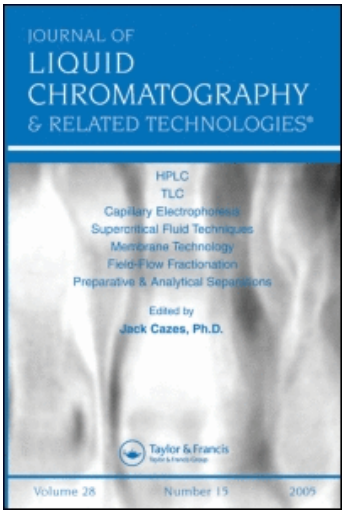

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Determination of Products in Hydroxyl Addition of Halophenols by Ion Pairing Chromatography

Ming Y. Ye[ab]
[a] Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana [b] ManTech Environmental Technology, Inc., Ada, OK

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DETERMINATION OF PRODUCTS IN HYDROXYL ADDITION OF HALOPHENOLS BY ION PAIRING CHROMATOGRAPHY

MING Y. YE*

Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556

ABSTRACT

Methods for determination of the aromatic compounds formed in the hydroxyl addition of halophenols are described. The technique of ion pairing chromatography is used to identify dihydroxyhalobenzene isomers. These molecules are highly polar and closely related in structure, which are very difficult to separated with conventional reverse phase chromatography. Hydroxyl radicals were produced by γ-radiolysis of liquid water saturated wih nitrous oxide. Ferricyanide was used to oxidize halohydroxycyclohexadienyl to dihydroxyhalobenzene.

INTRODUCTION

Addition of hydroxyl radical to aromatic compounds has been investigated previously. [1], [2], [3] The results indicated that in basic

* Present address: ManTech Environmental Technology, Inc., P.O. Box 1198, Ada, OK 74820

solution the hydroxyl addition of halophenol and phenol mainly produced halophenoxyl and phenoxyl radical. [1], [2] The results also showed that in neutral and acitic solution hydroxyl adducts were stable and the position of hydroxyl attack depended on substituents on the aromatic ring. The products in the hydroxyl addition of phenol have been determined quantitively. [2] In this study the ·OH addition of halophenol was examed in detail.

Dihydroxyhalobenzene isomers are formed in the hydroxyl addition of halogen substituted phenol in neutral and acidic solution. [1] These molecules are highly polar and closely related in structure, which are very difficult to separated with conventional reverse phase chromatography. Ion pairing chromatography is a valuable technique for separating these products. In Ion paring chromatography, polar compounds are retained by ion exchange interaction and by partition through Van der Waals or other forces. Slight difference in molecular polarity can result in different retention in the stationary phase for these molecules.

EXPERIMENTAL

a. Gama Radiolysis

The irradiations 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. [4]

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. 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 HPLC in a few minutes after completion of the irradiation.

c. Chemicals and sample preparation

The solutions for γ-radiolysis were prepared in triply distilled water which was purged of oxygen, saturated with N_2O. p-Chlorophenol, p-fluorophenol and ferricyanide were from Aldrich. Chemicals used in the mobile phase of HPLC were methanol from Baxter, acetic acid from Fisher and tetrabutylammonium acetate from Fluka. The pH measurements were made with an Orion 811 pH meter calibrated with Fisher buffers.

RESULTS AND DISCUSSIONS

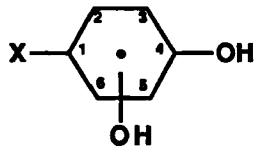
Ion Pairing Chromatography An ordinary C_{18} silica column was used in the analysis. The separation was accomplished by adding organic cations (tetrabutylammonium acetate, $TBA^+(OCOCH_3)^-$, 5 mM) to the eluent which will form ion pairs with sample anions. This ion pair then partitions between the mobile and stationary phases. This separation mechanism was also interpreted as that the eluent cation is adsorbed on the resin surface, thus making it an exchanger. [5], [6]

The hydrophobic ion pairing reagent (TBA^+) was selected because of the hydrophilic nature of sample anions. An organic modifier, CH_3OH, was added to the eluent to make the mobile phase more like the stationary phase and decrease retention times. A small amount of acetic acid (0.2%) was also added to the eluent to lower the pH. It is necessary to lower the eluent pH to about 4, because dihydroxybenzene can be easily oxidized at neutral and basic solutions. [1] The separation indicated that the desired sample anion charge is achieved at this pH. The eluent was purged with

helium to decrease the possibility of the oxidation of dihydroxybenzene and dihydroxyhalobenzene by the air in the eluent.

Determination of Products of Hydroxyl Addition Hydroxyl radicals are produced in the radiolysis of N_2O saturated aqueous solution. [2], [7] 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], [7] In the solution of 10 mM halogen substituted phenol the initial yield of hydroxyl radicals is about 5.9. [7]

In neutral and acidic solutions, ·OH adducts (halohydroxycyclohexadienyl radicals) are stable.

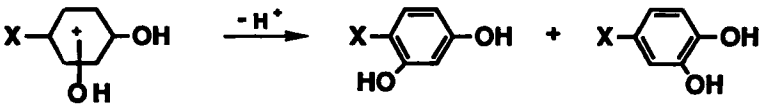


(X = F, Cl) (1)

To form dihydroxyhalobenzene from the initial OH adducts, halohydroxycyclohexadienyl radicals first have to loss electrons,

(2)

and then protons.



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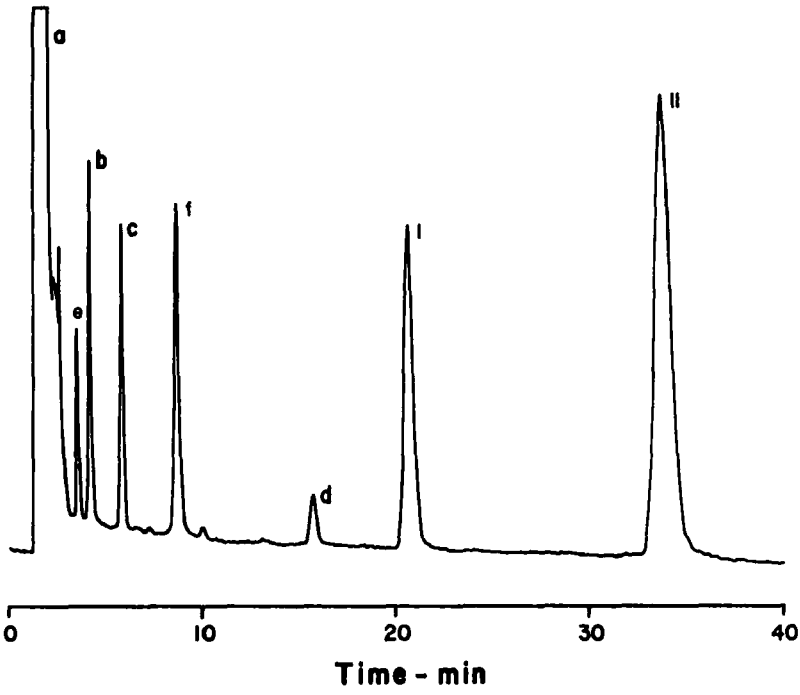
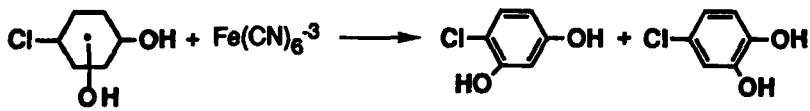


Figure 1 Chromatogram Observed in the Hydroxyl Addition of p-Chlorophenol Radiolysis of 10 mM p-chlorophenol with 1 mM ferricyanide (N_2O saturated; pH ~ 5). Detector: optical detector (210 nm); Mobile phase: methanol : water, 10 : 90 with 5 mM tetrabutylammonium acetate and 0.2% acetic acid; Flow rate: 1 ml/min. a. $K_3Fe(CN)_6$; b. hydroquinone; c. benzoquinone; d. phenol; e, f. unknown substances; I. 2,4-dihydroxychlorobenzene; II. 3,4-dihydroxychlorobenzene.

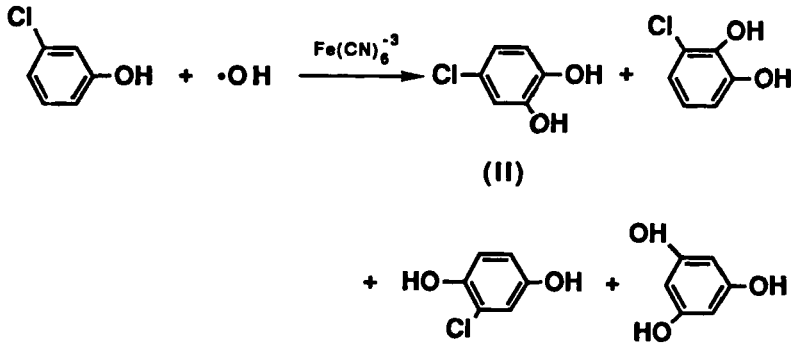
Ferricyanide was used to oxidize p-chlorohydroxycyclohexadienyl to 2, 4-dihydroxychlorobenzene and 3, 4-dihydroxychlorobenzene.



$$+ Fe(CN)_6^{-4} + H^+ \qquad (4)$$

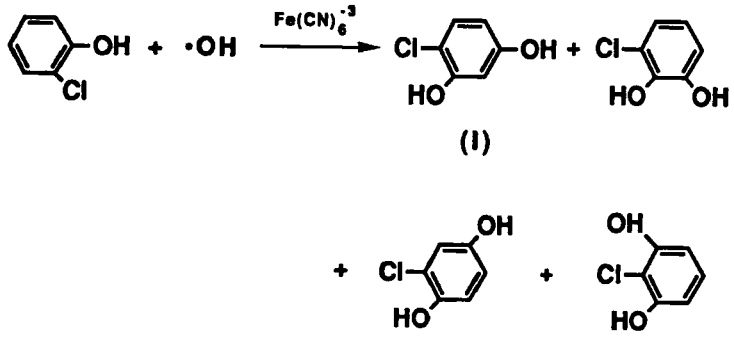
In the radiolysis of 10 mM p-chlorophenol solution with 1 mM ferricyanide at pH about 5, as it is expected from reactions (4), two isomers (I, II) are formed (Figure 1). Hydroquinone and benzoquinone were also found In Figure 1, which were formed by hydroxyl addition at C(1) position followed by elimination of hydrochloride. [1] Figure 2 shows the chromatogram obtained in the eluent with higher concentration of organic modifier than in Figure 1. To maximize the absorption of dihydroxychlorobenzene and to minimize the absorption from side products, the detector wavelength was set at 280 nm.

To identify the two isomers (peaks I and II in Figure 2), similar types of experiments were carried out in m-chlorophenol and o-chlorophenol solutions. 3,4-dihydroxychlorobenzene is expected to be produced as one of four isomers in the irradiation of N_2O saturated 10 mM m-chlorophenol with 1 mM ferricyanide.



(5)

2,4-dihydroxychlorobenzene should be formed as one of four isomers in the irradiation of o-chlorophenol solution.



Peak I was found in the irradiation of o-chlorophenol solution (Figure 3).

Peak II was found in the irradiation of m-chlorophenol solution (Figure 4).

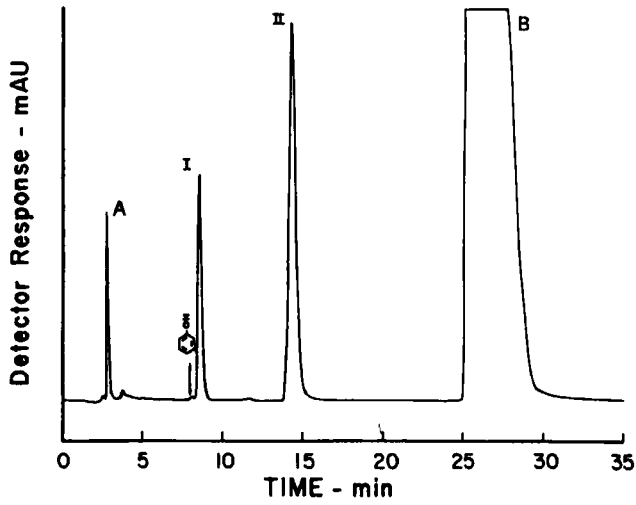


Figure 2 Chromatogram Observed in the Hydroxyl Addition of p-Chlorophenol Radiolysis of 10 mM p-chlorophenol with 1 mM ferricyanide (N_2O saturated; pH ~ 5). Detector: optical detector (280 nm); Mobile phase: methanol : water, 40 : 60 with 5 mM tetrabutylammonium acetate and 0.2% acetic acid; Flow rate: 1 ml/min.
I. 2,4-dihydroxychlorobenzene; II. 3,4-dihydroxychlorobenzene;
A. $K_3Fe(CN)_6$, B. p-chlorophenol.

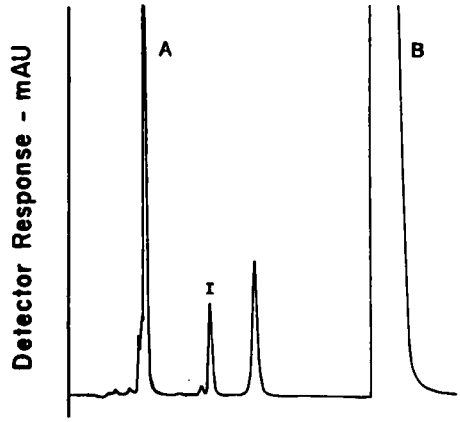


Figure 3 Chromatogram of Products in the Hydroxyl Addition of o-Chlorophenol Irradiation of 10 mM o-chlorophenol with 1 mM ferricyanide (N_2O saturated; pH ~ 5). The chromatographic condition was described in Figure 2. I. 2,4-dihydroxychlorobenzene; A. ferricyanide; B. o-chlorophenol

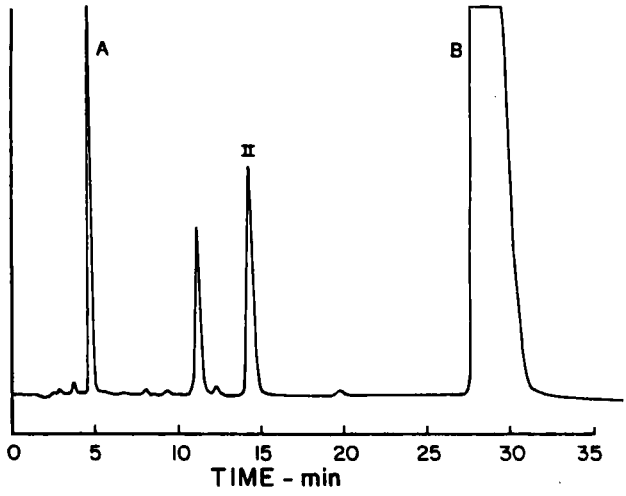


Figure 4 Chromatogram of Products in the Hydroxyl Addition of m-Chlorophenol Irradiation of 10 mM m-chlorophenol with 1 mM ferricyanide (N_2O saturated; pH ~ 5). The chromatographic condition was described in Figure 2. II. 3,4-dihydroxychlorobenzene; A. ferricyanide; B. m-chlorophenol.

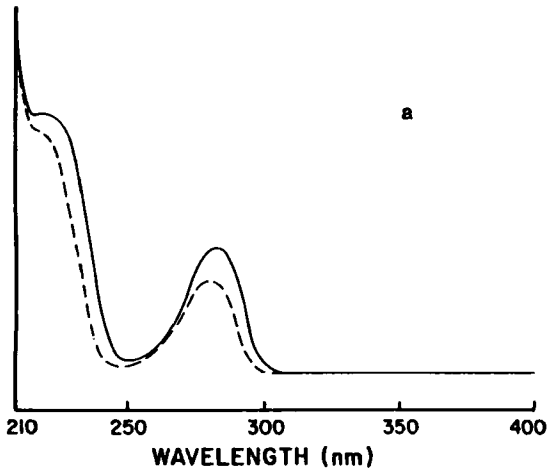


Figure 5a Absorption Spectra of 3,4-Dihydroxychlorobenzene and 2,4-Dihydroxychlorobenzene, 3,4-dihydroxychlorobenzene (___) and 2,4-dihydroxychlorobenzene (-----) observed in the irradiation of 10 mM p-chlorophenol with 1 mM ferricyanide at pH ~ 5. Spectra were recorded during the course of chromatographic analysis.

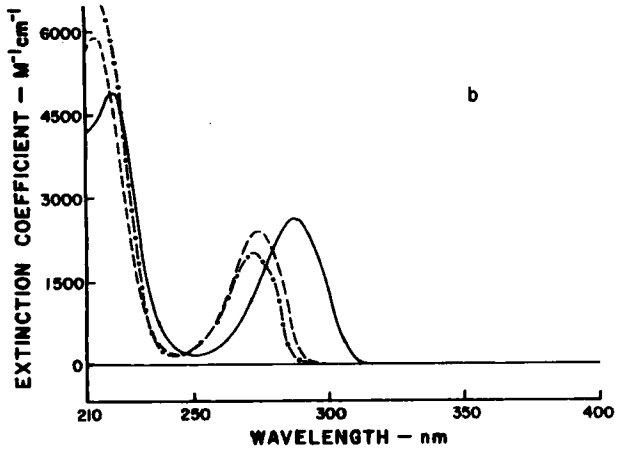


Figure 5b Absorption Spectra of Hydroquinone, Catechol, and Resorcinol Hydroquinone (___), catechol (-----) and resorcinol (– . – .) Spectra were recorded during the course of chromatographic analysis.

Thus peak I is indentified as 2,4-dihydroxychlorobenzene and peak II is 3,4-dihydroxychlorobenzene.

The spectra of peaks I and II are given in Figure 5a. In comparison with the spectra of catechol and resorcinol in Figure 5b, the similarity of optical absorptions of 2,4-dihydroxychlorobenzene and 3,4-dihydroxychlorobenzene is understandable. The maximum absorptions of the spectra are at 280 nm, a shift of 10 nm to longer wavelength in comparison with that of catechol and resorcinol. The shift can be interpreted as the result of the substitution of hydrogen atom by chlorine.

In Figures 2 we can see that the yield of 3,4-dihydroxychlorobenzene is much higher than that of 2,4-dihydroxychlorobenzene, which must be due to the ortho and para directing effect of OH group in the aromatic ring. Lack of 3,4-dihydroxychlorobenzene and 2,4-dihydroxychlorobenzene standards prevents us from making quantitative measurement of these two products formed in radiolysis.

Similar studies were carried out with p-fluorophenol. In the radiolysis of 10 mM p-fluorophenol solution with 1 mM ferricyanide at pH about 5, as it is expected that 3,4-dihydroxyfluorobenzene and 2,4-dihydroxyfluorobenzene were found in the irradiated sample. As it was found in the case p-chlorophenol, the yield of 3,4-dihydroxyfluorobenzene is much higher than that of 2,4-dihydroxyfluorobenzene.

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