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Conversion of Hydroxyphenyl to Phenoxyl Radicals: A Radiolytic Study of the Reduction of Bromophenols in Aqueous Solution[1]

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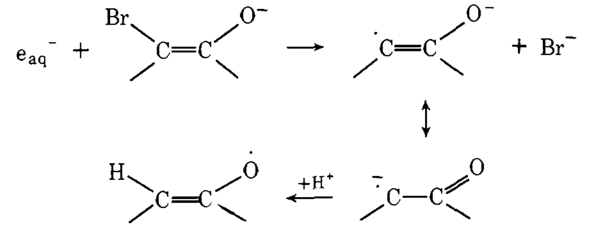
Abstract: Both steady-state ESR and spin trapping experiments demonstrate that hydroxyphenyl radicals are produced in the reaction of hydrated electrons with the bromophenols. Conductometric and optical pulse radiolysis studies show that the anionic forms of the ortho and para hydroxyphenyl radicals protonate rapidly at the radical site to produce phenoxyl radical. At pH 11.5 the protonation periods are respectively 14 and 4.1 μs. The meta isomer protonates at least an order of magnitude more slowly. Protonation is not observed for the neutral forms of these radicals. The important feature required for protonation appears to be the existence of appreciable negative charge density at the radical site. The rapid protonation of the *p*-hydroxyphenyl radical anion observed here provides a reference with which to compare other reactions of this radical and it has been possible to estimate a rate constant of 6×10^5 M^{-1} s^{-1} for its abstraction of H from *tert*-butyl alcohol and 4×10^7 M^{-1} s^{-1} for its addition to nitromethane. In the case of *p*-bromophenol, the phenoxyl radicals resulting from the initial protonation undergo a tertiary electron transfer reaction with *p*-bromophenoxide with a rate constant of 2.0×10^8 M^{-1} s^{-1}, so that the optical absorption spectra of the three bromophenoxyl radicals produced by OH reactions were also examined and are reported here. Because of this tertiary transfer, phenoxyl radicals cannot be observed in steady-state ESR experiments on these systems. Studies of the dependence of the width of the ESR lines of phenoxyl radical produced from phenol on the phenol concentration show that electron transfer between the radical and the substrate occurs with a rate constant of 1.9×10^8 M^{-1} s^{-1}.

Introduction

Studies[2] of the attack of e_{aq}^- on bromotetronate anion make it clear that the radical anion initially produced by the reductive elimination of Br^- protonates very rapidly at the radical site. Presumably this protonation results from appearance of appreciable negative charge at the radical carbon, i.e., as shown in the reaction below. Similarly, in the radicals produced as the result of electron attack on *p*- and *o*-bromophenolate, but not in the case of the meta isomer, one expects that there will be appreciable negative charge at the radical site and protonation seems likely. It was, therefore, decided to carry out optical and conductometric pulse radiolysis studies on the radiation chemistry of solutions of the bromophenols to examine for protonation of the radicals produced initially. It was indeed found that in their anionic forms the *p*- and *o*-hydroxyphenyl radicals protonate rapidly on the ring carbon to form phenoxyl radical. Protonation of the meta isomer is at least an order of magnitude slower. It was also found that in their neutral forms, these radicals do not observably undergo protonation. These observations explain the fact that hydroxyphenyl radicals were observed in steady-state ESR experiments on *m*-bromophenol,[3] but not in the cases of the other isomers. The results of pulse radiolytic and steady-state ESR experiments on the three bromophenols are described in the following. The studies on *p*-bromophenol make it apparent that electron transfer between phenoxyl radicals and phenoxide is fairly rapid ($k \sim 10^8$ M^{-1} s^{-1}), so that information on this transfer reaction is also included.



Experimental Section

p-Bromophenol (Eastman Chemical Co.) and *o*- and *m*-bromophenol (Aldrich Chemical Co.) were used without further purification. Phenol, *tert*-butyl alcohol, and the inorganic compounds used were Baker Analyzed Reagents. For studies involving the reaction of e_{aq}^-, the water used was triply distilled from basic permanganate and acid dichromate with a final distillation in a quartz system. Oxygen was removed by purging with nitrogen containing <0.01% oxygen.

The optical pulse radiolysis system described by Patterson and Lilie[4] was used. The software used in this system has now been modified to make it feasible to average a large number of experiments and to store and display 100 points on each trace for a more detailed examination of the overall kinetics. Dosimetry was by measurement on the N_2O

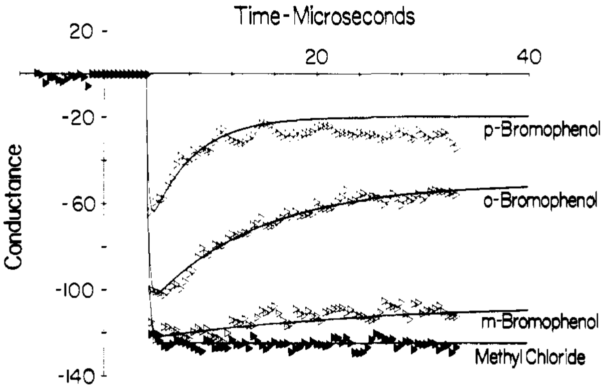


Figure 1. Pulse conductivity experiments on 0.4 mM bromophenol solutions containing 0.2 M *tert*-butyl alcohol at pH 11.5. Experimental results represent differences between N_2 and N_2O saturated solutions with each data point being the average observed over 100 pulses, with the sample being changed between pulses. The results for methyl chloride represent the differences between methyl chloride and N_2O saturated solutions, both containing 0.2 M *tert*-butyl alcohol to remove >96% of the OH. Conductances are normalized to a difference of -125 mhos cm^2 equiv^{-1} for the CH_3Cl solutions, assuming a yield of 2.75 for electron attack on the bromophenolates and 3.16 for CH_3Cl. The conductivity detector is gated off for 4 μs after the beginning of a 0.5 μs pulse. The curves are calculated by integration of eq 4-6, as described in the text. A gate of 4 μs and experimental time constant of 0.2 μs are assumed in the calculations.

saturated thiocyanate system at 480 nm with the extinction coefficient and yield of $(SCN)_2^-$ assumed to be 7600 M^{-1} cm^{-1} and 6.0, respectively. Extinction coefficients were calculated based on assumed yields of 6.0 for OH produced in N_2O saturated solutions and of 2.7 produced from e_{aq}^- at electron scavenger concentrations ~3 mM. In general, spectra were taken at dose levels of 300-600 rads/pulse, where the initial radical concentration was 2-4 × 10^{-6} M. Spectral data were examined for underlying contributions using the Hewlett-Packard 9830 programs described by Schuler and Buzzard.[5]

Conductometric pulse radiolysis experiments were carried out using the 10-MHz conductivity bridge described by Lilie and Fessenden.[6] The bridge has been modified to give response ~4 μs after the pulse. The data were digitized with a Biomation 8100 transient recorder and processed with a PDP-8 computer for signal averaging purposes by methods similar to those used in the optical experiments. The observed conductances were compared with those found in basic methyl chloride solutions, with the yield for HCl production in the latter case assumed to be 3.1.[7] These experiments were carried out at doses ~1000 rads/pulse, where the radicals produced from the bromophenol were at a concentration of ~3 × 10^{-6} M.

ESR spectra were taken using the steady-state in situ radiolysis method described by Eiben and Fessenden.[8] Line widths of the phenoxyl radical were examined in the second-derivative presentation obtained by use of field modulations at 100 kHz and 200 Hz. In this mode, instrumental broadening of the lines caused by the modulation is more severe than with first-derivative spectra. However, correction for this effect amounted to only about 20% in the transfer rate constant under the conditions used.

Conductivity Experiments

Protonation of the radicals initially formed by electron attack on the bromophenoxides is directly manifest in the pulse conductivity studies, since the additional changes that occur as a result of charge transfer processes have little effect on the conductivity. The results from experiments on 0.4 mM bromophenol at pH 11.5 (containing 0.2 M *tert*-butyl alcohol to remove the OH radicals)[9] are illustrated in Figure 1. The conductivity detector is gated off for a period of 4 μs following the electron pulse. Even so it is perturbed somewhat by the pulse, giving a negative going component that recovers with a period ~4 μs, as noted in experiments on N_2O saturated solutions containing *tert*-butyl alcohol. Methyl chloride solutions show a similar negative component, but after corrections have been made for the changes observed in the N_2O-saturated solutions the net results (solid points in Figure 1) show a stepwise increase in the conductivity with the pulse as observed in the DC measurements.[7] N_2O saturated solutions of the bromophenols containing 0.2 M *tert*-butyl alcohol (where >99% of e_{aq}^- should react with the N_2O and >96% of the OH should react with the alcohol) give traces similar to those in the absence of the bromophenols. The data points in Figure 1 correspond to the observed differences between N_2 and N_2O saturated solutions of the bromophenols and presumably represent the net effect of electron attack on these solutes.

Qualitatively it can be seen in Figure 1 that after the initial decrease there is a pronounced recovery in the conductance in the cases of the *o*- and *p*-bromophenols. Very little secondary change is observed for *m*-bromophenol. In basic solution, the protons produced as the complement of e_{aq}^- are rapidly neutralized so that one expects a sharp decrease in conductance with the pulse, as is noted for the methyl chloride solutions. After the hydrated electrons have reacted with the solute and bromide has been eliminated

$$e_{aq}^- + BrC_6H_4O^- \xrightarrow{k_1} Br^- + \cdot C_6H_4O^- \qquad (1)$$

the net change, assuming that the equivalent conductances of $BrC_6H_4O^-$ and $\cdot C_6H_4O^-$ are similar, should be the difference between the equivalent conductances of Br^- (78 mhos cm^2 equiv^{-1}) and OH^- (198 mhos cm^2 equiv^{-1}) (for methyl chloride $\Lambda(Cl^-) - \Lambda(OH^-) = 120$ mhos/cm^2 equiv^{-1}). It is indeed seen that the results for *m*-bromophenol and methyl chloride are very similar, indicating immediately that protonation is only of minor importance in this instance.

As protonation of the hydroxyphenyl radical anion produced in reaction 1 occurs, the conductance will increase as the result of release of OH^- to the solution. If reaction 2 is quantitative one expects the conductance increment to become slightly

$$\cdot C_6H_4O^- + H_2O \xrightarrow{k_2} C_6H_5O\cdot + OH^- \qquad (2)$$

positive, since the net effect of reactions 1 and 2 is to replace bromophenoxide ions with bromide ($\Lambda(Br^-) - \Lambda(BrC_6H_4O^-) \simeq 20$ mhos cm^2 equiv^{-1}). Recovery of the conductivity is, however, not complete, because of a side reaction that is very likely the abstraction of hydrogen from the *tert*-butyl alcohol by the hydroxyphenyl radicals, i.e.,

$$\cdot C_6H_4O^- + RH \xrightarrow{k_3} C_6H_5O^- + R\cdot \qquad (3)$$

The hydroxyphenyl radicals can also add to the bromophenol in a process parallel to reaction 3, but from the rate constant information available this path should be only ~25% as important. Since the conductance should not change significantly as the result of addition, one can effectively incorporate this complication as a contribution to k_3.

From the conductances observed at 20 μs it is apparent that reaction 2 accounts for only ~60% of e_{aq}^- in the case of *p*-bromophenol and ~45% in the case of the ortho isomer. Experiments at higher *tert*-butyl alcohol concentrations, in fact, show that reaction 3 becomes much more important. Unfortunately, one cannot use *tert*-butyl alcohol concentrations significantly lower than 0.2 M because of the necessity of removing the OH radicals.[9] At long times (~200 μs) the conductance again decreases as the result of disproportionation of the phenoxyl radicals produced in reaction 2. This latter effect is beginning to be manifest at 30 μs in the data of Figure 1 on the para isomer.

It should be possible to describe the conductance changes quite well by integrating the differential equations that describe the above chemical scheme, i.e.,

$$d[e_{aq}^-]/dt = P_e - k_1[e_{aq}^-][S] \qquad (4)$$

where [S] is the concentration of the bromophenol and P_e is taken equal to the rate for production of e_{aq}^- during the pulse and subsequently as zero;

$$\frac{d(\cdot C_6H_4O^-)}{dt} = k_1[e_{aq}^-][S] - k_2[\cdot C_6H_4O^-] - k_3[\cdot C_6H_4O^-][RH] \quad (5)$$

([RH] = *tert*-butyl alcohol concentration); and

$$\frac{d(OH^-)}{dt} = \frac{d(C_6H_5O\cdot)}{dt} = k_2[\cdot C_6H_4O^-] \quad (6)$$

The curves given in Figure 1 were calculated by numerically integrating eq 4–6 on a Hewlett-Packard 9830 calculator using a program that included a mathematical simulation of the gated detector and the apparatus time constant. From the ionic stoichiometry the conductance increments were calculated as $-120 + 140\ [C_6H_5O\cdot]$ mhos cm^2 equiv^{-1}.

For *p*-bromophenol, the conductivity level reached after ~20 μs is essentially determined by the ratio of $k_3[RH]/k_2$, which can be estimated from the data of Figure 1 to be ~0.5. For *o*-bromophenol this ratio is ~1.2 and for *m*-bromophenol >10. Incorporation of these relations into the calculations leaves the values of k_2 as the only undetermined parameters. For *p*-bromophenol the initial conductance change depends critically on the protonation period, so that one has little freedom in choosing a value for k_2. The period is, of course, also determined by this k_2, so that the calculations are very much overdetermined. The best fit to the data gives k_2 for *p*-bromophenol as $1.7 \times 10^5\ s^{-1}$ ($t_{1/2} = 4.1\ \mu s$) and for *o*-bromophenol as $0.5 \times 10^5\ s^{-1}$ ($t_{1/2} = 13\ \mu s$). These periods should be accurate to ±20%. Both sets of data indicate a value for k_3 in the range 3–4 $\times 10^5\ M^{-1}\ s^{-1}$. If a value of this magnitude is applicable in the case of the meta isomer, then both the initial change in the conductance and the fact that only a slight further change (increase) is observed out to 40 μs show that the rate constant for protonation of the *m*-hydroxyphenyl radical is less than $10^4\ s^{-1}$ ($t_{1/2} > 100\ \mu s$).

Spectra of the Intermediates

Since the phenoxyl radical expected to be formed in reaction 2 has a very characteristic spectrum,[5,10] it should be possible to follow the protonation in pulse radiolysis experiments. However, in preliminary studies on solutions similar to those used in the conductivity experiments, it was found that the spectrum observed for 0.4 mM *p*-bromophenol at ~100 μs after the pulse was not that of the phenoxyl radical but rather that of *p*-bromophenoxyl (see Figure 4). It is clear from the detailed studies reported below that this latter radical is formed in a tertiary electron transfer process, i.e.,

$$C_6H_5O\cdot + BrC_6H_4O^- \xrightarrow{k_7} C_6H_5O^- + BrC_6H_4O\cdot \quad (7)$$

This electron transfer, of course, does not result in any change in the number of ions in solution and will have little effect on the results of the conductivity experiments. Contributions from reaction 7 make the kinetic spectrophotometry very complicated, so that it is desirable to have detailed spectra of each of the phenoxyl radicals expected in these systems. These spectra have been obtained by oxidation of the corresponding phenols with OH.[11] At pH 11 the H atom adducts also contribute significantly in the region of 360–420 nm so that spectra were also taken in the presence of sufficient *tert*-butyl alcohol to remove most of the OH radicals.

Spectra of the Bromophenoxyl Radicals. Irradiation of an N_2O saturated 1 mM *p*-bromophenol solution at pH 11 gave the spectrum of Figure 2 (solid points). At this pH the reaction of OH (produced with a *G* of 6.0) is expected to result mainly in the formation of *p*-bromophenoxyl radical.

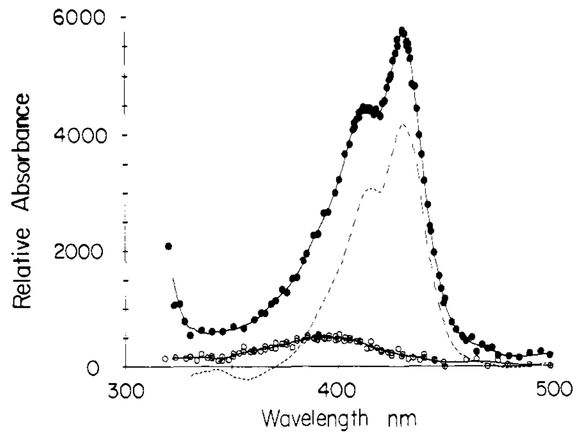


Figure 2. Spectra observed in the pulse radiolysis of 1 mM *p*-bromophenol solutions at pH 11: ●, saturated with N_2O; ○, also containing 0.4 M *tert*-butyl alcohol to remove OH radicals; (- - -), the contribution from *p*-bromophenoxyl after subtracting the contributions from the H atom adduct and semiquinone. These latter corrections were made as described in ref 5.

$$\cdot OH + BrC_6H_4O^- \xrightarrow{75\%} OH^- + BrC_6H_4O\cdot \quad (8)$$

Steady-state experiments on the production of Br$^-$, however, indicate that ~25% of the OH attacks at the bromine position.[12] This reaction should result in the formation of the benzosemiquinone radical.

$$\cdot OH + BrC_6H_4O^- \xrightarrow{25\%} Br^- + \cdot O\text{-}C_6H_4O^- + H^+ \quad (8a)$$

Pulse radiolysis experiments in which ascorbate was used to remove the bromophenoxyl radicals selectively[13] showed, indeed, that semiquinone is produced from OH in the expected yield. At pH 11 the hydrogen atom adduct to *p*-bromophenol, as observed for solutions to which 0.4 M *tert*-butyl alcohol had been added, absorbs significantly in the range of 350–450 nm (open circles in Figure 2). Even though the yield is small (G(H) = 0.6) the corrections are appreciable because the extinction coefficients are in the range of 1000–5000 $M^{-1}\ cm^{-1}$. In the experiments with e_{aq}^- the contribution is even more important because of the relatively lower yield of radicals produced from e_{aq}^- ($G \sim 2.7$). In Figure 2 the residual spectrum, after subtracting the contributions from the H atom adduct and from the semiquinone, is given by the dashed curve. This spectrum, corrected for the 75% contribution of *p*-bromophenoxyl radical, is repeated in Figure 3 for comparison with the spectrum of phenoxyl radical[5] and those of the *o*- and *m*-bromophenoxyl radicals as obtained in similar experiments. It is seen that the spectra of phenoxyl and *o*-bromophenoxyl radicals are very similar, so that the tertiary transfer reaction will have very little effect on the resulting spectrum and cannot easily be followed. In contrast, the spectrum of *p*-bromophenoxyl radical is considerably more intense than that of phenoxyl and shifted toward the red so that the two radicals can be readily distinguished and the electron transfer followed. The *m*-bromophenoxyl radical has a somewhat less intense spectrum, but one that is distinctively different from that of phenoxyl. The extinction coefficients at their principal maxima are for phenoxyl 3000 $M^{-1}\ cm^{-1}$ at 402 nm, for *p*-bromophenoxyl 5900 $M^{-1}\ cm^{-1}$ at 430 nm, for *o*-bromophenoxyl 2550 $M^{-1}\ cm^{-1}$ at 400 nm, and for *m*-bromophenoxyl 2000 $M^{-1}\ cm^{-1}$ at 425 nm.

Spectrophotometry of the Reduction Products. In the reaction of e_{aq}^- with *p*-bromophenoxide at pH 11.5, *p*-bromophenoxyl radical is an important intermediate 40–60 μs after

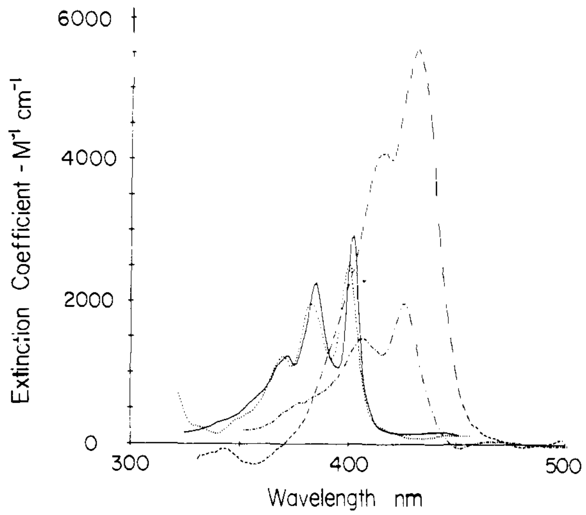
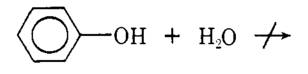


Figure 3. Spectra of phenoxyl (—), *p*-bromophenoxyl (- - -), *m*-bromophenoxyl (- • - • -), and *o*-bromophenoxyl (• • • •) radicals as determined in experiments similar to Figure 2. Extinction coefficients are determined on the basis of an OH yield of 6.0 for N_2O saturated solutions.

the pulse, as is seen in Figure 4A. After correcting for the large contribution from the H atom adduct, the spectrum (dashed curve in Figure 4A) is essentially identical with that of *p*-bromophenoxyl radical produced from OH (dotted curve), but only 59% as intense as that expected for a quantitative conversion. It is clear that there is appreciable loss of radicals as the result of reaction 3 or other side reactions. Spectra taken nearer to the pulse show a contribution from phenoxyl radical (the spectrum observed 3-5 μs after the pulse is illustrated by the solid points in Figure 5) and it is clear that phenoxyl radical is an intermediate in the reaction sequence. The spectrum observed 11-15 μs after the pulse (open diamonds in Figure 5) shows contributions from both phenoxyl and bromophenoxyl radicals. Considerations of all the rate constants involved (see below) show that the different stages in this sequence cannot be separated completely and that 0.4 mM *p*-bromophenol is an optimum concentration for examining the various stages. At lower solute concentrations electron scavenging (reaction 1) is too slow and at higher concentrations the transfer (reaction 7) is too rapid, and direct oxidation of the bromophenoxide by OH cannot be prevented easily.

Studies of the reaction of e_{aq}^- with *p*-bromophenol at pH 7 show no evidence for formation of phenoxyl or *p*-bromophenoxyl radicals (lower experimental data in Figure 4A). The spectrum observed at this pH is largely that of the H atom adduct, which is shifted to lower wavelength from that observed at pH 11.5 (see Figure 2). The *p*-hydroxyphenyl radical, in its neutral form, does not appear to protonate at the radical site to any detectable extent.



(2a)

Experiments with *o*-bromophenol give results that can be interpreted similarly. Experiments at pH 11.5 (solid circles in Figure 4C) show maxima at 382 and 401 nm that can be attributed to either phenoxyl or *o*-bromophenoxyl radical. There is very little change in the spectrum after ~20 μs, so that it is not possible to draw any significant conclusion about the importance of reaction 7. Again the contributions from the H atom adduct are very important and the residual attributable to phenoxyl or *o*-bromophenoxyl given by the dashed curve is only 45% of that expected for quantitative conversion. Experiments at pH 7 (open squares in Figure 4C) give a spectrum that is predominantly that of the H adduct at this pH. There is no evidence of phenoxyl radical, so that protonation of the neutral form of the ortho radical is unimportant.

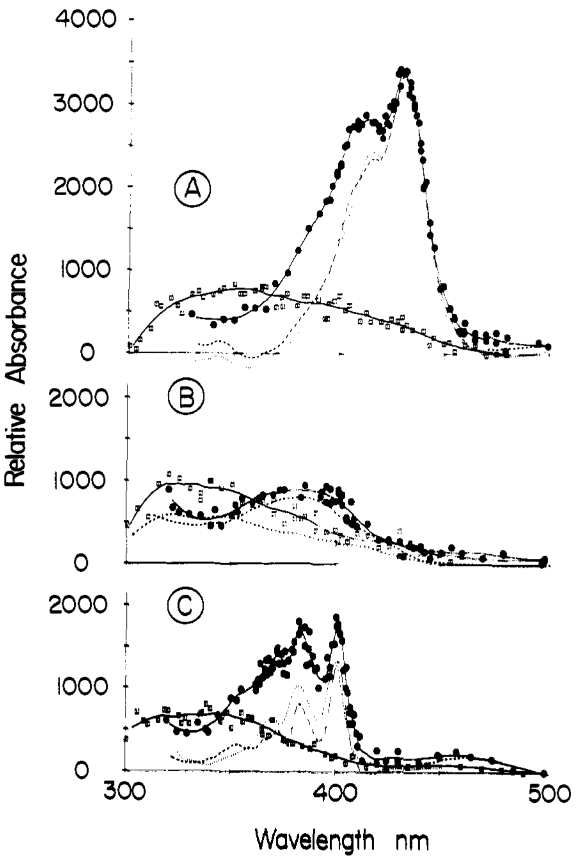


Figure 4. Spectra observed 40-60 μs after the pulse irradiation of N_2 purged 0.4 mM solutions of (A) *p*-bromophenol, (B) *m*-bromophenol, and (C) *o*-bromophenol at pH 11.5, ●; all at pH 7.0, ◻. Solutions contained 0.4 M *tert*-butyl alcohol to remove the OH radicals. The dashed curves in A and C are the residual after correcting for the contribution from the H atom addition product. The dotted curves are 59 and 45% of the spectra of corresponding bromophenoxyl radicals given in Figure 3. In B, the spectrum is mainly ascribed to the H atom adduct, as indicated by the dashed curves for solutions also saturated with N_2O.

In contrast to the above, experiments with *m*-bromophenol show no evidence for formation of either phenoxyl or *m*-bromophenoxyl radicals (4B) either at pH 7 or 11. Here the spectra observed are mainly those of the H atom adduct (spectra obtained in the presence of N_2O are given by the dashed curves).

Kinetic Spectrophotometry

***p*-Bromophenol.** The kinetics of the reactions in 0.4 mM *p*-bromophenol solutions was followed at the maxima of the phenoxyl (402 nm) and *p*-bromophenoxyl (430 nm) absorptions and the data are reported in Figure 6. At this concentration the reaction period of the electron is 0.6 μs ($k(e_{aq}^- + p\text{-bromophenoxide} = 2.9 \times 10^9\ M^{-1}\ s^{-1})$).[14] The time profile of the electron absorption was followed at 470 nm and can be described quite well by integrating eq 4 using an appropriate value for the extinction coefficient (4000 M^{-1} cm^{-1} at 470 nm) and an electronic time constant of 0.2 μs. The growth of the absorptions at 402 and 430 nm have periods ~3 and ~10 μs, respectively, but a detailed analysis is complicated, since reactions 1, 2, 3, and 7 all have similar periods. The kinetics were examined in more detail by numerically integrating the appropriate differential equations that describe each of the reaction intermediates on a Hewlett-Packard 9830 calculator. These equations include eq 4 and 5 given above. Because of the

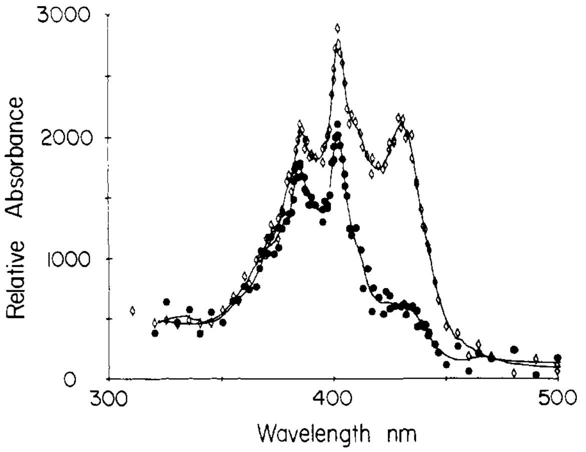


Figure 5. Spectra observed 3–5 μs (●) and 11–15 μs (◇) after the pulse irradiation of a 0.4 mM solution of *p*-bromophenol at pH 11.5 (containing 0.2 M *tert*-butyl alcohol). The sharp peak at 402 nm is ascribed to phenoxyl radical and the peak at 430 nm that grows in more slowly to *p*-bromophenoxyl radical. At longer times, the contribution from phenoxyl radical disappears and the spectrum of Figure 4A is ultimately observed.

transfer reaction, eq 6 must be replaced by

$$\frac{d(C_6H_5O\cdot)}{dt} = k_2[\cdot C_6H_4O^-] - k_7[C_6H_5O\cdot][BrC_6H_4O^-] \tag{6a}$$

The formation of *p*-bromophenoxyl is described by

$$\frac{d(BrC_6H_4O\cdot)}{dt} = k_7[C_6H_5O\cdot][BrC_6H_4O^-] + k_8[OH][BrC_6H_4O^-] \tag{9}$$

where the last term is included to account for the direct production of bromophenoxyl by OH. In the systems studied here, most of the OH radicals are removed by reaction with the *tert*-butyl alcohol,

$$OH + RH \rightarrow H_2O + R\cdot \tag{10}$$

so that the contribution of the last term in eq 9 is small. Since the H atom adduct formed in the reaction

$$H + BrC_6H_4O^- \xrightarrow{k_2} Br\dot{C}_6H_5O^- \tag{11}$$

absorbs significantly at 402 nm, its contribution must also be computed. In this study, essentially all of the H atoms react with the *p*-bromophenol so that

$$d[Br\dot{C}_6H_5O^-]/dt = k_{12}[H][BrC_6H_4O^-] \tag{12}$$

Since the H atom and OH radicals build up and decay on the time scale of the pulse, the steady-state approximation cannot be used in evaluating eq 9 and 12, but rather, one must integrate the appropriate expressions describing the formation of these intermediates, i.e.,

$$d[H]/dt = P_H - k_{12}[H][BrC_6H_4O^-] \tag{13}$$

$$d[OH]/dt = P_{OH} - k_8[OH][BrC_6H_4O^-] - k_{10}[OH][RH] \tag{14}$$

where P_H and P_{OH} are the H and OH production rates during the pulse and zero afterwards. Equations 4, 5, 6a, 9, 11, 13, and 14 were integrated simultaneously, the concentrations of each absorbing intermediate (electron, phenoxyl, and bromophenoxyl radicals and H atom adduct; the hydroxyphenyl radical was assumed to have no significant absorption) were multiplied by the appropriate extinction coefficients, and the resultant sum of the absorbances was substituted into a differential equation that simulated the detector response. Integration of the latter gave the expected time dependence of the absorption. Incorporation of the contribution from the H atom adduct into the calculations is extremely important, since this accounts for about one-third of the absorption observed at 402 nm (extinction coefficient for the H adduct is 4600 M^{-1} s^{-1}). As it turns out, all of the rate constants and extinction coefficients needed in these calculations are known from other studies, except the rate constants for reactions 2, 3, and 7. Since the absorption of *p*-bromophenoxyl in Figure 4A is only 60% of that expected, this scheme requires that for 0.2 M *tert*-butyl alcohol, $k_3[RH] = 0.67k_2$. The calculated increase of absorption at 430 nm is insensitive to the exact value of k_2 (given that $k_2 \sim 2 \times 10^5$ s^{-1} from the preliminary observations) and, as can be seen in Figure 6, the data at this wavelength can be fitted quite well with $k_7 = 2.0 \times 10^8$ M^{-1} s^{-1}. At this point, only k_2 remains to be determined. The calculation is quite sensitive to the value of k_2 since one is required to fit the magnitude of the dip that occurs as the electron reacts, the period of the rise as the phenoxyl and bromophenoxyl radicals grow in, and, more importantly, the delay of this latter rise. This delay is critically dependent on k_2. Optimizing the fit, k_2 is determined to be 1.7×10^5 s^{-1}. If k_2 were significantly greater, then the rise at 402 nm would occur at earlier times and effectively wipe out the observed dip. If k_2 were smaller, then the slower buildup of product would result in a much more pronounced dip after the electron decay. Iterating the calculations once gives best values of $(1.7 \pm 0.3) \times 10^5$ s^{-1} (or $t_{1/2} = 4.1 \pm 0.6$ μs) for k_2 and $(2.0 \pm 0.5) \times 10^8$ M^{-1} s^{-1} for k_7. The pseudo-first-order rate constant for the reactions removing the phenyl radicals is 1.2×10^5 s^{-1}. If this removal is attributable entirely to reaction 3, then $k_3 = 6 \times 10^5$ M^{-1} s^{-1}.

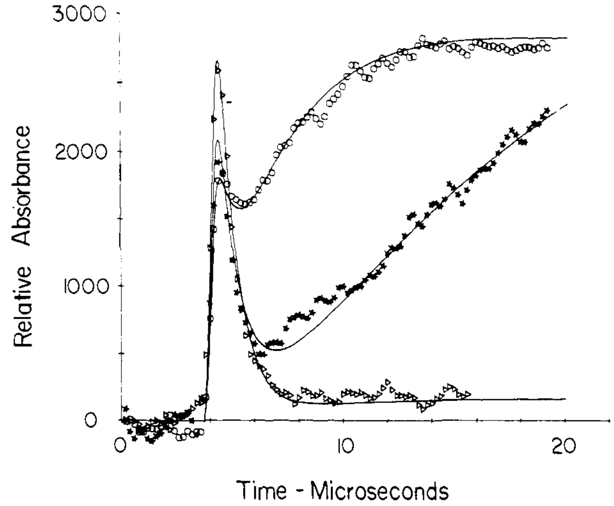


Figure 6. Time dependence of the absorption at 402 (○), at 430 (★), and at 470 nm (△) observed for a 0.4 mM solution of *p*-bromophenol at pH 11.5 (N_2 purged containing 0.2 M *tert*-butyl alcohol). The latter illustrates the growth and decay of the electron absorption. The long-term growth at 430 nm results from the electron transfer from *p*-bromophenoxide to phenoxyl radical. The time dependence observed at 402 nm is the complex dependence resulting from reactions 1, 2, 7, 8, and 11. Curves are calculated as described in the text.

o-Bromophenol. Because of the similarity of the spectra of phenoxyl and *o*-bromophenoxyl radicals (see Figure 3), the kinetics of the protonation of the *o*-hydroxyphenyl radical was followed at the isosbestic point at 400 nm and the data are reported in Figure 7. The growth and decay of the e_{aq}^- as observed at 470 nm can be reproduced quite well by integration of eq 4 with k_1 taken as 2.3×10^9 M^{-1} s^{-1} (the literature value is 1.9×10^9 M^{-1} s^{-1}).[14] Using this value the cusp observed at 400 nm can be reproduced with $k_2 = 5 \times 10^4$ s^{-1} (taking

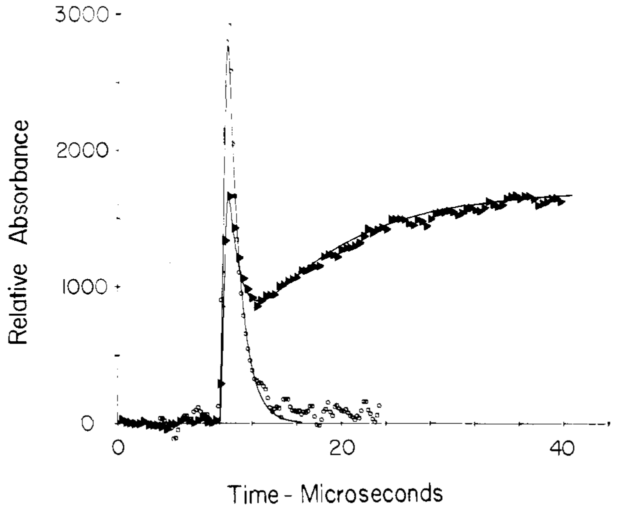


Figure 7. The time dependence of the absorption at 400 (▲) and at 470 nm (○) observed for a 0.4 mM solution of *o*-bromophenol at pH 11.5 (N_2 purged; containing 0.2 M *tert*-butyl alcohol). Curves are calculated as described in the text.

$k_3[RH] = 1.2k_2$ as determined by the limiting value of the absorption at 40 μs). The indicated value for k_3 is $3 \times 10^5\ M^{-1}\ s^{-1}$. While the extinction coefficient of the H adduct is smaller here than in the case of the para derivative (ϵ_{400} 2100 $M^{-1}\ cm^{-1}$), the contribution to the absorption is again very significant (~50% of the signal at the minimum observed at 400 nm). From the fit of the data, k_2 can be given as $(5 \pm 1) \times 10^4\ s^{-1}$ ($t_{1/2} = 14 \pm 3$ μs).

The *o*-bromophenoxyl radical absorbs slightly more than phenoxyl in the region 390–400 nm and less in the region of 400–405 nm. Detailed examination of the growth and decay at 395 and 404 nm gave curves similar in shape to that given in Figure 7. It is clear from these studies that the protonation reaction is so slow and is overlapped by the subsequent transfer reaction that one can say very little about the kinetics of the transfer reaction in this case. The spectrum reported in Figure 4C indicates a slight contribution from phenoxyl radical, so that transfer may be considerably slower than in the case of the para radical.

Confirmation by Transfer to Ascorbate. Since both phenoxyl and the bromophenoxyl radicals oxidize ascorbate ion rapidly, it is possible to estimate the yield of these radicals by examining the production of the ascorbate radical at 360 nm. These studies are reported in detail elsewhere.[13] The yields of phenoxyl radicals are estimated from these studies to be $0.6G_{e_{aq}^-}$ for the *p*-bromophenol and $0.45G_{e_{aq}^-}$ in the case of the *o*-bromophenol. Reduction of the meta isomer shows that a species is produced which slowly oxidizes ascorbate, but it is possible to estimate $0.1G_{e_{aq}^-}$ as an upper limit to the formation of phenoxyl radicals in this case. These results are all in accord with the present observations.

ESR Observations

A previous paper[3] on the ESR spectra of phenyl radicals covered those derived from the bromophenols as well as many others. However, discussion of a number of points not covered in that work can be included here in support of the mechanisms introduced above. Indirect detection of the phenyl radicals from all three isomers was possible in basic solution (pH 12) by spin trapping with the *aci* anion form of nitromethane, $CH_2{=}NO_2^-$. Adducts of the form $RCH_2\dot{N}O_2^-$ were detected in all three cases and the ESR parameters were consistent with those for a number of other adducts in which the radical R was clearly of the phenyl type (see Table IV of ref 3). Phenoxyl radicals have not been observed to add to $CH_2{=}NO_2^-$. Experiments were carried out with 5–10 mM bromophenol and 1–10 mM nitromethane. Good signals of the adducts of $CH_2{=}NO_2^-$ were obtained with 1 mM *o*- or *m*-bromophenol, but with the para compound 10 mM was necessary. This difference in behavior is consistent with the shorter lifetime of the para isomer of $\cdot C_6H_4O^-$ before protonation to phenoxyl radical (reaction 2). From the observed dependence on $CH_2{=}NO_2^-$ concentration it is evident that the reaction of the *p*-hydroxyphenyl radical with about 5 mM $CH_2{=}NO_2^-$ competes with its conversion to $C_6H_5\dot{O}$. On the basis of a 4 μs protonation period, the rate constant for the addition to $CH_2{=}NO_2^-$ is ~$4 \times 10^7\ M^{-1}\ s^{-1}$.

Attempts were also made to directly observe the ESR spectra of radicals formed from the bromophenols. In basic solution the meta isomer gave readily detectable lines of the phenyl radical $\cdot C_6H_4O^-$ as reported in Table I of ref 3. Thus little protonation of this isomer occurs on the time scale of the ESR experiments. No detectable ESR lines of either phenyl or phenoxyl radicals were found with the ortho and para isomers. Initially, the failure to observe the phenoxyl radical was puzzling, but subsequent observation of the electron transfer to form bromophenoxyl radical explains this failure. The bromophenoxyl radicals should not be detectable because of broad lines caused by the effects of the bromine hyperfine splitting and quadrupole moment.

In neutral solution, where the *p*-hydroxyphenyl radical does not protonate, it was possible to detect its ESR lines. As reported in ref 3, all simple phenyl radicals show considerable perturbation of the line intensities as a result of CIDEP. This effect causes the high-field lines to become more intense than wou'd otherwise be the case and reduces or even inverts the low-field lines. With *p*-bromophenol this effect caused the low-field group of lines to be undetectable. (The central group of lines was obscured by the signal from the irradiated cell.) In spite of this problem, a good estimate of the hyperfine parameters was possible, since other available data on phenyl radicals allows a very good estimate of the *g* factor. The spectrum should consist of a triplet of triplets as a result of the pairs of ortho and meta protons. The high-field group consisted of a 4.90-G triplet, which is assigned to the meta protons. The separation of the high-field line group from the center of the spectrum can be calculated to be 16.8 G to within 0.1 G. These parameters are in good agreement with those of phenyl radical itself ($a_o = 17.4$, $a_m = 6.2$ G).[3] A similar experiment in neutral solution with *o*-bromophenol did not give detectable lines. Here the asymmetry of the radical plus the possibility of a small splitting by the OH proton probably explains the low intensity. No experiment in neutral solution was attempted with the meta compound.

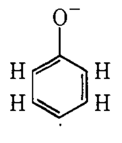
Electron Transfer between Phenoxyl Radical and Phenoxide. The above demonstration of a rapid electron transfer reaction involving phenoxyl radical and bromophenoxide ion (reaction 7; for *p*-bromophenoxide ($k_7 = 2.0 \times 10^8\ M^{-1}\ s^{-1}$)) suggests that such a reaction may also occur with phenoxide ion itself,

$$C_6H_5\dot{O}(1) + C_6H_5O^-(2) \rightarrow C_6H_5O^-(1) + C_6H_5\dot{O}(2) \quad (15)$$

where the labels 1 and 2 mark individual molecules or radicals. This reaction cannot be detected by optical spectroscopy, since no chemical change is involved. However, ESR spectroscopy provides a unique capability to do so because the spin state of the protons in the radical effectively labels a particular radical or molecule. Upon occurrence of the transfer reaction the ESR line of radical (1), on the average, moves to a new position corresponding to the nuclear spin state of molecule (2) which becomes radical (2). The change in the ESR spectrum causes a broadening of the ESR lines, which is detectable at rates of transfer above about $10^6\ s^{-1}$. The line broadening is evident either directly through line-width measurements or through the reduction in signal height. Measurements were made with various concentrations of phenol at pH 11.5. Data for both peak height and excess line width are given in Figure 8. The peak height is plotted in the fashion appropriate to second-derivative spectra. With a width of 1.0 kHz for the unbroadened line, these two sets of data should have the same slope as is found. Correcting for the fact that not all of the transfer reactions result in a change in the nuclear spin assignment, the slope corresponds to a rate constant for reaction 15 of 1.7 × 10^8 M^{-1} s^{-1}.[15] Since some line broadening from over-modulation is inevitable in this mode of operation, further processing of the data was undertaken to correct for this effect. The estimated correction raises the rate constant for reaction 15 from the value of 1.7 × 10^8 M^{-1} s^{-1}, corresponding to the slope in Figure 8, to 1.9 × 10^8 M^{-1} s^{-1}. This value is believed accurate to about this difference or ±15% and is esentially identical with that of 2.0 × 10^8 M^{-1} s^{-1} observed in the optical experiments for transfer between *p*-bromophenoxide and phenoxyl radical. In a discussion of a number of transfer reactions involving organic radicals,[16] Meisel estimates that for an exchange reaction involving a neutral radical and its parent anion where $\Delta G_{ab}{}^{\circ} = 0$, the rate constant should be about 0.5 × 10^8 M^{-1} s^{-1}. The somewhat higher rate constant observed here can be accommodated if the reaction radius is ~20% higher than the 5.0 Å assumed in Meisel's calculations.

Conclusions

As indicated in the introduction, radicals which have the structure $-\dot{C}{=}C(O^-)-$ can have appreciable negative charge at the radical site. In their oxyanion forms both the *o*- and *p*-hydroxyphenyl radicals exhibit structures with related features, so that protonation might be expected on the radical carbon; e.g., for the *p*-hydroxyphenyl radical anion the structures I–III should contribute to the overall wave function.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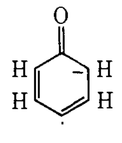
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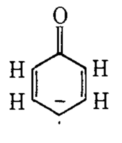
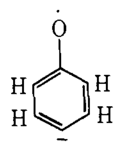

III

It can be seen that it is possible for structure III to accept a proton from water to produce phenoxyl radical. Because the negative charge in the phenoxides is in the π system, direct contribution from the alternative structure (IV) would not


IV

seem to play an important role; i.e., the feature controlling the protonation reaction is the conjugation of the charge and not the delocalization of the unpaired electron. It is known,[3] of

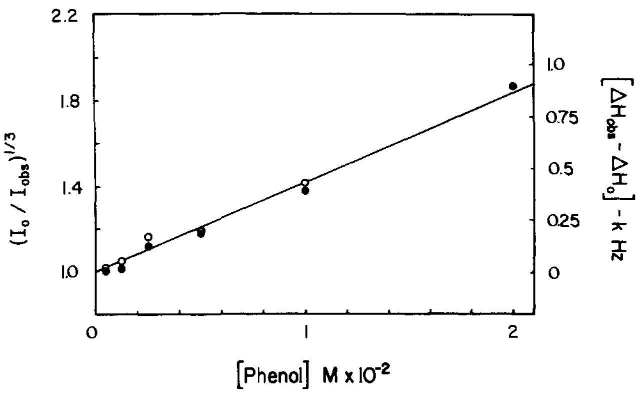


Figure 8. Effect of phenol concentration on the intensity (●) and incremental width (○) of the ESR lines of phenoxyl radical as observed in steady-state experiments. I_0 and ΔH_0 are taken as the limiting values at low concentration. Line width is given in the experimental units of the proton NMR frequency (1 G = 4.26 kHz). The linear dependence of $I_{obsd}{}^{-1/3}$ and incremental line width on phenol concentration corresponds to a transfer rate constant of 1.9 × 10^8 M^{-1} s^{-1} (see text).

course, that the unpaired electron in phenyl radicals is localized in an sp^2 hybrid in the plane of the ring. The requisite feature is absent in the meta radical, so that protonation is expected to be considerably slower.

The protonation observed here provides a reference reaction with which to compare other reactions involving phenyl radicals in competitive studies. As noted above, the absolute rate for hydrogen abstraction from *tert*-butyl alcohol and for its addition to nitromethane can be determined by reference to this reaction. It is anticipated that a number of other rate constants will be similarly measured. It is also important to note that reaction 2 allows one to prepare phenoxyl radicals in the absence of phenol and in the present study has made it possible to study the electron transfer reaction between the bromophenoxide and phenoxyl radical.

References and Notes

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