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Inter- and Intramolecular Redox Reactions of Substituted Phenylperoxyl Radicals in Aqueous Solutions

G. I. Khaikin,[†] Z. B. Alfassi,[‡] and P. Neta*

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Substituted phenylperoxyl radicals ($XC_6H_4OO^{\bullet}$) were produced from 4-bromoanisole, 4-bromophenol, and 4-bromo-*N,N*-dimethylaniline (XC_6H_4Br) in irradiated aqueous alcohol solutions. The process involves reductive debromination of these compounds by reaction with solvated electrons and subsequent reaction of the substituted phenyl radicals ($XC_6H_4^{\bullet}$) with O_2. The rate constants for reaction of 4-$MeOC_6H_4^{\bullet}$ with O_2 and with several alcohols and for reactions of 4-$MeOC_6H_4OO^{\bullet}$ with various reductants were determined. The 4-$MeOC_6H_4OO^{\bullet}$ radical decays with a second-order rate law and partially yields the 4-$MeOC_6H_4O^{\bullet}$ radical. On the other hand, 4-$HOC_6H_4OO^{\bullet}$ undergoes an intramolecular electron transfer, through its deprotonated form, $^-OC_6H_4OO^{\bullet}$, to yield the 4-$HOOC_6H_4O^{\bullet}$ radical. $Me_2NC_6H_4OO^{\bullet}$ undergoes both intramolecular transformation and radical−radical processes, but its protonated form, $Me_2HN^+C_6H_4OO^{\bullet}$, undergoes mainly radical−radical reactions.

Introduction

A number of substituted phenylperoxyl radicals have been studied by pulse radiolysis[1−4] and have been shown to oxidize ascorbate, chlorpromazine, $ABTS^{2-}$ [2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) ion], and several phenolic compounds. The rate constants for these reactions are higher than those for oxidation of the same compounds by similarly substituted alkylperoxyl radicals.[5] Little is known, however, about the fate of arylperoxyl radicals upon their self decay. In principle, they may decay via mechanisms similar to those for aliphatic peroxyl radicals,[6] i.e., formation of an unstable tetroxide and subsequent elimination of O_2. This may lead to formation of two identical phenoxyl radicals,

$$2\,C_6H_5OO^{\bullet} \rightarrow C_6H_5OOOOC_6H_5 \rightarrow 2\,C_6H_5O^{\bullet} + O_2 \tag{1}$$

or their combination products (mainly hydroxylated biphenyl).[7]

$$2\,C_6H_5OO^{\bullet} \rightarrow C_6H_5OOOOC_6H_5 \rightarrow (C_6H_4)_2(OH)_2 + O_2 \tag{2}$$

Since both phenylperoxyl and phenoxyl radicals have distinct absorption spectra in the visible range, it should be possible to examine whether the decay of phenylperoxyl occurs via reaction 1 by using kinetic spectrophotometric pulse radiolysis. For this study we chose three substituted phenylperoxyl radicals, namely the 4-methoxy, 4-hydroxy, and 4-dimethylamino derivatives. The phenoxyl radicals that may be produced from these peroxyl radicals exhibit characteristic intense absorptions that have been studied previously[8,9] and thus can serve as a diagnostic tool for the mechanism under study.

The phenylperoxyl radicals were produced in irradiated solutions by reductive debromination of 4-bromoanisole, 4-bromophenol, and 4-bromo-*N,N*-dimethylaniline with solvated electrons ($k_3 \sim 10^9-10^{10}$ L mol^{-1} s^{-1}),[10] followed by the rapid reaction of the phenyl radical with oxygen ($k_4 \sim 10^9$ L mol^{-1} s^{-1}).[1−4] For example,

$$CH_3OC_6H_4Br + e_{aq}^- \rightarrow CH_3OC_6H_4^{\bullet} + Br^- \tag{3}$$

$$CH_3OC_6H_4^{\bullet} + O_2 \rightarrow CH_3OC_6H_4OO^{\bullet} \tag{4}$$

The 4-hydroxyphenyl radical, formed by reduction of 4-bromophenol, has been shown to convert in alkaline solutions into the phenoxyl radical, $k_6 = 1.7 \times 10^5$ s^{-1}.[11]

$$^{\bullet}C_6H_4OH + OH^- \rightarrow {}^{\bullet}C_6H_4O^- + H_2O \tag{5}$$

$$^{\bullet}C_6H_4O^- + H_2O \rightarrow C_6H_5O^{\bullet} + OH^- \tag{6}$$

To minimize the contribution of this intramolecular electron transfer process, we buffered the solutions near pH 7 so that the hydroxyphenyl radical will react with O_2 to form the hydroxyphenylperoxyl (as in reaction 4) with no significant formation of phenoxyl.

In this study, we measured the rate constant for reaction 4. Then we utilized this reaction as a reference for measuring the rate constants for reaction of $CH_3OC_6H_4^{\bullet}$ with three alcohols by competition kinetics. We determined the rate constants for oxidation of several compounds by the peroxyl radical $CH_3OC_6H_4OO^{\bullet}$, and finally, we studied the self decay of the peroxyl radicals derived from the above three compounds.

Experimental Section

The pulse radiolysis experiments were carried out under the same conditions as those described before.[1,2] Absorption spectra were monitored in aerated or oxygen-saturated solutions, containing the bromoaromatic compound and an alcohol or sodium formate as scavengers for the H and OH radicals. In these experiments we used a high dose rate (in the range 50−200 Gy/pulse) because the molar absorptivities of these radicals were relatively low ((1−2) × 10^3 L mol^{-1} cm^{-1}),[1−4] and they were produced in low yields. Since the yields were low and could not be accurately determined, owing to various competing reactions ($e_{aq}^- + O_2$, $Ph^{\bullet}$ + alcohol), the molar absorptivities

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[†] On leave from the Institute of Electrochemistry, Russian Academy of Sciences, Moscow.

[‡] Permanent address: Ben-Gurion University of the Negev, Beer Sheva, Israel.

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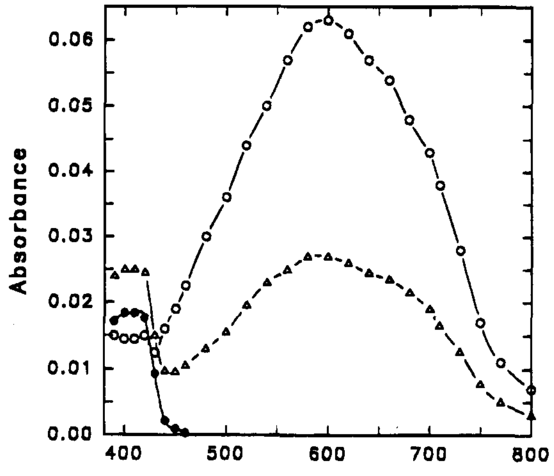

Figure 1. Transient absorption spectra recorded by pulse radiolysis of air-saturated aqueous solutions of 4-bromoanisole (2.5 × 10^{-3} mol L^{-1}) containing *t*-BuOH (2.5 mol L^{-1}) and phosphate buffer (2 × 10^{-3} mol L^{-1}) at pH 7 recorded ~0.5 μs (○) and 140 μs (▽) after the pulse. The solid symbols are the difference between the absorbance at 140 μs and the initial absorbance (the latter was corrected for the expected decay based on the observed decay at longer wavelengths).

have not been determined. The kinetic measurements were carried out at various dose rates. The measurements with $ABTS^{2-}$ were done with lower dose rates (5–10 Gy/pulse) since $ABTS^{•-}$ has a high molar absorptivity (3.5 × 10^4 L mol^{-1} cm^{-1} at 417 nm).[12] When measuring the rate constants for reactions of radicals with various compounds, we corrected for competing reactions (such as radical–radical decay or radical reaction with other species) by measuring the first-order formation rates with at least three different concentrations of reactant, varying by about a factor of 4, and then deriving the second-order rate constants from linear plots of the first-order rate constants vs concentration. Aliphatic peroxyl radicals and $O_2^{•-}$, produced along with the phenylperoxyl, do not interfere with the spectral and kinetic measurements because they absorb only in the UV and react considerably more slowly than phenylperoxyl radicals. However, they must contribute to the decay kinetics of peroxyl radicals, i.e., ArOO• + ArOO• is always mixed with ArOO• + ROO•. There are two major sources of uncertainty in the derived rate constants: the statistical uncertainty in the first- and second-order fits, which was generally between 2% and 10%, although in a few cases it was higher, and uncertainties in the measurements of volumes and weights, which we estimate as ≤10%. The overall estimated standard deviations are given in the table along with the rate constants. All other experimental details were as described before.[1,2]

Results and Discussion

4-Methoxyphenylperoxyl Radical. Pulse radiolysis of 4-bromoanisole in aerated aqueous solutions containing either an alcohol or formate ions, as scavengers for the OH radicals, results in the formation of a transient species absorbing in the visible range (Figure 1). The spectrum exhibits a broad peak with λ_{max} at (630 ± 10) nm in predominantly aqueous solutions (containing 0.1 mol L^{-1} formate ions or 0.25 mol L^{-1} *t*-BuOH or *n*-PrOH and buffered at pH 7) but at (600 ± 10) nm with high alcohol fraction (25% *t*-BuOH). This spectrum is ascribed to the 4-methoxyphenylperoxyl radical formed by reactions 3 and 4 and is in agreement with the previously reported spectrum.[3,4] The slight blue shift found upon increasing alcohol fraction is in accord with previous observations of the spectra of other phenylperoxyl radicals in water/alcohol mixtures.[2,13]

TABLE 1: Rate Constants for Reactions of Phenyl and Phenylperoxyl Radicals with Various Reactants in Aqueous Solutions

radical	reactant	k, L mol^{-1} s^{-1} [a]
4-$CH_3OC_6H_4^•$	O_2	(1.3 ± 0.3) × 10^9
	CH_3OH	(7.6 ± 1.6) × 10^5
	CH_3CH_2OH	(2.7 ± 0.6) × 10^6
	$(CH_3)_2CHOH$	(6.5 ± 1.3) × 10^6
4-$CH_3OC_6H_4OO^•$	SO_3^{2-}	(1.9 ± 0.4) × 10^6
	4-$CH_3OC_6H_4OH$	(2.4 ± 0.5) × 10^6
	4-HOC_6H_4OH	(5.0 ± 1.0) × 10^6
	ascorbate	(9.4 ± 1.9) × 10^7
	$ABTS^{2-}$	(1.5 ± 0.3) × 10^9
4-$CH_3OC_6H_4O^•$	SO_3^{2-}	<1 × 10^6 [b]
	ascorbate	(5.2 ± 1.0) × 10^7 [b]
	$ABTS^{2-}$	(1.0 ± 0.3) × 10^7 [c]
4-$(CH_3)_2NC_6H_4OO^•$	$ABTS^{2-}$	(5.1 ± 1.0) × 10^8

[a] Measured at pH 6.7–6.9, except where noted. [b] Measured at pH 8 by following the decay of the 4-methoxyphenoxyl radical absorption at 420 nm as a function of substrate concentration. [c] Measured at pH 5.9 by following the formation of the $ABTS^{•-}$ radical absorption at 415 nm as a function of $ABTS^{2-}$ concentration; k was much lower at pH 8.

The rate constant for reaction of the 4-methoxyphenyl radical with O_2 (reaction 4) was determined by following the formation of the peroxyl radical absorption at 600–630 nm in solutions containing 4-bromoanisole, *t*-BuOH (0.1 mol L^{-1}), and various O_2 concentrations (2–9) × 10^{-4} mol L^{-1}, assuming a solubility of 1.3 × 10^{-3} mol L^{-1} for pure O_2 under ambient conditions). The rate constant was found to be k_4 = (1.3 ± 0.3) × 10^9 L mol^{-1} s^{-1}, slightly lower than the value reported previously.[4]

Rate constants for reactions of the 4-methoxyphenyl radical with three alcohols, e.g.,

$$CH_3OC_6H_4^{•} + CH_3OH \rightarrow CH_3OC_6H_5 + {}^{•}CH_2OH \quad (7)$$

were measured by competition kinetics using reaction 4 as a reference (since the species involved in reaction 7 cannot be readily followed by optical absorption measurements). The yield of peroxyl radical, i.e., the absorbance at 600 nm, was determined in air-saturated solutions in the absence (A_0) and presence (A) of various alcohol concentrations. The rate constants were calculated from linear plots of A_0/A vs [ROH] according to the equation, $A_0/A - 1 = (k_7[ROH])/(k_4[O_2])$, and are given in Table 1 for ROH = MeOH, EtOH, and 2-PrOH. They are lower than those reported previously[4] by about a factor of 2, owing to the fact that our reference rate constant, k_4, is lower than that used in the previous study by about the same factor. The relative reactivities, however, are practically identical in the two studies, i.e., MeOH:EtOH:2-PrOH = 1:4:9. This order of reactivity for H-abstraction by phenyl radicals from these alcohols is predictable based on bond dissociation energies and on comparison to reactivities of other radicals.[14]

Rate constants for oxidation of ascorbate (Asc), phenols, and sulfite by the phenylperoxyl radical were determined by following the decay of the 600 nm absorption as a function of reactant concentration.

$$CH_3OC_6H_4OO^{•} + Asc^{-} \rightarrow CH_3OC_6H_4OO^{-} + Asc^{•} \quad (8)$$

The rate of oxidation of $ABTS^{2-}$ was determined by following the buildup of absorption of the product radical at 415 nm.

$$CH_3OC_6H_4OO^{•} + ABTS^{2-} \rightarrow CH_3C_6H_4OO^{-} + ABTS^{•-} \quad (9)$$

The results are summarized in Table 1. The values found for ascorbate and $ABTS^{2-}$ are similar to those reported previously for other substituted phenylperoxyl radicals.[1] The finding that $CH_3OC_6H_4OO^•$ reacts with $CH_3OC_6H_4OH$, although relatively slowly, to form $CH_3OC_6H_4O^•$ suggests a higher reactivity for $CH_3OC_6H_4OO^•$ as compared to $CH_3OC_6H_4O^•$. This was confirmed by measuring the rate constants for oxidation of sulfite, ascorbate, and $ABTS^{2-}$ by the 4-methoxyphenoxyl radical (in N_2O-saturated solutions containing 0.1 mol L^{-1} NaN_3). All three values (Table 1) are found to be lower than those for the 4-methoxyphenylperoxyl radical. This is in contrast with the behavior noted before, where the reactivity of phenoxyl (with ascorbate and $ABTS^{2-}$)[15,16] was considerably higher than that of phenylperoxyl.[1] The different behavior is clearly due to the electron-donating effect of the 4-methoxy group, which increases the electron density on the phenoxyl oxygen but has a smaller effect on the more distant peroxylic oxygen. In the latter case, the mesomeric effect is very small so that the inductive effect of the methoxy group predominates, i.e., it acts as an electron-withdrawing substituent. The reduction potential for $C_6H_5O^•/C_6H_5O^-$ (0.97 V vs NHE at pH 7)[17] is higher than that for $C_6H_5OO^•/C_6H_5OO^-$ (estimated to be ~0.7 V),[13] but the reduction potential for $4\text{-}MeOC_6H_4O^•/4\text{-}MeOC_6H_4O^-$ (0.72 V at pH 7)[17] must be considerably lower than that for $4\text{-}MeOC_6H_4OO^•/4\text{-}MeOC_6H_4OO^-$. This is most clearly demonstrated by the rate constants for oxidation of $ABTS^{2-}$. The reduction potential for $ABTS^{2-}/ABTS^{•-}$ is 0.68 V vs NHE.[12] This compound is oxidized rapidly by all substituted phenylperoxyl radicals studied. It is oxidized more rapidly by $C_6H_5O^•$ but very slowly by $4\text{-}MeOC_6H_4O^•$. In the latter case, because the reduction potentials of the two pairs are close and the value for $4\text{-}MeOC_6H_4O^•$ is pH dependent, the rate constant was found to be strongly pH dependent; the value of 1.0×10^7 L mol^{-1} s^{-1} was measured at pH 5.9, but the reaction was much slower and was difficult to follow at pH 8.

The decay of the broad, 500–700 nm, absorption of the 4-methoxyphenylperoxyl radical is accompanied by a buildup of absorption in the 400 nm range (Figure 1). The spectra at different times after the pulse could not be better resolved by monitoring at lower wavelengths since other absorptions in the UV, which are much more intense, mask the spectra of interest. Nevertheless, the buildup around 400 nm suggests the formation of some 4-methoxyphenoxyl radicals upon the decay of the peroxyl radical. The process, however, is not quantitative. Since the phenoxyl radicals produced also decay on the same time scale as the peroxyl radicals, only a small absorbance is formed at 400 nm, which subsequently decays. The kinetic traces of the decay of the peroxyl radical monitored at 600 nm fit a second-order rate law better than a first-order one, and k was dependent on the radical concentration (dose per pulse) but not on the alcohol or bromoanisole concentrations. These findings suggest that the peroxyl radicals decay by second-order processes to yield phenoxyl radicals as well as other products. The low yield of phenoxyl radicals may indicate that reaction 2 has a greater contribution than reaction 1 but may be due also to the presence of other radicals in this system, i.e., $RO_2^•$ (from the alcohol) and $O_2^{•-}$, which contribute to the decay process by reacting with the phenylperoxyl radical. From the decay kinetics under various conditions, we derive an average value of $2k/\epsilon = (1.9 \pm 0.4) \times 10^6$, and by taking[3,4] $\epsilon = 2 \times 10^3$ L mol^{-1} cm^{-1} we obtain $2k = 3.8 \times 10^9$ L mol^{-1} s^{-1}. This value, however, cannot be ascribed solely to reactions 1 and 2 since the other peroxyl radicals formed in these solutions must contribute to the observed decay kinetics.

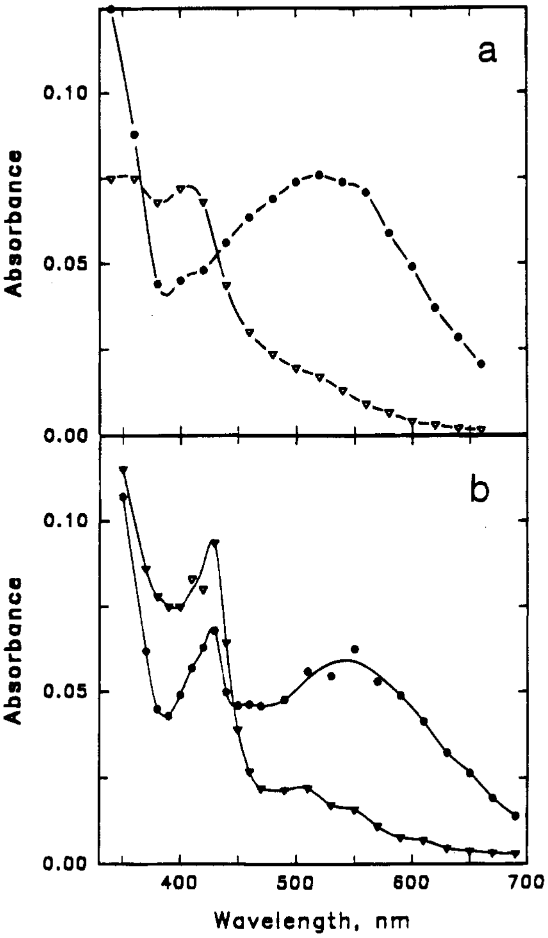

Figure 2. Transient absorption spectra recorded by pulse radiolysis of O_2-saturated aqueous solutions of 4-bromophenol: (a) 2×10^{-3} mol L^{-1} 4-bromophenol, 0.5 mol L^{-1} *t*-BuOH, 5×10^{-3} mol L^{-1} phosphate buffer at pH 7.6, recorded 0.5 μs (●) and 20 μs (▽) after the pulse; (b) 6.5×10^{-3} mol L^{-1} 4-bromophenol, 2 mol L^{-1} *t*-BuOH, 3×10^{-2} mol L^{-1} phosphate buffer at pH 7.6, recorded 0.2 μs (●) and 10 μs (▽) after the pulse.

4-Hydroxyphenylperoxyl Radical. The transient absorption spectra recorded by pulse radiolysis of 4-bromophenol solutions under different conditions indicated that the formation of the 4-hydroxyphenylperoxyl radical was followed by a rapid decay that was strongly dependent on conditions, including the concentration of the phosphate buffer. It was also clear that the decay of the peroxyl radical absorption was accompanied by buildup of absorption near 400 nm. Figure 2 shows the transient spectra recorded at different times after the pulse with two different solutions of 4-bromophenol. In both cases, the spectra recorded at short times (0.5 μs in (a) and 0.2 μs in (b)) exhibit a broad absorption with λ_{max} at 520–540 nm. At longer times (10–20 μs), this absorption decays while the absorption near 400 nm increases. The spectrum at low buffer concentration (Figure 2a) has no initial peak near 400 nm whereas that obtained at high buffer concentration (Figure 2b) shows an initial peak at 430 nm that increases with time. All of the above peaks are observed under O_2 and are eliminated by deoxygenating the solution, indicating that both the 520–540 nm and the 430 nm peaks are a consequence of the reaction of the phenyl radical with O_2. The former peak is ascribed to the peroxyl radical, by comparison to earlier results,[1-4] and the latter peak to a phenoxyl radical. The appearance of the 430 nm peak at short times under high buffer concentrations is a result of the rapid decay of the peroxyl radical in this solution. The incomplete appearance of the 430 nm peak at low buffer concentrations is a result of the slower decay of the peroxyl radical and the contribution of competing processes. The decay of the peroxyl radical at 500–600 nm was found to follow a first-order rate law very closely. The rate constant was nearly independent of the radical concentration (k_{obs} increased by <50% upon increasing the dose per pulse by a factor of >20) and was not affected by the 4-bromophenol concentration (between 1×10^{-3} and 1×10^{-2} mol L^{-1}) but was linearly dependent on buffer concentration at constant pH (using total phosphate concentration between 0.2 and 2×10^{-3} mol L^{-1}).

These results suggest that the 4-hydroxyphenylperoxyl radical undergoes a base-catalyzed intramolecular electron transfer to yield the 4-hydroperoxyphenoxyl radical:

$$HOC_6H_4OO^{\bullet} + HPO_4^{2-} \rightarrow {}^{-}OC_6H_4OO^{\bullet} + H_2PO_4^{-} \quad (10)$$

$${}^{-}OC_6H_4OO^{\bullet} \rightleftharpoons {}^{\bullet}OC_6H_4OO^{-} \quad (11)$$

$${}^{\bullet}OC_6H_4OO^{-} + H_2PO_4^{-} \rightarrow {}^{\bullet}OC_6H_4OOH + HPO_4^{2-} \quad (12)$$

The pK_a of $HOC_6H_4OO^{\bullet}$ is expected to be lower than that of phenol (10.0) because of the electron-withdrawing effect of the dioxyl group, and by comparison to the pK_a values of other 4-substituted phenols,[18] it may be estimated to lie between 8.5 and 9.5. The pK_a of ${}^{\bullet}OC_6H_4OOH$ may be slightly lower than that for aliphatic hydroperoxides, which is near 12,[19] because of electron withdrawing by the phenyl group. The reaction of the peroxyl radical with the hydrogen phosphate ion results in partial ionization of the phenolic OH group. Subsequently, an intramolecular electron transfer occurs between the phenolic and the peroxyl moieties, resulting in partial formation of the phenoxyl radical. Protonation of the hydroperoxide (reaction 12), which has a higher pK_a value than that of the peroxyl radical, will pull reaction 11 to the right. From the linear dependence of the observed rate constant on phosphate concentration, we derive a second-order rate constant of $(4.0 \pm 1.0) \times 10^8$ L mol^{-1} s^{-1} for reaction 10. The intercept found (1.8×10^5 s^{-1}) may be due to deprotonation of the phenolic group of the radical by reaction with water or to other modes of decay of the peroxyl radicals. Because of the rapid intramolecular process in the 4-hydroxyphenylperoxyl radical, it was not possible to examine the second-order decay of this radical to find out whether any phenoxyl radical is produced by such a process nor was it possible to study oxidation of other compounds by this peroxyl radical.

4-(*N,N*-Dimethylamino)phenylperoxyl Radical. Pulse radiolysis of 4-bromo-*N,N*-dimethylaniline in aerated aqueous solutions containing alcohol leads to the formation of the peroxyl radical, $(CH_3)_2NC_6H_4OO^{\bullet}$. The spectrum of this species has $\lambda_{max} = (600 \pm 10)$ nm in neutral solutions (Figure 3), but at pH 3 the peak is found at a lower wavelength, $\lambda_{max} = (500 \pm 10)$ nm, indicating the presence of a protonated species, $(CH_3)_2HN^{+}C_6H_4OO^{\bullet}$.

$$(CH_3)_2NC_6H_4OO^{\bullet} + H^{+} \rightarrow (CH_3)_2HN^{+}C_6H_4OO^{\bullet} \quad (13)$$

This shift is in line with earlier findings that the peaks for most substituted phenylperoxyl radicals are near 500 nm, except for those containing a 4-substituent with lone pairs at the α-position that can interact with the ring π-system, which results in a considerable red shift.

Decay of the peroxyl radical results in formation of transient species absorbing at 500 nm (Figure 3). This absorption may be ascribed to several possible products.

(a) Second-order decay of the peroxyl radicals by a mechanism parallel to reaction 1 may produce the dimethylaminophenoxyl radical.

$$2(CH_3)_2NC_6H_4OO^{\bullet} \rightarrow 2(CH_3)_2NC_6H_4O^{\bullet} + O_2 \quad (14)$$

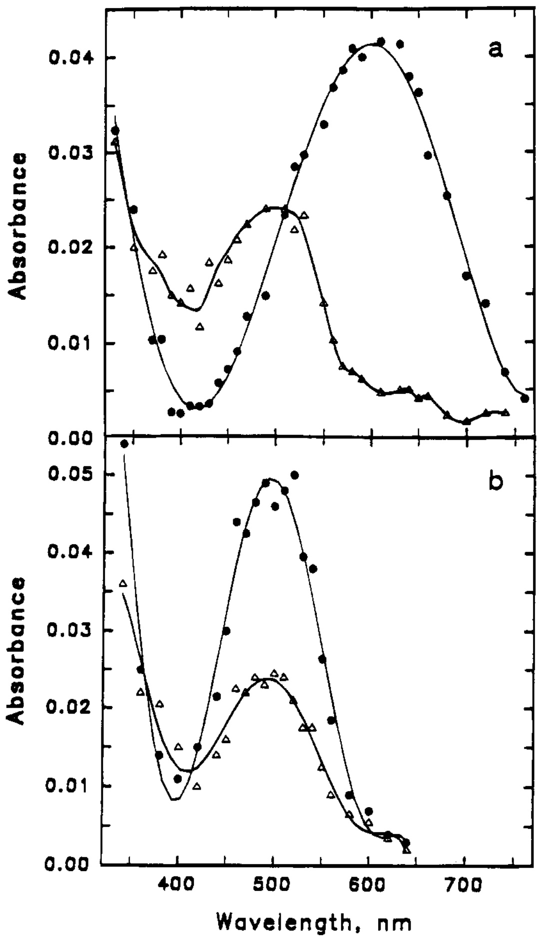

Figure 3. Transient absorption spectra recorded by pulse radiolysis of O_2-saturated aqueous solutions of 4-bromo-*N,N*-dimethylaniline ($\leq 1 \times 10^{-3}$ mol L^{-1}) containing MeOH (0.4 mol L^{-1}): (a) at pH 6.7 (1×10^{-2} mol L^{-1} phosphate buffer), recorded ~0.5 μs (●) and 10 μs (△) after the pulse; (b) at pH 3.1 (with $HClO_4$), recorded ~1.5 μs (●) and 10 μs (△) after the pulse.

This radical has been produced by oxidation of 4-(*N,N*-dimethylamino)phenol and reported to have λ_{max} at 495 nm.[9] We prepared it by pulse radiolytic oxidation of this compound with $N_3^{\bullet}$ radicals at pH 7 and found a similar value, $\lambda_{max} = (510 \pm 10)$ nm.

(b) Decay of the peroxyl radical by a mechanism parallel to reaction 2 will produce stable adducts that are not likely to exhibit significant absorption at 500 nm.

$$2(CH_3)_2NC_6H_4OO^{\bullet} \rightarrow [(CH_3)_2NC_6H_3OH]_2 + O_2 \quad (15)$$

(c) Intramolecular electron transfer, similar to that discussed above for the hydroxy derivative, will produce the radical cation $HOOC_6H_4N(CH_3)_2^{\bullet+}$.

$$(CH_3)_2NC_6H_4OO^{\bullet} \rightleftharpoons (CH_3)_2N^{\bullet+}C_6H_4OO^{-} \quad (16)$$

$$(CH_3)_2N^{\bullet+}C_6H_4OO^{-} + H_2PO_4^{-} \rightarrow (CH_3)_2N^{\bullet+}C_6H_4OOH + HPO_4^{2-} \quad (17)$$

This species is also expected to absorb near 500 nm, by comparison to the radical cation of *N,N*-dimethylaniline.[20]

(d) Oxidation of the parent compound, 4-bromo-*N,N*-dimethylaniline, by the peroxyl radical will produce the radical cation $BrC_6H_4N(CH_3)_2^{\bullet+}$.

$$(CH_3)_2NC_6H_4OO^\bullet + (CH_3)_2NC_6H_4Br \rightarrow (CH_3)_2NC_6H_4OO^- + (CH_3)_2N^{\bullet+}C_6H_4Br \quad (18)$$

This radical cation is also expected[20] to absorb near 500 nm. We produced it by oxidizing the compound with $N_3^\bullet$ radicals and found it to have an absorption with λ_{max} at (500 ± 5) nm. Since pathways a, c, and d lead to products absorbing in the same range, we have to distinguish between the various mechanisms through the kinetic behavior.

The decay of the peroxyl radical, monitored at 620 nm with aerated solutions containing 20% *t*-BuOH and 4×10^{-3} mol L^{-1} phosphate buffer at pH 7.1, was found to obey neither a pure first-order rate law nor a second-order one. Individual traces fitted first order better than second order, but the rate constant was dependent on the initial radical concentration, indicating a considerable second-order component. A plot of $1/t_{1/2}$ vs initial radical concentration (calculated from the absorbance by using $\epsilon = 1200$ L mol^{-1} cm^{-1})[4] gave a straight line from which we derive $k = 3.5 \times 10^4$ s^{-1} for the first-order contribution and $k = 3 \times 10^9$ L mol^{-1} s^{-1} for the second-order contribution. The observed rate constant was independent of the concentration of the starting material (varying by a factor of 8), ruling out reaction 18. Therefore, the first-order component of the decay indicates that the intramolecular process, reaction 16, has a pronounced contribution. This process, however, is not as rapid under the current experimental conditions ($t_{1/2} \sim 20$ μs) as that found with the hydroxy derivative (reactions 10−12, $t_{1/2} \sim 1-4$ μs) and is accompanied by second-order radical−radical reactions involving all the radicals present in this system, i.e., reactions 14 and 15 as well as mixed radical decay. The contribution of reaction 14, to yield the phenoxyl radical $(CH_3)_2NC_6H_4O^\bullet$, cannot be estimated because of the overlapping absorptions of the two radical products (from reactions 14 and 16).

At pH 3, where the peroxyl radical is protonated, the first-order component of the decay kinetics becomes insignificant and the process fits second-order kinetics quite well. The peroxyl radical absorption at 500 nm (Figure 3b) decays over 50−100 μs to yield a species that also absorbs at 500 nm and that decays over several milliseconds. The two decay processes are well resolved, and their rate constants can be calculated independent of each other. The faster process is a nearly pure second-order decay of the peroxyl radicals, with $2k/\epsilon \sim 4 \times 10^6$, and the fact that the product of this process absorbs at 500 nm indicates the importance of pathway a in this case.

$$2(CH_3)_2HN^+C_6H_4OO^\bullet \rightarrow 2\,(CH_3)_2HN^+C_6H_4O^\bullet + O_2 \quad (19)$$

Since the molar absorptivity of this phenoxyl radical[9] product is 3−4 times as high as that of phenylperoxyl radicals[1−4] and the remaining absorbance after the first decay process is only ~50% of the initial value, we can estimate that only 10−15% of the radicals decay via reaction 19. The remaining radicals decay to stable products via reaction 15 and reaction with other radicals present in this system.

In summary, phenylperoxyl radicals decay partially via the mechanism represented by reaction 1 to produce phenoxyl radicals. They may also decay via reaction 2 to stable products, but the contribution of this reaction cannot be assessed in the present system, where decay by reaction with aliphatic radicals present in solution also contributes to the overall process. In certain cases, phenylperoxyl radicals were found to decay by intramolecular electron transfer, leading to reduction of the peroxyl to hydroperoxide and oxidation of a substituent present on the same ring. For example, the 4-hydroxyphenylperoxyl radical formed the 4-hydroperoxyphenoxyl radical (reactions 10−12) and the (4-dimethylamino)phenylperoxyl formed the (4-hydroperoxy)dimethylanilinium radical cation (reactions 16 and 17). The former process was relatively fast and predominant whereas the latter process was slower and thus was accompanied by other decay routes.

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References and Notes

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