COMMENTS

A Time-Resolved Raman Study of the Reaction of OH Radicals with *p*-Phenylenediamine†

Sir: Hydroxyl radicals react with most organic materials largely by addition to the ring to form hydroxycyclohexadienyl radicals which in many cases can be observed directly by optical[1] or ESR methods[2] or can be oxidized further to form hydroxylated products.[3] For aromatics substituted with amino groups the OH adducts decay rapidly to form radical cations.[4] Direct oxidation to the radical cation by electron transfer to OH also is possible. Experimental evidence distinguishing these initial and secondary processes largely comes from transient absorption studies where characteristic differences between the spectra of the initial and final intermediates provide a ready means for obtaining kinetic information. In a previous study of the reaction of OH with aromatic diamines[5] the absorption spectrum attributed to the OH adducts was reported to be virtually identical with that of the radical cations, differing only in intensity. This situation contrasts with other cases where the radical cations characteristically absorb at a longer wavelength than do the OH adducts. In view of the apparent lack of features that distinguish the reported spectra of the radical cation from that of the OH adducts, the reaction of OH radicals with aromatic diamines needs to be reexamined by a structure-sensitive technique. Here we apply pulse radiolysis methods with time-resolved resonance Raman detection to examine the intermediates formed in the OH oxidation of *p*-phenylenediamine. These studies show that in neutral and basic solution the OH adducts, if formed, have a very short lifetime, that the absorption spectrum previously assigned to the OH adduct is, in fact, that of the radical cation, and that this radical cation does not protonate in moderately acidic solutions.

The time-resolved optical absorption and Raman techniques used in this laboratory have been described previously in detail.[6,7] The OH radical was produced by pulse radiolysis of N_2O-saturated water and reacted with *p*-phenylenediamine (Aldrich) present at concentrations of 0.1–20 mM. Comparative studies using $N_3^•$ radical as a secondary oxidant were carried out in 0.1 M N_3^- solutions. The initial radical concentrations were $\sim 3 \times 10^{-6}$ M in the absorption and $\sim 10^{-4}$ M in the Raman studies. The time resolution in both experiments was limited by the irradiation pulse width, ~10 and ~100 ns, respectively. Absorbances were referenced to that of $(SCN)_2^{•-}$ in the thiocyanate dosimeter.[9] Raman band intensities were compared under similar irradiation conditions.

p-Phenylenediamine is not protonated in neutral or basic solutions (pK_as of the conjugate acids are 3.3 and 6.1). It can be readily oxidized by chemical methods to produce the radical cation which absorbs in the near-ultraviolet and visible regions with maxima at 300, 370, 460, and 490 nm.[10] Pulse radiolysis studies show that at wavelengths longer that 400 nm essentially identical spectra are observed 2 μs after the pulse for direct oxidation by OH and for indirect oxidation by $N_3^•$ where electron transfer is implicated[8] (Figure 1). These spectra are similar to those observed in the chemical oxidation studies. As indicated in Figure 1 there is, in the case of OH oxidation, a small contribution attributable to the H atom addition product in the 360-nm region which is observed for the solution containing 0.1 M *tert*-butyl alcohol. No change in the spectral characteristics with time, other than attributable to radical decay in second-order reactions, are observed at microsecond and longer times. At this point it seems likely that the decrease in spectral intensity previously reported on the 10-μs scale[5] reflects radical decay.

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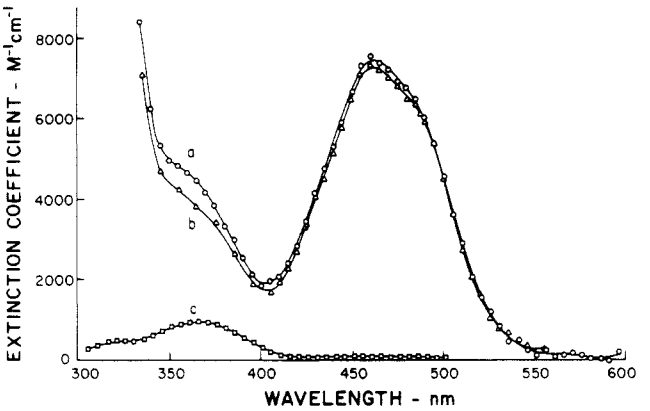

Figure 1. Absorption spectra observed 1.0 μs after irradiating a 1 mM *p*-phenylenediamine solution (N_2O saturated) at pH 7.8 (a) and for solutions also containing 0.1 M NaN_3 (b) or 0.2 M *tert*-butyl alcohol (c). The latter represents the spectrum of the H atom adduct which contributes to (a) but not to (b) where the radical cation is produced directly by electron transfer.

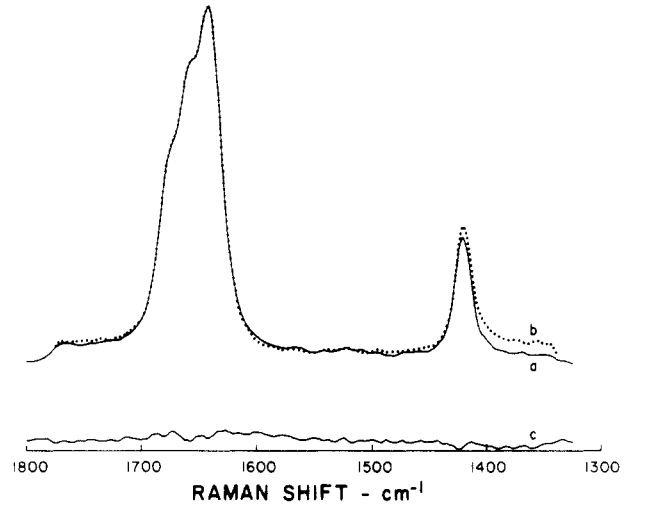

Figure 2. Raman spectra obtained 100 ns after the electron pulse with excitation at 460 nm for a pH 8.0 solution 2 mM in *p*-phenylenediamine and saturated with N_2O (solid spectrum) and also containing 0.1 M NaN_3 (dotted spectrum). There is no significant signal in the difference between the two recordings, showing that the yields of the radical cation are similar.

Raman spectra (Figure 2) recorded ~150 ns after the pulse with excitation at 460 nm show that the absorption band in this region is attributable to the radical cation. The more prominent Raman features at 1674, 1658, 1642, and 1422 cm^{-1} are assignable

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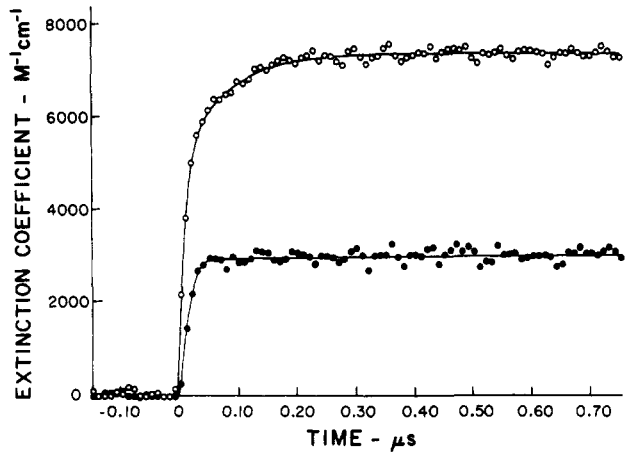

Figure 3. Time dependence of the relative absorbance observed at 480 nm (○) and at 385 nm (●) for a solution containing 10 mM *p*-phenylenediamine at pH 7.8 saturated with N_2O. The rise observed at 385 nm corresponds to the expected period for reaction of OH with *p*-phenylenediamine. The growth of the signal at 480 nm represents the delayed production of about 15% of the radical cation with a period of 50 ns.

to the *p*-phenylenediamine radical cation.[10] As shown in Figure 2, Raman spectra obtained with •OH and N_3• oxidation are identical in vibrational structure and similar in intensity. With OH oxidation the intensity of these bands increases by ~5% at 1 μs. Weaker Raman spectra exhibiting the same Raman bands were obtained with 530-nm excitation. Because the absorption is considerably lower at this wavelength, the possibility of photochemical complications is reduced. We also find that the signal intensity is proportional to the laser pulse power. There is no indication in our studies for any contribution from photolysis of the transient at 460 nm. In summary, these Raman experiments give no evidence for any contributions to the 460-nm absorption band from radicals other than *p*-phenylenediamine radical cations.

The intensity of the Raman bands in the 1300–1800-cm^{-1} region at pH 9 decayed according to second-order kinetics with a first half period ~20 μs at an initial radical concentration of ~2×10^{-4} M. This decay rate corresponds to a second-order rate constant of ~3×10^8 M^{-1} s^{-1}; i.e., the combination reactions are about a factor of 4 slower than those of phenoxyl radicals.[7] In the optical experiments, where the initial radical concentration was only ~3×10^{-6} M, the initial decay rate was correspondingly slower, showing that even at micromolar concentrations decay is predominately due to second-order reactions.

It is clear from these studies that at microsecond times the transient present in the OH oxidation of *p*-phenylenediamine is the radical cation and not the OH adduct as previously reported. Raman studies in acidic solution show that the radical cation persists down to at least pH 2, so that the pK_a of the conjugate acid cannot be 5.9, as previously reported. However, because *p*-phenylenediamine is protonated in acidic solution, the reaction mechanism becomes more complicated, as will be discussed elsewhere, and the previously observed dependence of signal amplitude probably reflects the change in chemistry which follows the protonation of the substrate. In retrospect, it seems clear that the reported pK of 5.9 reflects the second pK of the *p*-phenylenediamine (6.1) rather than that of the radical which must have a $pK_a < 2$.

At this point the principal question remaining is whether OH oxidation in neutral and basic solution takes place via electron transfer or by addition followed by elimination of OH^-. Optical studies on a 20 mM solution, where the OH reaction period is ~5 ns, show that ~85% of the radical cation is produced on the same time scale as •OH attack on the substrate. The kinetic trace at 460 nm (Figure 3) shows, however, that there is a delayed growth of the radical cation with an additional 15% being produced with a period ~50 ns. This additional radical cation can be attributed to a mechanism involving OH addition followed by OH^- elimination or to a electron transfer to an oxidizing radical produced in the initial reaction. The kinetic trace at 360 nm given in Figure 3, where the OH adduct is expected to absorb, does not show a similar growth, indicating that the adduct and cation radicals have similar extinction coefficients at this wavelength.

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