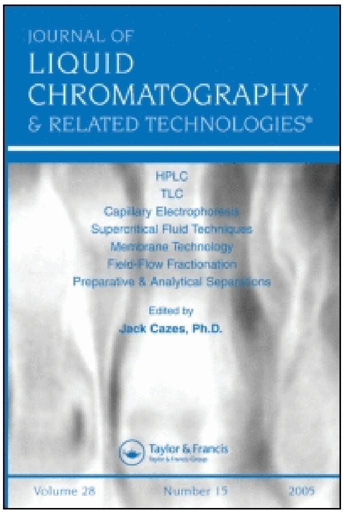

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Determination of Products in Hydroxyl Addition of Phenol Using High-Performance Liquid Chromatography

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DETERMINATION OF PRODUCTS IN HYDROXYL ADDITION OF PHENOL USING HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Methods for quantification of the products formed in the hydroxyl addition of phenol by reverse phase chromatography are described. The sample was detected by electrochemical detector connected in tandem with UV detector. HPLC analysis indicated that the probabilities (p) for attachment of OH to the para, ortho and meta positions are 11 : 8 : 1. The hydroxyl radical is seen to exhibit a strong preference for addition at the positions activated by the OH group. This preference results from the electrophilic character of hydroxyl radical.

INTRODUCTION

Hydroxyl radicals can react with phenol by addition to the aromatic ring. In neutral and acidic solutions, the hydroxyl adducts are stable. (1) The

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positions of OH radicals attack are dependent on the nature of the substituents on the benzene ring. Using High performance liquid chromatography (HPLC) to determine the products formed in these reactions provide useful information for synthetic chemistry.

The major products in the hydroxyl addition of phenol are hydroquinone, catechol and resorcinol. The method developed for quantification of these products is reverse phase chromatography with electrochemical and UV detections.

EXPERIMENTAL

a. Gama Radiolysis

The irradiations were carried out inside 2 cylindrical ^{60}Co r-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. (2)

b. HPLC Analysis

The instrumentation used included a Waters 510 pump, a Rheodyne 7010 injection valve with a 100 ul loop, a Waters Lichrosorb RP-18 radial compression column, an HP 1040A high speed spectrophotometric detection system and a Princeton Applied Research Corporation M400 electrochemical detector. Chromatographic signals and spectra data were stored on flexible disc through HP9121 flexible disc drive then transfered to VAX-780 computer, where the raw data were evaluated.

Irradiated samples were introduced into the ion chromatography and HPLC in a few minutes after completion of the irradiation.

c. Chemicals and sample preparation

The solutions for r-radiolysis were prepared in triply distilled water which was purged of oxygen, saturated with N_2O. Phenol and ferricyanide was from Aldrich. Chemicals used in the mobile phase of HPLC were acetonitrile and acetic acid from Fisher. The pH measurements were made with an Orion 811 pH meter calibrated with Fisher buffers.

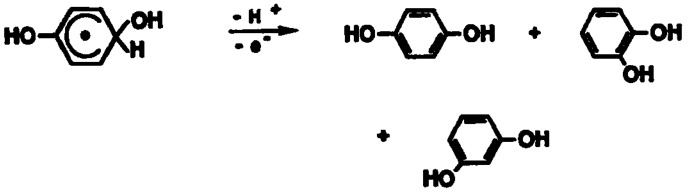
RESULTS AND DISCUSSIONS

Hydroxyl radicals are produced in the radiolysis of N_2O saturated aqueous solution. (3)

$$e^-_{aq} + N_2O + H_2O \longrightarrow \cdot OH + N_2 + OH^- \qquad (1)$$

The yield of hydroxyl radicals depends on the concentration of solutes and the rate constants for the reaction of hydroxyl radicals with the solutes. (1), (3) In the solutions of 10 mM phenol, the initial yield of hydroxyl radicals is about 5.9. In neutral and acidic solutions ·OH adducts (hydroxylated hydroxycyclohexadienyl radicals) are stable.

(2)



(3)

Figure 1 shows the chromatogram observed in the radiolysis of 10 mM phenol solution at pH 5.6. Hydroquinone (peak a), resorcinol (peak b) and catechol (peak c) were produced in the irradiated sample with yields of

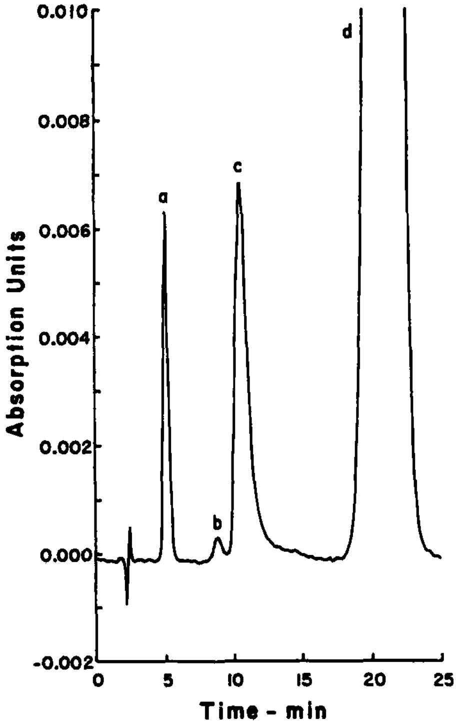


Figure 1 Chromatogram Observed in Hydroxyl Addition of Phenol

10^{-2} M phenol solution at pH 5.2 (N_2O saturated) irradiated with ^{60}Co r–rays at a dose rate of 2.8 X 10^{16} eV g^{-1} s^{-1} of 1.7 x 10^{19} eV g^{-1}.
Column: Waters Lichrosorb RP-18 radial compression column.
Elution: 2% acetonitrile and 0.2% acetic acid in water.
Flow rate: 1 ml/min.
Principal peaks are (a) hydroquinone, (b) resorcinol, (c) catechol and (d) phenol.

TABLE 1

YIELDS OF DIHYDROXYBENZENES IN THE REACTION OF ·OH WITH PHENOL[1]

Solute	pH	hydroquinone	catechol	resorcinol
phenol[2]	5.6	0.63 (11%)	1.35 (23%)	0.03 (0.5%)
phenol with[3] $K_3Fe(CN)_6$	5.2	1.73 (29%)	2.49 (42%)	0.31 (5%)

1. The numbers in parentheses are yields per ·OH produced, based on G(·OH) = 5.9.
2. 10 mM phenol at pH 5.6 saturated with N_2O.
3. 10 mM phenol with 1 mM $K_3Fe(CN)_6$ at pH 5.2 saturated with N_2O.

0.63, 0.03 and 1.35 (Table 1), amounting to 11, 0.5 and 23% of G(OH), respectively.

The total yield of three products is 2.01, which accounts for 34% of OH radicals initially produced. Ferricyanide can be used to oxidize hydroxycyclohexadienyl to dihydroxybenzene. (1), (4) In the presence of 1 mM ferricyanide, at pH 5.2, as illustrated by the chromatogram in Figure 2, one observes that the signals of hydroquinone and catechol double and the signal of resorcinol increases about 10 times. The spectra of hydroquinone, catechol and resorcinol observed in the irradiation are shown in Figure 3. The yields of these three products are hydroquinone, 1.73, catechol, 2.49, resorcinol, 0.31, amounting to 29%, 42% and 5% of G(·OH), respectively

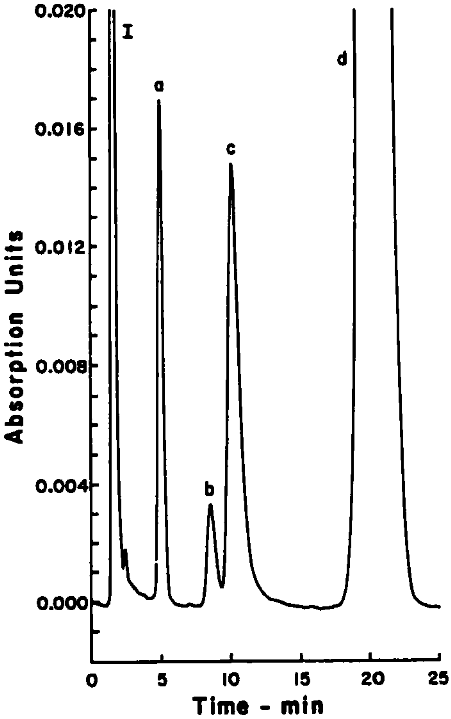


Figure 2 Chromatogram Observed in Hydroxyl Addition of Phenol with Ferricyanide

10^{-2} M phenol solution with 1 mM ferricyanide at pH 5.2 (N_2O saturated) irradiated with ^{60}Co r–rays at a dose rate of 2.8 x10^{16} eV g^{-1} s^{-1} of 1.7 x 10^{19} eV g^{-1}.
HPLC conditions were described in Figure 1.
Principal peaks are (I) ferricyanide, (a) hydroquinone, (b) resorcinol, (c) catechol and (d) phenol.

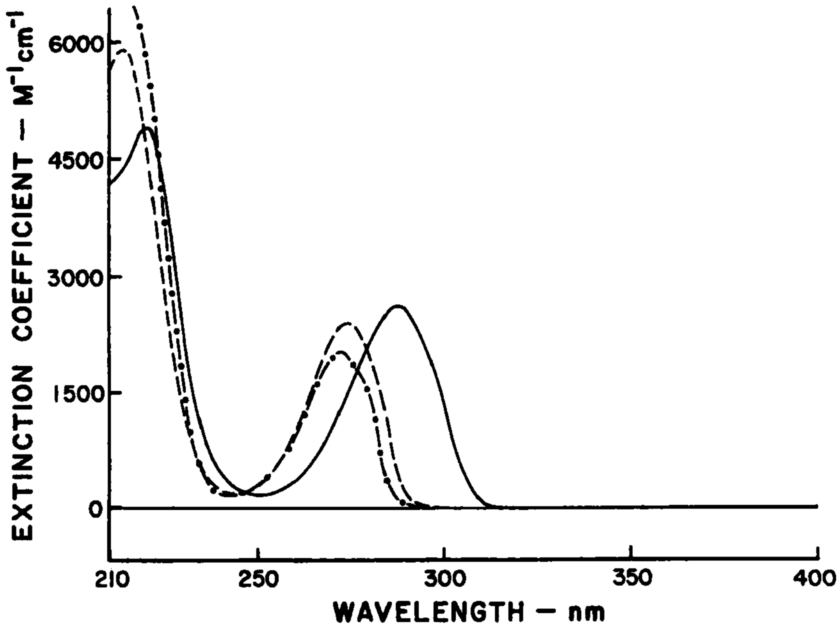


Figure 3 Absorption Spectra of Hydroquinone, Catechol, and Resorcinol

Hydroquinone (———), catechol (-----) and resorcinol (– · – · –) Spectra were recorded during the course of chromatographic analysis.

(Table 1). The sum of the yield of hydroquinone and catechol accounts for 72% of G(·OH), which shows that the addition of hydroxyl radicals to the ortho and para sites are the main processes in the oxidation of phenol by ·OH. Thus the probabilities (p) for attachment of OH to the para, ortho and meta positions is 11 : 8 : 1. The OH radical is seen to exhibit a strong preference for addition at the positions activated by the OH group. This preference results from the electrophilic character $^{(5)}$ of ·OH. A complete material balance is obtained if it is assumed that 23% of the OH radicals

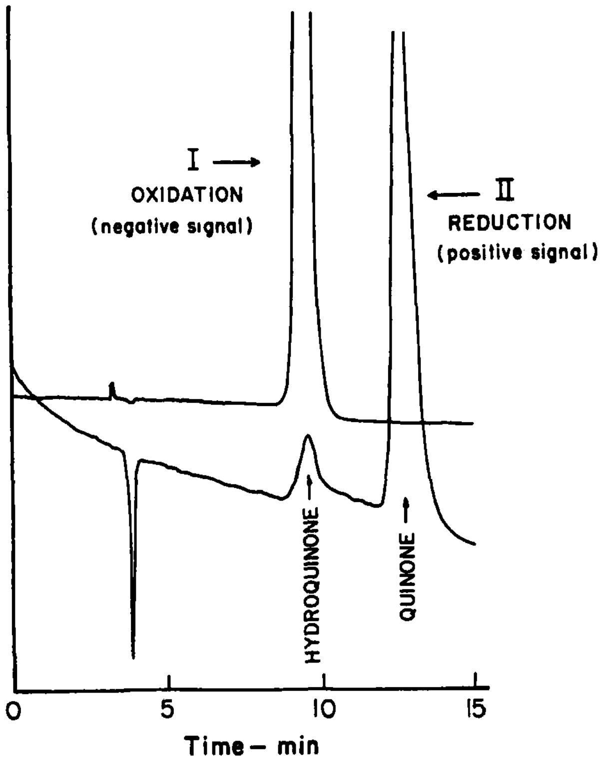


Figure 4 Electrochemical Signals of Hydroquinone and Benzoquinone

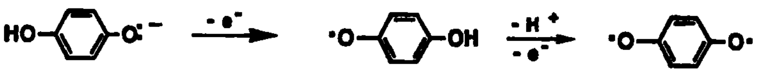
Electrode: Glassy carbon.
Oxidation potential applied: 650 mV.
Reduction potential applied: -500 mV.

react at the ipso position of phenol. Addition at this position is expected to be followed rapidly by elimination of water to yield phenoxyl radical. It is noted that the yields of both hydroquinone and catechol in the pure phenol solution were less than half in comparison to that in the presence of ferricyanide. The explanation of this difference is that part of dihydroxycyclohexadienyl radicals formed in the absence of ferricyanide undergoes elimination of water. The yield of resorcinol is extremly low in the absence of ferricyanide, which indicates that 3-hydroxy-hydroxycyclohexadienyl radical is relatively unstable.

Dihydroxybenzenes were not observed in any significant yield in the radiolysis of phenol solution at basic solution, pH about 11. Presumably, most of the dihydroxycyclohexadienyl radicals form phenoxyl radicals at basic as the result of rapid elimination of OH^-.

The experiment was also carried out in 10 mM phenol solution with 0.1 M NaN_3 at pH 5.6. There are no dihydroxybenzenes found in the solution. The result confirms that azide radicals react with phenol only by electron transfer. (6)

In neutral and basic solutions, hydroquinone, catechol and resorcinol are rapidly oxidized by dissovled oxygen to benzoquinone. (1)



(4)

(5)

The mobile phase was 0.2% acetic acid and 2% acetonitrile, and was purged with ultra high purity nitrogen. The standard solutions of hydroquinone, catechol, resorcinol and benzoquinone were prepared with 3% of acetic acid solution, purged with ultra high purity nitrogen and kept in a refugerator (4 °C).

An electrochemical detector has high sensitivity towards hydroquinone and benzoquinone. Figure 3 shows the oxidation signal of hydroquinone (7 uM) and reduction signal of benzoquinone (12 uM). Since the mobile phase used is 0.5% acetic acid aqueous solution which is electrically conductive, no additional buffer was added.

ACKNOWLEDGMENTS

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