

**Studies on Phenolic Compounds as Potential Iodine Mitigants  
in Nuclear Reactor Containment**

by

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A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree of

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Department of Chemistry

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## **Abstract**

Radioactive iodine is a by-product formed during the production of energy in a nuclear power plant. Because of its volatility and biological activity, it has been identified as one of the more hazardous nuclides formed. In the event of a loss-of-coolant accident (LOCA), aqueous iodide can be converted into the volatile  $I_2$ , which may escape into the environment. The possibility of using additives such as phenols as mitigants, a chemical means of minimizing iodine release, was investigated. Bench-scale studies were performed using halophenols, particularly 2-chlorophenol, a compound which was shown to be capable of suppressing iodine volatility. Steady-state irradiations of 2-chlorophenol under various conditions, combined with kinetic studies and product analysis (HPLC, GC/MS and synthetic work), have been utilized to determine the reaction pathways.

The aqueous electron is identified as a very important species in the mitigation scenario, as it has the ability to reduce halogenated phenols into reactive hydroxyphenyl radicals plus the corresponding halide ion. The synthesis of 3'-chloro-2,4'-dihydroxybiphenyl was performed in order to verify the presence of a ring coupling mechanism which is the result of the electron reaction.

The formation of hydroxylated products, such as chlorohydroquinone and 3-chlorocatechol, was identified as an important part of the iodine mitigation scheme, as this process would be in direct competition with iodide oxidation. The formation of these products is discussed in terms of their effect on the iodine mitigation scheme.

Determining the rate of iodination of several halogenated phenols helped to understand the consequences of the radiolysis products, while helping to ascertain the structural characteristics important to this reaction. Time resolved pulsed radiolysis was utilized to determine that iodophenols and iodoanisoles all react with the aqueous electron at about  $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , a rate which is much faster than that of other halogenated phenols. Hydroxyl radicals reactions were generally slower.

The conclusion is that iodine mitigation by phenolic compounds occurs by several distinct mechanisms, both radical and non-radical processes. These reactions are expected to be similar to that of all aromatic compounds in the containment building.

## TABLE OF CONTENTS

Title .....	i
Acknowledgements .....	ii
Abstract .....	iii
Table of Contents .....	v
<b>Chapter 1: INTRODUCTION .....</b>	<b>1</b>
1.1 The Radioiodine Problem .....	1
1.2 Water and Radiation .....	3
1.3 Hydrolysis of Iodine .....	5
1.4 Radiolytic Reactions of Iodine Species .....	5
1.5 Radiolysis of Organic Compounds .....	6
1.6 Reactions of Iodine With Organic Compounds .....	12
1.7 Pulse Radiolysis .....	15
1.8 Purpose .....	16
<b>Chapter 2: EXPERIMENTAL .....</b>	<b>17</b>
2.1 Pulse Radiolysis .....	17
2.2 Steady State Radiolysis .....	18
2.3 HPLC .....	18
2.4 GC/MS .....	19
2.5 Kinetics by UV/Vis Spectrophotometer .....	19
2.6 Stopped Flow Spectrophotometer .....	20
2.7 Ion Chromatography .....	21
2.8 Preparation of Organic Compounds .....	21
<b>Chapter 3: RESULTS AND DISCUSSION .....</b>	<b>27</b>
3.1 Product Analysis .....	27
3.2 Kinetics .....	41
3.2.1 Time Resolved Pulse Radiolysis .....	41
3.2.2 Halide ion Production .....	47
3.2.3 Electrophilic Substitution Reaction .....	53
3.3 Iodine Mitigation .....	62
<b>Chapter 4: CONCLUSIONS .....</b>	<b>69</b>
<b>Chapter 5: RECOMMENDATIONS .....</b>	<b>72</b>
<b>References .....</b>	<b>74</b>
<b>Appendix .....</b>	<b>79</b>



## **1 Introduction**

### **1.1 The Radioiodine Problem**

Radioactive iodine is a by-product formed during the production of energy in a nuclear power plant. These plants derive their energy from uranium by a process known as fission, which occurs when a  $^{235}\text{U}$  atom captures a neutron. It then becomes unstable, splits, and releases energy, neutrons and fission fragments. These fragments may themselves be unstable and rearrange their nuclei through several forms of radioactive decay. As a uranium atom can split in many ways, many different fission products are possible. Although there are several iodine isotopes produced,  $^{131}\text{I}$  is the most hazardous because of its 8.02 day half-life.

In the event of a loss of coolant accident (LOCA) of a nuclear reactor, the ability to cool the core is lost, leading to the release of fission products into the reactor containment buildings. Species may be released into the gas phase as a function of their volatilities, may be released as aerosols, or transported as solutes in the primary coolant. Safety research in this field is important in order to find ways to mitigate the effects of released fission products.

As iodine forms  $\text{CsI}$  (a water soluble salt) in the fuel, it is easily transported by water. The aqueous iodide ion may be oxidized in the presence of a radiation field into  $\text{I}_2$ , which is a volatile material and quite reactive towards organic contaminants, eventually forming volatile organic iodides such as methyl iodide.

These volatile species are of concern, especially when volatile radioactive iodine species may be released into the containment buildings, or in the case of a more serious accident, such as the one experienced at Chernobyl or Three Mile Island, when radioiodine is released into the environment. Iodine has an significant role among fission product releases and important research efforts are being invested in the understanding of its behaviour.

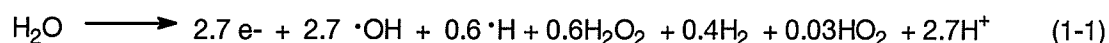
Radioiodine has been described as the most important nuclide that could be released in the event of an accident [1]. The reason for particular concern about iodine is that its radioactive isotopes, especially  $^{131}\text{I}$ , pose a substantial health risk. Human bodies contain 10 to 20 mg of iodine, more than 90% of which is located in the thyroid gland. Radioactive iodine bioconcentrates as it passed through the food chain from soil to vegetation to cattle to humans, or algae to fish, etc. As radioactive iodine accumulates in an organism, it concentrates in the thyroid gland, where a significant radiation dose may be received. Health problems, including thyroid cancer, can result [2, 3]. Thus, it is of interest to keep iodine in less reactive, less volatile states in a reactor containment building.

Hydrazine, a powerful reducing agent, has been one additive that has been used to achieve this goal [4]. Preliminary tests show that some organic compounds can reduce the amount of gas phase iodine in irradiated iodide solutions [5]. These additives have been termed mitigants. Phenol, tert-butyl alcohol and sodium formate were among earlier mitigants tested. Sodium formate and tert-butyl alcohol were dismissed, as they quickly broke down to release iodine

into the gas phase. As phenol showed promising results, various substituted phenols were tested to determine the effect of functional groups. This work will focus on understanding the mechanism through which these phenols act as mitigants.

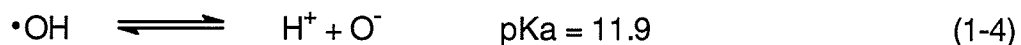
## 1.2 Water and Radiation

Water molecules absorb energy from  $\beta$ (electrons) and  $\gamma$  radiation producing radicals and ions according to equation 1-1. In an aqueous solution these radicals



and ions are responsible for most of the radiation induced chemical reactions. The coefficients in Equation 1-1 represent radiochemical yield (G-value), which is the number of species produced per 100 eV absorbed by the system. These values refer to a neutral solution (pH=7) and are widely accepted [6]. Generally, hydroxyl radicals and hydrogen peroxide are the important oxidizing products, while electrons and hydrogen atoms are the reducing products.

Changes in pH can have an affect on the yields of the primary radical species. In acidic solution, electrons are scavenged by protons to form atomic hydrogen,  $\cdot\text{H}$ . Thus, pH values less than 2 are generally used for studies requiring electron scavenging. In basic solution several dissociations are possible as pKa values are approached.



Also, a higher yield of electrons is achieved by the action of hydrogen atoms on hydroxide ions.



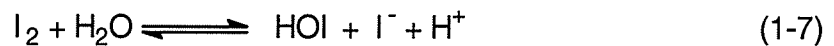
Because so many reactive species are produced in irradiated solutions, the selective scavenging of certain radicals is necessary to simplify the system. One common procedure is to saturate a solution with  $\text{N}_2\text{O}$  prior to irradiation.  $\text{N}_2\text{O}$  is fairly soluble in water (25 mM), and is very reactive with aqueous electrons ( $k = 9.1 \times 10^9 \text{ s}^{-1}\text{M}^{-1}$ ) [7]. This serves to capture electrons while simultaneously increasing the yield of hydroxyl radicals.



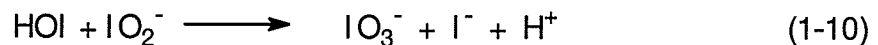
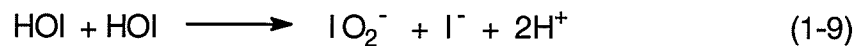
As oxygen is able to add an electron rapidly to form superoxide radical anion ( $\text{O}_2^{\cdot-}$ ), solutions must be purged of air if electron reactions are to be observed. Several hydroxyl radical scavengers have been used but the most common ones are tert-butyl alcohol and 2-propanol.

### 1.3 Hydrolysis of Iodine

Iodine undergoes hydrolysis according to reaction 1-7, quickly followed by reaction 1-8 [8]. These equilibria explain the formation of  $I_3^-$  when  $I_2$  is dissolved in water, and explain the formation of HOI in basic solution.



Hypoiodous acid (HOI) can disproportionate (1-9) and eventually form iodate ( $IO_3^-$ ) (1-10), another less hazardous, non-volatile form of iodine [9].



These equilibria are pH-sensitive and are complicated by the primary products of water radiolysis.

### 1.4 Radiolytic Reactions of Iodine Species

There have been many papers on this subject by workers involved in reactor safety and design [9, 10 and references within]. Of the many radiolytic reactions that are possible, only the more relevant ones will be considered here. One important scheme of reactions is the oxidation of  $I^-$  by the hydroxyl radical.

Equations 1-11 through 1-13 show how  $I_3^-$  is produced, which, as we have seen in equation 1-8, is in equilibrium with  $I_2$ .



There is also a mechanism by which  $I_2$  is reduced back to  $I^-$ :



In a neutral solution the roles of the electron and the hydroxyl radical are approximately balanced. Thus, the  $I_2$  produced will be only a small steady state amount. If the  $I_2$  is allowed to escape into the gas phase, it is no longer susceptible to the reactions induced by the radiolytic water products. However, in the presence of other additives, the equilibria between  $I^-$  and  $I_2$  will be altered. Thus, it is important to understand the effect of organic compounds on the system. This topic has been the subject of some discussions (The Third CSNI Workshop on Iodine Chemistry in Reactor Safety) and has been identified as an area that needs more investigation.

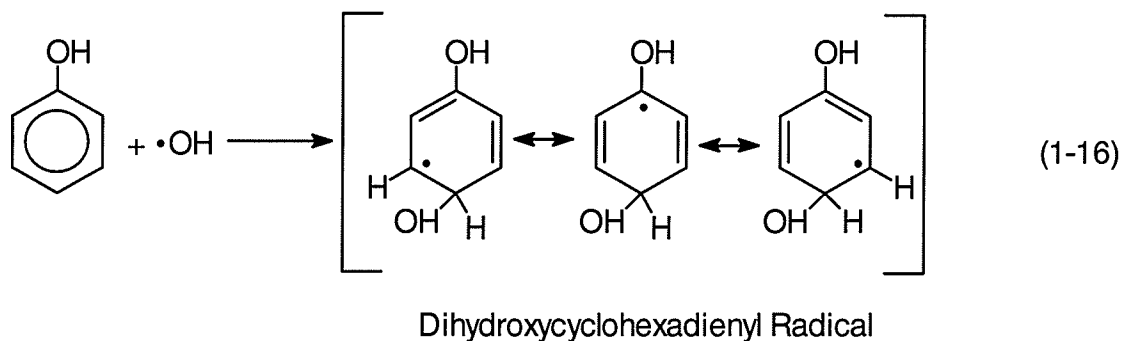
### 1.5 Radiolysis of Organic Compounds

In order to understand how organic compounds may change the reactivity

of the aqueous iodine system, it is important to recognize what happens during the aqueous radiolysis of organic molecules. In dilute solutions, water absorbs most of the energy from the radiation. Therefore it is the action of the radiolysis products of water that causes reaction on dissolved organic compounds.

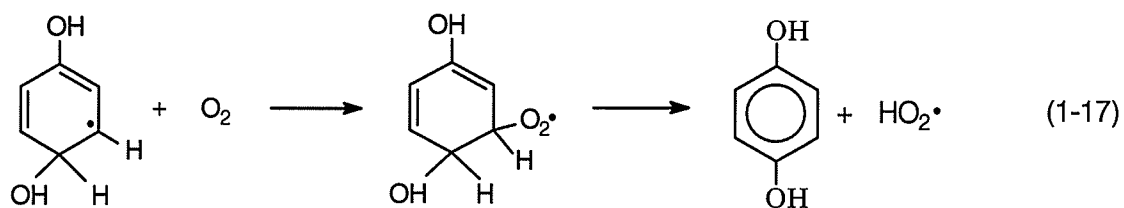
Aliphatic and aromatic compounds undergo different reactions with hydroxyl radicals. The tendency is for the hydroxyl radical to abstract hydrogens from aliphatic compounds, while hydroxylation of the ring occurs for aromatic compounds [11]. It is this latter property that is of interest with regards to iodine mitigation. If the hydroxyl radicals can be scavenged by aromatic rings, less oxidation of  $I^-$  can take place. Phenols have been shown to rapidly react with hydroxyl radicals [12].

The radiolysis products of phenol have been examined by several groups. [13-16]. Some studies have been done in order to determine the radiolytic decomposition of phenols in wastewater. While the major products have been found to be hydroquinone, catechol and 1,2,4-trihydroxybenzene, traces of resorcinol and 2,2'-dihydroxybiphenyl were also found. Through pulse radiolytic studies [16], the initial intermediate of the hydroxylation of phenol was found to be a dihydrocyclohexadienyl radical (1-16), a radical stabilized by resonance. The G-value for this  $\cdot OH$ -adduct was determined to be 2.66, which is very close to the G-value of hydroxyl radicals in pure water (2.7)[15]. This suggests that addition to the ring is the main mode of reaction of the hydroxyl radical, rather than the direct formation of phenoxy radicals.



This reaction has been compared to aromatic electrophilic addition because it has shown good correlation with the Hammett relationship, with a  $\rho$  value of -0.41 [12]. As the hydroxyl group on phenol is *ortho/para* directing, the hydroxyl radical tends to add to those positions preferentially [17].

The fate of this  $\cdot\text{OH}$ -adduct depends upon the reaction conditions. If oxygen is present, it will quickly add to the dihydroxycyclohexadienyl radical producing an unstable peroxy radical [15]. Elimination of  $\text{HO}_2\cdot$  will soon follow to yield the hydroxylated ring.

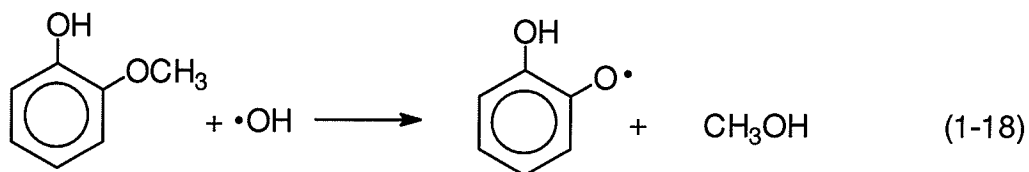


Without oxygen, pulse radiolytic studies have shown that elimination of water to

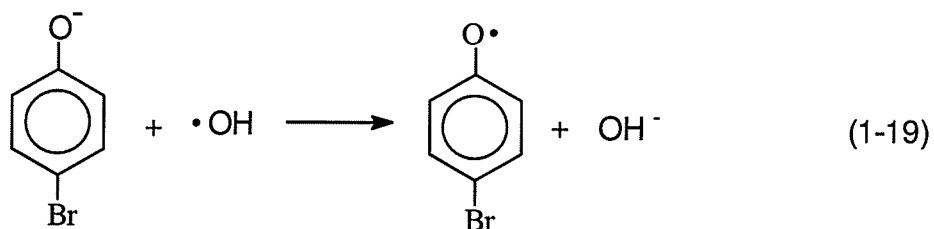


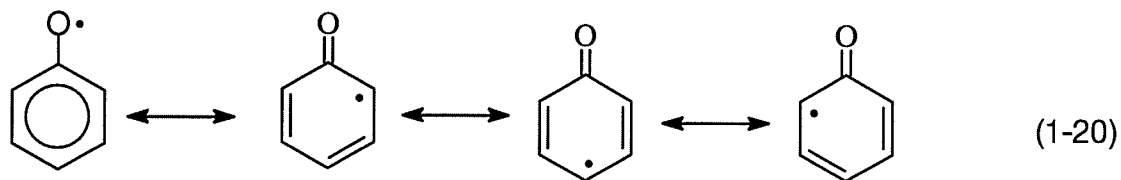
yield a phenoxy radical (1-19) is both acid and base catalyzed [16,18]. Disproportionation-type reactions have been proposed to account for hydroxylated products that are observed in the absence of oxygen [19-22].

Hydroxyl radicals can also attack a carbon containing a substituent, the *ipso* position. This can result in the substituent being replaced by OH. This type of oxidative displacement has been observed for halogens, methoxy, nitro and amino groups [23, 24]. The rate of this type of attack increases if there is an activating group in an *ortho* or *para* relationship.



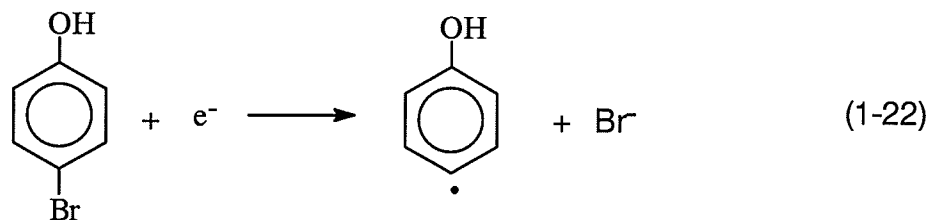
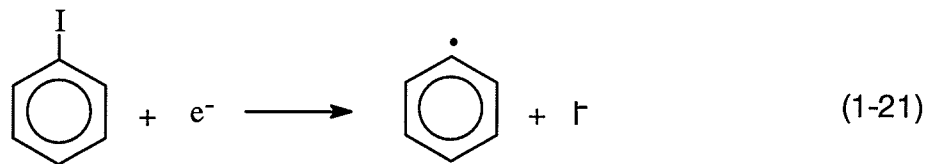
Under very basic conditions (pH>11), phenols exist mainly as the corresponding phenoxide ion, and will react with hydroxyl radicals to yield phenoxy radicals (Equation 1-19) which are more stable due to several resonance structures (Equation 1-20) [16, 18].



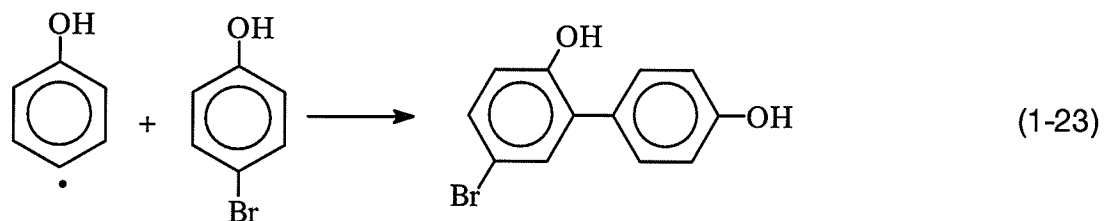


Phenoxy radicals have been proposed as the source of dimers that are sometimes found as a radiolysis product [25, 26, 19]. Phenolic compounds have been used as food additives and other applications as antioxidants as they form stable radicals and stop radical chain reactions [27]. These phenoxy radicals usually disappear via coupling or disproportionation. Coupling products can be found in large quantities if enough phenoxy radicals can be produced at one time (as in a pulse radiolysis experiment), but few dimers are usually detected during a lower dose rate steady state experiment [26].

Organic compounds that contain halogen atoms are susceptible to reaction with an electron due to the high electronegativity of halogens and their relatively weak bond strength [28, 6]. Halophenols, particularly chlorophenols, have been studied as model compounds in studies for radiation induced pesticide degradation and wastewater treatment [19, 29, 30]. The result of the electron reaction is the formation of a halide ion and a radical; while in the case of an aryl halide, phenyl radicals result [31, 32, 33].



The fate of these phenyl and hydroxyphenyl radicals depends on other components in the solution. With a hydrogen donor such as tert-butyl alcohol or 2-propanol, the radical is quantitatively converted into the corresponding phenol or benzene by hydrogen abstraction [32, 34]. There is also evidence that shows that these radicals can react with the starting material (phenol or aryl halide) to form biphenols or biphenyls. For example, 4-bromophenol exhibits this behaviour [33, 35].



Some radicals may also be trapped by  $\text{I}_2$  [6, 36]. The reaction rate of electrons with an unsubstituted phenol, benzene or toluene has values typically orders of magnitude less than that for halogenated derivatives [28].

Hydrogen atoms can also add to aromatic rings, to yield cyclohexadienyl radicals or to displace halogens [29, 34]. However, since the G-value for hydrogen is 0.6, this process is less important.

Some compounds such as phenol and catechol, have already been identified as radiolytic products of 2-chlorophenol [34]. However, a more detailed product analysis is required to understand the role of 2-chlorophenol as a mitigant.

#### 1.6 Reactions of Iodine with Organic Compounds

Iodine is capable of reacting with many types of organic molecules and functional groups. These reactions, and the synthetic utility of iodine, have been reviewed in a chapter of "Synthetic Reagents" by J.S. Pizey [37]. The reaction of molecular iodine with phenols and amines has been extensively studied [38]. In the presence of an oxidant such as nitric acid, hydrogen peroxide, or peracetic acid, iodination of less activated ring systems, such as benzene and toluene, can also take place.

The kinetics and mechanism of the iodination of phenols have been studied by several groups [39-42]. The rate of the iodination of phenol was found to depend upon the concentrations of phenol,  $I_2$ ,  $I^-$ ,  $H^+$ , and the buffer. A general rate equation (Equation 1-24) has been found to describe the dependence of rate on various experimental conditions.

$$\frac{d[I_2]}{dt} = k \frac{[Phenol] [I_2]}{[H^+] [I^-]} + k' \frac{[Phenol] [I_2] [Buffer]}{[H^+]^2 [I^-]} \quad (1-24)$$

However, in the presence of iodide ion, the amount of  $I_2$  available to react is lowered due to the equilibrium that yields  $I_3^-$  (Equation 1-8). Since the reaction will be followed using the variation in optical absorbance of  $I_3^-$ , equation 1-24 should take this equilibrium into account and be written in terms of  $I_3^-$ .

$$I_2 + I^- \rightleftharpoons I_3^- \quad K_{eq}=700 \quad \text{therefore,} \quad \frac{d[I_2]}{dt} = \frac{d[I_3^-]}{dt} \left( \frac{1}{(K_{eq}) [I^-]} \right)$$

Since  $I_2$  is in equilibrium with  $I_3^-$ , the total change in  $I_2$  is given by  $[I_2 + I_3^-]$  [43].

Thus the rate equation is really:

$$\frac{d[I_2]}{dt} + \frac{d[I_3^-]}{dt} = \frac{k[I_2] [Phenol]}{[I^-] [H^+]} + \frac{k'[I_2] [Phenol] [Buffer]}{[I^-] [H^+]^2}$$

So in terms of  $I_3^-$  this equation is:

$$\frac{d[I_3^-]}{dt} \left( \frac{1}{(K_{eq}) [I^-]} + 1 \right) = \frac{k[I_3^-] [Phenol]}{(K_{eq}) [I^-]^2 [H^+]} + \frac{k'[I_3^-] [Phenol] [Buffer]}{(K_{eq}) [I^-]^2 [H^+]^2}$$

or

$$\frac{d[I_3^-]}{dt} = \left( \frac{k}{(K_{eq}) [I^-] + 1} \right) \frac{[I_3^-] [Phenol]}{[I^-] [H^+]} + \left( \frac{k'}{(K_{eq}) [I^-] + 1} \right) \frac{[I_3^-] [Phenol] [Buffer]}{[I^-] [H^+]^2} \quad (1-25)$$

As a result, rates obtained by observing the disappearance of  $I_3^-$  should be multiplied by a factor of  $K_{eq}[I^-]+1$  to obtain the real rate of  $I_2$  disappearance.

A wide variety of theories have been discussed about the exact nature of the attacking iodine species [42, 44, 45, 46]. Some that have been suggested include  $I_2$ , HOI,  $I^+$  and  $H_2OI^+$ . At high pH values this reaction proceeds very quickly, which may be a reflection of the degree of ionization of the phenol as the corresponding pKa value is approached. It also may be an indication of which iodine species is more abundant, as in basic solution,  $I_2$  is converted into hypoiodous acid (HOI).

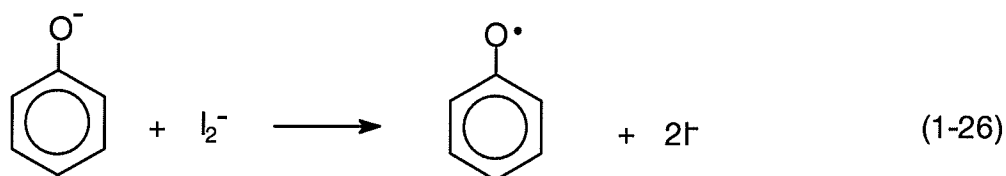
The rate determining step in the mechanism is the breaking of the C-H bond of the iodocyclohexadienone intermediate. This has been confirmed by studies finding a kinetic isotope effect on the iodination of phenol-2,4,6- $d_3$  [42].

Product distribution studies have shown that the ration of *ortho* to *para* isomers depends upon pH [45, 47]. At higher pH values, the *ortho* isomer is favoured. This affect has been attributed to different rates of proton transfer in the reaction intermediates.

Application of the Hammet equation has been limited to *meta* and *para* substituted phenol, as *ortho* substituents are generally more difficult to correlate. [39, 40, 48]. As expected for an electrophilic addition, the  $\rho$  value is negative, meaning that the electron withdrawing groups slow the reaction, and electron releasing groups speed the reaction relative to phenol itself.

The present work will explore how this reaction may apply to the iodine mitigation concept and how it may be affected by ionizing radiation. The application of the rate equation to 2-chlorophenol will be studied and rates of other phenolic compounds will be compared.

In addition to the thermal reaction of iodine with aromatic compounds, there are also some free radical reactions that can take place. The radical anion  $I_2^{\cdot-}$ , which is generated by the aqueous radiolysis of iodide, can react with phenoxide ions by an electron transfer to produce phenoxy radicals and  $I^-$  (Equation 1-26) [49, 50]. This reaction has been studied by pulse radiolysis for p-chlorophenol,



p-cresol, p-bromophenol and other phenols. It was found that the rate of this reaction depended heavily on the pH of the solution, since the  $I_2^{\cdot-}$  reacts with the corresponding phenoxide ion [49].

### 1.7 Pulse Radiolysis

Pulse radiolysis is an important tool for radiation chemistry. It is a technique, much like flash photolysis, that is used to observe transients of fast radiation induced reactions. Electrons, free radicals and excited state molecules

are formed by a short, high energy electron pulse and are observed by optical absorption or other means. One of the main uses of this technique is in measuring reaction kinetics. Conventional kinetic techniques cannot be used as many free radical reactions take place on the nanosecond to microsecond time scale.

Pulse radiolysis first became applicable in about 1960, when accelerators capable of delivering sufficiently short pulses became available, and has since become a well established technique within radiation chemistry. Over the years, several books have become available on the subject [51-54].

### 1.8 Purpose

The purpose of this study is to gain an understanding of how some aromatic compounds may behave in irradiated aqueous solutions in the presence of various iodine species. This will give insight into how iodine volatility is affected by aromatic compounds, whether present as an added mitigant, as part of a polymer chain or as an impurity in the water. This knowledge is needed to predict what may happen in the containment building of a nuclear reactor in the event of a LOCA. Product identification and kinetic data are necessary to unravel possible mechanistic pathways and determine what other factors may be of importance. Emphasis is placed on halogenated phenols, particularly 2-chlorophenol, as it has shown to delay the formation of volatile iodine [5].



## **2 Experimental**

### **2.1 Pulse Radiolysis**

The pulsed radiolysis experiments were performed at the Radiation Laboratory of the University of Notre Dame. This computerized pulsed radiolysis system and has been described in detail in several journals [7, 55, 56]. The system consists of a LINAC accelerator delivering 10 ns pulses of 8 MeV electrons for absorbed doses of approximately 200-400 rads (2-4Gy). Solutions were pumped continuously through a 1 cm cell that was directly in line with the electron beam. The flow rate was such that fresh solution would be in the cell for each pulse. The analyzing light, generated by a pulsed xenon arc lamp, passed through the cell perpendicularly to the electron beam before arrival at a SPEX monochromator and kinetic photomultiplier. Signals were averaged over 10-30 pulses to obtain the kinetic traces. The traces were then fitted for pseudo first order constants, which were then plotted against concentration to get the second order constants.

Doses were calibrated by correlating the output of a current integrator to the absorbance of  $(\text{SCN})_2^-$  ( $\lambda_{\text{max}} = 472 \text{ nm}$ ) which is generated in a  $\text{N}_2\text{O}$  saturated solution of  $\text{SCN}^-$ . Doses were calculated using the known G-value (6.14) and molar extinction coefficient (7580) [55]. Rate constants for hydrated electron reaction were determined at 700 nm using a 3-71 Corning cutoff filter to filter light below 400 nm eliminate interference from lower wavelengths.

Water was purified by a Millipore Milli-Q water system. Chemicals were

obtained from Aldrich except for the tert-butyl alcohol (Fisher Scientific) and the 2-iodophenol (Lancaster). The chemicals were of the highest purity commercially available and were used as received. Solutions were buffered at a pH of 4.7 with 0.005 M  $\text{KH}_2\text{PO}_4$  and purged with high purity  $\text{N}_2\text{O}$  or  $\text{N}_2$  just before irradiation.

## 2.2 Steady State Radiolysis

Irradiations were performed in an AECL Gammacell-220  $^{60}\text{Co}$  source with a dose rate of 0.38 kGy/hr (calibrated on November 1, 1993), as determined by the Fricke Dosimeter system [6]. A 500 ml Pyrex cell with a teflon/rubber septum for syringe sampling was used for all irradiations. Prior to irradiation, the cell was baked at  $500^\circ\text{C}$  to remove organic films from the surface. Solutions were purged with ultra high purity argon,  $\text{N}_2\text{O}$  or air before irradiation. All solutions were made up with purified water from a Millipore Milli-Q water purification system with chemicals from Aldrich, except for tert-butyl alcohol and 2-propanol, which were from Fisher Scientific. Fisher Scientific pH probes were used for pH determinations and sodium hydroxide or sulphuric acid was used to adjust pH. For analysis by GC/MS, entire irradiated solutions (250 ml) were acidified, extracted with ether and concentrated by rotary evaporation.

## 2.3 HPLC

Two Waters 510 solvent pumps, a Waters WISP 712 autosampler, a Hewlett Packard 1050 multiwavelength UV/Vis detector were interfaced through

a Waters System Interface Module to a NEC 286 Computer. A gradient elution scheme of water and acetonitrile was used to elute the samples through a Supelco DB C18 column. Components were detected at 220 nm. Concentrations were determined relative to standard solutions made up from pure compounds. The program, Baseline (Waters), was used for calibration and data manipulation.

#### 2.4 GC/MS

The GC/MS analyses were performed on a Hewlett Packard 5970 series Mass Selective Detector outfitted with a Hewlett Packard 5890 Gas Chromatograph equipped with a 12 or 25 m HP-1 methylsilica column. This system was used for identification of radiolysis and synthetic products. One microliter of the sample was injected onto the column by a glass Hamilton syringe. A 2 minute solvent delay provided enough time for a variety of solvents (chloroform, methylene chloride, methanol, ether, THF) to pass the mass spectrometer before it turned on. The temperature of the injection port was 200°C. The column temperature, initially at 35°C, was increased to 275°C over a period of 27 minutes.

#### 2.5 Kinetics by UV/Vis Spectrometer

Kinetic studies were performed on a Hewlett Packard 8450A UV/Vis spectrophotometer system. Solutions of 2-chlorophenol (approximately 33 ml) were poured into a temperature controlled, 10 cm quartz cell. Fisher pH probes

were used for pH determination and sodium hydroxide or hydrochloric acid was used to adjust to the desired pH. After small aliquots (0.33 ml) of an  $I^-/I_2$  stock solution ( $[I_2] = 1e-3$  M,  $[I^-] = 5e-2$  M) were added, the cell was quickly mixed and the instrument was activated. The system was set up to take absorbance measurements at specific intervals depending upon the speed of the reaction. An excess of  $I^-$  in the solution ensured that some of the  $I_2$  was converted to  $I_3^-$ , which has a much greater extinction coefficient. As a result, the reaction was followed at a wavelength of 350 nm, which corresponds to  $I_3^-$ . The slope of the plots of  $\ln(\text{absorbance})$  vs. time yielded the pseudo first order rate constants.

## 2.6 Stopped Flow Spectrophotometer

A HiTech stopped flow unit was used for measuring the rate of reactions that were too fast for the Hewlett Packard spectrophotometer system. The pneumatically driven syringes inject a 1:1 mixture of two solutions into the cell, therefore the initial solutions were made up to result in the same concentrations that were used in the Hewlett Packard system. The optical cell had a shorter path length, but in the interest of duplicating the conditions on the Hewlett Packard spectrophotometer, the  $I_3^-$  concentration was not increased. As a result, the change in absorbance was smaller, but did not cause difficulties. The software provided with the system collected and fit the data to result in a pseudo first order rate constant.

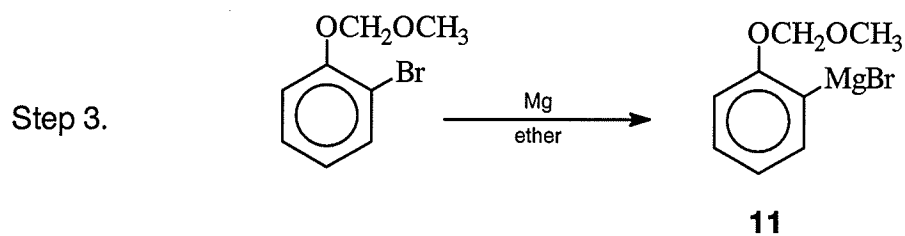
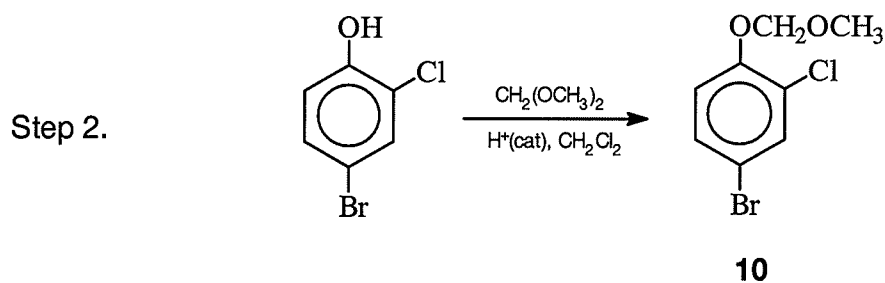
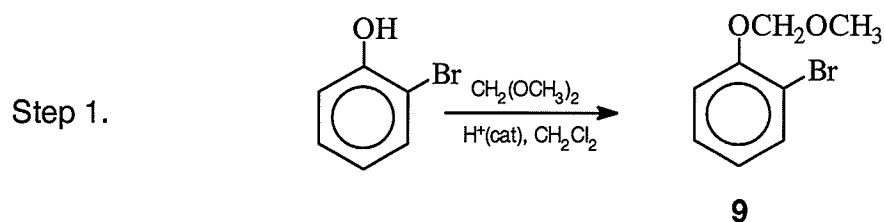
## 2.7 Ion Chromatography

A Dionex QIC system was used in the analysis of iodide and chloride. A mobile phase of 1.7 mM NaHCO<sub>3</sub> and 1.8 mM Na<sub>2</sub>CO<sub>3</sub> was used to elute samples through a Dionex AS4A anion column. Samples (0.5 ml) were diluted if necessary to fit onto a calibration curve made up of standards between 1 and 30 ppm. Peaks were integrated by a Dionex analysis program and the areas were used for unknown determination.

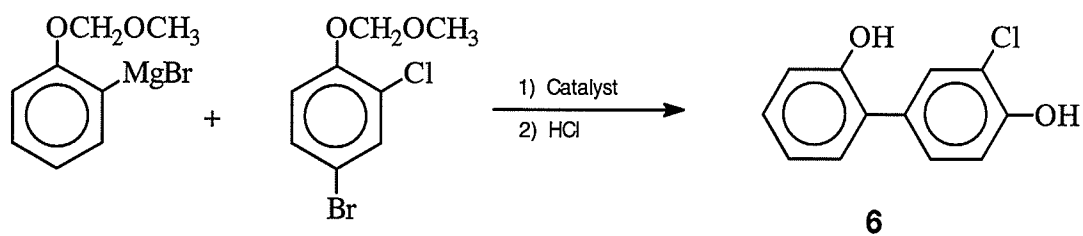
## 2.8 Preparation of Organic Compounds

A plan to synthesize chlorinated biphenol **6** was devised featuring a palladium catalyzed coupling of a Grignard reagent [57] and a brominated chlorophenol is shown (Scheme 2-1). The coupling reaction was first tested by successfully performing a documented reaction between phenyl magnesium bromide and 1,4-bromochlorobenzene to form 4-chlorobiphenyl. The catalyst, Iodo-(p-fluoro)-bis(triphenylphosphine) palladium (II), is known to be selective for coupling at the bromine bond in the presence of a chlorine-carbon bond [58]. Proton NMR spectra were recorded on a Bruker AM-300 or a 500 MHz instrument. Exact masses were recorded on a Fisons Instruments V.G. 7070E-HF Double Focussing Forward Geometry instrument at the University of Manitoba. Whatman aluminum backed 0.25 mm pre-coated silica gel TLC plates were used for analytical purposes, while 1 mm Analtech Silica Gel GF glass backed plates were utilized for preparative procedures.

Scheme 2-1



Step 4.



Preparation of Iodo-(p-fluoro)-bis(triphenylphosphine) palladium (II)

Iodo-(p-fluoro)-bis(triphenylphosphine) palladium (II) was prepared following a literature procedure [59, 60]. A mixture of tetrakis(triphenylphosphine) palladium(0) (1 g, 0.87 mmol) and of p-fluoriodobenzene (150  $\mu$ l, 1.3 mmol) and 12 ml toluene was stirred at room temperature for approximately 2 hours. Toluene was removed by rotary evaporation. The crude product was then triturated in ether and recrystallized from chloroform/hexane to yield white/yellow crystals (~0.5 g, 70% yield) that decomposed at 170°C.

Preparation of ether 9 (Step 1: Refer to Scheme 2-1)

The phenolic group on 2-bromophenol was protected with the methoxymethyl group by a procedure utilizing an acid catalyzed acetal exchange involving dimethoxy methane. The phenol (~ 5 g, 34.5mmol), dimethoxymethane (10 ml, 113 mmol) and catalytic amounts of p-toluenesulphonic acid were refluxed for 72-84 hours in methylene chloride (150 ml) [61]. Although time consuming, this procedure required little attention and is safer in comparison to any methods involving chloromethyl methyl ether. Methanol was removed from the system by 4Å molecular sieves contained in a Soxlet extractor on the principle that methylene chloride and methanol form an azeotrope boiling at 37.8°C. After rotary evaporation of the solvents, the crude product was extracted with 1 M NaOH, dried over MgSO<sub>4</sub>, and then purified by fractional distillation at reduced pressure. About 3 ml (50% yield) of ether 9 was collected at 138°C at 40 mmHg. Yield was not

maximized.

$^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.55 (d, 1H, aromatic), 7.25 (t, 1H, aromatic), 7.15 (d, 1H, aromatic), 6.89 (t, 1H, aromatic), 5.25 (s, 2H, O-CH<sub>2</sub>-O), 3.53 (s, 3H, OCH<sub>3</sub>). Mass spectrum,  $m/e$  (rel %): 218(425), 216(437), 188(2), 186(1), 157(1), 145(2), 143(2), 119(1), 78(1), 77(2), 76(2), 75(2), 74(1), 64(3), 63(5), 62(1), 50(3), 45(100), 39(2), 38(3).

#### Preparation of Ether 10 (Step 2)

4-Bromo-2-chlorophenol was protected following the same procedure as for 2-bromophenol (above). Ether **10** was collected at 152°C at 30 mmHg during the reduced pressure distillation (~50% yield). Yield was not maximized.

$^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.51 (s, 1H, aromatic), 7.30 (d, 1H, aromatic), 7.06 (d, 1H, aromatic), 5.22 (s, 2H, O-CH<sub>2</sub>-O), 3.51 (s, 3H, OCH<sub>3</sub>). Mass spectrum,  $m/e$  (rel %): 252(4), 250(3), 222(1), 207(1), 191(1), 179(1), 177(1), 112(1), 110(1), 75(3), 74(2), 63(5), 62(3), 61(1), 50(1), 46(2), 45(100), 37(1).

#### Preparation of 3'-chloro-2,4'-dihydroxybiphenol 6 (Steps 3 and 4)

The Grignard reagent **5** was prepared in the usual way by adding the protected bromophenol **9** (0.5 ml, 3.4 mmol) dropwise to magnesium turnings (0.1 g, 4.1 mmol) suspended in anhydrous THF (~5 ml). While making the Grignard reagent in diethyl ether, the reaction was often difficult to start and never went to



completion, usually terminating when a precipitate appeared. This was attributed to moisture in the anhydrous ether (Aldrich) or to low solubility of the Grignard reagent in diethyl ether. This problem was alleviated by changing the solvent to freshly distilled THF. The reagent was then transferred to another dropping funnel. A 3-necked flask was then charged with the catalyst (0.03g, 0.035mmol), protected bromochlorophenol **10** (0.5 ml, 3.1mmol) and THF (~4ml). The resulting mixture was left to react for 72 hours. Aqueous hydrochloric acid was then slowly added and the mixture was stirred overnight. This step also serves as a deprotection step. The mixture was then extracted with ether. The combined organic phase was washed with saturated NaH<sub>2</sub>CO<sub>3</sub> solution and water, then dried over MgSO<sub>4</sub>. Evaporation of the solvent yielded a dark red/brown mixture. As the coupling reaction between such species was not discussed in the available literature, the yield of this reaction was not known. The first attempt resulted in very little product. Using a longer reaction time and a higher ratio of catalyst, the yield improved. As the mixture contained several unknown components, attempts were made to purify the product by TLC. After elution on a preparative TLC plates (chloroform/ethyl acetate 9:1), the silica gel was removed (band at R<sub>F</sub>=0.46), extracted with ether and concentrated by rotary evaporation. Two more repetitions of this procedure yielded small amounts of 3'-chloro-2,4'-dihydroxybiphenol **6** (< 5 mg). A yield of 5-10% is estimated.

<sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ: 7.48 (s, 1H, aromatic), 7.31 (d, 1h, aromatic), 7.25 (t, 1H, aromatic),

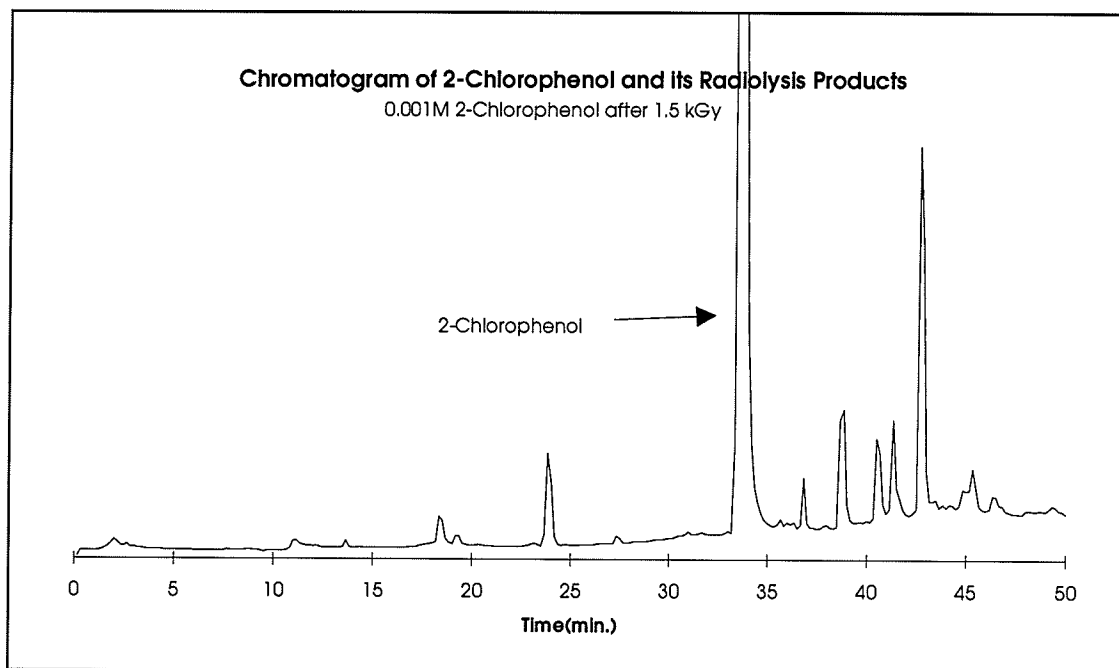
7.21 (d,1H,aromatic), 7.12 (d,1H,aromatic), 6.98 (t, 1H, aromatic), 6.95 (d, 1H, aromatic), 5.68 (s, 1H, OH), 5.11(s,1H,OH). Mass spectrum, *m/e* (rel %): 222(31), 221(14), 220(100), 185(58), 184(19), 167(7), 157(29), 139(7.39), 128(25), 127(17), 126(6), 102(7), 101(6), 77(10), 75(8), 64(13), 63(12), 51(13.8). Exact mass/mass spec.: calculated 220.029, found 220.027.

### **3 Results and discussion**

#### **3.1 Product Analysis**

In this section, the major radiolysis products of 2-chlorophenol will be identified. Discussion will include possible formation pathways and interpretation of product yields relative to various solution compositions.

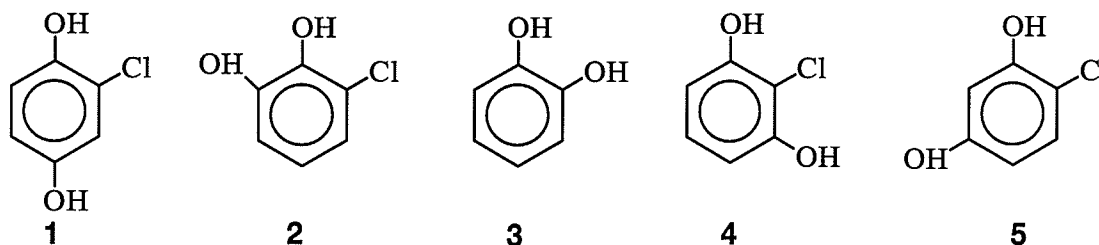
When irradiations are performed on solutions of the substrate, a multitude of products appear. As these products may have different structures and reactivities than the initial substrate, it is important to identify and possibly quantify them. Electron and hydroxyl radical scavenging is helpful in determining how different products are formed [11].



**Figure 3-1**

Scavenging hydroxyl radicals before they can oxidize  $I^-$  to  $I_2$  is one of the

modes of iodine mitigation. To prove this, oxidized products must be identified. Solutions can be saturated with  $N_2O$  to single out the effects of hydroxyl radicals. As the chlorine atom on the ring of 2-chlorophenol is only weakly deactivating, it is not likely to alter the activated sites on the ring. Although five possible structures (1-5) can be proposed, the hydroxyl radicals are expected to



preferentially add to the *ortho* and *para* positions relative to the phenolic oxygen.

Samples of these compounds were obtained, where possible, to help with identification of the radiolysis products. Retention times and spectral data from HPLC and GC/MS show that compounds **1**, **2** and **3** are present in the radiolysis mixture. Compound **5**, 4-chlorocatechol, was not found as a radiolysis product. The reduction product, phenol, was also identified as a product.

As chlorohydroquinone **1** could be analyzed easily by HPLC, dose profiles were constructed under a series of conditions (Figure 3-2). Purging with  $N_2O$  scavenges most of the electrons, and at the same time doubles the yield of hydroxyl radicals. Therefore more hydroxylated products would be expected. Comparison of the production of chlorohydroquinone in pure water to that of  $N_2O$

saturated water demonstrates the problem of maintaining halogenated products in an electron environment. Only a small steady state amount of chlorohydroquinone is produced in pure water, as it is susceptible to dehalogenation by the reaction

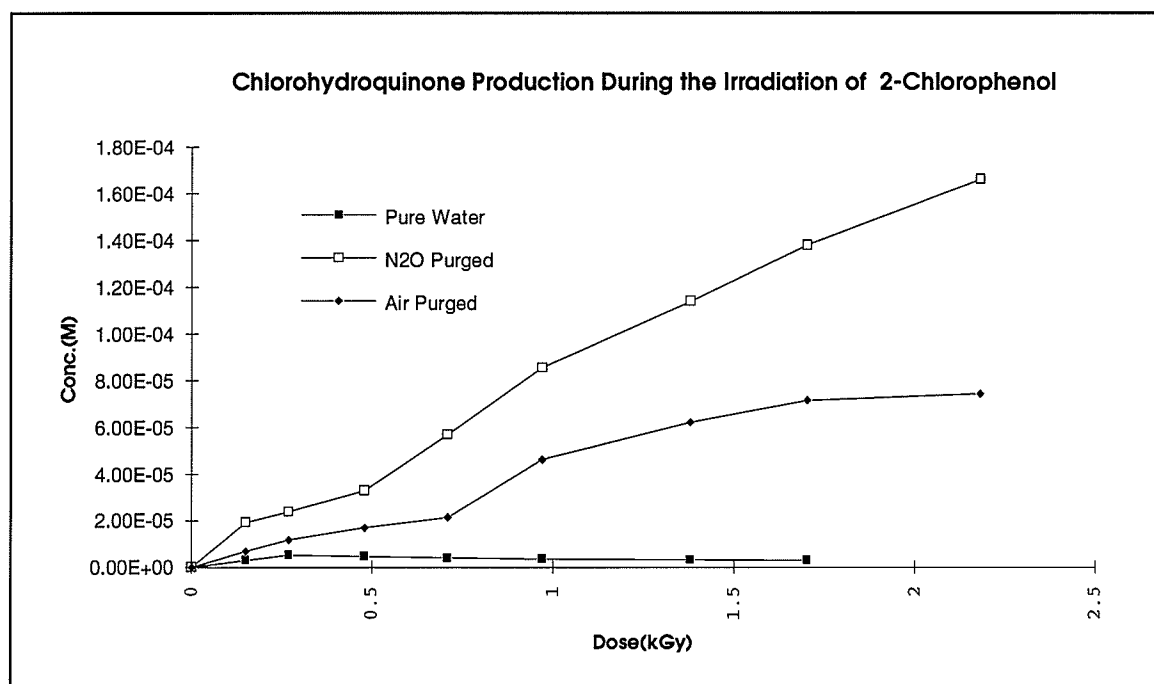


Figure 3-2

with aqueous electrons. In the aerated environment,  $O_2$  is present, allowing hydroxylation to occur faster as another mechanism comes into effect.

To observe the products of the reaction of the substrate with the aqueous electron, tert-butyl alcohol is used to scavenge the hydroxyl radicals. The only reaction that can take place is for the electron to add to the ring and subsequent loss of halogen. In this solution, the major product formed is phenol. The tert-butyl alcohol seems to serve two purposes. When the yield of phenol in pure water is compared to that of a 0.4 M tert-butyl alcohol solution, it is evident that

either tert-butyl alcohol increases phenol production or that hydroxyl radicals somehow reduce the buildup of phenol. Other researchers found that in the presence of an effective hydrogen donor, the hydrophenyl radicals are quantitatively converted into phenol [33].

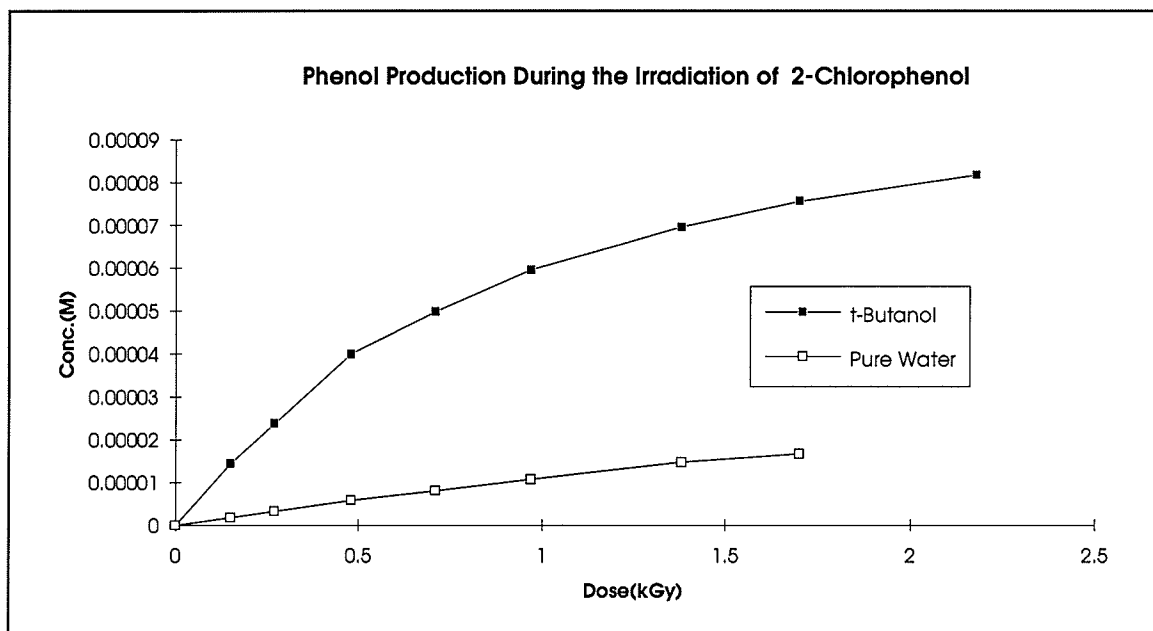
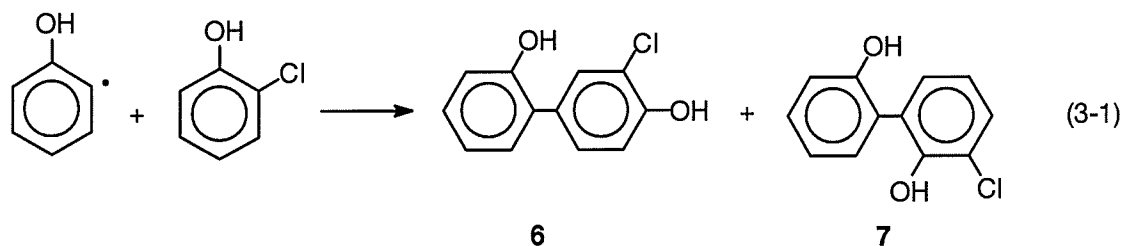


Figure 3-3

It is possible that the small amount of phenol produced in pure water comes from hydroxyphenyl radicals abstracting phenolic hydrogen from a 2-chlorophenol molecule or perhaps  $\text{HO}_2\cdot$  is involved. The difference in slopes of these graphs correspond to a G-value of  $\sim 0.8$ . This number represents the yield of hydroxyphenyl radicals that do not form phenol, but meet an alternate fate.

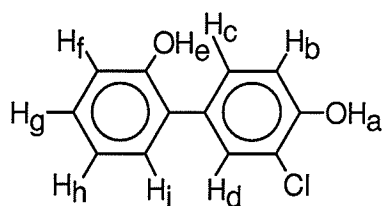
In the absence of excess hydrogen donors, peaks appear at longer retention

times in the HPLC chromatograms, suggesting the presence of larger molecules. It was then hypothesized that hydroxyphenyl radicals can attack the starting material to form various isomers of chlorobiphenol, for example compounds **6** and **7**. Precedence for this hypothesis comes from a similar system [33, 35].



Peaks with molecular weights consistent with these structures were observed in the GC/MC data. Attempts to synthesize compounds **6** and **7** were carried out in order to verify the hypothesis.

The  $^1\text{H}$  nmr spectra of the product of Scheme 2-1 is consistent with the expected absorptions of chlorobiphenol **6**. The absorptions and their assignments are given in Table 3-1. The assignments were based upon the protons position relative to the OH group on the ring. Protons in an *ortho* or *para* relationship to an OH group will be further upfield than those with a *meta* relationship (ie.  $\text{H}_h$  and  $\text{H}_i$  are the absorptions furthest upfield). The effect of the chlorine is to shift protons from that ring downfield. For example,  $\text{H}_d$  and  $\text{H}_c$  are the absorptions furthest downfield.



**Table 3-1**

**<sup>1</sup>H nmr Absorptions and Assignments**

Absorption (ppm)	Multiplicity	Assignment
7.48	singlet	H <sub>d</sub>
7.31	doublet	H <sub>c</sub>
7.25	triplet	H <sub>g</sub>
7.21	doublet	H <sub>i</sub>
7.12	doublet	H <sub>b</sub>
6.98	triplet	H <sub>h</sub>
6.95	doublet	H <sub>f</sub>
5.68	singlet	H <sub>e</sub>
5.11	singlet	H <sub>a</sub>



Homodecoupling data serve to confirm the aromatic assignments (See Appendix) by showing which absorptions are related. For example, the data clearly display a relationship between the absorptions at 7.48, 7.31 and 7.12. Peaks with this type of coupling and splitting are consistent with the expected patterns. The data also support the assignments given to the other ring by displaying the relationship between the doublet at 7.21 and triplet at 6.98 and between the doublet at 6.95 and triplet at 7.25. The phenolic protons correspond to wider peaks further upfield from the aromatic absorptions (between 5 and 6 ppm). It is evident from the full NMR spectrum that several impurities are present in the sample, possibly water and stopcock grease.

The mass spectrum of the product (Figure 3-4) is compared to that of the radiolysis product's in Figure 3-5. Also, the retention times on GC and HPLC correspond to a peak suspected to be compound **6**. These data support the speculation that chlorobiphenol **6** is one of the radiolysis products of 2-chlorophenol in argon saturated water. As the chlorinated biphenols are susceptible to the dehalogenation reaction with the aqueous electron, only a small steady state amount would be produced and biphenols would be the expected product.

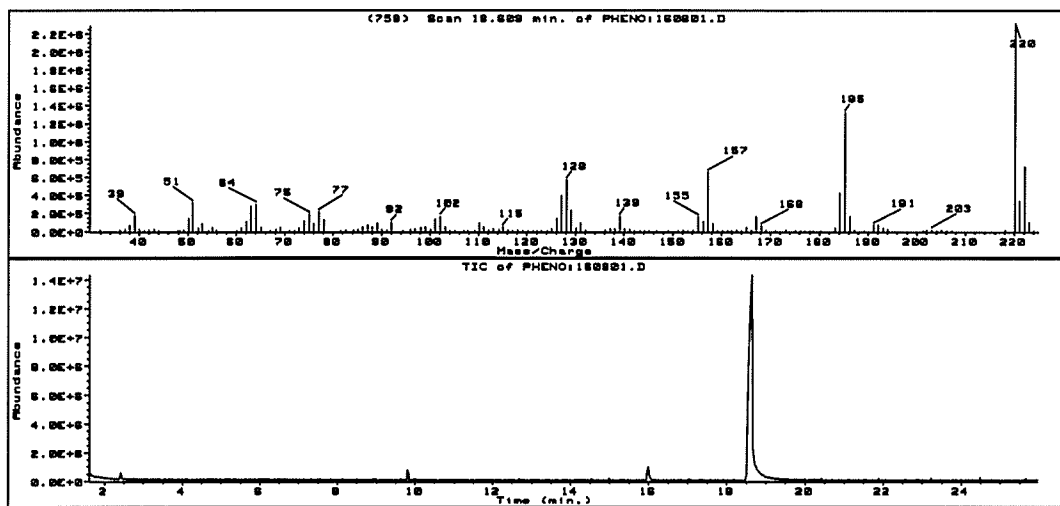


Figure 3-4 Chromatogram and Mass Spectrum (18.6 min.) of Synthetic Product.

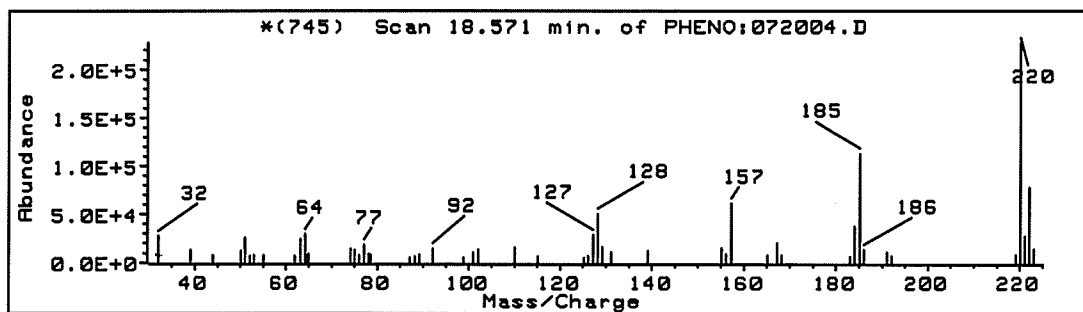
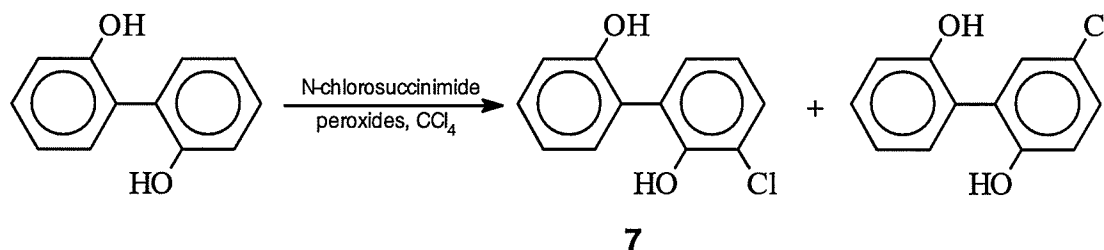


Figure 3-5 Mass spectrum of radiolysis product at 18.6 minutes.

Synthesis of another one of the suspected chlorinated biphenols, 3-chloro-2,2'-dihydroxybiphenyl was attempted (Scheme 3-2). The starting material in this case, 2,2'-biphenol (easily obtained), was treated with N-chlorosuccinimide. This free radical chlorination formed di- and tri-chlorinated species as well as the two expected monochlorinated products, as demonstrated by analysis of the product. Separation of these isomers on a silica gel column to obtain a pure sample of 3-chloro-2,2'-dihydroxybiphenyl proved to be difficult. Although this procedure had potential, it was abandoned at this point. However, GC/MS and HPLC data of the mixture show a product with a retention time and mass spectrum consistent with one of the radiolysis products (Figures 3-6 and 3-7). As this product is a structural isomer of chlorobiphenol **6**, it displays a similar mass spectrum. However, the spectra from the two products can be distinguished (see peak at  $m/e$  192). This product was not isolated and characterized by NMR or elemental analysis, but it is likely that chlorobiphenol **7** is also a radiolysis product.

Scheme 3-2.



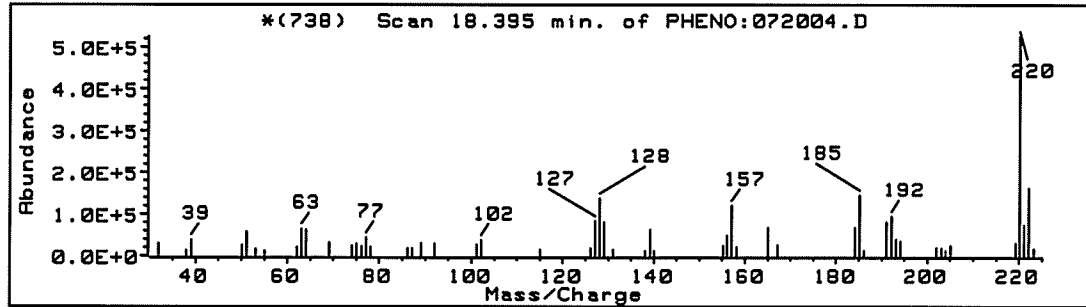


Figure 3-6 Mass spectrum of chlorination product at 18.4 minutes.

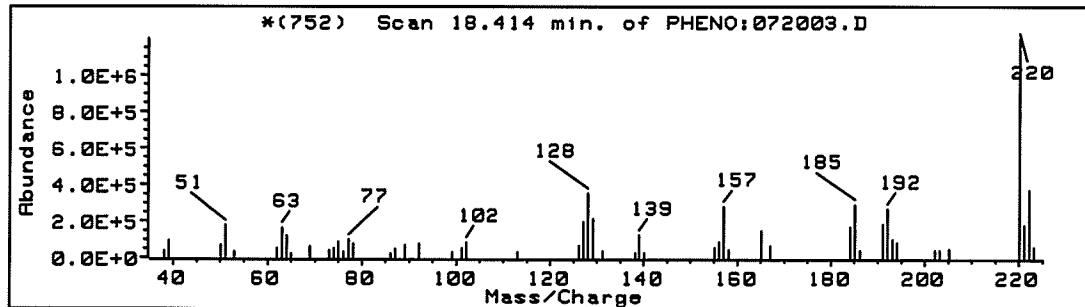
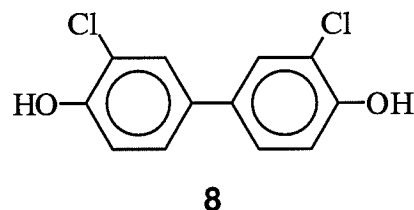
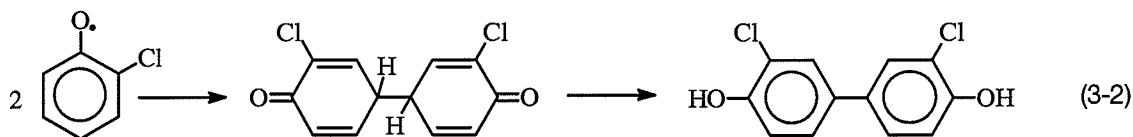


Figure 3-7 Mass spectrum of radiolysis product at 18.4 minutes.

The GC/MS data also give evidence for dimerization. Small peaks corresponding to structures such as compound **8** appear later in the chromatogram. The formation of these compounds can be explained by the



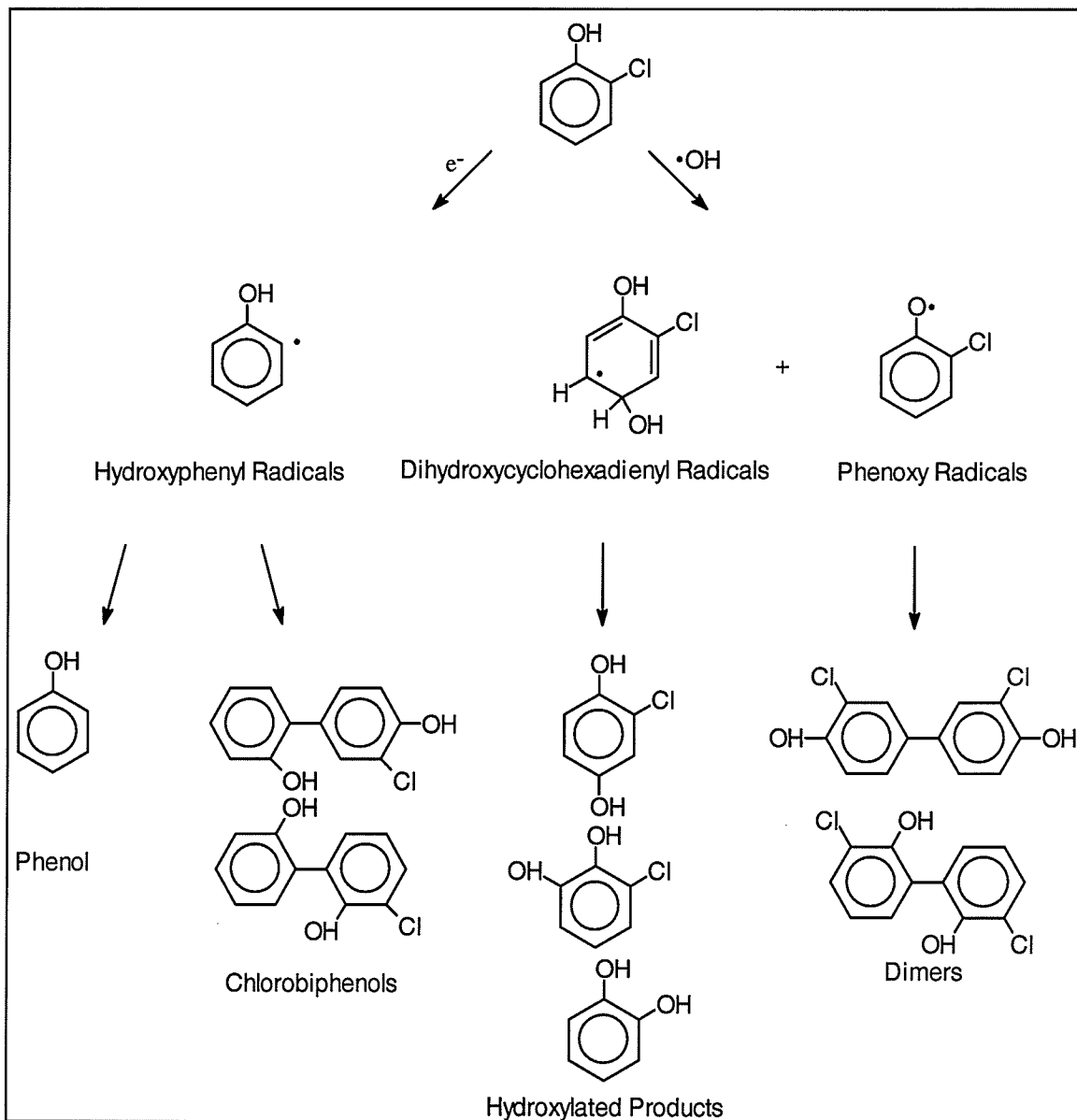
dimerization of phenoxy radicals (Equation 3-2) [19, 25, 26]. In a steady state experiment, dimerization of phenoxy radicals is likely to be an infrequent event, as the population of radicals at any one time would be small. This reaction would become more important as the dose rate increases.



Existence of these larger molecules may have an effect on the stability of the organic compound in a radiation field and give insight into the mitigant behaviour of chlorophenol. After further irradiation, compounds consisting of three or more aromatic rings may even be formed. Instead of breaking down into small, volatile compounds, the opposite seems to be true to some extent. Larger organic iodides would be less volatile than small molecular weight iodo compounds.

The following scheme outlines the major radiolytic pathways of our model compound in pure water:

Varying conditions such as pH, air content, and other additives will affect



**Figure 3-8**

these pathways. In air saturated solutions, the production of hydroxylated products is greater than in argon purged solutions, but the formation of dimers and

biphenols such as **6** and **7** are interrupted. The initial product between a hydroxyphenyl radical and oxygen is likely a peroxy radical. Peroxy radicals are generally more stable than the radicals from which they are derived [6]. Perhaps it will then abstract a phenolic hydrogen, dimerize or disproportionate. In a  $N_2O$  saturated system, there are few electrons to react with the chlorophenol. Thus, there are also few hydroxyphenyl radicals with which to produce chlorobiphenols. However, as the yield of hydroxyl radicals has doubled, there would be more dihydroxycyclohexadienyl radicals and more phenoxy radicals to dimerize. The dimerization pathway would still account for only a small amount of material. If enough of an organic substrate, such as an alcohol, is added into the system, the hydroxyphenyl radicals have a hydrogen donor and would be converted into phenol. Steady state experiments with tert-butyl alcohol have confirmed that the production of chlorobiphenols such as **6** and **7** is diminished. The pH of the solution may have various effects, depending upon its degree of alkalinity or acidity. If the solution is only moderately acidic (pH = 4-5), the yields of primary radiolysis products would be unaffected. However, some rates would change. For example, since most of the phenol will be protonated at this pH, addition of a hydroxyl radical would be slower than in a neutral solution. The conversion of the adduct into a phenoxy radical, being acid and base catalyzed, would happen faster [16, 18]. Under more acidic conditions (pH <4), electron yield will drop and will approach zero at about a pH of 1. At the same time, the yield of hydrogen atom will rise. Under basic conditions (pH >10), most of the phenol will be deprotonated

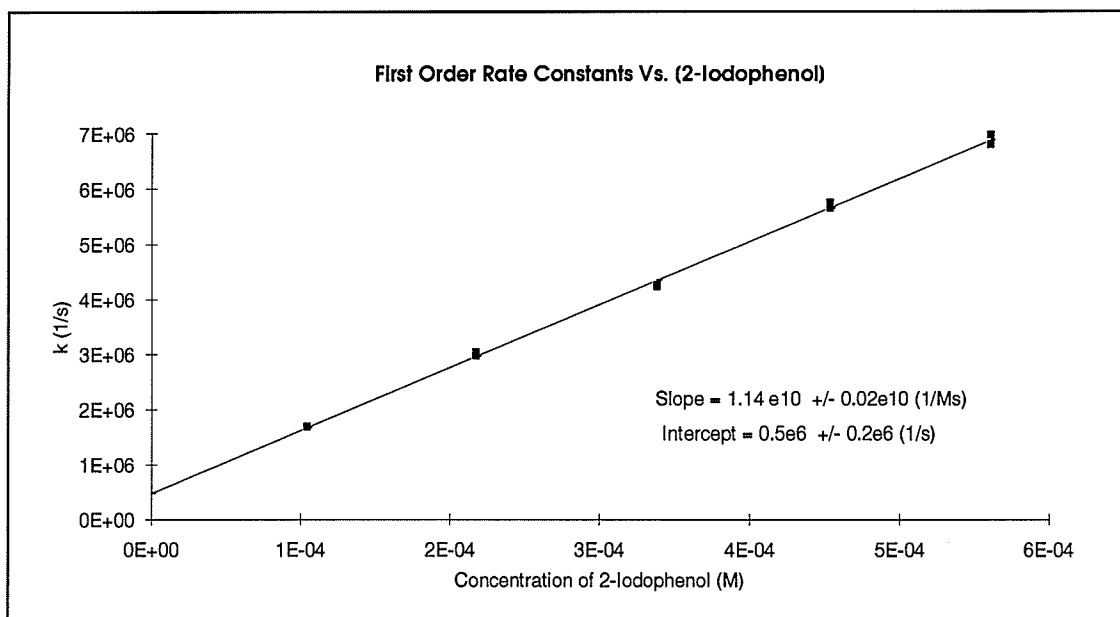
and will be converted into a phenoxy radical by the hydroxyl radical. The electron yield will also slightly rise.



### 3.2 Kinetics

#### 3.2.1 Time Resolved Pulse Radiolysis Studies

Time resolved pulse radiolysis studies were performed to obtain rate constants for the addition of the aqueous electron with iodophenols and iodoanisoles. This was achieved by collecting pseudo first order traces of the buildup and decay of the aqueous electron absorption. Aqueous electrons are known to have a strong absorption with  $\lambda_{\text{max}} = 700 \text{ nm}$  [6]. A fit program allowed the extraction of first order decay constants. As only micromoles of electron are produced in each pulse, the substrate is in great excess.



**Figure 3-9** Plot to determine second order rate constant for the 2-iodophenol + electron reaction.

An example of the trace is given in the appendix. It shows the rapid buildup of absorbance due to hydrated electrons when radiation is pulsed, then its decay over a period of about 2 us. Figure 3-9 shows the 2-iodophenol concentration dependence used to calculate the second order rate constants. These rate constants are given in Table 3-2 along with rates of other halophenols for comparison. The rate of reaction of the electron with the iodophenols is faster than that of the other halophenols. Iodine seems to fit into the pattern of reactivity that one would predict by relative carbon-halogen bond strengths. The rates for all of the iodoaromatic species (Tables 3-2 and 3-3) are very comparable. The significance of these rate differences is that the iodo-substituted species will have a kinetic advantage over the chloro-substituted species in a competition for hydrated electrons.

The question remains whether each electron addition yields an iodide ion. This question will be addressed in the next section. Previous data [34, 62] demonstrate that the yields of fluoride ion and chloride ion are not quite quantitative with the production of electrons. However, the yield of bromide ion in the electron reaction with bromophenols is quantitative. If bond strength is the important factor, then it would follow that iodide yield would be quantitative.

Table 3-2

Reaction Rates of Halophenols with the Aqueous Electron

Substrate	k (M <sup>-1</sup> s <sup>-1</sup> )	Reference
2-chlorophenol	1.3e09	[34]
3-chlorophenol	1.9e09	[34]
4-chlorophenol	1.5e09	[34]
2-bromophenol	7.3e09	[34]
3-bromophenol	6.0e09	[34]
4-bromophenol	6.3e09	[34]
2-iodophenol	(1.14 ± 0.02)e10	This work.
3-iodophenol	(1.04 ± 0.04)e10	This work.
4-iodophenol	(1.0 ± 0.2)e10	This work

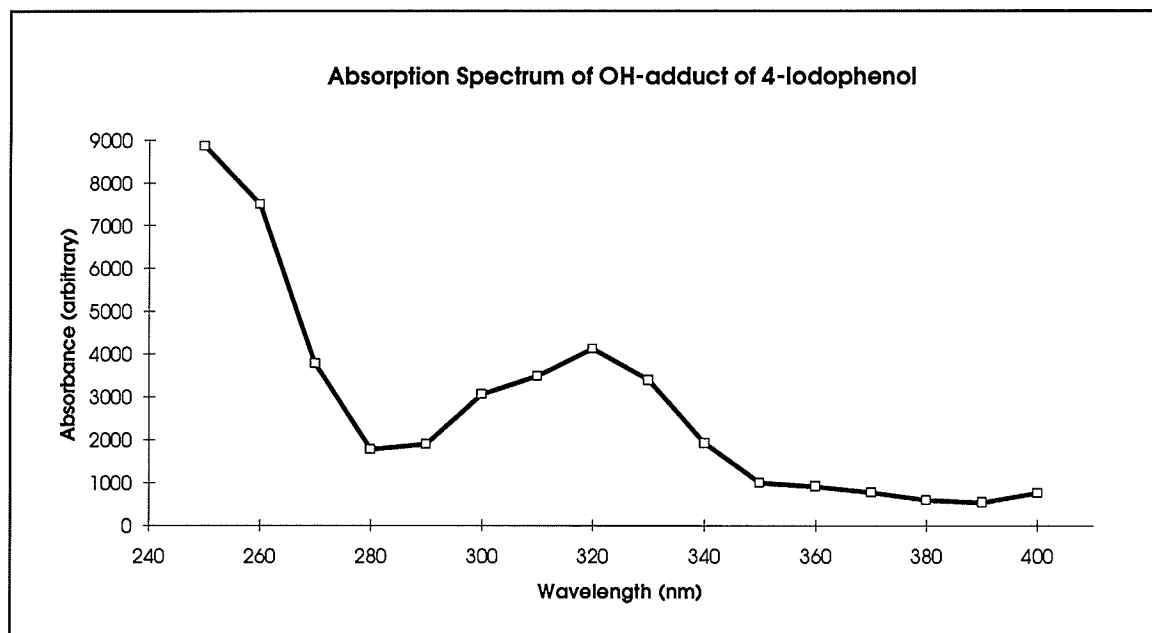
Notes: Errors are estimated by the standard error from the plot slopes.  
pH = 5

Table 3-3

Reaction Rates of Iodoaromatic Compounds with the Aqueous Electron

Substrate	k (M <sup>-1</sup> s <sup>-1</sup> )	Reference
2-Iodoanisole	(1.04 ± 0.07)e10	This work.
3-Iodoanisole	(1.06 ± 0.08)e10	This work.
4-Iodoanisole	(1.09 ± 0.02)e10	This work.
Iodobenzene	1.2e10	[68]
4-Iodobenzoate ion	9.1e09	[68]

There are very little data on the rates of hydroxyl radical attachment to halogen substituted phenols. Rate of hydroxyl radical attachment to iodophenol rings was also determined by pulse radiolysis. This was done by following the rapid pseudo first order growth of the absorbance of the hydroxyl radical adduct of each species in  $N_2O$  saturated solutions. The problem is that hydroxyl radicals can attack several sites on the ring, including the site containing the halogen, leading to several different intermediates. To find an appropriate wavelength, an absorbance spectrum was obtained of the transient absorbing about 1  $\mu s$  after the pulse.



**Figure 3-10**

This absorption spectrum is most likely a composite spectrum of several isomeric dihydrocyclohexadienyl radicals [63], plus a small contribution from the hydrogen atom adduct. A wavelength of 320 nm was selected and second order rate

constants were calculated after several substrate concentrations were run. Table 3-4 summarizes the data.

These rate constants are likely very sensitive to pH. As these reactions have been compared to electrophilic reactions [12], one would expect faster rates at higher pH due to higher ratios of dissociated phenol. The solutions were buffered at a pH of 5 to ensure that most of the phenol was present as the protonated form.

As some hydroxyl radicals will displace halogens and other substituents, it may be helpful to know what percentage of the total hydroxyl radical yield will follow this route. This will be addressed in the following section.

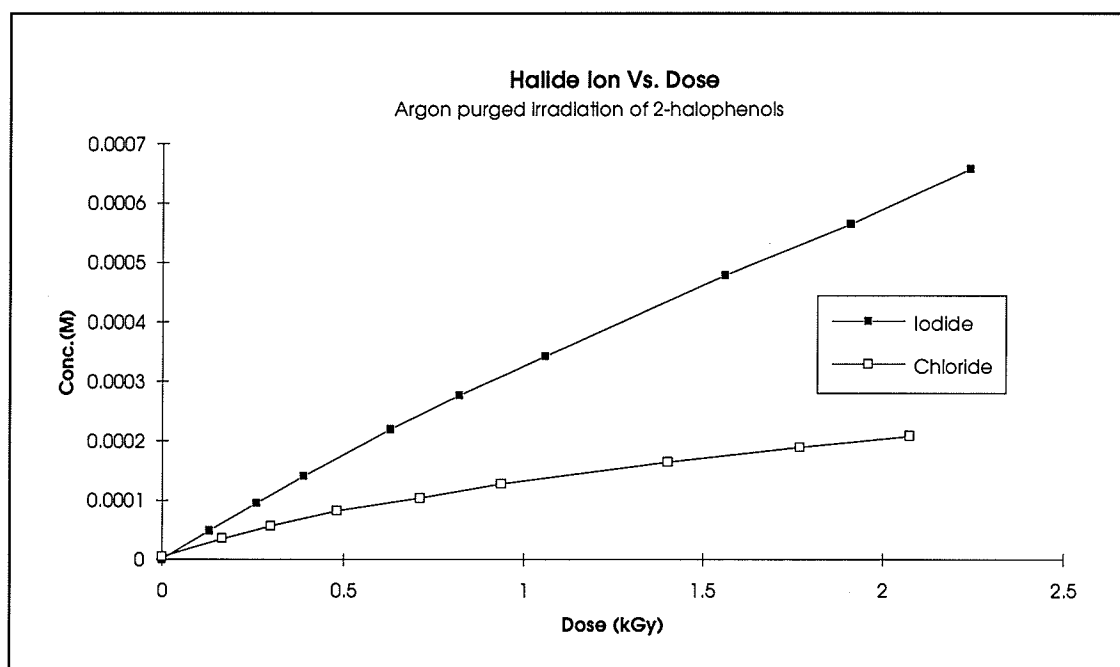
**Table 3-4**

**Reaction Rates of Phenols with the Hydroxyl Radical**

<b>Substrate</b>	<b>pH</b>	<b>Rate (<math>M^{-1}s^{-1}</math>)</b>	<b>Reference</b>
2-iodophenol	4.7	$(9.6 \pm 0.5)e9$	[This Work]
3-iodophenol	4.7	$(8.9 \pm 0.3)e9$	[This Work]
4-iodophenol	4.7	$(9.3 \pm 0.6)e9$	[This Work]
2-chlorophenol	6.5-7.7	$1.2e10$	[29]
4-chlorophenol	6.5-7.7	$1.5e10$	[19]

### 3.2 Halide Ion Production

The concentration of halide ion in irradiated solutions was investigated to determine the rate and mechanism of halide detachment from the ring. Radiochemical yields of fluoride, chloride and bromide liberation from halophenols are available [34], but no data are available on iodide.



**Figure 3-11**

While solutions of different types were being irradiated, samples were taken and analyzed by ion chromatography. Figure 3-11 shows the relative rate of halide removal between 2-iodophenol and 2-chlorophenol. In pure, argon purged water, the buildup of the halide ion is a result of a combination of reactions. Although the electron reaction is probably the most important source of halide ion, the hydrogen

atom and hydroxyl radical reaction may also contribute. The G-value for iodide production in pure water was calculated to be about 3.5 while that for chloride was approximately 2. To determine the contributions of each species towards iodine cleavage, solutions were made up with the radical scavengers 2-propanol, tert-butyl alcohol and/or N<sub>2</sub>O. The G-value of each run was determined from the slope of the plots of halide vs. dose. If the plot was slightly curved, the initial slope was determined by fitting the curve to a quadratic function and taking the linear term coefficient as the slope. A 5-10% error is estimated in these values (ie. ΔG-value ~ 0.2).

$$\text{Radiochemical Yield} = \frac{\text{molecules}}{100\text{eV}} = \frac{M}{\text{kGy}} (9650) \quad (3-3)$$

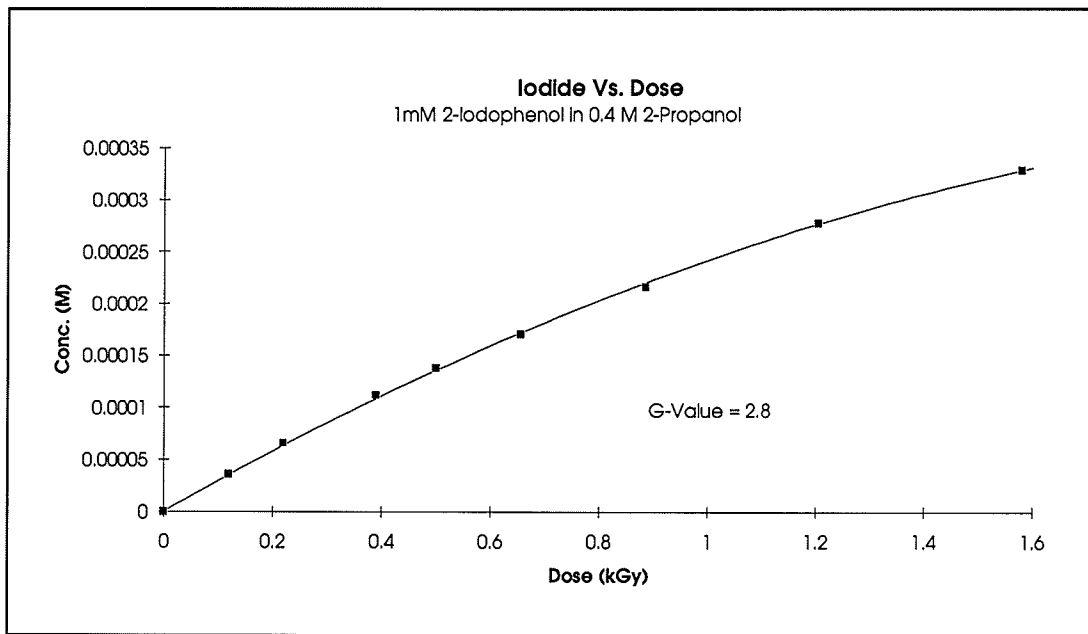


Figure 3-12

Figure 3-12 shows the dose dependence of iodide concentration in a



solution where electrons predominate. The initial slope corresponds to an iodide yield of 2.9. Since 0.4 M 2-propanol scavenges 99% of the hydroxyl radicals and 75% of the hydrogen atoms, a small correction is made to account for the small amount of iodide being produced from radicals that are not scavenged. Thus resulting in a yield of 2.8, which is only slightly smaller than the iodide yield in pure water. This would suggest that electrons are of major importance towards the removal of iodine from the ring.

In previous work [34, 62], the hydroxyl radical has been shown to contribute to the production of halide ions by direct substitution. The trend seems to be that as the halogen gets larger, the rate of substitution gets slower (fluoride>chloride>bromide). It follows that iodine will be even less substituted by hydroxyl radicals on an aromatic ring. To test this theory, a N<sub>2</sub>O saturated solution

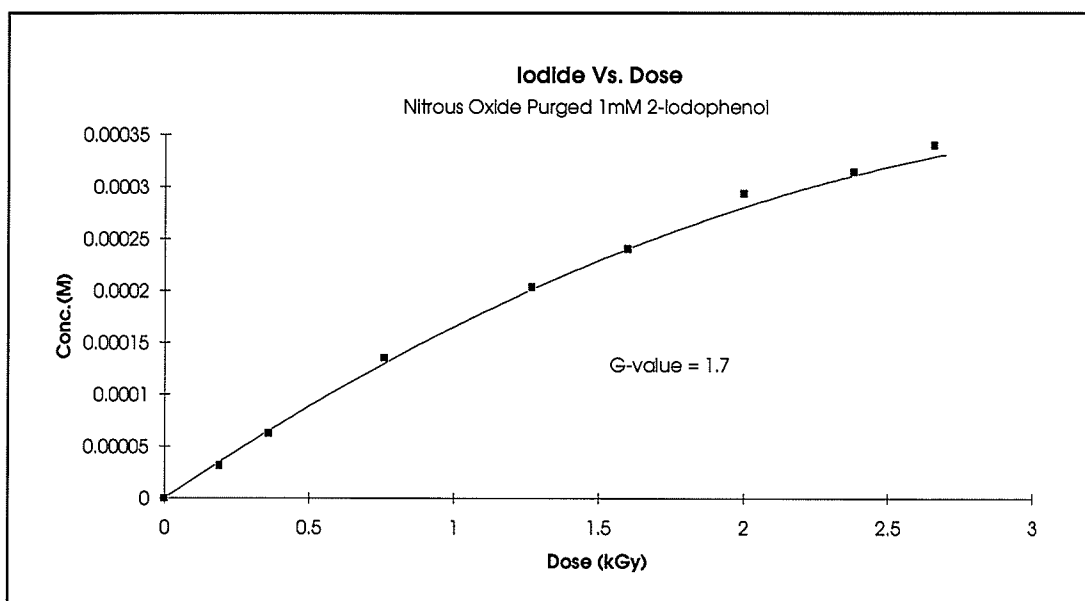


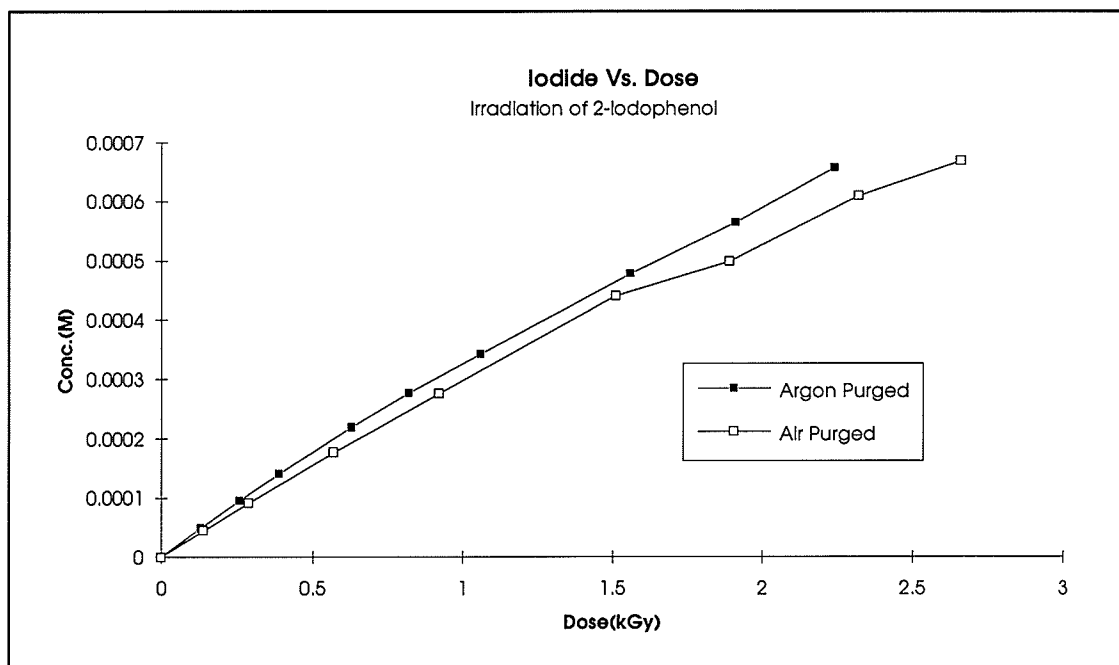
Figure 3-13

of 2-iodophenol was irradiated. The iodide results are shown in Figure 3-13. As the graph is curved, the initial slope was used for G-value determination. In this solution the electrons are scavenged by  $N_2O$  but the hydroxyl radical yield is approximately doubled to a value of 5.5, therefore the  $I^-$  production due to hydroxyl radicals would be doubled. The initial slope corresponds to a yield of 1.7, which is a combination of hydrogen and hydroxyl radicals.

If both tert-butyl alcohol and  $N_2O$  are present, then only the hydrogen atoms remain. A yield of 0.4 for the production of iodide is extracted from this irradiation. This value is small as one would expect, but seems a bit high since the radiochemical yield of hydrogen atoms is only 0.6. This result suggest that there may be another mechanism at work besides physical substitution on the ring, such as an electron transfer from the hydrogen atom [64]. For comparison, solutions of 4-iodophenol and 3-iodophenol were also irradiated. The results are similar.

If electrons are the major pathway for iodine cleavage, oxygen may have an effect because it is an effective electron scavenger. Figure 3-14 shows that there is only a minor difference between the iodide yield in argon and air saturated solutions. This could be due to an electron transfer from superoxide radical to the iodophenol. A similar observation has been made for the 4-bromophenol decomposition [35].

Non-irradiated control solutions demonstrated that the iodide and chloride liberation is due to the radiation. Solutions of 2-iodophenol, 3-iodophenol, 4-iodophenol and 2-chlorophenol were analyzed 24 hours after being made. The



**Figure 3-14**

corresponding halide ion was undetectable in each case.

One source of error in these determinations can be caused by pH changes since solutions generally become more acidic during irradiations. The presence of protons can cause a decrease in the yield of electrons. With a yield of about 2.7, almost every electron produced by radiation that escapes into the bulk of the solution generates a corresponding iodide ion. A yield of 0.6 due to hydroxyl radicals means that ~23% of the total hydroxyl radicals will react at the site containing an iodine atom. This seems reasonable as there are 2 other major sites of attack on the ring.

In summary, the removal of iodide from the ring happens quite readily. Calculation of G-values in various solutions allow the estimation that the liberation of iodide is approximately 75% due to electrons (2.7), ~15% due to hydroxyl radicals

(0.6) and ~10% due to hydrogen atoms (0.4). Chloride is liberated at a slower rate.

This could be attributed to relative bond strengths of the halogens [34].

### 3.2.3 Electrophilic Substitution Reaction

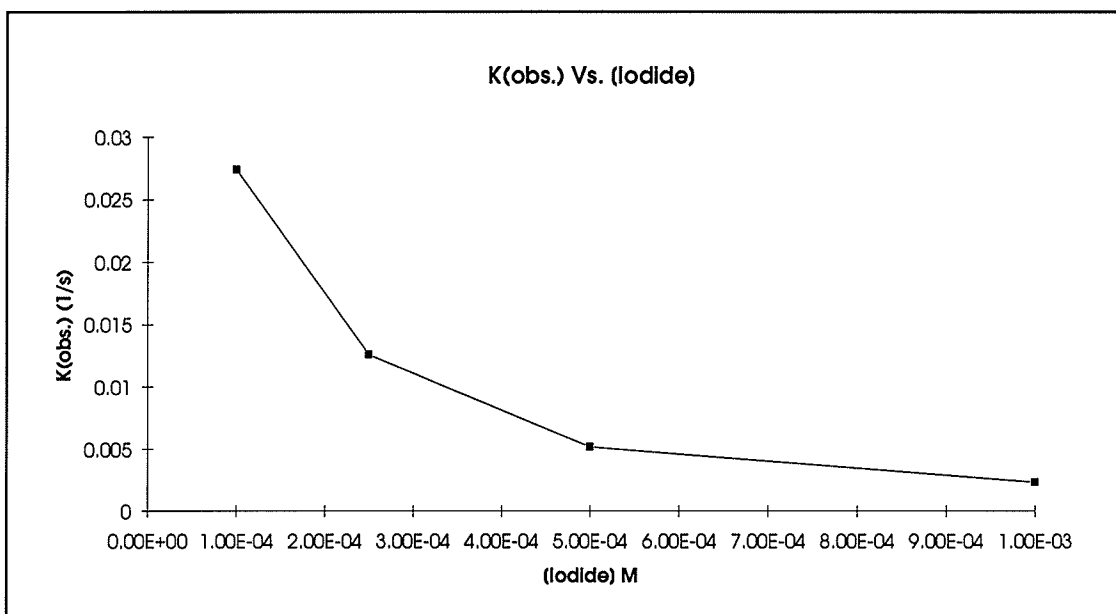
As phenols can react with Iodine via electrophilic substitution reactions under mild conditions, it would be helpful to study these reactions to assess their importance in terms of iodine mitigation. Many iodinations have been studied kinetically, and it is likely that 2-chlorophenol, and perhaps many other phenols, will obey the same general rate equation. After confirming this, rate constants of the reaction between I<sub>2</sub> and 2-chlorophenol will be determined. Rate of the 2-chlorophenol iodination will then be compared with that of other halogenated phenols.

Pseudo first order rate constants were attained by treating I<sub>2</sub> with an excess of 2-chlorophenol while following the reaction spectrophotometrically. Plots of k<sub>obs</sub> vs. various concentrations of I<sup>-</sup> displays a typical inverse function (Figure 3-15), as would be predicted for the rate equation. Thus a plot of 1/[I<sup>-</sup>] gives a straight line with a slope of:

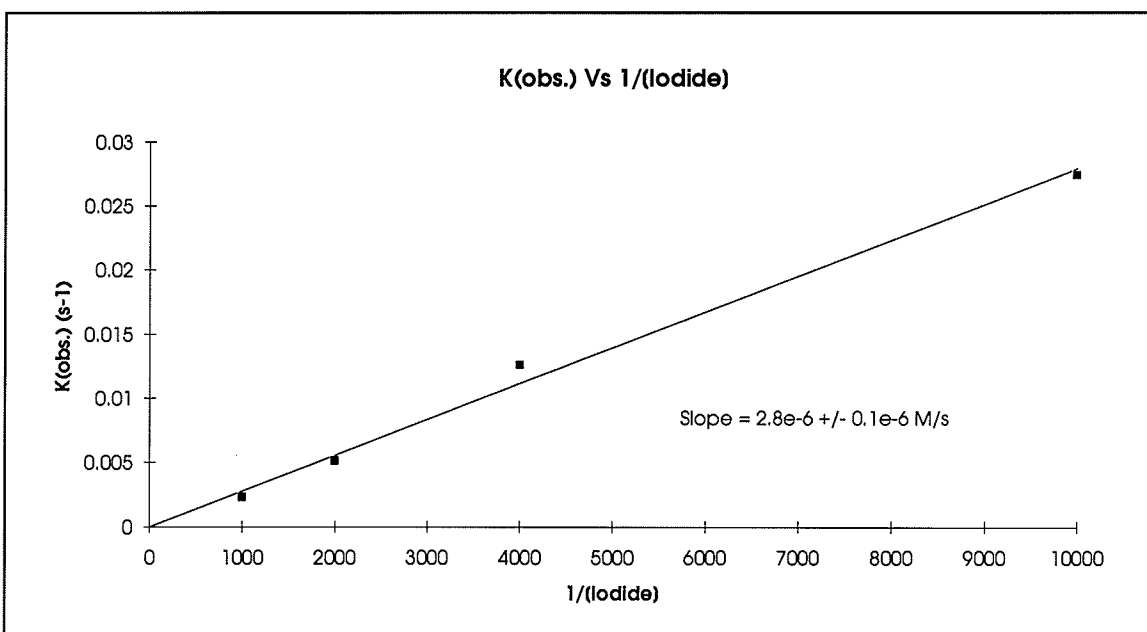
$$2.8e-6 = \frac{k[\text{phenol}]}{[H^+]} + \frac{k'[\text{Phenol}][\text{Buffer}]}{[H^+]^2} \quad (3-4)$$

The pH dependence of this reaction is displayed by a plot of k<sub>obs</sub> vs. [H<sup>+</sup>] (Figure 3-17). As pH rises, the reaction gets faster. This inverse relationship is described in the rate equation. The plot of k<sub>obs</sub> vs. 1/[H<sup>+</sup>] is linear and has a slope equal to:

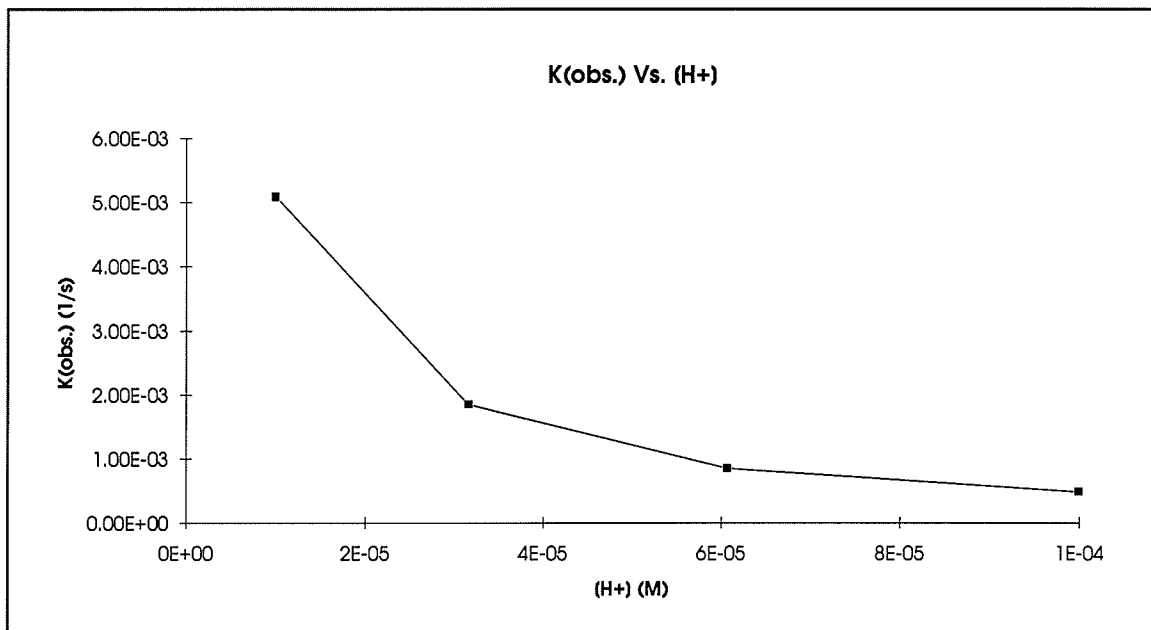
$$5.2e-8 = \frac{k[\text{phenol}]}{[I^-]} + \frac{k'[\text{Phenol}][\text{Buffer}]}{[H^+]} \quad (3-5)$$



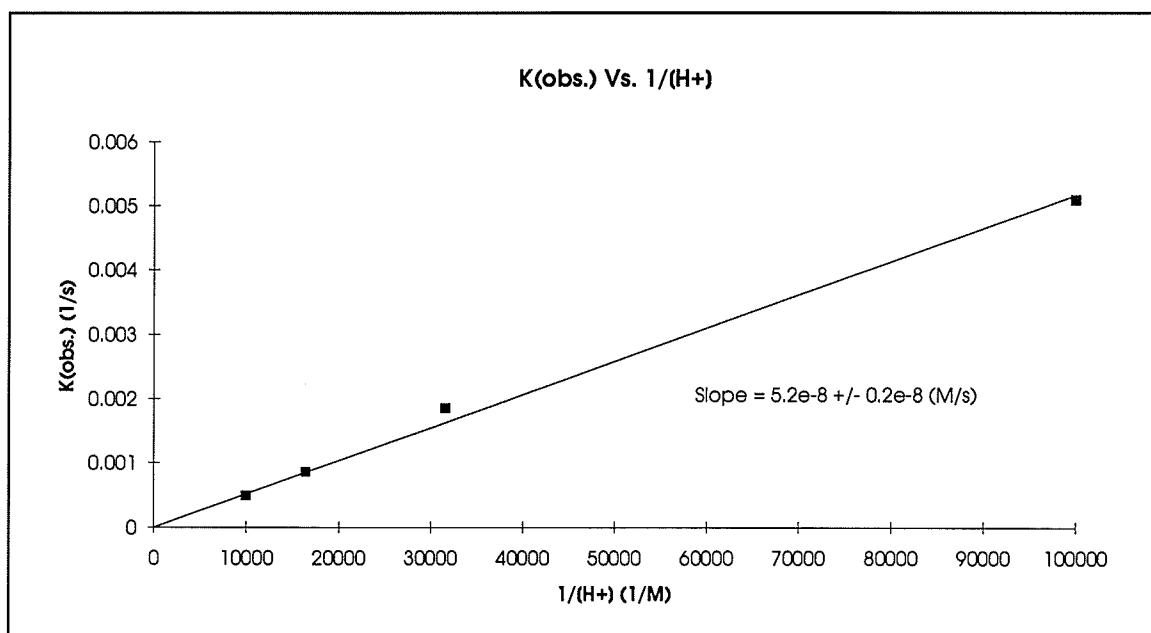
**Figure 3-15** - Conditions: 0.01M Acetate buffer, pH=5,  $1e-3M$  2-chlorophenol,  $25^{\circ}C$



**Figure 3-16** Conditions: 0.01M Acetate buffer, pH=5,  $1e-3M$  2-chlorophenol,  $25^{\circ}C$ .



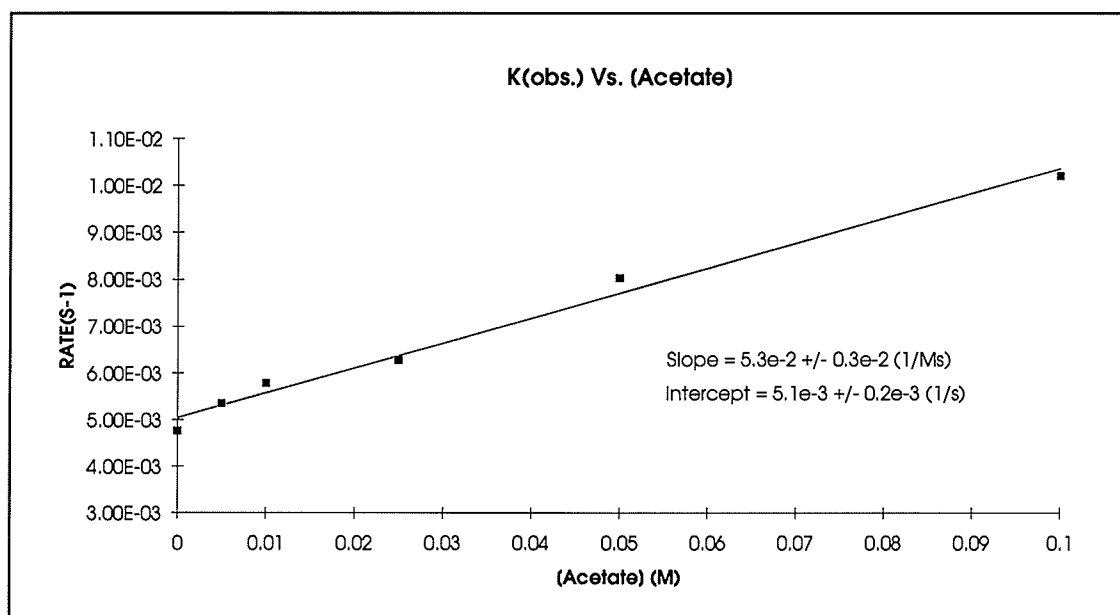
**Figure 3-17** - Conditions: 0.01M Acetate buffer, 5e-4M Iodide, 1e-3M 2-chlorophenol, 25°C.



**Figure 3-18** - Conditions: 0.01 M Acetate Buffer, 5e-4 M Iodide, 1e-3 M 2-chlorophenol, 25°C.

These relationships will be used to double check the  $k$  and  $k'$  values obtained in the plots of  $k_{\text{obs}}$  vs [Buffer] plots.

The general rate equation contains a buffer term since concentrations of various buffers have been shown to have an effect on the reaction rate. Various buffered solutions were run to determine to what degree the reaction may be catalyzed. An acetate buffer was tried first, as its pH range gives rates conveniently measurable by the HP spectrophotometer.



**Figure 3-19** - Conditions: pH=5, 1e-3 M 2-chlorophenol, 1e-5 M iodine, 25°C.

If all of the species are held constant except for concentration of buffer used,  $k$  can be obtained from the y-intercept and  $k'$  can be obtained from the slope:

$$\text{Intercept} = 5.1e-3 \text{ s}^{-1} = \frac{k[\text{Phenol}]}{[\text{H}^+][\text{I}^-]} \quad \therefore k = (2.6 \pm 0.3) e-8 \text{ M s}^{-1}$$



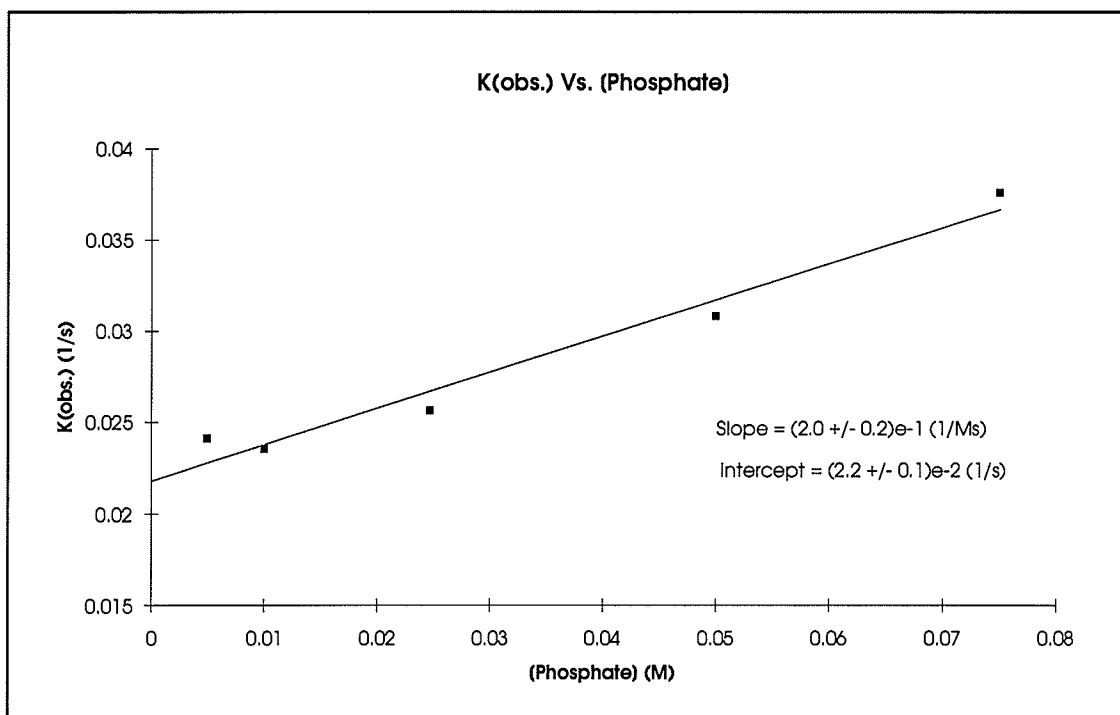
$$\text{Slope} = 5.3e-2 \text{ s}^{-1}\text{M}^{-1} = \frac{k'[\text{Phenol}]}{[\text{H}^+]^2 [\text{I}^-]} \quad \therefore k' = (2.7 \pm 0.5) e^{-12} \text{ M s}^{-1}$$

These  $k$  and  $k'$  values were then found to be reasonable after substituting them into the slope equations for the  $1/[\text{I}^-]$  and  $1/[\text{H}^+]$  plots (Equations 3-4 and 3-5). If very accurate rates are needed, many more points are required to achieve a better plot. Another buffer at a different pH and iodide concentration (phosphate, pH=6,  $[\text{I}^-]=1e-3\text{M}$ ) was tested to compare  $k$  values. The rate constants,  $k$ , are comparable taking their errors into consideration.

$$\text{Intercept} = 2.2e-2 \text{ s}^{-1} = \frac{k[\text{Phenol}]}{[\text{H}^+] [\text{I}^-]} \quad \therefore k = (2.2 \pm 0.3) e^{-8} \text{ M s}^{-1}$$

$$\text{Slope} = 2.0e-1 \text{ s}^{-1}\text{M}^{-1} = \frac{k'[\text{Phenol}]}{[\text{H}^+]^2 [\text{I}^-]} \quad \therefore k' = (2.0 \pm 0.2) e^{-13} \text{ M s}^{-1}$$

The  $k'$  value taken from the phosphate plot is smaller than that of the acetate plot. This demonstrates the species dependence of the buffer term. A quick calculation will show that the buffer's effect is almost negligible at concentrations less than  $10^{-3}$  M, and very small at  $10^{-2}$  M, which is the standard concentration used for most of these experiments. The error in these rate constants derives mainly from two sources, the scatter in the plot and the pH measurements.



**Figure 3-20** - Conditions: pH=6,  $1 \times 10^{-3}$  M 2-chlorophenol,  $1 \times 10^{-5}$  M iodine,  $25^\circ\text{C}$ .

Several other halogenated phenols were tested to determine the effect of different halogens on the ring in different positions. The results of these tests are given in Table 3-5. This may help determine why some phenols have shown more mitigating behaviour than others.

As these reactions were performed in the presence of  $5 \times 10^{-4}$  M iodide, a correction of  $1.35 (K_{\text{eq}}[\text{I}^-] + 1)$  must be applied to account for the fact that some of the total  $\text{I}_2$  added is tied up as  $\text{I}_3^-$  (see Equation 1-25).

**Table 3-5**

**Pseudo First Order Reaction Rates of Various Phenols**

<b>Substrate</b>	<b>pKa [65]</b>	<b>k<sub>obs</sub> (s<sup>-1</sup>)</b>
phenol	9.95	(1.06 ± 0.03)e-2
2-fluorophenol	8.82	(4.79 ± 0.06)e-3
2-chlorophenol	8.11	(6.3 ± 0.3)e-3
2-bromophenol	8.39	(8.7 ± 0.1)e-3
2-iodophenol	8.47	(1.20 ± 0.03)e-2
4-chlorophenol	9.20	(1.13 ± 0.05)e-3
4-iodophenol	9.20	(2.28 ± 0.09)e-3

**Note:** 1e-3 M halophenol, 5e-4 M I<sup>-</sup>, 1e-2 M Acetate buffer, pH-5.1, 25°C. Average of 3 runs. Error is estimated by the standard deviation between these runs.

The trend in Table 3-5 is such that the rate increases for rings with less electronegative halogens such as iodine and bromine. This is easily explained since the reaction is an electrophilic substitution process and thus is somewhat controlled by electron density in the ring. However, the data show that 2-iodophenol is faster (or very close considering error) than unsubstituted phenol. This suggests that the pKa of each phenol also plays a role and also supports the theory that the deprotonated phenol is the species that reacts with I<sub>2</sub>, not the protonated phenol reacting with HOI. Phenols with a lower pKa would have a higher population of phenoxide ion present at a given pH, therefore they would undergo a faster reaction. Nevertheless, all of the halogen substituted phenols have a lower pKa than unsubstituted phenol. Obviously, it can be concluded that pKa is not the only consideration.

Position of the halogen on the ring also has an effect on their reactivity. Both *para*-chlorophenol and *para*-iodophenol are slower than their *ortho* isomers. In both *para* and *ortho* isomers, the halogen is *meta* to the potential bonding sites. The position, however, affects the electron density at the oxygen, causing differences in pKa. The rate difference could also be explained if the *para* position is the more preferred location for substitution.

Under a radiation field, these reaction rates will change according to how the abundances of the various iodine species change by reacting with the radiolysis products of water. It may also be interesting to determine how another direct effect of radiation, hydroxylation of the aromatic ring, could affect the

**Table 3-6**

**Pseudo First Order Reaction Rates of Various Phenols**

<b>Substrate</b>	<b><math>k_{\text{obs}}</math> (<math>\text{s}^{-1}</math>)</b>
chlorohydroquinone	$30.9 \pm 0.6$
3-chlorocatechol	$219 \pm 9$

**Note:**  $1\text{e-}3$  M halophenol,  $5\text{e-}4$  M  $\text{I}^-$ ,  $1\text{e-}2$  M Acetate buffer, pH-5.1,  $25^\circ\text{C}$ . Average of 15 shots. Error is estimated by the standard deviation between these runs.

system. Two hydroxylation products of 2-chlorophenol, chlorohydroquinone and 3-chlorocatechol, were tested on the stopped-flow instrument under the same conditions (Table 3-6). These dihydroxyl species react orders of magnitude faster than 2-chlorophenol. Another strong electron donating group further activates the ring for electrophilic substitution. The significance of this result towards the iodine mitigation scheme is that hydroxylation of the aromatic rings is greatly facilitated. Not only are the hydroxyl radicals scavenged, but also the rings' ability to scavenge molecular iodine is increased.

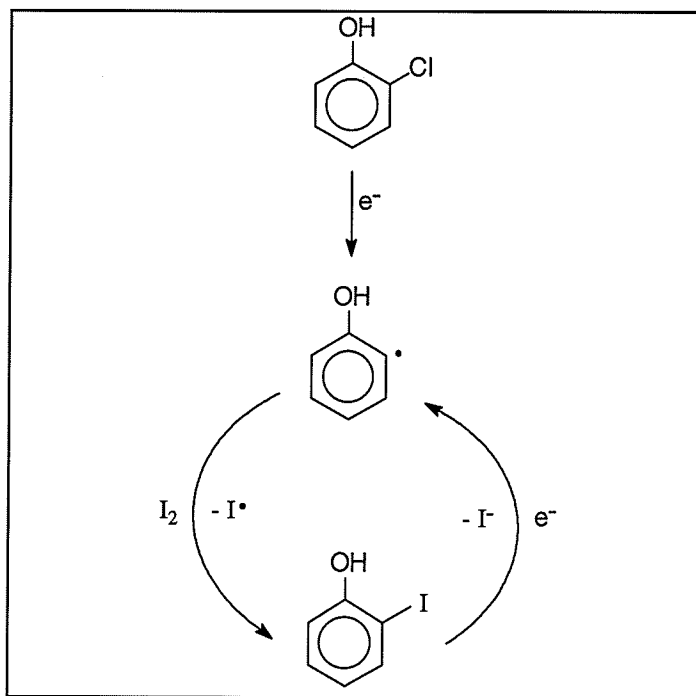
In summary, the rate of iodination of these phenols depends on the compound's pKa, the electronegativity of the halogen and its position on the ring.

### 3.3 Iodine Mitigation

The mitigation of molecular iodine is a combination of many mechanisms involving several species. It involves the confrontation of two complex radiolytic systems. The chlorophenol can disrupt the oxidation of iodide, and can consume  $I_2$  when it is formed. However, if iodine gets attached to the ring, it can be converted to iodide by the electron reaction. This is a convenient process from the point of view of mitigation of iodine in containment.

Besides the electrophilic addition reaction, another pathway to consume  $I_2$  could be through the reactive hydroxyphenyl radical. If  $I_2$  added to hydroxyphenyl radicals the subsequent electron reaction will not only dehalogenate the iodine on

the ring to yield the harmless iodide ion, but also will generate another hydroxyphenyl radical. Pulse radiolytic studies, discussed previously, showed that iodophenols will react about 10 times faster than chlorophenols. This will aid in the competition for electrons. This suggests the possibility that there may be a catalytic cycle by which iodine is converted to iodide using the aromatic ring and electrons (Figure 3-21). This is more difficult to prove because of the thermal



**Figure 3-21**

reaction (electrophilic addition) of the two species. This problem can be overcome by using a less activated aromatic ring. A methoxy group in place of the -OH on

the phenol will accomplish this. Chloroanisole reacts slowly, if at all, with molecular iodine without the aid of a secondary oxidant. The chlorine will be removed from the ring as in the 2-chlorophenol, resulting in a methoxyphenyl radical. Thus, if it is irradiated in the presence of  $I_2$ , 2-chloroanisole should be converted to 2-iodoanisole. The existence of 2-iodoanisole in the irradiated solution was confirmed by comparing retention times on (HPLC and GC) and mass spectral data to that of the pure compound. One difficulty in this test is that any 2-iodoanisole produced is also susceptible to reacting with electrons, leaving only a small amount to be detected. Figure 3-22 shows the results of this test.

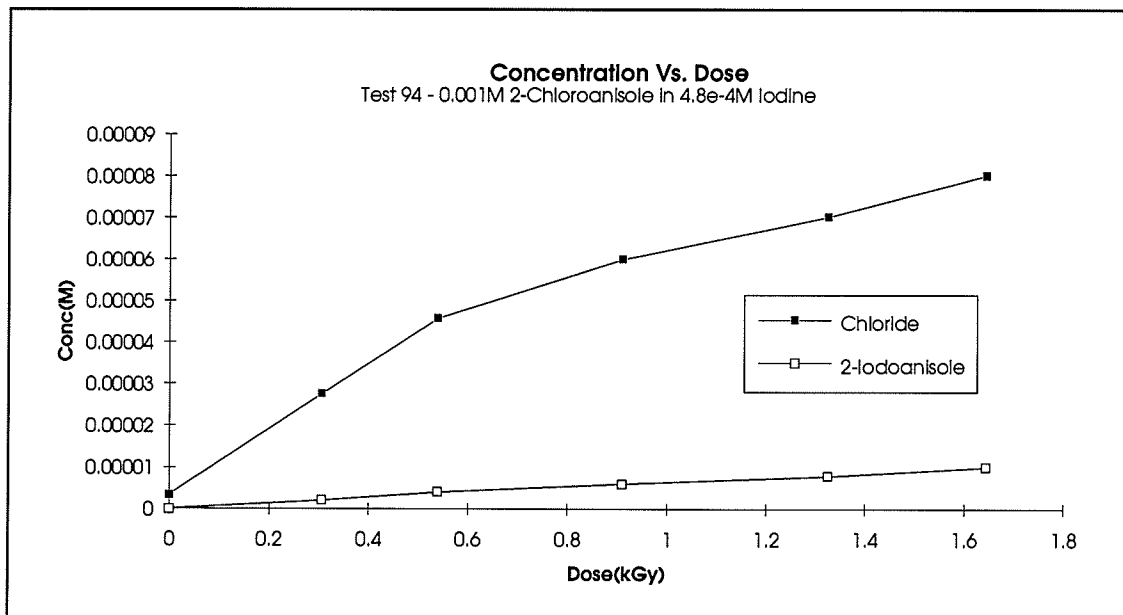


Figure 3-22

Although the iodoanisole concentration seems to increase with dose, the amount is much less than the amount of chloride ion liberated. This effect



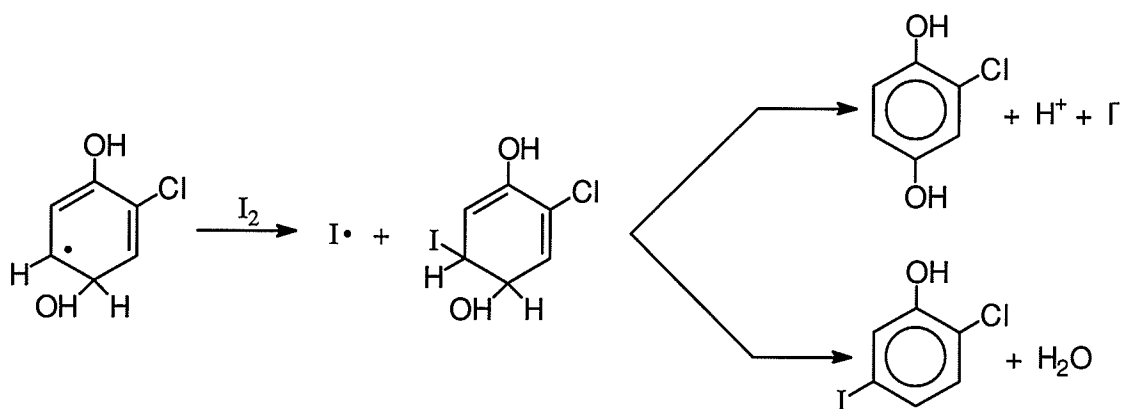
suggests that either chloride is produced faster than by electrons alone, or that the methoxy phenyl radicals can react with something other than  $I_2$ . Both possibilities are probably true. Small amounts of chloride ion can be produced by hydroxyl radicals and hydrogen atom as well as electron. Also, the methoxyphenyl radicals can react with another ring to form some sort of dimethoxy biphenyl species. There is a competition between the  $I_2$  and other rings (mostly 2-chloroanisole) for the methoxyphenyl radicals. As the concentration of 2-chloroanisole is about twice that of the iodine, the preferential formation of dimethoxy biphenyls compounds can be rationalised if the two rates are about equal.

Unfortunately, this experiment could not be done under conditions where electrons predominate. Iodine would have to compete with tert-butyl alcohol to scavenge the radical. But, since the concentration of tert-butyl alcohol is so high, anisole, and not iodoanisole, would probably result. In addition, the presence of hydrogen donors would also interfere with dimerization processes. In an oxygenated solution,  $I_2$  and  $O_2$  would have to compete for the radicals.

Although the hydroxyphenyl radical reactions with iodine may be orders of magnitude quicker than the thermal reaction, there will be only a small amount of the hydroxyphenyl radical present at any time. Initially, 2-chlorophenol will be in excess. Thus, the non-radical reaction of phenol and iodine would be of great importance.

There will, of course, be other radicals which may be able to react with  $I_2$ . One of these could be the hydroxyl radical adduct of the phenol

(dihydroxycyclohexadienyl radical). If iodine could add to this radical, it could likely be followed by some sort of elimination ( $\text{H}_2\text{O}$  or  $\text{HI}$ ) to regain aromaticity (Figure 3-23). Under these conditions, phenoxy radicals would also be present; however,



**Figure 3-23**

they are not very reactive. The reaction between oxygen and a phenoxy radicals ( $\text{PhO}\cdot$ ) is known to be very slow in comparison with the second order dimerization reaction. This trait is one of the reasons why phenols make effective antioxidants [66, 67]. Their reaction with  $\text{I}_2$  would probably be equally as weak.

Although the overall mitigation scheme involves many possible reactions, competition for several species should be considered before the impact of a reaction is evaluated. One of the major conflicts between the two systems is the competition for hydroxyl radicals. Iodide reacts with the hydroxyl radical at a rate of  $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [68], while 2-chlorophenol reacts with hydroxyl radicals at a rate of  $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . As the rates are very similar, this means that 2-chlorophenol will have to be in about 100 times in excess of the iodide ion to ensure that less than 1% of the hydroxyl radicals react with iodine. As the irradiation continues the

competition may shift as the concentration of 2-chlorophenol drops while products are forming. As most of the products are phenols or dihydroxyl species, the organic compounds will still compete effectively for the hydroxyl radicals. However, it would be helpful to know the rates of each of the products.

The competition for electrons has less impact as reductions of any of the species involved are favourable towards iodine mitigation. Iodine, oxygen, chlorinated phenols and iodinated phenols will all react with the hydrated electron.

Figure 3-24 displays a summary of the reactions involved in the mitigation of molecular iodine by 2-chlorophenol discussed thus far. At the centre of this scheme is the oxidation of iodide ion to molecular iodine, passing through the  $I_2^-$  intermediate. Also shown are the various pathways that either prevent the oxidation from occurring, or reduce the amount of iodine that does get produced. Of course all of these products will be subjected to the primary radiolysis products of water to undergo further oxidation or reduction.

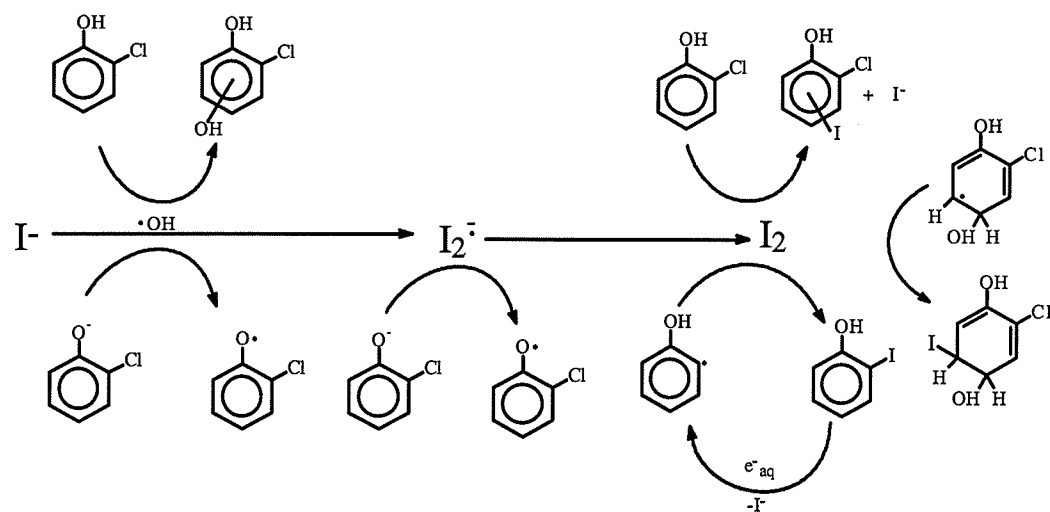


Figure 3-24

#### **4 Conclusions**

Mitigation of molecular iodine by halogenated phenols is a complex collection of reactions by species generated in the radiolysis of iodide and the radiolysis of the phenol. Although some non-radical reactions are involved, most of the interesting changes in the solution are brought about by the radiolysis products of water, primarily hydroxyl radicals and aqueous electrons.

The identification of the radiolysis products and verification of the process in which the product was formed is as essential step in understanding the system. Most products are the result of reaction with the electron or the hydroxyl radical.

The major products of the reaction of 2-chlorophenol with the hydroxyl radicals are chlorohydroquinone and 3-chlorocatechol. The implication of the presence of hydroxylated products in terms of iodine mitigation is that hydroxyl radicals have an alternate reaction to the oxidation of the iodide ion. This competition is governed by rates and concentration of the phenol and iodide. Although the formation of iodine can be greatly reduced on the basis of this reaction alone, some molecular iodine is always produced. Also, it is helpful to know what will happen when the radiolysis products start building up.

Reaction rates of chlorophenols with the hydroxyl radicals are of the order of  $1.2 \times 10^{10}$  to  $1.5 \times 10^{10} \text{ s}^{-1}\text{M}^{-1}$ . Iodophenols react somewhat slower, with rates ranging from  $8.9 \times 10^9$  to  $9.6 \times 10^9 \text{ s}^{-1}\text{M}^{-1}$ . However, not every reaction results in a hydroxylated product, since a phenoxy radical and a hydroxide ion may also be produced. This depends upon the pH and the presence of oxygen. Since the

iodide ion reacts with hydroxyl radicals at a rate of  $1.1 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$ , 2-chlorophenol will need to be at a concentration of about 100 times the concentration of iodide ion to be an effective hydroxyl radical scavenger.

The major product of the electron reaction is chloride ion, and either phenol or chloro-dihydroxybiphenyls depending upon the solution composition of the solution. The formation of 3'-chloro-2,4'-dihydroxybiphenyl was confirmed by the synthesis and subsequent comparison of data to that of the radiolysis product. Also, the formation of an isomer, 3-chloro-2,2'-dihydroxybiphenyl, is suspected. While the presence of chloride and phenol confirm a dehalogenation reaction, the formation of chlorobiphenols support the idea of a reactive hydroxyphenyl radical as an intermediate. This hydroxyphenyl radical is a reactive species that may scavenge molecular iodine. The dehalogenation reaction is important because it provides a means of releasing iodide from an aromatic ring as iodide. Although a catalytic reaction to scavenge iodine and release iodide ion utilizing the electron reaction is possible, the phenyl radicals are subject to reaction with the starting material, which is initially in excess.

The electrophilic reaction of iodine with phenols provides a means of destroying the molecular iodine before it can escape into the gas phase. As all of the known radiolysis products are also phenols of some sort, there will likely be an electrophilic substitution reaction with each of them. Kinetic studies on two of the radiolysis products, chlorohydroquinone and 3-chlorocatechol, have demonstrated that the reaction may also be much faster than the original substrate.

Halogens will be removed from the ring as the corresponding halide ions. This process is important to the iodine mitigation scheme as it provides a pathway of reducing molecular iodine to iodide ion utilizing the aromatic ring. The yield of iodide in a deaerated solution of 2-iodophenol is approximately 3.5, most of which is due to reduction by the aqueous electron. The remainder is due to hydroxyl radicals and hydrogen atoms. In comparison, chloride yield from 2-chlorophenol is about 2. This difference may be attributed to relative carbon-halogen bond strength.

Rates of reaction of iodinated aromatic compounds with the aqueous electron are about  $1.1 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$  at a pH of 5. Rates appear to follow a progression down the halogen group in the order of bond strength. Iodinated compounds are the fastest.

Pulse radiolysis experiments are important to study rates and radical intermediates. Unavailability of an appropriate instrument has limited progress in this aspect of the study. Acquiring rates of reaction of hydroxyphenyl radicals, phenoxy radicals and  $\text{I}_2^-$  are among some of the experiments to be tried.

Knowledge of the reactions of phenols with iodine species in the presence of radiation are not limited to the concept of mitigation. Other aromatic compounds may be present in a containment building, all of which will display similar radiation chemistry. Hydroxylation of any aromatic ring may occur, forming a phenolic compound which may have chemistry similar to the compounds in the present study.

## **5 Recommendations**

Pulse radiolysis experiments are important to study rates and radical intermediates. Unfortunately, the unavailability of an appropriate instrument has limited progress in this aspect of the study. For example, it was discovered that the hydroxylation products of 2-chlorophenol undergo iodination faster than 2-chlorophenol itself. The question is whether this holds true for the addition of hydroxyl radicals. Iodine atoms ( $I\cdot$ ), are generated by the oxidation of iodide ions. Do they have any interaction with phenolic compounds? Rates of reaction of hydroxyphenyl radicals, phenoxy radicals and  $I_2\cdot^-$  would be valuable experimental data. These reactions cannot be monitored unless observed in their appropriate time scale. More kinetic data of this sort will show what reaction pathways are the most important. Steady state experiments show complementary data on the final products of these reactions.

The matrix of possible conditions is very large. The presence of air, alcohols and pH have been identified as having some effect on the system. Another possibly important factor in this system is dose rate. As the population of radicals at any given time is increased, the chances of dimerization and radical recombinations increase. Another possible investigation could be on the effect of hydrogen peroxide on both the products and electrophilic substitution reaction. During this study, it became apparent that oxygen could change the radiolysis products of 2-chlorophenol, including increased rate of hydroxylation. Also, the formation of chlorobiphenols decreased, presumably because oxygen adds to the



hydroxyphenyl radical. It would be desirable to elucidate the next step in this process and determine the ultimate products in it.

One problem with using organic compounds in a radiation field is that eventually the rings will split and decay into small compounds and  $\text{CO}_2$ . It would be helpful to study exactly how this happens and how it can be minimized so that better mitigating molecules can be chosen. If this ring-splitting mechanism requires oxygen [69], it could be desirable to determine how much the stability of aromatic rings is increased in deaerated solutions.

A possible reaction that could be added to the iodine mitigation scheme is the addition of iodine to the hydroxyl radical adduct of 2-chlorophenol. However the experiment could not be done with 2-chlorophenol because of the electrophilic addition reaction. One would have to use a nitrous oxide saturated solution of 2-chloroanisole and then look for the appropriate product.

The system studied involves many species interacting in many ways. With further experimental data, the impact of a phenolic mitigant in containment may be fully understood.

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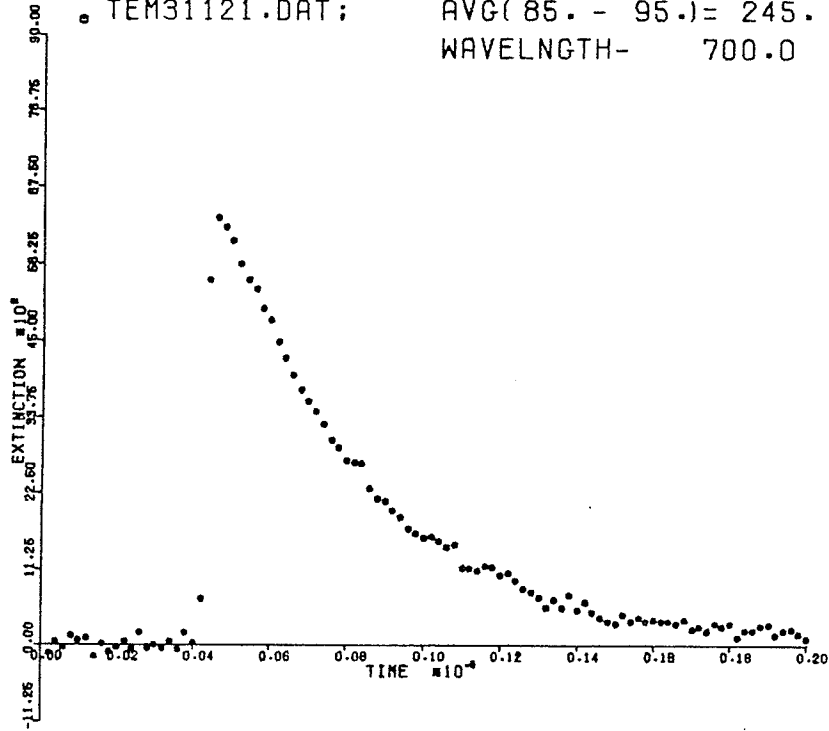
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**APPENDIX**

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Pulse Radiolysis Trace  
Absorbance at 700 nm (aqueous electron)



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BRUKER

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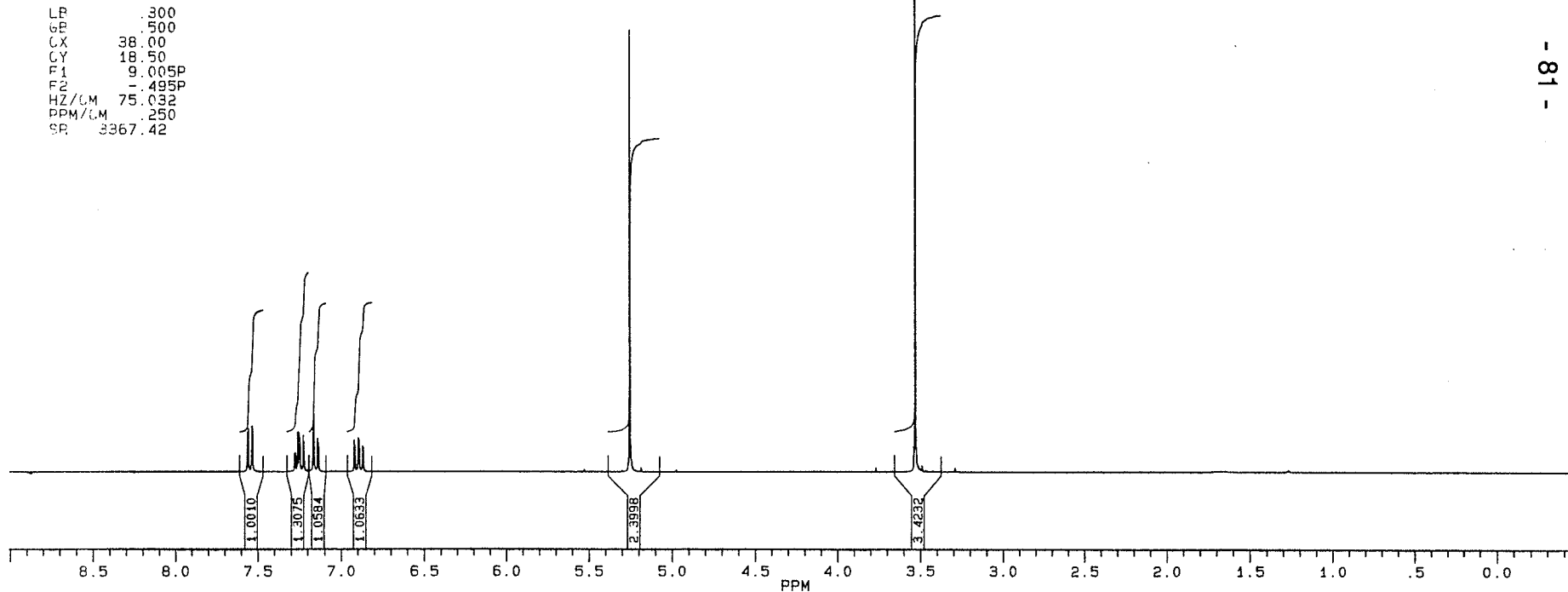
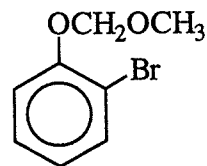
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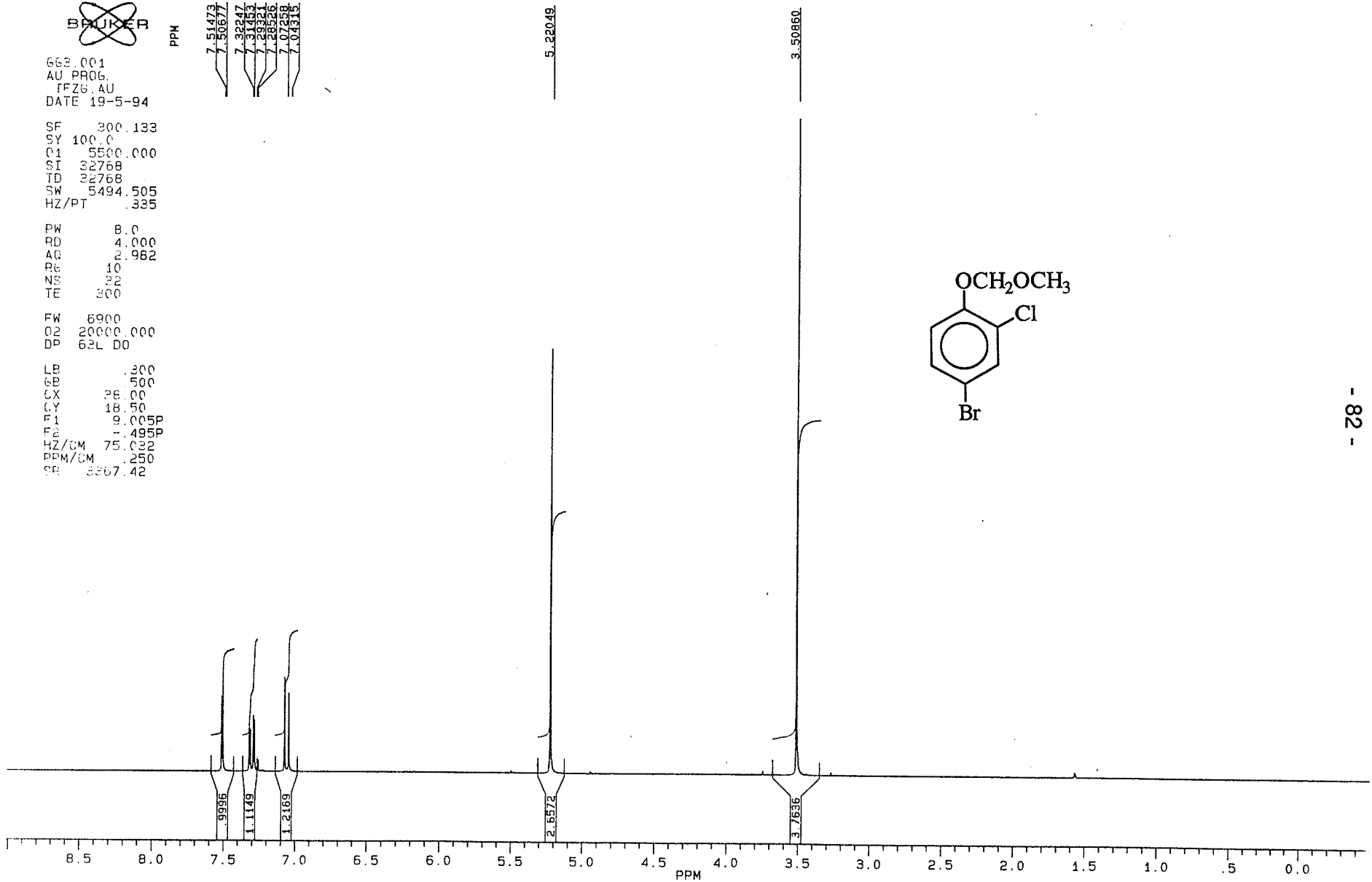
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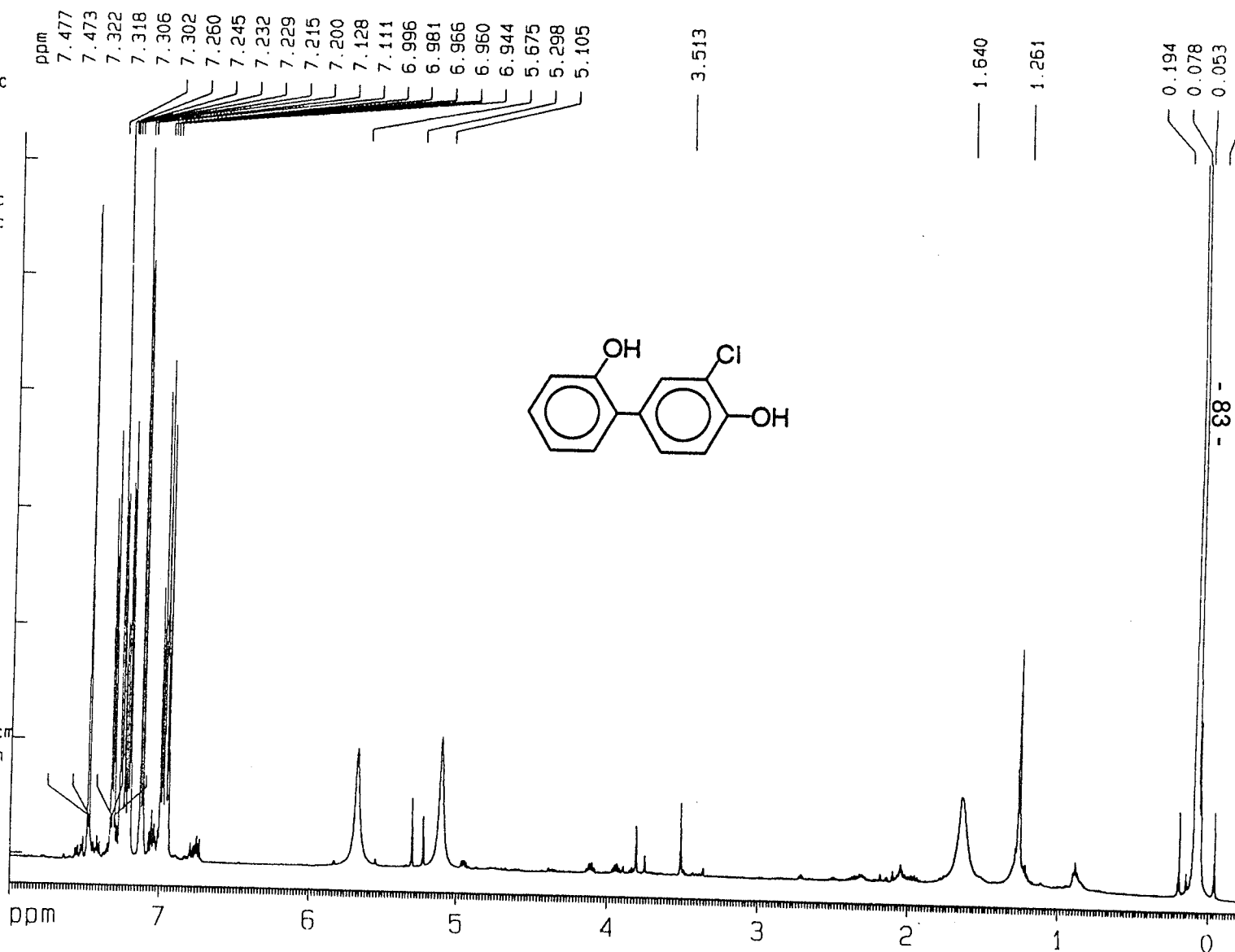
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Current Data Parameters

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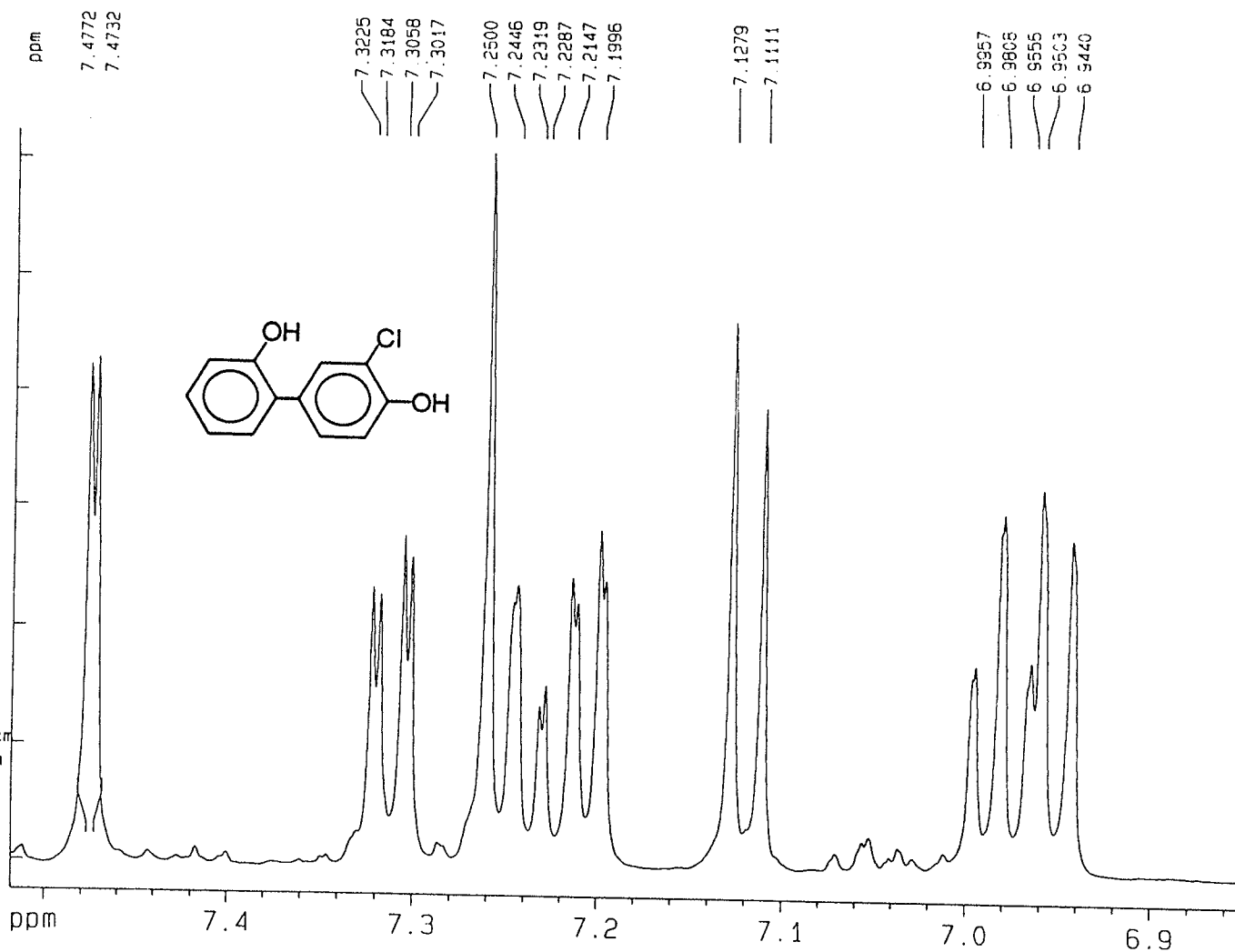
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Glenn Glowa sample #2 1-H at 500 MHz in CDCl3 at 300K



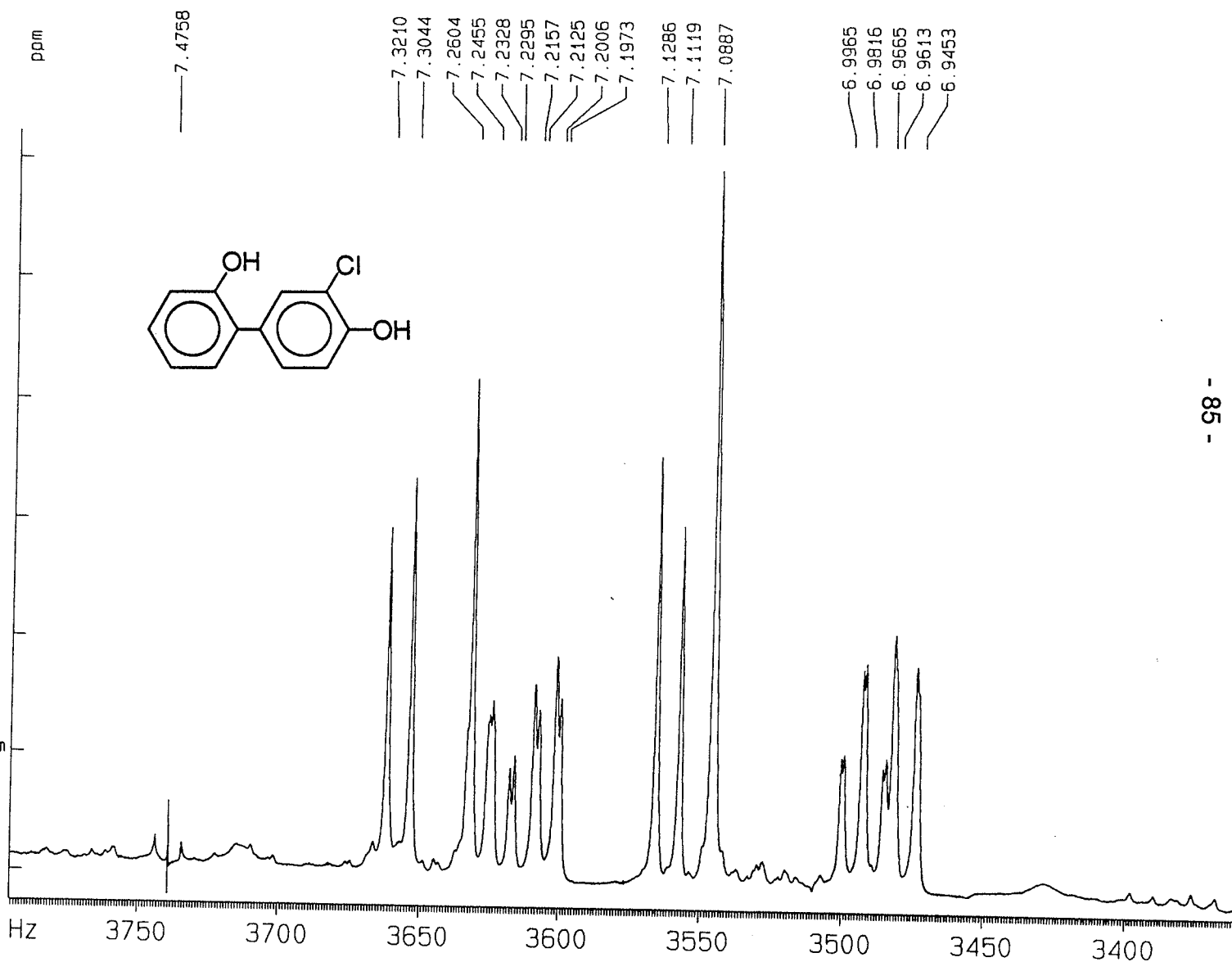
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P1 10.0 usec  
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### G. Glowa SAmple 2 Homodecoupling at 7.47 ppm

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Current Data Parameters

NAME srin-glowa2  
 EXPNO 5  
 PROCNO 1

Glowa #2 homodecoupling at 7.31 ppm

F2 - Acquisition Parameters

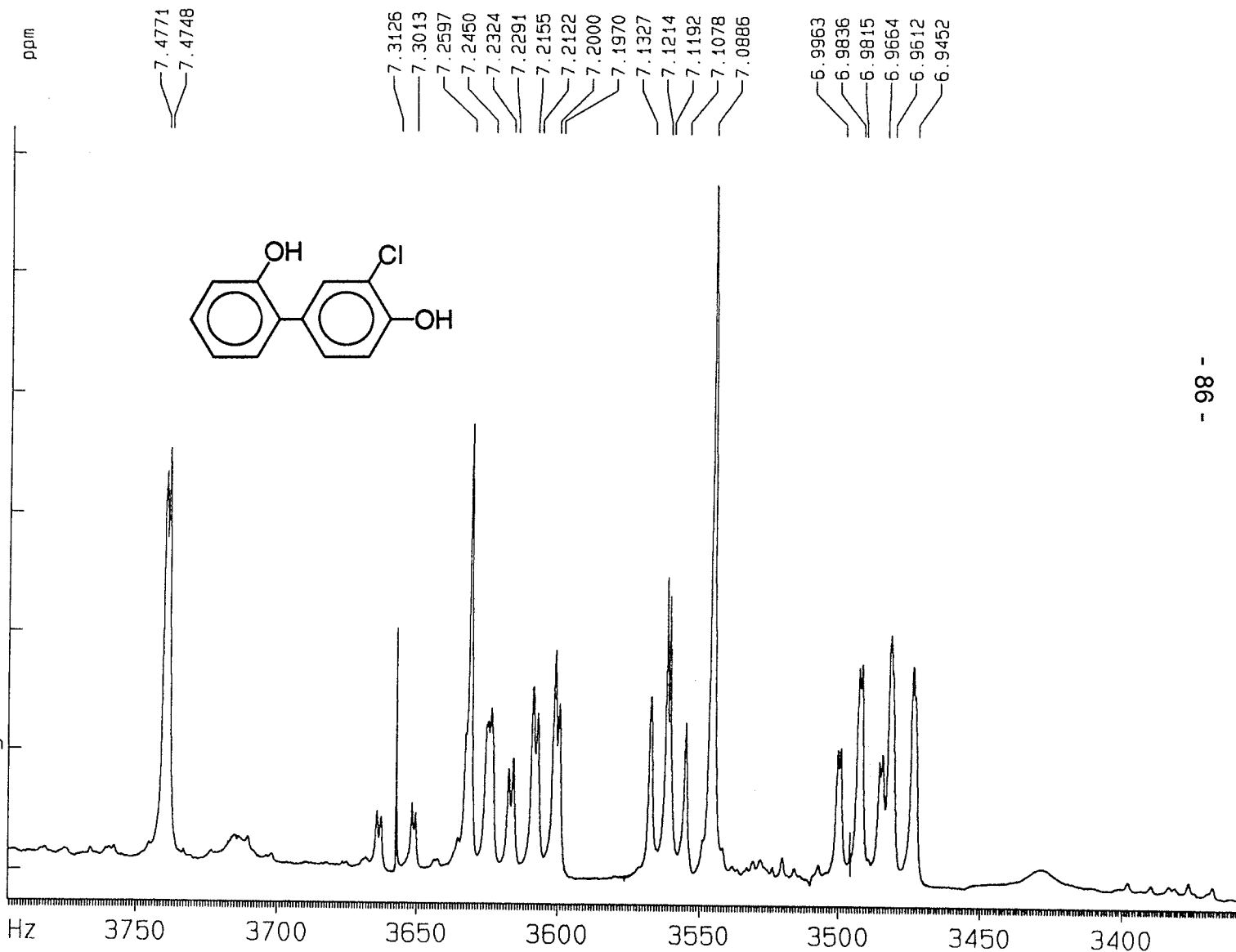
Date 940912  
 Time 14.22  
 PULPROG zghdh2  
 SOLVENT CDCl3  
 AQ 18.6941643 sec  
 FIDRES 0.026746 Hz  
 DW 1141.0 usec  
 RG 128  
 NUCLEUS 1H  
 HL1 4 dB  
 D12 0.0000200 sec  
 D1 10.0000000 sec  
 P1 10.0 usec  
 DE 1426.3 usec  
 SFO1 500.1389970 MHz  
 SWH 438.21 Hz  
 TD 16384  
 NS 8  
 DS 1

F2 - Processing parameters

SI 32768  
 SF 500.1354205 MHz  
 WDW EM  
 SSB 0  
 LB 0.05 Hz  
 GB 0  
 PC 4.00

1D NMR plot parameters

CX 20.00 cm  
 F1P 7.589 ppm  
 F1 3795.59 Hz  
 F2P 6.713 ppm  
 F2 3357.37 Hz  
 PPMCM 0.04381 ppm/cm  
 HZCM 21.91060 Hz/cm



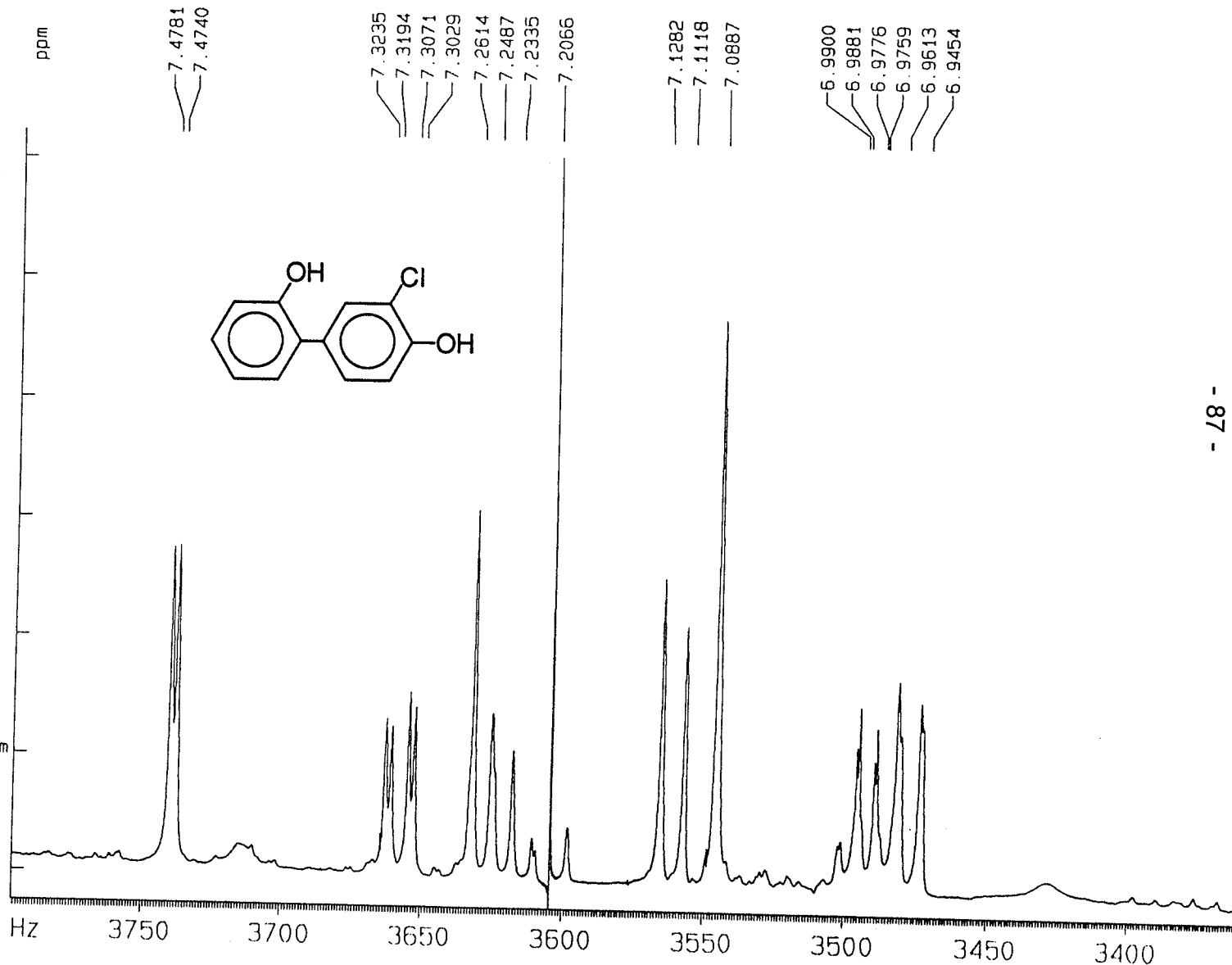
Current Data Parameters  
 NAME srin-glowa2  
 EXPNO 6  
 PROCNO 1

G. Glowa's sample #2 homodec. at 7.2 ppm

F2 - Acquisition Parameters  
 Date 940912  
 Time 14.26  
 PULPROG zgpdh2  
 SOLVENT CDCl3  
 AQ 18.6941643 sec  
 FIDRES 0.026746 Hz  
 DW 1141.0 usec  
 RG 128  
 NUCLEUS 1H  
 HL1 4 dB  
 D12 0.0000200 sec  
 D1 10.0000000 sec  
 P1 10.0 usec  
 DE 1426.3 usec  
 SF01 500.1389970 MHz  
 SWH 438.21 Hz  
 TD 16384  
 NS 8  
 DS 1

F2 - Processing parameters  
 SI 32768  
 SF 500.1354205 MHz  
 WDW EM  
 SSB 0  
 LB 0.05 Hz  
 GB 0  
 PC 4.00

1D NMR plot parameters  
 CX 20.00 cm  
 F1P 7.589 ppm  
 F1 3795.59 Hz  
 F2P 6.713 ppm  
 F2 3357.37 Hz  
 PPMCM 0.04381 ppm/cm  
 HZCM 21.91060 Hz/cm



Current Data Parameters

NAME srin-glowa2  
EXPNO 7  
PROCNO 1

F2 - Acquisition Parameters

Date 940912  
Time 14.43  
PULPROG zgpg30  
SOLVENT CDC13  
AQ 18.6941643 sec  
FIDRES 0.026746 Hz  
DQ 1141.0 usec  
RG 128  
NUCLEUS 1H  
HL1 4 dB  
D12 0.0000200 sec  
D1 10.0000000 sec  
P1 10.0 usec  
DE 1426.3 usec  
SF01 500.1389970 MHz  
SWH 438.21 Hz  
TD 16384  
NS 8  
DS 1

F2 - Processing parameters

SI 32768  
SF 500.1354205 MHz  
WDW EM  
SSB 0  
LB 0.05 Hz  
GB 0  
PC 4.00

1D NMR plot parameters

CX 20.00 cm  
F1P 7.589 ppm  
F1 3795.59 Hz  
F2P 6.713 ppm  
F2 3357.37 Hz  
PPMCM 0.04381 ppm/cm  
HZCM 21.91060 Hz/cm

G. Glowa's sample #2 homodec. at 6.92 ppm

