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Hydroxyl Radical as a Probe of the Charge Distribution in Aromatics: Phenol

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Initial radiation chemical yields of 1.48 (2), 0.24 (2), and 2.01 molecules per 100 eV of absorbed energy are reported for addition of $^{\bullet}$OH radical to each of the ortho, meta, and para positions of phenol. These yields represent 91% of the yield of 5.96 expected for $^{\bullet}$OH addition to 5 mM phenol and are in general agreement with other previous measurements. Pulse radiolysis experiments show that phenoxy radical is produced in a yield of ∼0.42 as a result of addition of $^{\bullet}$OH at phenol's ipso position. The total of these yields (5.84) accounts for the addition of virtually all of the expected $^{\bullet}$OH radicals. The relative yields for addition to the ortho, meta, and para positions provide a measure of the charge distribution in phenol that correlates quite well with the unpaired spin distribution in phenoxyl radical. This correlation indicates that the OH substituent similarly affects the charge distribution on the aromatic ring of phenol and the unpaired spin distribution in the phenoxyl radical.

Introduction

Because of its electrophilic character[1] $^{\bullet}$OH radical is expected to add preferentially at the electron-rich centers of aromatics. As a result it can act as a probe of the charge distribution in an aromatic. Studies of the distribution of the isomeric hydroxycyclohexadienyl radicals produced by $^{\bullet}$OH addition to aromatics should, therefore, provide information on their charge distributions. In selected cases this information can be obtained from pulse radiolysis[2] or ESR studies.[3] A more general approach involves determination of the radiation chemical yields of the hydroxylated products after oxidation of the initial hydroxycyclohexadienyl radicals. The distribution of dihydroxybenzenes produced in the case of phenol provides a reference for other studies involving hydroxylated aromatics.

Raghavan and Steenken,[2] in studies using quinones to oxidize the adducts at the ortho and para positions, showed that, as expected, $^{\bullet}$OH preferentially adds at those positions at the expense of very little addition at the meta or hydroxyl (ipso) positions. The Raghavan−Steenken paper[2] provides an excellent discussion of the kinetics involved in these experiments. While various other oxidants have been used,[2,4] ferricyanide is usually the oxidant of choice because it has been shown to oxidize hydroxycyclohexadienyl radicals to phenol quantitatively.[5] Ye[6] in chromatographic (HPLC) studies and Albarran and Schuler[7] in capillary electrophoresis (CE) studies, using ferricyanide as the radical oxidant, similarly found that addition preferentially occurs at the ortho and para positions. Tripathi and Su, using time-resolved Raman measurements, showed that in the case of 4-carboxyphenol ∼12% of $^{\bullet}$OH addition occurs at its ipso position.[8] Pulse radiolysis studies carried out during the present investigation (see below) show that $^{\bullet}$OH attack at the ipso position of phenol is of a similar magnitude.

Because the distribution found in the case of phenol is important as a reference for the effect of OH substituents on the charge distribution in hydroxylated aromatics, we critically reexamined the radiolysis of aqueous solutions of phenol containing ferricyanide to determine the initial yields of the hydroxylated products and report the results here. The distribution of the initial yields of the dihydroxybenzenes found in the present study, which is similar to the distributions previously reported, provides a sound basis for considering the effects of substituents on the charge distribution in other aromatics. The present results are particularly important in indicating that the charge distribution in phenol is very similar to the unpaired spin distribution in phenoxyl radical, i.e., that the electronic structure of the aromatic ring in phenol is similarly affected by OH and $^{\bullet}$O substituents.

Experimental Section

Phenol (Mallinckrodt) was sublimed. HPLC analysis showed that there were no significant impurities, including the dihydroxybenzenes and benzoquinone, in the resultant sample. Reference samples of quinone, catechol, and 1,2,3-, 1,3,5-, and 1,2,4-trihydroxybenzene were from Aldrich and used as received. Resorcinol and hydroquinone (Aldrich) were recrystallized from methanol. 2-Hydroxyquinone was prepared by hexachloroiridate oxidation of 1,2,4-trihydroxybenzene.[9] The experimental procedures were similar to those used in other recent studies of radiolytic hydroxylation of aromatics.[10−13] Aqueous solutions containing 5.0 mM phenol and 2.7 mM ferricyanide were freshly prepared before each experiment. The pH of these solutions was ∼7, so the phenol (p$K_a \approx 9.95$) was essentially in its protonated form. Because loss of water from the OH adducts to form phenoxyl radical is both acid[14] and base catalyzed,[15] it is important that these experiments be carried out in near neutral solutions. HPLC analysis of these solutions showed no significant contributions of the products expected in the radiolytic experiments. All solutions were purged of dissolved air and saturated with N_2O before irradiation. The N_2O served to convert hydrated electrons to $^{\bullet}$OH radicals and the ferricyanide to oxidize the intermediate cyclohexadienyl radicals to the corresponding hydroxylated aromatics.

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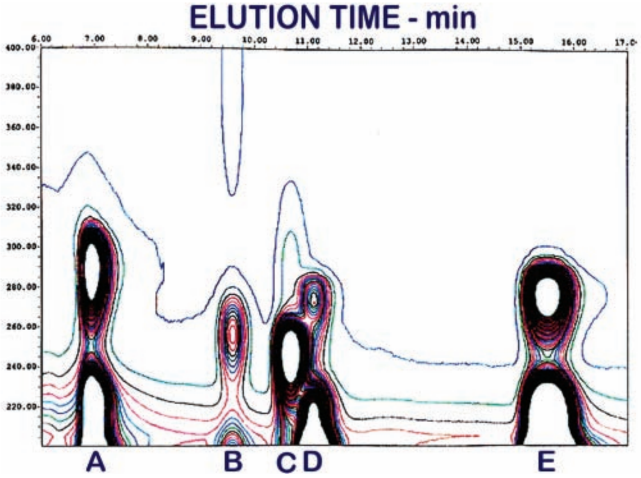

Figure 1. Contour plot (50 contours from 0 to 0.1 mAU) of a 5 mM solution of phenol containing 2.7 mM ferricyanide irradiated to a dose of 834 Gy: (A) hydroquinone, (B) hydroxyquinone, (C) quinone, (D) resorcinol, (E) catechol.

Irradiations were at 22 °C at a dose rate of 92.7 Gy/min. At this dose rate the total yield for reaction of $^{\bullet}$OH with 5 mM phenol is expected to be ~55 μM/min. Initial radiation chemical yields, in units of molecules per 100 eV of absorbed energy, were determined as described below in the Results section. A radiation chemical yield of 1 corresponds to 1.032×10^{-7} mol/J. Immediately after irradiation samples were analyzed by liquid chromatography (HPLC). The HPLC analyses employed a Waters Millennium system equipped with a diode array detector. A 150 × 4.6 mm Phenomenex 3 μm Luna C-8 column was used for product separation. Samples were 100 μL. Resolution was adequate using an eluent containing ~0.01 M perchloric acid and 5% methanol. Spectra, recorded from 200 to 450 nm at 1 s intervals, provided 3-D chromatographic data from which spectra and chromatograms could be extracted. Areas of appropriate chromatographic peaks were determined using the Millennium software. Concentrations were determined from these areas using sensitivities determined with reference samples. After the hydroxylated products were eluted the concentration of methanol in the eluent was increased to remove unreacted phenol.

Pulse radiolysis experiments were carried out at the Notre Dame Radiation Laboratory's 8 MeV LINAC facility as previously described.[16] Irradiation of N_2O-purged solutions 5 mM in phenol with a 2 ns pulse at a dose of ~8 Gy/pulse produced initial $^{\bullet}$OH concentrations ≈ 5 μM. Time-resolved absorption traces were recorded spectrophotometrically and processed as described in ref 16. Pulse radiolysis of a 5 mM phenol solution also containing 200 mM sodium azide provided reference information on the spectrum and yield of phenoxyl radical.

Results

Product Analysis Studies. Figure 1 displays a contour plot of the chromatographic data for a 5 mM phenol solution containing 2.7 mM ferricyanide irradiated to a dose of 838 Gy. At this dose only five products are apparent. They include the three expected products: hydroquinone at A, resorcinol at D, and catechol at E. Additionally, quinone is apparent at C. It is produced by partial oxidation of hydroquinone by the ferricyanide used as the radical oxidant. Even though its concentration is much lower (<10%) than those of the other products it is very apparent in the figure because it absorbs relatively strongly at 247 nm.

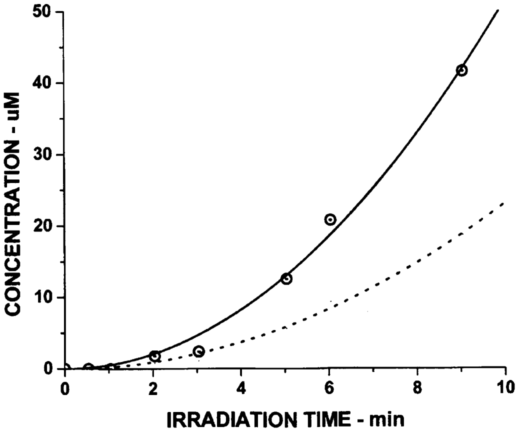

Figure 2. Dose dependence of the concentration of hydroxyquinone produced in the radiolysis of 5 mM solutions of phenol. The solid curve is a quadratic that shows the hydroxyquinone to be produced as a secondary product. The dashed curve represents the estimated dose dependence of 1,2,3-trihydoxybenzene also produced as a secondary product (see text).

The product observed at B in the figure is conclusively identified as hydroxyquinone by comparison of its spectrum and retention time with a sample prepared by the hexachloroiridate oxidation of 1,2,4-trihydroxybenzene. It has an extinction coefficient comparable to that of quinone[9] and is apparent in the chromatograms even though it is produced only in very low yield. As indicated in Figure 2 its concentration is quadratically dependent on dose, so it is clearly produced as a secondary product. Since 1,2,4-trihydroxybenzene is not observed it is apparent that it is rapidly and totally oxidized to hydroxyquinone by the ferricyanide present. 1,2,3-Trihydroxybenzene is also expected as a significant secondary product but is not apparent in Figure 1 because it is produced only from catechol and resorcinol and absorbs much less strongly than the other products. It elutes just in front of hydroquinone and is observed at higher doses. 1,3,5-Trihydroxybenzene is not expected to be observable at the doses used in these experiments because it is only produced from resorcinol in very low yield.

The dose dependence of the concentrations of the products resulting from OH addition to phenol ($[P_i]_D$), at the positions ortho, meta, and para to the OH substituent, is illustrated by the open symbols in Figure 3. The sum of the hydroquinone and quinone concentrations is taken to represent attack at the para position. The dotted curve represents optimized fits of the data to the functional dependence (eq 1) that takes into account the competition between the reaction of $^{\bullet}$OH with phenol and the initial products and also loss of the products in the secondary reactions

$$[P_i]_D = f_i \cdot G(P_t)_0 \cdot D\{2(\ln(1 + QD)/Q) - D\}^{16,18} \qquad (1)$$

In eq 1 $G(P_t)_0$ represents the yield of the total of the initial and f_i the fractional contribution of a specific product.

The solid symbols in Figure 3 represent the concentration of each of the components corrected for the concentration of the secondary products derived from them. Because hydroxyquinone is produced from each of the primary products, its contributions are estimated by apportioning the observed concentration of hydroxyquinone according to the relative yields of hydroquinone, resorcinol, and catechol and the number and relative reactivity of the sites determined by studies in progress of the radiolytic oxidation of the initial products. We estimate that 65% of the secondary reactions (23% from catechol, 6% from resorcinol, and 36% from hydroquinone) results in formation

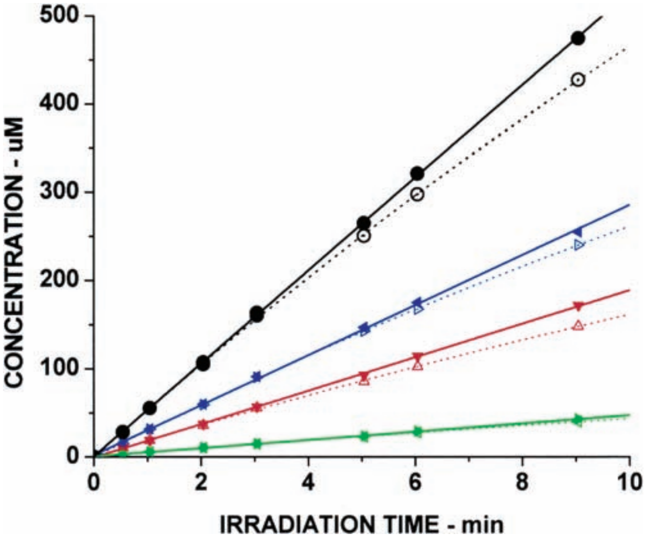

Figure 3. Open symbols illustrate the dose dependence of the concentration of (red) hydroquinone plus quinone, (blue) catechol, (green) resorcinol, and (black) total of the initial products at a dose rate of 92.7 Gy/min. The dotted curves represent the optimized fit of the data to eq 1. The solid symbols represent the data corrected for the secondary products (see text) and the solid lines the linear fit of these latter data.

of 1,2,4-trihydroxybenzene, which is rapidly oxidized by ferricyanide and observed as hydroxyquinone. Although 1,2,3-trihydroxybenzene is estimated to be produced in 35% of the secondary reactions (32% from catechol and 3% from resorcinol) it has a weak absorbance and is observable only at very high doses. Because 1,3,5-trihydroxybenzene is produced only from resorcinol it does not contribute significantly to the corrections for secondary processes.

The solid lines in Figure 3 represent linear fits to the corrected data. It is seen that they are tangent to the observed dose dependences at zero dose. Their slopes correspond to radiation chemical yields of 2.95 for catechol, 0.48 for resorcinol, and 2.01 for hydroquinone. We estimate that these yields are accurate to the order of a few percent as indicated by their agreement with the initial yields of 3.01, 0.50, and 1.98 determined by fitting the observed concentration dependences of the dihydroxybenzenes with eq 1. They are also in general agreement with previous measurements after appropriate corrections have been made (see discussion). The total of these yields, 5.44, represents 91% of the yield of 5.96 expected for $^{\bullet}$OH scavenging by 5 mM phenol.[17]

Pulse Radiolysis Studies. Because the total initial yield of the dihydroxybenzenes is only 91% of that expected it is apparent that addition of $^{\bullet}$OH at the ipso position of phenol is also significant. Such addition is expected to produce phenoxy radicals as the result of rapid elimination of water from the adduct. Since phenoxyl radicals are readily reduced to phenol, no observable product is expected. However, in pulse radiolysis experiments phenoxyl radicals can be observed to be produced at a diffusion-controlled rate (i.e., $t_{1/2} \approx 20$ ns in 5 mM phenol). Figure 4 displays the spectral data observed 250−750 ns after pulse irradiating a 5 mM solution of phenol at pH 7.

The absorption band at 335 nm in spectrum A is a composite of the spectra of the hydroxycyclohexadienyl radicals produced. As expected, these radicals decay according to second-order kinetics with a first half period of ~300 μs. The absence of a significant absorption at 335 nm in spectrum B is expected because azide radical oxidizes phenolics by electron transfer rather than by addition.[19]

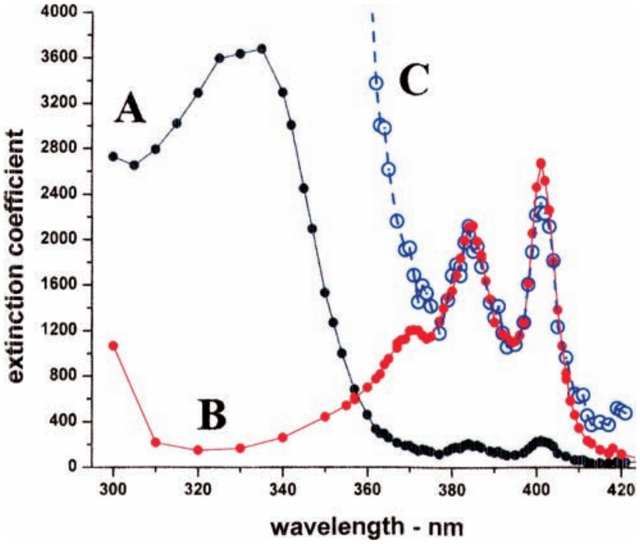

Figure 4. Absorption spectra observed in the pulse radiolysis of (A) a 5 mM phenol solution at pH ≈ 7 and (B) also containing 200 mM sodium azide. (C) Spectrum A magnified by a factor of 10. A was recorded 250−750 ns and B 2.5−7.5 μs after the pulse at which times oxidation was complete.

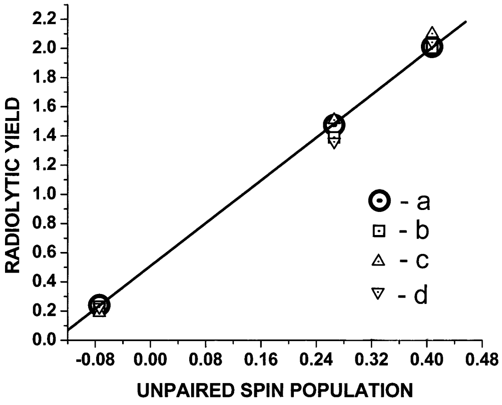

Figure 5. Correlation of the initial yields of catechol, resorcinol, and hydroquinone with the unpaired spin population located at the ortho, meta, and para positions of phenoxyl radical: (a) present results, (b) from ref 7, (c) from ref 6, and (d) from ref 2. The yields given in refs 2 and 6 have been scaled by factors of 0.93 and 1.21 (see text).

The weak absorption in the 370−410 nm region in Figure 4 appears simultaneously with the absorption at 335 nm. The spectrum in this region (C) has been magnified by a factor of 10, which shows it to be mainly attributable to phenoxyl radical. Comparison of spectra B and C shows that the yield of phenoxyl radical is an order of magnitude lower when $^{\bullet}$OH rather than $^{\bullet}$N$_3$ is used as the oxidant. Since $^{\bullet}$N$_3$ oxidizes phenol quantitatively[19] the relative absorbances of B and C at 401 nm indicate that ~7% of the $^{\bullet}$OH radicals ($G \approx 0.42$) add to phenol at its ipso position. Together with the other yields reported above, virtually all (~98%) of the expected yield of 5.96 is accounted for. In summary, the relative yields for addition of $^{\bullet}$OH to each of the ortho, meta, para, and ipso positions of phenol are in the ratios of 0.25:0.04:0.34:0.08.

Discussion

We previously commented that the charge distribution in the cresols is closely related to the unpaired spin distribution in the corresponding phenoxyl radicals.[20] In Figure 5 the radiation chemical yields per position determined in the present study (a, open circles) are plotted against the unpaired spin population

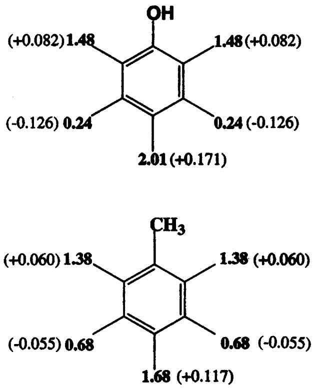

Figure 6. Bold numbers represent the radiation chemical yields for •OH addition at the ortho, meta, and para positions of phenol and toluene. The differences between the estimated negative charges at the various positions and 0.166 are given parenthetically.

at the corresponding ring positions in phenoxyl radical determined by ESR measurements. The latter values are taken as 0.4 times the proton hyperfine constant at those positions in mT.[21] Yields previously obtained in CE studies for 5 mM phenol solutions,[7] where ferricyanide was used as the radical oxidant, are given by b in the figure. Ye's data,[6] where ferricyanide was also used as the oxidant, show a similar trend but a total yield of only 4.45. These yields, scaled by a factor of 1.21 to take into account the lower total, are given by c. The yields reported by Raghavan and Steenken for 15−20 mM phenol solutions using quinones as the radical oxidant[2] are given by d. They have been scaled by a factor of 0.943 because of the 6% higher scavenging yield expected at the higher phenol concentration.[18] The overall agreement between these various results conclusively shows that the partial rates for addition at each of the ortho, meta, and para positions to the neutral form of phenol to be in a ratio of 0.74:0.12:1.

The linear relationship in Figure 5 shows that the distribution of charge in phenol, indicated by the present and previous studies, correlates very well with the unpaired spin distribution in phenoxyl radical. We also indicated[20] a similar correlation between the product distribution in the reaction of •OH radicals with *meta*-cresol and the unpaired spin distribution in 3-methylphenoxyl radical. This similarity is not too surprising because a methyl substituent is usually considered to have a relatively minor effect on the electronic structure of an aromatic ring. However, this is not the case for *ortho*- and *para*-cresol, where the yields for addition at the positions meta to the OH substituent are substantially greater than expected from the correlation in Figure 5. In those cases the ortho/para configuration of the OH and methyl substituents appears to result in a compensatory effect on the charge distribution. At this point one cannot predict the effects of substituents on the relative yields for •OH attack solely on the basis of ESR data. Clearly more extensive studies are in order.

The present studies provide a measure of the excess negative charge on the ortho and para positions of phenol and the corresponding deficiency at its meta positions. The excess/deficiency is given parenthetically in Figure 6 relative to a negative charge of 0.166 at the ring positions in the benzene radical anion.

Comparative data for toluene,[7,13] also given in the figure, show that its methyl substituent has an effect about one-half as strong in directing negative charge to the para and ortho position as does an OH substituent. In both cases the product distributions indicate that the excess charge on the para position is approximately twice that on the ortho positions. Because the negative charge deficiency at the meta position of phenol is appreciable and close to being saturated it is somewhat surprising that the methyl substituent in toluene does not have a somewhat greater effect on the rate for •OH addition at its meta position.

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(18) For a derivation of eq 1, see the appendix in ref 16. Q in eq 1 is a fitting parameter that describes the curvature of the plot and is given by $k_2 \cdot G(\mathrm{P_t})_0/(k_1 \cdot [\mathrm{S}])$, k_1 and k_2 are the second order rate constants for reaction of •OH with phenol and the products, and [S] is the phenol concentration.

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