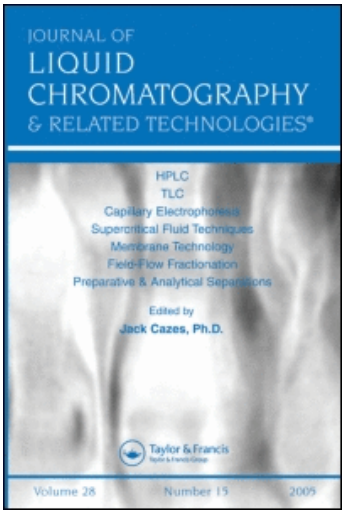

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DETERMINATION OF OXIDATION PRODUCTS IN RADIOLYSIS OF HALOPHENOLS WITH PULSE RADIOLYSIS, HPLC, AND ION CHROMATOGRAPHY

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ABSTRACT

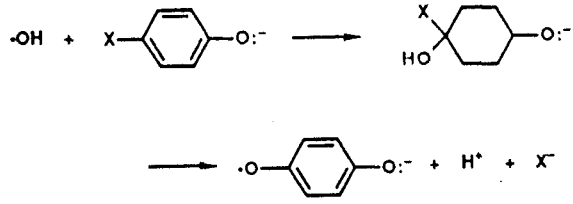
Hydroxyl radicals react with halogen substituted phenols by several different ways. One is addition of OH radicals to the aromatic ring, which is followed by elimination of hydrogen halide, H_2O or OH^-. The positions of OH radicals attack are dependent on the nature of the halogen which affects the electronic distribution in the ring. The oxidation of fluorophenols, chlorophenols and bromophenols with hydroxyl radicals in N_2O saturated solution has been investigated with pulse radiolysis and γ-irradiation experiments. The intermediates of the reactions were studied by pulse radiolysis. The products created in the γ-irradiation of aqueous solutions of halophenols were analyzed by ion chromatography and high performance liquid chromatography (HPLC). With the combination of time-resolved and steady-state experiments a complete and detailed description of radiolytic oxidation of halophenols by hydroxyl radicals was obtained.

INTRODUCTION

Above pH 11 the reaction of hydroxyl radical with halophenols results mainly in the formation of halophenoxyl radical (1),(2) via electron transfer,

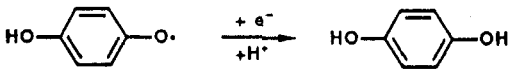
(1)

or addition of ·OH to the ring followed by rapid elimination of OH⁻. (3) However, when ·OH attacks at the site of halogen release of hydrogen halide to form p-benzosemiquinone radical anion results. (1), (4)



(2)

In acidic solutions (pH 3 ~ 4), we find the initial ·OH adducts are moderately stable and can be oxidized to form dihydroxyhalobenzene as products. In the presence of an electron donor, such as ascorbic acid, in acidic solution (pH ~ 3) benzosemiquinone radicals formed by ·OH reaction at the halogen position can be reduced to hydroquinone, catechol and resorcinol, e.g.,



(3)

The relative contributions for OH radical attack at the different positions were examined by the detection of benzosemiquinone radicals with pulse radiolysis and the production of halide ions and complementary hydroquinone, resorcinol and catechol with HPLC.

MATERIALS AND METHODS

Time resolved experiments were carried out using the Notre Dame Radiation Laboratory's computerized pulse radiolysis system as described in detail elsewhere. (5), (6) A Biomation 8100 was used for A/D conversion of the optical signals except in the case of experiments below 1 - us full scale. The absorbance measurements given here are compared to $(SCN)_2^-$ with a reference value of 7580 M^{-1} cm^{-1} taken for the extinction coefficient at 472 nm and a yield of 6.14 in N_2O saturated solution. (7) Most experiments were carried out at an initial radical concentration of 3×10^{-6} M.

Steady State Experiments

a. Gama Radiolysis Experiments

For steady state experiments, the irradiation were carried out inside 2 cylindrical ^{60}Co γ-ray sources at absorbed dose rates of 1.24×10^{17} and 1.38×10^{18} eVg^{-1} min^{-1}, respectively. Absorbed doses were determined by reference to the Fricke dosimeter. (8)

b. High Performance Liquid Chromatography (HPLC) and Ion Chromatography

Hydroquinone, catechol and resorcinol produced in the irradiation were analyzed by HPLC using Waters Lichrosorb RP-18 radial compression column. Princeton Applied Research Corporation M400 electrochemical detector, which has considerably greater sensitivity for these products than an optical detector, was used for quantification. A Hewlett-Packard HP 1040A diode array detector was used basically to record the spectra for identification.

Halide ions, F^-, Cl^- and Br^- were determined with ion chromatography. The ion chromatography mainly consists of a Waters 590 programmable solvent delivery unit, a Waters 430 conductivity detector, and Waters IC-PAK anion column. All quantitative results, HPLC and ion chromatography, were from comparison of peak area with reference samples run under identical chromatographic conditions. In γ-radiolysis, irradiated samples were introduced into the ion chromatography and HPLC in a few minutes after completion of the irradiation.

Solutions for both the pulse radiolysis and r-radiolysis studies were prepared in triply distilled water which was purged of oxygen, saturated with N_2O. The pH was adjusted by addition of Backer Analysis KOH and Aldrich $HClO_4$, and determined with an Orion 811 pH meter calibrated with Fisher buffers. All halophenols and ascorbic acid were from Aldrich. Sodium azide was from Fluka. The chemicals used in the mobile phases of the

ion chromatography and HPLC were acetonitrile UV from American Burdick and Jackson, tetrabutylammonium acetate from Fluka, acetic acid from Fisher and 1-octanesulfonic acid from Kodak.

RESULTS AND DISCUSSIONS

Time-resolved Studies

The hydroxyl radicals react simultaneously via several competing pathways, e.g., addition to an aromatic ring (reaction 2) or by direct electron transfer (reaction 1). In the pulse radiolysis of a N_2O saturated 2 mM p-chlorophenol solution at pH 10.3, the spectrum has contributions from p-chlorophenoxyl, benzosemiquinone and also cyclohexadienyl radicals resulting from hydrogen atom addition (open circles in Figure 1). (9), (10).

In neutral and basic solutions the ascorbic acid anion is a very good reducing agent and reacts with halophenoxyl radicals very rapidly (3) so that it can be used to remove the halophenoxyl radicals and convert them to the halophenoxides or halophenols.

The rate constants for oxidation of ascorbate anion by halophenoxyl radicals are in the range 4 to 13 X 10^8 M^{-1} s^{-1}. (2) For the series of para-substituted phenoxyl radicals the rate constants increase monotonically with the electron withdrawing power of the substituent (F < Cl < Br). (11) The spectrum observed in the pulse radiolysis of 2 mM p-chlorophenol solution with 0.2 mM ascorbate shows absorption maxima of para-semiquinone at 428 nm and of the ascorbate radical at 360 nm (triangles in Figure 1).

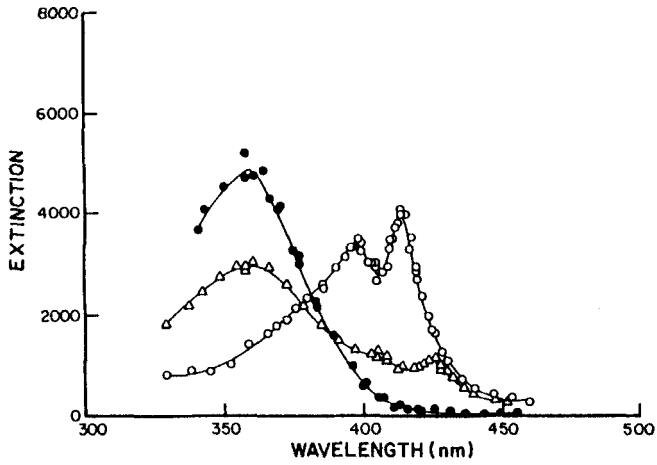


FIGURE 1 Absorption Spectra of Benzosemiquinone Radical Anions and Ascorbate Radicals

Spectra observed 55-75 usec after pulse radiolysis of 2 mM p-chlorophenol solution (N_2O saturated; pH 11.3): in the neat solution (o); containing 0.2 mM ascorbic acid (Δ). Spectrum of scorbate radical (●) observed in pulse radiolysis of 0.2 mM ascorbate acid solution with 0.1 M NaN_3 (N_2O saturated; pH 11.2). It is quit clear that the absorption (Δ) at 428 nm is predominantly that of the p-benzosemiquinone radical which is estimated to be produced with 16% yield in the neat solution.

Because ascorbate also reacts with hydroxyl radicals rapidly the loss of OH radicals by such reaction has to be considered. The rate constant of the reaction is 5.61×10^9 M^{-1} s^{-1} determined in this study by pulse radiolysis. This value is somewhat higher than the previously reported value of 4.1×10^9 M^{-1} s^{-1}. (2) In the irradiation of 2 mM p-chlorophenol and 0.2 mM ascorbate solution at pH 10.2, comparison of the pseudo first order rate constants of the reactions of hydroxyl radicals with halophenoxide and ascorbate anions (Table 1), predicts that only

7.4% of OH radicals should react with ascorbate anions. Irradiation of a N_2O saturated 0.2 mM ascorbic acid and 0.1 M NaN_3 solution at pH 10.6 gave the spectrum of ascorbate radical (solid points in Figure 1). The spectrum is similar to that obtained in a previous study (2) which shows an absorption band with a maximum at 360 nm. The absorption above 400 nm is low (< 500 M^{-1} cm^{-1}) so that one can observe any contribution from p-benzosemiquinone formed in reaction 2. At pH 10.6 a rate constant of 4.8 X 10^9 M^{-1} s^{-1} has been measured for the oxidation of ascorbate anions by azide radicals by pulse radiolysis in our study, which is close to that with hydroxyl radicals, 5.61 x 10^9 M^{-1} s^{-1} from this study.

Figure 1 shows the spectrum observed 55-75 us after the pulse irradiation of a solution of 2.0 mM p-chlorophenol and 0.2 mM ascorbic acid (N_2O saturated; pH 10.2). The reaction period of electron transfer from ascorbate anions to p-chlorophenoxyl in this solution is ~ 4.7 us. The p-benzosemiquinone produced in the irradiation has a maximum absorption at 428 nm with a relative absorbance of 1108 M^{-1} cm^{-1}. From the extinction coefficients of benzosemiquinone, 6900 M^{-1} cm^{-1}, (12) and ascorbate radical, 76 M^{-1} cm^{-1}, at 428 nm (Figure 1), we estimated the yield of benzosemiquinone to be 0.88 which amounts to 16 % of G(·OH) (G(·OH) = 5.5). A correction of 7.4% for ·OH loss by reacting with ascorbate was considered. Similar experiments were carried out for p-fluorophenol and p-bromophenol and the results are given in Table 1.

TABLE 1

Product Yields in the Pulse Radiolysis of Aqueous Solutions of Halophenoxides

Solute [1]	G_{BQ} [2]	k x 10^{-9} $M^{-1}s^{-1}$ ($C_6H_5O^- + \cdot OH \rightarrow$)	k^3 x 10^{-9} $M^{-1}s^{-1}$ ($XC_6H_5O\cdot + Asc^- \rightarrow$)
p-fluorophenoxide	1.38	8.7	4.6
p-chlorophenoxide	0.88	4.6	7.3
p-bromophenoxide	0.66	5.7	8.3

1. 2 mM halophenol solutions containing 0.2 mM ascorbic acid at pH ~ 10.5. All solutions saturated with N_2O.

2. Yields are given in units of G (molecules/100 eV). Averages of 3 experiments.

3. The rate constants are taken from the reference 2.

The yield of m-benzosemiquinones was very low in the radiolysis of the meta-substituted phenols and the optical signals are too weak to be measured by pulse radiolysis. With the ortho-substituted phenols analogous measurements are not possible because the o-benzosemiquinone radical absorbs strongly only at wavelengths below that of ascorbate (<350 nm).

Halide Ion Production

Halide ions produced in reaction 2 in the irradiation of halophenol solutions saturated with N_2O have been determined quantitatively by ion chromatography. Yield-dose plots for the formation of halide ions in 2 mM para-substituted phenol

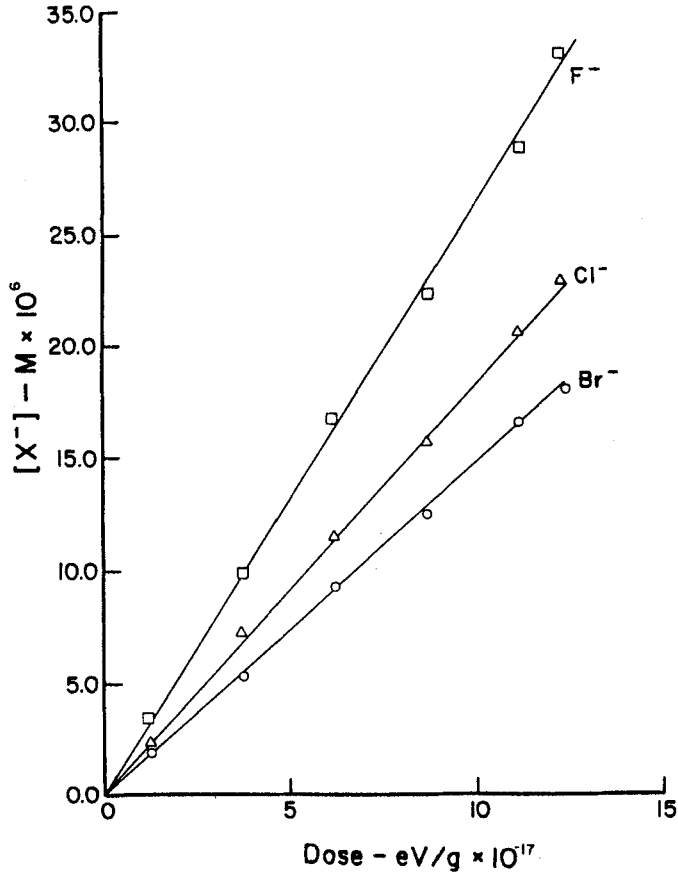


FIGURE 2 Production of Halide Ions as a Function of Dose

Production of fluoride (□), chloride (Δ) and (o) bromide ions in 1 mM p-fluorophenol, p-chlorophenol and p-bromophenol (N_2O saturated, pH ~ 11) as a function of dose at dose rate of 1.24×10^{17} eV g^{-1} min^{-1} (^{60}Co). Slopes correspond to net radiation chemical yields of 1.43, 0.83 and 0.70.

TABLE 2

Product Yields in the Oxidation of Halophenols [1]

Solute [2]	G_X^- [3] pH~10	G_X^- [3] pH~3	G [3]	G' [4]
p-fluorophenol	1.43	1.46	1.33	1.39 (25%)
p-chlorophenol	0.83	0.85	0.78	0.83 (15%)
p-bromophenol	0.70	0.72	0.65	0.67 (12%)
o-fluorophenol	1.04	1.02	0.93	0.98 (18%)
o-chlorophenol	0.79	0.76	0.75	0.76 (14%)
o-bromophenol	0.40	0.43	0.35	0.39 (7%)
m-fluorophenol	0.35	0.39	0.34	0.36 (7%)
m-chlorophenol	0.25	0.23	0.22	0.23 (4%)
m-bromophenol	0.15	0.16	0.14	0.15 (3%)

1. Dose delivered by ^{60}Co γ-ray source at 1.40×10^{18} eVg^{-1} min^{-1}. Yields are given in units of G (molecules/100 eV).

2. 2 mM halophenol solutions containing 0.2 mM ascorbic acid. All solutions saturated with N_2O.

3. G_X^-: yields of halide ions. G: yields of hydroquinone, catechol and resorcinol. G_X^- and G were averaged from four experiments.

4. Yields were averaged from Table 1, G_X^- and G in this Table. The numbers in parentheses are yields per ·OH produced, based on G(·OH)=5.5.

solutions are shown in Figure 2. The production of halide ions are linear with dose over the range 1.2 to 12 X 10^{17} eVg^{-1} in 2 mM halophenol solutions. Table 2 gives the yields of halides (G_X^-) produced in the irradiation of 2 mM halophenol solutions at pH ~ 10 saturated with N_2O. Experiments were also carried out in acidic solutions (pH ~ 3) and the results are shown in Table 2 (G_X^-). A correction was made for e_{aq}^- loss by reacting with H^+

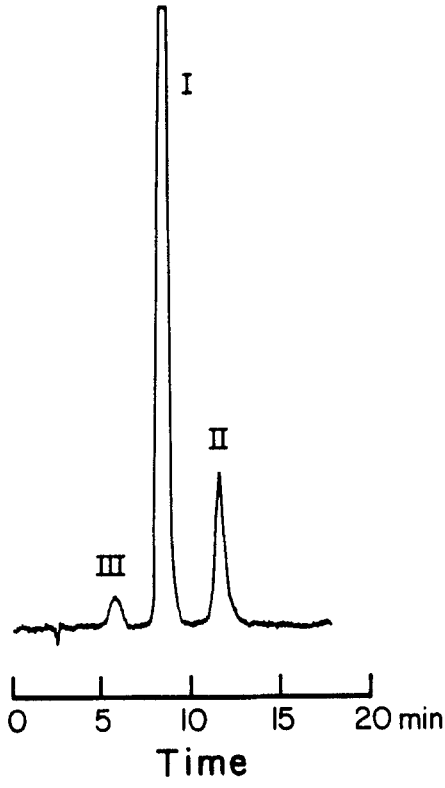


FIGURE 3 Chromatogram Observed in Hydroquinone Solution

0.51 mM hydroquinone solution (N_2 purged neutral pH).
Detector: optical.
Mobile phase: 5 mM tetrabutylammonium acetate.
Principal peaks: I. hydroquinone, II. 1,4-benzoquinone, III. unknown.

at pH ~ 3. It is clear that the production of halide ions does not strongly depend on the solution pH. This is surprising and indicates that OH and O^- substituents have similar effects. The pKas of halophenols are about 9. (13)

Production of Hydroquinone, Catechol and Resorcinol

In neutral and basic solutions, hydroquinone is rapidly oxidized by dissolved oxygen to 1,4-benzoquinone. In Figure 3, hydroquinone (signal I) and 1,4-benzosemiquinone (signal II) were found in the chromatogram of hydroquinone solution at neutral pH. However, in acidic solutions purged with N_2 (pH < 4) hydroquinone is stable. Similarly, catechol is also very easily oxidized by air in neutral and basic solution. Resorcinol is more stable than hydroquinone and catechol. In order to measure the yield of hydroquinone, catechol and resorcinol accurately the experiment has to be performed in acidic solution and in presence of reducing agents. Ascorbic acid is a very efficient reducing agent. It converts hydroxyphenoxyl radicals to hydroquinone, catechol and resorcinol at acidic solution (pH ~ 3).

(4)

Hydroquinone was found in the irradiation of N_2O saturated 2 mM p-fluorophenol solutions with 0.2 mM ascorbic acid at pH ~ 3 (Figure 4). The yields of hydroquinone, catechol and resorcinol were given in Table 2 (G).

Comparisons and Discussions

The averaged values of benzosemiquinone radicals (Table 1), halide ions, hydroquinone, catechol and resorcinol (Table 2) are

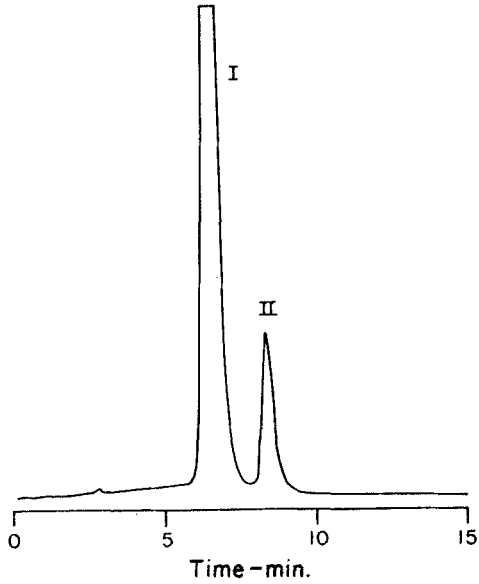


FIGURE 4 Hydroquinone Produced in Radiation

Radiolysis of 1 mM 4-fluorophenol solution containing 0.1 mM ascorbic acid (N_2O saturated; pH 3.2)
Detector: electrochemical.
Mobile phase: as in Figure 3.
I. ascorbic acid, II. hydroquinone (8.2×10^{-6} M).

given in Table 2 (G'). These yields determined by three different detection methods essentially agree. For example, in the p-fluorophenol system, the yield of benzosemiquinone radicals determined by pulse radiolysis is 1.42, fluoride determined by ion chromatography is 1.45 and hydroquinone determined by HPLC in the presence of ascorbate is 1.33. The averaged value of these three yields is 1.40, amounts to 25% of G(·OH). From these yields one can see that the addition of hydroxyl radicals

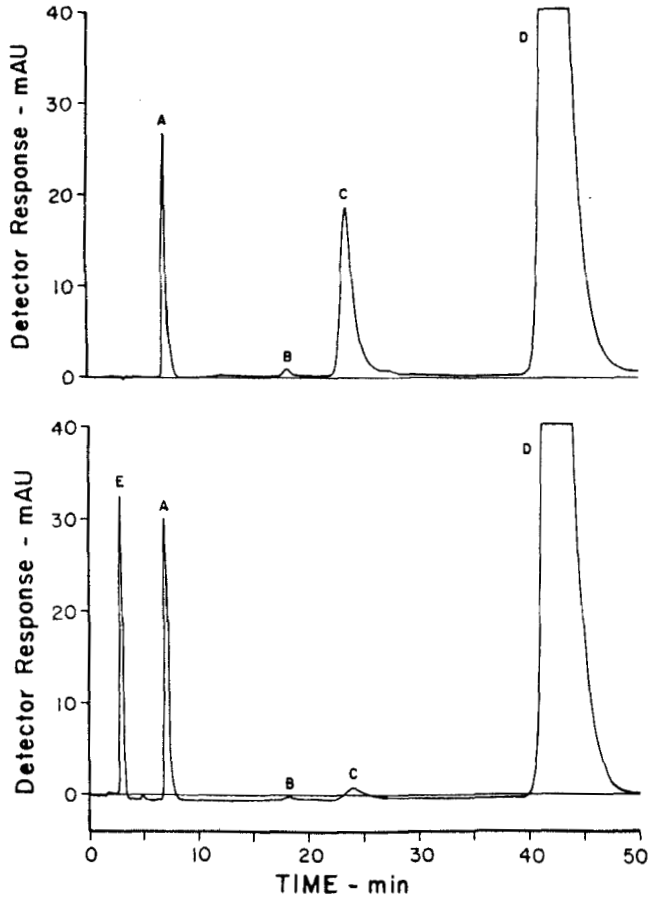


FIGURE 5 Chromatogram of Products in the Oxidation of p-Fluorophenol with Hydroxyl Radical

Irradiation of 4 mM p-fluorophenol, in the absence of ascorbic acid at pH ~ 5 (5a and 5c *); in the presence of ascorbic acid at pH ~ 3 (5b), saturated with N_2O.
Optical detector, wavelength: 281 nm
Mobile phase: 0.3% acetic acid.

A. hydroquinone, B. 2,4-dihydroxyfluorobenzene,
C. 3,4-dihydroxyfluorobenzene, D. p-fluorophenol,
E. ascorbic acid, HQ. hydroquinone, BQ. benzoquinone.

* Figure 5c is the detailed part of Figure 5a at wavelength 248 nm where benzoquinone has a very strong absorption (21,000 $M^{-1}cm^{-1}$).

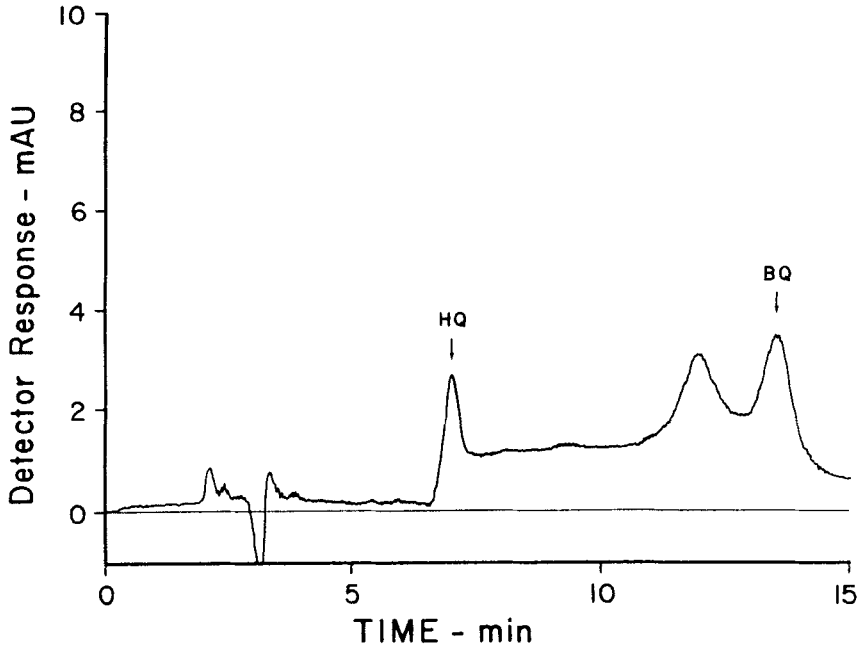


FIGURE 5c

apparently depends on substituents in the order of halogen size, F > Cl > Br. We interpret this as resulting from steric hinderance on the approach of OH radical to the substituent positions. Similar conclusions can be obtained from ortho- and meta-substituents (Table 2). By comparing the yields in para-, ortho- and meta-fluorine substituents we find that the attack of OH radicals is dependent on the halogen position relative to the OH group on the aromatic ring (p > o > m), which must result from the distribution of electron density in the aromatic system.

TABLE 3

Product Yields in the Oxidation of Halophenols under Varying Conditions [1]

Solute [2]	pH	G(catechol)	G_{X^-}
o-fluorophenol	5.2	0.59	1.04
o-fluorophenol	3.5	0.76	1.02
with 0.2 mM ascobate	10.0	0.20	1.03
with 0.2 mM ascorate	3.6	0.93	1.02
o-chlorophenol	5.3	0.49	0.77
o-chlorophenol	2.9	0.53	0.75
with 0.2 mM ascobate	10.1	0.12	0.77
with 0.2 mM ascorate	3.3	0.75	0.76
o-bromophenol	5.5	0.11	0.41
o-bromophenol	3.5	0.15	0.44
with 0.2 mM ascobate	10.3	0.04	0.44
with 0.2 mM ascorate	3.4	0.39	0.43
with 0.4 mM ascobate	3.1	0.37	0.45

1. Dose delivered by ^{60}Co γ-ray source at 1.40×10^{18} eVg^{-1} min^{-1}. Yields are given in units of G (molecules/100 eV).

2. 2 mM halophenol solutions saturated with N_2O.

Similar trends are found in chlorine and bromine substituents (Table 2).

Side Reactions in Acidic Solutions

In experiments with para- and ortho-substituted phenols without ascorbic acid at pH ~ 5, only low yields of hydroquinone and catechol were found (Table 3). The low yields of these products must result from the oxidation of hydroxycyclohexadienyl radicals after they are formed in the reaction 2. In the

irradiation of 4 mM p-fluorophenol at pH ~ 5 (Figure 5a), the yield of hydroquinone is about 12% lower than that with ascorbic acid (Figure 5b). Benzoquinone was found in this irradiated sample (Figure 5c). These experiments demonstrate conclusively that ascorbate efficiently reduces hydroxyphenoxyl radicals to hydroquinone and catechol and removes oxidants in the systems. In Figure 5a, two other peaks (B and C) were found, which were very small in Figure 5b. These two peaks have been determined to be 2,4-dihydroxyfluorobenzene (peak B) and 3,4-dihydroxyfluorobenzene (peak C), which are apparently formed by ·OH adducts. The detail of this study will be given in our next paper.

CONCLUSIONS

The studies of pulse radiolysis, ion chromatography and HPLC are in good agreement. The results indicate that the positions of hydroxyl radical attack are determined by

(1) electronic distribution in the aromatic system (p > o > m);

(2) the size of halogen, steric factor (F > Cl > Br).

The addition of hydroxyl radicals and the elimination of hydrogen halides do not depend on the solution pH. In acidic solution, pH ~ 3, in presence of a reducing agent, such as ascorbic acid, hydroxyphenoxyl radicals can be reduced to hydroquinone or catechol or resorcinol. Without ascorbic acid at pH ~ 5 the initial hydroxyl adducts are stable and the products formed from such adducts are found in the irradiated samples.

The studies illustrate that radiation chemical methodology is very useful for some problems which are difficult to dissolve by ordinary techniques. When one combines time-resolved and steady-state studies radiation chemistry can provide a more complete information to a problem in chemistry.

ACKNOWLEDGMENTS

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