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Directing Effects of Phenyl Substitution in the Reaction of OH Radical with Aromatics: The Radiolytic Hydroxylation of Biphenyl[†,1]

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The initial yields for formation of 2-, 3- and 4-hydroxybiphenyl following the radiolytic oxidation of biphenyl in the presence of ferricyanide are, respectively, 2.19, 1.13 and 1.55 molecules/100 eV. These yields reflect relative rates of 0.71:0.37:1 for •OH radical attack on each of the ortho, meta, and para positions of biphenyl. Comparison of the corresponding partial rate constants to that for benzene shows that phenyl substitution has a significant effect in directing •OH addition to the ortho and para positions of aromatic systems. Comparison with phenol shows that a phenyl substituent has only a slightly smaller effect than does OH in increasing the partial rate constant at the ortho and para positions but is substantially less effective in decreasing the rate of •OH reaction at the meta position.

We have examined the distribution of products in the radiolytic hydroxylation of biphenyl in order to obtain information on the directing effect of phenyl substitution on the site of addition of •OH radicals to aromatic systems. This information is particularly needed for discussions of concerted effects of OH and phenyl substitution in studies of reactions of •OH with hydroxybiphenyls which are in progress.[2] In the studies reported here ferricyanide was used to oxidize the three phenyl-substituted hydroxycyclohexadienyl radicals initially produced to stable products which could then be analyzed by chromatographic methods. This approach is similar to that previously used to examine the radiolytic oxidation of benzene to phenol, which was found to be quantitative,[3] and to determine the relative rates for •OH reaction at the α- and β-positions of naphthalene.[4] The initial product yields reported here show that addition to the 2-, 3-, or 4-positions of biphenyl is near to quantitative and that the phenyl group has a substantial effect on directing •OH addition to the ortho and para positions. Background kinetic data on the reactions of the intermediates, obtained by pulse radiolytic methods, are also reported.

Experimental Section

Biphenyl has only a very limited solubility in water (5.1×10^{-5} M) so that the present experiments had to be carried out at very low concentrations and correspondingly low doses. Biphenyl concentrations were determined by absorption spectrophotometry based on an extinction coefficient of biphenyl of 15 700 M^{-1} cm^{-1} at 248 nm as determined for a solution 40 μM in biphenyl. On purging biphenyl is volatilized rapidly from aqueous solutions so that the solutions used in the kinetic experiments were closely monitored spectrophotometrically. In the product analysis studies, solutions containing 10^{-4} M potassium ferricyanide were purged with N_2O in a septum-sealed irradiation cell and subsequently saturated with biphenyl. The N_2O served to convert e_{aq}^- to OH radicals. Irradiation was at ~25 °C in a ^{60}Co source at a dose rate, calibrated with the Fricke system,[5] of ~1100 rad/min (~1.14×10^{15} eV g^{-1} s^{-1}). At this dose rate •OH radicals are produced in a N_2O-saturated solution at a rate ~ 6 μM/min. Biphenyl was from Matheson, Coleman and Bell and potassium ferricyanide from J. T. Baker. Water was purified by the triple distillation process used in conventional radiation chemical experiments.

It was found that the reverse-phase HPLC methods used to separate hydroxylated aromatics in other studies[2,4] did not adequately resolve the 3- and 4-hydroxybiphenyls expected in the present experiments. Because of this difficulty a normal-phase method employing a 10-cm Waters 4-μM Nova-Pak silica column was used in the separations with cyclohexane containing 5% ethyl acetate used as the eluent. Detection was with a Waters 990+ diode array system with the data digitally recorded in three-dimensional format. Spectra and chromatographic displays could then be readily reconstructed from the recordings. Secondary products were examined by the reverse-phase chromatographic methods used to study the radiolytic oxidation of the hydroxybiphenyls.[2]

Because a nonaqueous mobile phase was used in the analytical separations, the products produced in the irradiated aqueous solutions were extracted into an equal volume of the mobile phase. This extraction avoided problems with the column which occurred on direct injection of the aqueous phase. The distribution coefficients measured in separate experiments showed that greater than 90% of the products were extracted into the organic phase. Single extractions were used and appropriate corrections applied for distribution between the two phases. The chromatographic sensitivities were calibrated with reference samples of 2- and 4-hydroxybiphenyl obtained from Fluka and 3-hydroxybiphenyl from Eastern Kodak. The 3-hydroxybiphenyl contained ~5% 4-hydroxybiphenyl impurity for which a correction was made.

Pulse radiolysis experiments were carried out at the Radiation Laboratory LINAC facility, as previously described.[6] Doses of ~600 rad/pulse produced an initial radical concentration of ~3 μM. Signal-averaging methods were used to develop the desired detail. Dosimetry was based on the N_2O-saturated thiocyanate dosimeter using a radiation chemical yield of 6.13 molecules/100 eV [7] and an extinction coefficient of 7580 cm at 472 nm for $(SCN)_2^-$.[8]

Results and Discussion

Pulse Radiolysis Experiments. The absorption spectrum recorded ~10 μs after the pulse for a solution 46 μM in biphenyl is given by the solid points in Figure 1. This spectrum is predominantly due to the phenyl-substituted hydroxycyclohexadienyl radicals produced as the result of •OH addition to biphenyl. The extinction coefficients given represent the weighted average of the three isomeric radicals produced based on an overall radiation chemical yield of 5.3, as is appropriate at the low concentration of biphenyl for the reactions of •OH radicals

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[†] From the M.S. dissertation of X. Chen, University of Notre Dame, August 1992.

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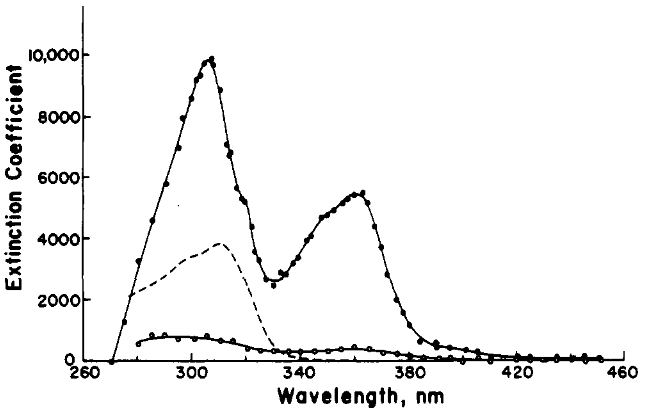


Figure 1. Absorption spectra recorded ~10 μs after pulse irradiation of (●) a 50 μM N_2O-saturated aqueous solution of biphenyl and (○) also containing 50 μM *tert*-butyl alcohol to scavenge selectively the OH radicals. The extinction coefficient scale is based on thiocyanate dosimetry with the radical yield taken as 5.3. The dashed spectrum is that of hydroxycyclohexadienyl obtained in similar experiments with benzene.

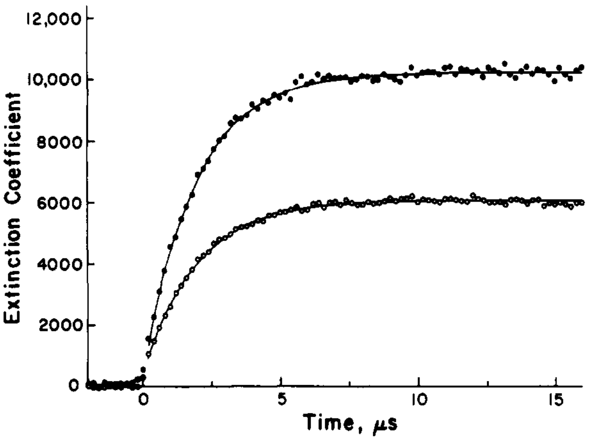


Figure 2. Time dependence of the absorbances at (●) 305 and (○) 360 nm observed in the pulse radiolysis of a 50 μM solution of biphenyl (N_2O saturated). Solid curves correspond to growth half periods of 1.35 and 1.33 μs.

produced in N_2O-saturated solutions.[9] This spectrum exhibits major peaks at 305 and 360 nm and weak side bands at 320 and 345 nm. The peaks at 305 and 360 nm have been reported previously by Sehested and Hart.[10] For comparison the spectrum of hydroxycyclohexadienyl radical, obtained in similar experiments with benzene, is also given by the dashed spectrum in the figure. It is noted that this radical does not exhibit any significant absorption above 340 nm.

The spectrum recorded under identical conditions after addition of 0.05 M *tert*-butyl alcohol to scavenge the •OH radicals is given by the open points in Figure 1. From the available rate information[11] it is estimated that the alcohol should remove ~98% of the •OH radicals but only ~2% of the H• atoms, so it is clear that the contribution of the H• atom addition product to the spectrum observed in the absence of the *tert*-butyl alcohol is only minor. Sehested and Hart[10] have reported from studies at pH 3 that the H• atom adducts to biphenyl absorb at 360 nm with an extinction coefficient of 5000 M^{-1} cm^{-1}. As is seen in the lower spectrum in Figure 1, there is no absorption in neutral solution that is similar to that reported by Sehested and Hart. However, we do find such an absorption in more acidic solutions. Further experiments are required to determine the origin of this latter absorption which very likely involves a protonated form of the H• atom adduct.

Figure 2 illustrates the growth kinetics at 305 and 360 nm for a solution 5.0×10^{-5} M in biphenyl. The solid lines in the figure represents exponential growth of the signals with essentially identical half periods of 1.35 and 1.33 μs. A common period should, of course, be observed since both represent the loss of •OH even though different product radicals may be involved. The observed pseudo-first-order rate constant of 5.2×10^5 corresponds to a second-order rate constant for reaction of •OH with biphenyl of $(1.04 \pm 0.05) \times 10^{10}$ M^{-1} s^{-1}. This value agrees very well with the value of $(0.9 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} given by Sehested and Hart.[10]

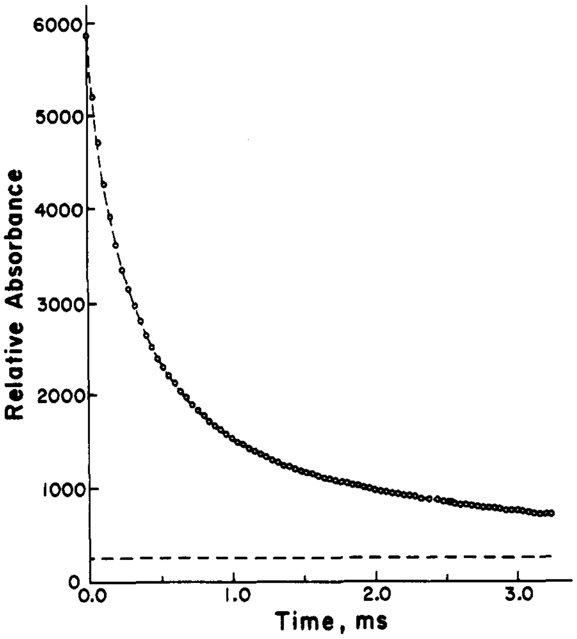


Figure 3. Decay of the signal at 360 nm at an initial radical concentration of 3.3 μM. Curve through experimental points corresponds to a second-order decay ($2k = 1.0 \times 10^9$ M^{-1} s^{-1}) superimposed on a background signal of 290 M^{-1} cm^{-1} indicated by the dashed line.

At an initial radical concentration of 3.3×10^{-6} M the signal at 360 nm decays as is shown in Figure 3. The solid curve in the figure corresponds to a second-order reaction having a rate constant ($2k$) of 1.0×10^9 M^{-1} s^{-1} for reaction between two phenyl-substituted hydroxycyclohexadienyl radicals. This value is only slightly less than that for reaction between two hydroxycyclohexadienyl radicals (1.2×10^9 M^{-1} s^{-1}) determined in parallel studies during the course of this work.[12] There appears to be no significant kinetic or steric barrier to the second-order reactions of the phenyl-substituted radicals.

Pulse radiolytic studies of biphenyl solutions also containing ferricyanide showed that oxidation of the •OH adducts by ferricyanide is only modestly rapid. It is, in fact, more than an order of magnitude slower than for oxidation of the •OH adducts to phenol.[13] Figure 4 illustrates the time dependences of the signals at 305 and 360 nm for solution 5×10^{-4} M in ferricyanide. These signals decay very nearly exponentially, as indicated by the solid traces in the figure, with however, rather different half periods of 8.8 μs at 305 nm and 17.2 μs at 360 nm. These periods correspond, respectively, to rate constants of 1.6×10^8 and 8.1×10^7 M^{-1} s^{-1}. The difference, which is very apparent in the figure, certainly indicates that different transients are principally responsible for the absorption maximum at these two wavelengths. Sehested and Hart[10] previously concluded from their observations that the various intermediates had similar spectra.

Loss of ferricyanide as measured at 420 cm, where it has an extinction coefficient of 1027 M^{-1} cm and ferrocyanide has negligible absorption, is more complicated. The time dependence illustrated in Figure 5 shows that approximately 70% of the expected loss occurs within 80 μs, with an additional loss of ~20% being observed on a somewhat longer time scale. The initial, more rapid, component has a half period of ~13 μs which approximates the average of the decays observed at 305 and 360 nm. It almost certainly represents the unresolved oxidation of

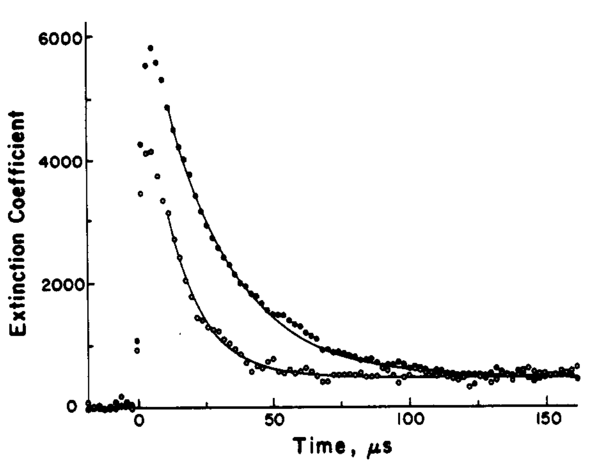


Figure 4. Time dependence of the absorbance following the pulse irradiation of a N_2O-saturated solution 50 μM in biphenyl and 0.5 mM in ferricyanide at (○) 305 and (●) 360 nm. Decays represented by the solid curves are exponential and have, respectively, half periods of 8.8 and 17.2 μs. Note that there is negligible manifestation of the 17.2-μs decay at 305 nm. Neither of these traces indicates any significant contribution from the component with a half period ~60 μs noted in Figure 5.

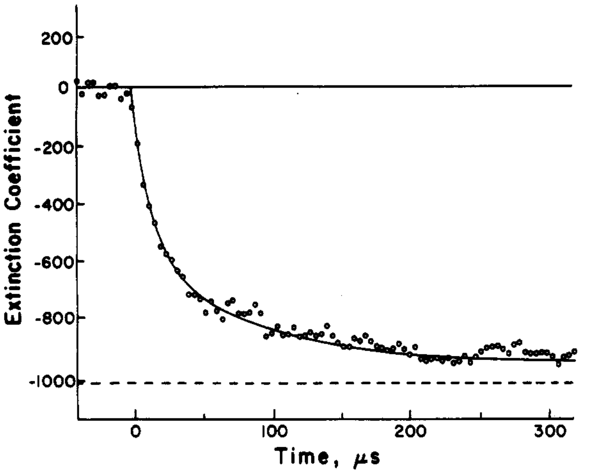


Figure 5. Time dependence of the absorbance at 420 nm following the pulse irradiation of a N_2O-saturated solution 50 μM in biphenyl and 0.5 mM in ferricyanide. The limiting value expected (−1027 M^{-1} cm^{-1}) if the reaction is quantitative and there is no superimposed background signal is given by the dashed curve. The signal initially decreases to about 70% of the expected limit with a half period of ~11 μs. An additional decrease of ~20% with a half period of ~60 μs is observed on the longer time scale.

the ortho and para isomers by the ferricyanide with an average rate constant of 1.1×10^8 M^{-1} s^{-1}. From the results reported below these isomers should have approximately equal contributions and total ~70% of the •OH reactions. This assignment is in accord with the findings of Raghavan and Steenken[13] that the ortho and para •OH adducts to phenol are more easily oxidized than the meta isomer. Correspondingly the slower component ($t_{1/2} \sim 60$ μs; $k \sim 2 \times 10^7$ M^{-1} s^{-1}) very likely represents the oxidation of the meta isomer. These rate constants are sufficiently high that at the dose rate used in the γ-radiolysis the radical concentration never rises above 10^{-10} M in the presence of 10^{-4} M ferricyanide so that second-order reactions should not compete with their oxidation.

We note here that in the case of the ortho and para isomers the unpaired spin can be delocalized onto the second ring, whereas such delocalization is not possible in the case of the meta isomer. This difference appears to be manifest in the rates of reaction with ferricyanide and in the absorption spectrum which is considerably more intense and strongly red shifted from that of hydroxycyclohexadienyl radical. In fact, since each of the absorption peaks at 305 and 360 nm appear to represent only a fraction of the intermediates, the extinction coefficients of the individual radicals at their respective maxima will be even greater than the values given in Figure 1 and considerably greater than for the unsubstituted radical. The absorption band at 360 nm is particularly useful in these studies because it occurs at a window in the ferricyanide spectrum. The decays given in Figure 4 indicate no significant contribution at 305 or 360 nm from the radical responsible for the slower oxidation. Since the unpaired spin is localized on one ring in the meta isomer, its spectrum is presumably similar to that of the unsubstituted hydroxycyclohexadienyl radical.

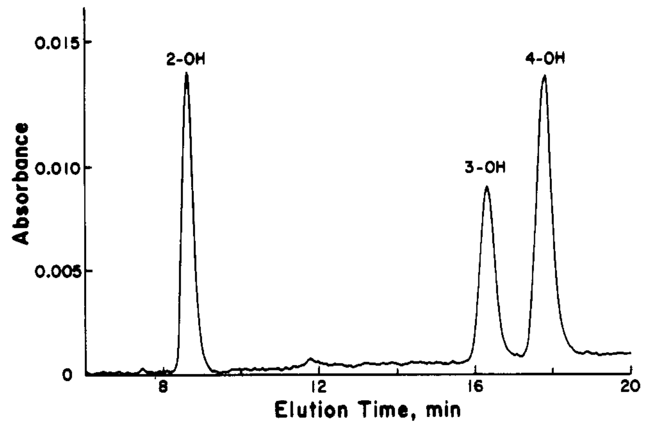


Figure 6. Chromatogram recorded at 250 nm of a saturated solution of biphenyl (N_2O saturated) also containing 10^{-4} M ferricyanide irradiated to a dose of 1200 rad. Elution was normal phase as described in text. The three major products, in order of elution 2-, 3-, and 4-hydroxybiphenyl as indicated, are chromatographically and spectroscopically identical to authentic samples.

In Figure 5 the absorption scale has been normalized to an overall yield of 4.93 for reaction of the cyclohexadienyl radicals with the ferricyanide to take into account corrections of 2% for loss of OH radicals and 5% for loss of hydroxycyclohexadienyl radicals in second-order combination reactions. The limiting loss of absorbance at ~3 ms (940 M^{-1} cm^{-1}) is 91% of the value expected (1027 M^{-1} cm^{-1}) if the reaction with ferricyanide were quantitative. Since one does not expect any appreciable absorption from products at 420 nm, this result would indicate that, as an approximate upper limit, ~9% of radicals do not reduce the ferricyanide on the millisecond time scale. While such a result is in accord with the chromatographic results reported below, it is subject to considerable uncertainty from a possible small positive background contribution to the absorbance at long times which could result from radicals or products unaccounted for by the above difference.

Product Analyses. A typical chromatogram recorded at 250 nm for a biphenyl solution containing 10^{-4} M ferricyanide is given in Figure 6. This sample was irradiated to a dose of 1200 rad. This chromatogram shows that the three expected hydroxybiphenyls are the predominant products at low doses. At higher doses dihydroxybiphenyls produced in the secondary oxidation of the initial products are also observed (Figure 7). These secondary products are those that predominate in the radiolytic oxidation of the hydroxybiphenyls.[2] As the radiolysis progresses, an appreciable drop-off in yield is expected to result from secondary reactions as the products build up and compete with biphenyl at the low concentration of the latter. Reaction of •OH with ferrocyanide produced in the reduction of the ferricyanide ($k = 1 \times 10^{10}$ M^{-1} s^{-1})[11] is particularly important. Figure 8 shows the concentrations of 2-, 3- and 4-hydroxybiphenyl as a function of dose. This figure clearly shows the expected drop-off in yield for doses greater than 1000 rad (0.6×10^{17} eV/g) where both the total organic product and ferrocyanide exceed 10% of that of biphenyl. Correcting for this drop-off, the initial slopes, given by the solid lines in Figure 8, correspond to radiation

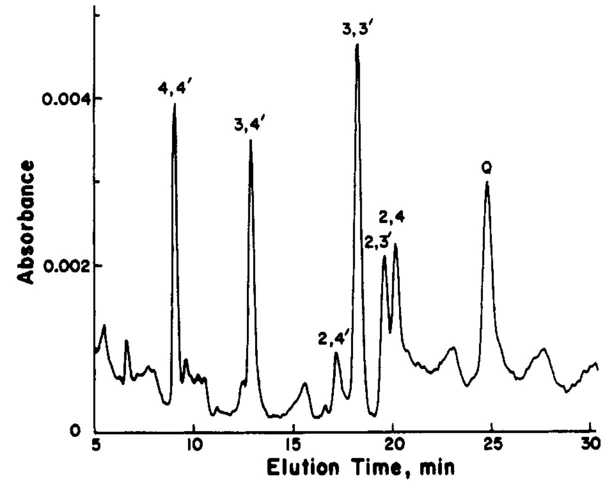


Figure 7. Reverse-phase chromatogram at 250 nm of the secondary products produced in the radiolytic oxidation of a saturated solution of biphenyl (N_2O saturated) also containing 10^{-4} M ferricyanide. Irradiation was at a dose of 5500 rad and separation as in ref 2. At the dose used the monohydroxylated products were only ~60% of those expected from the initial yields. Product identification was by reference to products observed in the oxidation of the hydroxybiphenyls. As indicated in the figure, the major secondary products are 4,4'-, 3,4'-, 3,3'-, 2,3'-, and 2,4-dihydroxybiphenyl and also 2-phenylquinone (Q) resulting from the tertiary oxidation of 2,5-dihydroxybiphenyl.

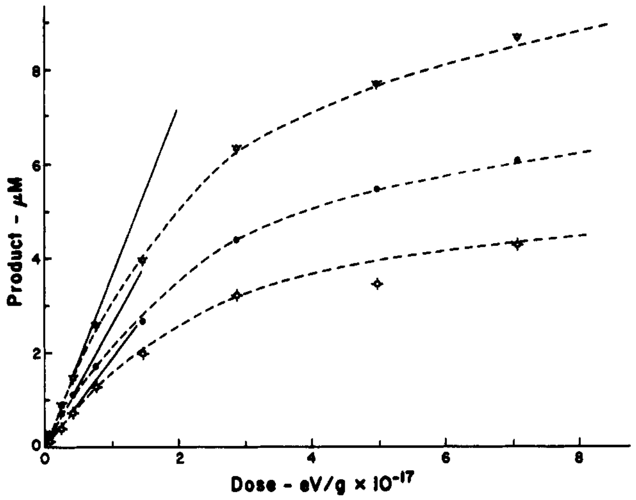
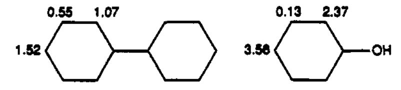


Figure 8. Product concentration as a function of dose for solutions saturated with biphenyl and N_2O also containing 10^{-4} M ferricyanide: (▲) 2-hydroxybiphenyl; (◼) 3-hydroxybiphenyl; (●) 4-hydroxybiphenyl. Initial slopes correspond to yields of 2.19, 1.13, and 1.55, respectively. Dashed lines represent a common dependence normalized for these initial yields.

chemical yields of 2.19, 1.13, and 1.55 for reaction of ${}^{\bullet}$OH at, respectively, the 2-, 3-, and 4-positions of biphenyl. The total, 4.87 is 92% of that of the yield of 5.3 expected at the low concentration of the biphenyl. Since previous studies[3] indicate that under similar conditions ${}^{\bullet}$OH addition to benzene is quantitative, the remaining 8% represents an approximate upper limit to reaction of ${}^{\bullet}$OH at the apical positions of biphenyl. As indicated above, the pulse radiolysis studies of ferricyanide containing solutions also indicate an oxidation yield slightly less than quantitative.

If the product concentrations are normalized by factors corresponding to the initial yields given above, then all data (expect for the point for 3-hydroxybiphenyl at 5 × 10^{17} eV/g) fall on a common curve; i.e., within experimental error the ratio of products is constant. This common dependence, which is represented in Figure 8 by the dashed curves, gives reasonable assurance that none of the products is selectively removed in the secondary reactions. This conclusion was confirmed in experiments in which yields of two of the hydroxybiphenyls were determined upon addition of 10 µM of the third. These experiments showed only the ~20% reduction expected from competition between the biphenyl and the added hydroxybiphenyl.

(A) Partial Rate Constants / 10^9 $M^{-1}s^{-1}$



(B) Relative Rate Constants

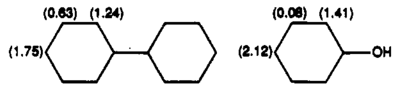


Figure 9. Partial and relative rate constants for reaction of ${}^{\bullet}$OH with biphenyl and phenol. Values in (B) are given relative to benzene as unity. The partial rate constant for reaction of ${}^{\bullet}$OH with benzene is taken at 1.3 × 10^9 M^{-1} s^{-1}. Observed values have been corrected by factors of 2(7.8/10.4) for biphenyl and 7.8/10.1 for phenol to take into account the number of reactive sites and total reaction rates.

The Directing Effect. The overall rate constant of 1.04 × 10^{10} M^{-1} s^{-1} indicates that reactions of ${}^{\bullet}$OH with biphenyl is diffusion controlled, i.e., that essentially all encounters result in reaction. Selection of the site of reaction thus must occur within the encounter complex. From the initial yields given above, the relative rates for attack at the individual ortho, meta and para positions are 0.71:0.37:1. It is clear that the ${}^{\bullet}$OH radical, which is known to be electrophilic,[14] is seeking out the electron-rich centers in the encounter complex. Based on the overall rate constant, the partial rate constants for reaction at the 10 individual ortho, meta, and para positions are, respectively, 1.07 × 10^9, 0.55 × 10^9, and 1.52 × 10^9 M^{-1} s^{-1} (see Figure 9A). These partial rate constants can be compared to the corresponding value of 1.3 × 10^9 M^{-1} s^{-1} for reaction of ${}^{\bullet}$OH with benzene for which the overall rate constant is 7.8 × 10^9 M^{-1} s^{-1}.[11] This comparison makes it clear that the phenyl substituent donates electrons to the para positions and withdraws electrons from the meta positions. However since these reactions are diffusion controlled, partial rate constants must be interpreted somewhat differently than those for thermally controlled reactions and comparisons must take into account the relative number of reaction sites available. Since the overall rate constant for reaction of ${}^{\bullet}$OH with biphenyl is 35% greater than for its rate with benzene, a more representative comparison would be with values which are 50% greater (i.e., by a factor of 2/1.33). The ratios of these values to the partial rate constant for ${}^{\bullet}$OH reaction with benzene (1.3 × 10^9 M^{-1} s^{-1}) are given parenthetically in Figure 9B. Such a comparison makes it clear that the phenyl group donates electrons to both the ortho and para positions but withdraws them from the meta positions.

It is instructive to compare the above with similar data for ${}^{\bullet}$OH reaction with phenol which has a comparable overall rate constant, 1.01 × 10^{10} M^{-1} s^{-1}.[12] In studies using quinones as the radical oxidants Raghavan and Steenken[13] have reported yields for reaction of ${}^{\bullet}$OH at the ortho, meta, and para positions of phenol of 2.88, 0.16, and 2.17, giving a ratio of 0.7:0.04:1 for the relative rates at the individual positions. These measurements were made for solutions 15 mM in phenol, at which concentration the total yield is expected to be 6.14.[9] These relative rates shown that phenyl and OH substitution affect the ortho/para ratio in about the same way but that OH has a pronouncedly greater effect on reaction at the meta position. Ye[15] found similar yields of 2.49 × 0.31 and 1.73 in the presence of ferricyanide. Based on Raghavan and Steeken's data and an overall rate constant of 1.01 × 10^{10} M^{-1} s^{-1}, partial rate constants of 2.37 × 10^9, 0.13 × 10^9, and 3.56 × 10^9 M^{-1} s^{-1} are obtained for ${}^{\bullet}$OH reactions at the ortho, meta, and para sites of phenol (Figure 9A). Ye's data indicate that the partial rate constant for reaction at the meta position may be a factor ~2 higher. In either case reaction at the meta position is substantially less than expected statistically.

The comparison given in Figure 9B, which takes into account the fact that biphenyl has twice as many reactive sites as does phenol, shows that an OH substituent increases the partial rate constant for reaction of •OH at the ortho and para sites only 20% more than does a phenyl substituent. However, it reduces the rate for reaction at the meta position by a factor of at least 4. The data are inconclusive on providing information on the relative effects of OH and phenyl on reaction at the position of substitution.

A General Comment

The study reported here represents a particularly good example of the use of radiation chemical methods to obtain information that is not readily available from more conventional studies. Because of its low solubility, studies of the reactions of biphenyl in aqueous environments have to be carried out at very low (micromolar) product concentrations. One also wishes to avoid complicating secondary reactions that are usually superimposed when, for example, chemical mixing or thermal methods are used to generate the desired intermediates. The present study illustrates very well how the radiolysis of aqueous solutions can be used to study the mechanism of •OH reactions in considerable detail. Radiolysis permits the introduction of a known number of radicals under sufficiently well-controlled conditions so that initial yields can be determined and quantitative measurements are possible. The approach used here also minimizes complications from unwanted secondary reactions that are almost certainly involved when thermal methods are used to prepare the reactive intermediates.

References and Notes

(1) The work described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Contribution No. NDRL-3524 from the Notre Dame Radiation Laboratory.

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