{\bullet}$ atom adduct, which does not decay into the cation radical. It can be seen from Figure 6 (absorbance scaled for $^{\bullet}OH$ radiation yield) that about 40% of the absorption at 480 nm evolves simultaneously with the

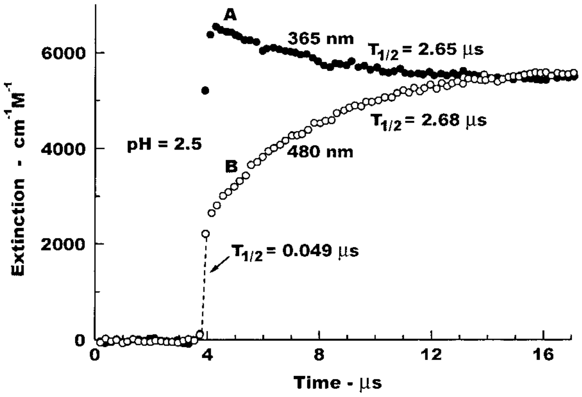


Figure 6. Temporal evolution of transient absorption on electron pulse irradiation of N_2-saturated aqueous solution containing 2 mM *p*-phenylenediamine at pH 2.5: (A) 365 nm (●); (B) 480 nm (○).

365 nm absorption. On the other hand, the remaining 60% grows with the decay of the 365 nm absorption, with a half period of ~2.7 µs.[18] On comparison with the $PDA^{\bullet+}$ formation in H^+-PDA (Figure 3), one estimates a drop of 25(±5)% in the yield (in terms of $^{\bullet}OH$ concentration) in the diffusion-controlled component (ET) and an increase of about the same magnitude in the adduct-mediated (AMET) component, as expected from the DOB mechanism. The H^+-catalyzed rate constant for the OH^- elimination from the $^{\bullet}OH$ adduct of H^+PDAH^+, estimated as $8(\pm 2) \times 10^7$ M^{-1} cm^{-1},[18,24] is extremely low compared to that of a diffusion-controlled process. We attribute this low value to the Coulombic barrier experienced by the proton in approaching the $^{\bullet}OH$ adduct. It is well-known that the $^{\bullet}OH$ addition occurs preferentially on the ortho and para positions of the substituted benzenes with substituent groups having strong pπ electron-donating properties (e.g., OH, NH_2).[1,2,25] A significant amount of $^{\bullet}OH$ addition at a position meta to $-NH_2$ in H^+PDA is not expected. Therefore, only one $^{\bullet}OH$ adduct (ortho) plays a dominant role in the cation radical formation via AMET, and the formation kinetics qualitatively resembles that in H^+PDAH^+ where only one adduct precursor is possible.

pH Dependence of Transient Absorption. As discussed in the preceding sections, the 460−480 nm transient absorption is associated with the *p*-phenylenediamine cation radical ($PDA^{\bullet+}$) in basic as well as acidic solutions, but its yield depends on the time of observation and pH. In basic solutions, the $^{\bullet}OH$ radical is totally (100%) consumed to produce the cation radical in less than 1 µs under the chemical conditions employed. On the other hand, the $^{\bullet}OH$ oxidation of H^+PDA at pH 4.5 produces only 55(±5)% of the cation radicals in 1 µs. In addition, 16% of the $^{\bullet}OH$ radicals are lost in forming the *p*-aminophenoxyl ($APhO^{\bullet}$) radical, with λ_{max} at 444 nm.[21] Therefore, the $PDA^{\bullet+}$ absorption at 460−480 nm, measured 1 µs after the electron pulse, decreases as the pH of the solution is lowered from 8 to 4.5. This pH dependence relates to the acid−base equilibrium of PDA but not to that of its $^{\bullet}OH$ adduct, as thought previously. This does not mean that the adduct radical (PDA−$^{\bullet}OH$) cannot protonate in acidic solutions. In all probability, its protonation pK_a would be very similar to that of the parent molecule.[12] However, there is no evidence that the $^{\bullet}OH$ adduct is formed in appreciable concentration in basic solutions or that it absorbs in the 460−480 nm region.

In mildly acidic solutions, conversion of the $^{\bullet}OH$ adduct into the cation radical ($PDA^{\bullet+}$) is complete in less than 40 µs (rate of 1.3×10^5 s^{-1}). The pH dependence of the 480 nm absorption, 40 µs after the electron pulse, can be explained in terms of the pH-dependent yield of the *p*-aminophenoxyl radical ($APhO^{\bullet}$), as illustrated in Figure 7. We ignore here the loss of radicals due to radical−radical reactions (about 10%). The yield of $APhO^{\bullet}$ was measured 1 µs after the electron pulse, by Raman spectroscopy, on radiolysis of N_2O-saturated 2 mM PDA solutions in the pH range 3−8. The fraction of the $^{\bullet}OH$ radical used in the $APhO^{\bullet}$ production increases from 0 to 14% (Figure 7A) as PDA converts into its acid form (H^+PDA). There is a corresponding decrease in the $PDA^{\bullet+}$ yield, estimated from the 480 nm absorption, 40 µs after the pulse (Figure 7B). The sum of the $PDA^{\bullet+}$ and $APhO^{\bullet}$ concentrations shows very little variation with pH ("A + B" of Figure 7). This sum represents the total radiation yield of $^{\bullet}OH$ if the loss of radicals by second-order reactions is not considered. The titration curves in parts A and B of Figure 7 reflect the protonation properties of the parent compound. However, the diagram in Figure 7B can be easily misinterpreted to be due to the acid−base equilibrium of the cation radical. Therefore, it is not surprising that the $^{\bullet}OH$ adduct and cation radicals of various aromatic amines have been erroneously assigned pK_a values very close to those of the parent molecules, using similar titration curves.[9]

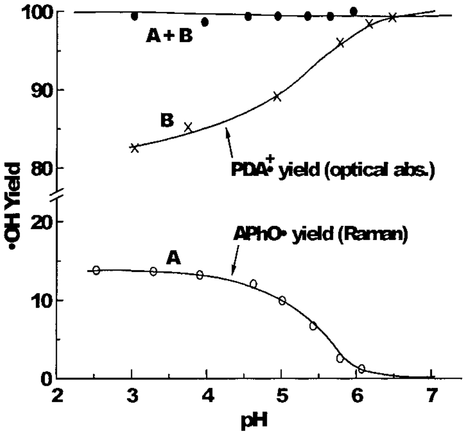


Figure 7. pH dependence of the yields of the *p*-phenylenediamine cation ($PDA^{\bullet+}$) and *p*-aminophenoxyl ($APhO^{\bullet}$) radicals, as determined by transient absorption and time-resolved Raman resonance Raman, respectively (see text).

Conclusions

The pH effect on the $^{\bullet}OH$ oxidation of *p*-phenylenediamine in water has been examined as a model system for elucidating the reaction mechanism in aromatic diamines. Our experimental approach differs from the earlier investigations, since it combines the commonly used transient absorption method with time-resolved resonance Raman spectroscopy. We present here the vibrational spectroscopic evidence of the $^{\bullet}OH$ addition, followed by deamination, in the acid form of an aromatic diamine, for the first time. Deamination does not occur in the basic form of the molecule. The identification of an aromatic oxy radical as an intermediate in the reaction of $^{\bullet}OH$ with protonated diamines (e.g., *p*-aminophenoxyl radical in *p*-phenylenediamine) provides a simple explanation for the marked pH dependence of the transient absorption spectra and kinetics.

An important finding of the work relates to the reaction mechanism where the $^{\bullet}OH$ radical exhibits dual oxidative behavior (DOB) with respect to the different protonation forms of an aromatic molecule. The transfer of a delocalized pπ electron from *p*-phenylenediamine (H^+PDA and H^+PDAH^+) to the $^{\bullet}OH$ radical occurs directly (ET) at a diffusion-controlled rate and via solvent-induced ionic fragmentation of the covalently bonded $^{\bullet}OH$ adducts (AMET or adduct-mediated electron transfer) on the microsecond time scale. The ET component of the DOB decreases, and AMET increases, on proton additions to amine. The effect can be conveniently described in terms of the ionization potential (IP) of the neutral molecule and free energy change ($\Delta G°$) on protonation. It appears that misidentification of the reaction intermediates has been primarily responsible for the AMET interpretation of the •OH oxidation of aromatic diamines.

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