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6. AUTHOR(S) Dr Anders W. Andren	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Water Chemistry Program University of Wisconsin-Madison 660 N. Park St., Madison, WI 53706	8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR- 8
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13. ABSTRACT (Maximum 200 words)

The overall objectives for this project is to improve and evaluate present assessment procedures which are designed to predict the transport and fate, including degradation pathways, of compounds of interest to the Air Force sphere. Specifically, our sub-objectives may be summarized to: (1) Continue to update and improve aqueous solubility, octanol-water partition coefficient, and vapor pressure predictive techniques as new property data appear in the literature. (2) Study the effect of cosolvents, cosolutes, colloids, and temperature on aqueous solubility of solutes of interests and evaluate/develop thermodynamic, semiempirical, and empirical predictive schemes. (3) Evaluate and develop structure-activity relationships to predict rates, mechanisms, and extent of environmental abiotic and biotic degradation of chemicals of environmental interest. (4) Provide realistic computer generated compound behavior profiles for a variety of these compounds. In this progress report we address what we feel are the most important environmental degradation pathways in addition to direct photolysis, namely liquid phase homogeneous and heterogeneous OH radical reactions. We have focussed our attention on chlorinated aromatic hydrocarbons (chlorobenzene), since these compounds cover a broad range of compounds that are of environmental interest. Results from

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these investigations will help us both in understanding environmental fate as well as in designing remedial action measures of CAHs.

MOLECULAR PROPERTIES AND FATE OF ORGANIC CHEMICALS

ANDERS W. ANDREN
DAVID E. ARMSTRONG
DAVID L. SEDLAK

WATER CHEMISTRY PROGRAM
UNIVERSITY OF WISCONSIN-MADISON
660 N. PARK ST., MADISON
WISCONSIN 53706

PROGRESS REPORT FOR THE PERIOD ENDING 9/14/1990

PROJECT OFFICER T. J. CERVANY, MAJOR
LIFE SCIENCE DIRECTORATE

A. BACKGROUND

One of the most useful environmental modeling approaches integrates data on physicochemical properties of a compound with hydrodynamic or aerodynamic transport models. This approach uses the results from such laboratory measurements or calculations as aqueous solubility, saturation vapor pressure, liquid and vapor molecular diffusivities, Henry's Law Coefficient, photolysis rate, UV absorption, sorption partition coefficient, abiotic and biotic degradation rates e.t.c. These data are then incorporated into various steady-state and time dependent transport models.

In implementing these models it quickly became apparent that much of the aforementioned data were lacking for many chemicals of environmental interest. Prohibitive logistical and economic constraints also prevents laboratories from determining these properties and reaction pathways for all chemical of interest.

Our laboratory has developed extensive experience and expertise in the determination of a variety of molecular properties. In this project we have moved on to more complicated systems, i. e. mixed solute/solvent. We have also begun to examine degradation pathways for hydrophobic organic chemicals. In particular, free hydroxyl radical reactions with model chlorinated aromatic compounds. We have studied both reaction kinetics, pathways, as well as prediction methods for reaction rates.

The overall objectives for this project is to improve and evaluate present assessment procedures which are designed to predict the transport and fate, including degradation pathways, of

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compounds of interest to the Air Forcesphere. Specifically, our sub-objectives may be summarized to: (1) Continue to update and improve aqueous solubility, octanol-water partition coefficient, and vapor pressure predictive techniques as new property data appear in the literature. (2) Study the effect of cosolvents, cosolutes, colloids, and temperature on aqueous solubility of solutes of interests and evaluate/develop thermodynamic, semiempirical, and empirical predictive schemes. (3) Evaluate and develop structure-activity relationships to predict rates, mechanisms, and extent of environmental abiotic and biotic degradation of chemicals of environmental interest. (4) Provide realistic computer generated compound behavior profiles for a variety of these compounds.

In this progress report we address what we feel are the most important environmental degradation pathways in addition to direct photolysis, namely liquid phase homogeneous and heterogeneous OH radical reactions. We have focussed our attention on chlorinated aromatic hydrocarbons (chlorobenzene), since these compounds cover a broad range of compounds that are of environmental interest. Results from these investigations will help us both in understanding environmental fate as well as in designing remedial action measures for CAHs.

B. INTRODUCTION

Chlorinated aromatic hydrocarbons (CAHs) have been introduced to the environment from a variety of anthropogenic sources. Many of these compounds are resistant to biodegradation and pose a

threat to biota and human populations. Understanding chemical mechanisms through which these compounds are degraded is critically important to describing their environmental fate and designing efficient, effective chemical treatment systems.

Hydroxyl radicals ($\text{OH}\cdot$) are some of the most effective known chemical oxidants of CAHs under laboratory conditions and may play an important role in the oxidation of CAHs in the environment. Hydroxyl radicals are responsible for most of the CAH degradation in the troposphere (1,2) and are present in many surface waters (3). In water treatment systems which employ ozone, secondary reactions which result in the production of $\text{OH}\cdot$ may be an important oxidant source (4).

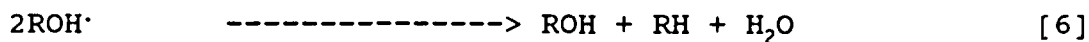
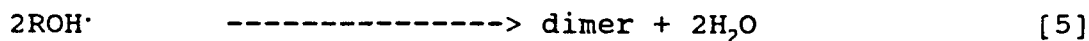
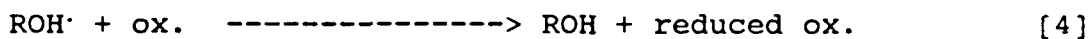
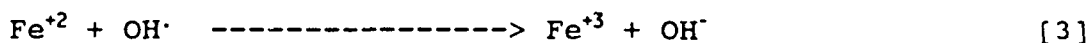
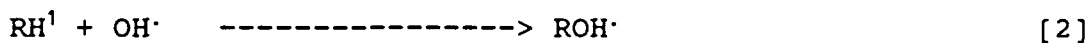
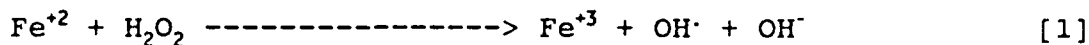
Recently, it has been proposed that hydroxyl radicals generated by the reaction of hydrogen peroxide and ferrous iron (Fenton's Reagent) may be a viable means of treating water, soil and sediments contaminated with CAHs (5,6). Under laboratory conditions it has been demonstrated that Fenton's Reagent is capable of oxidizing a variety of aromatic hydrocarbons (see 7-9 for examples) and preliminary reports indicate that pilot scale Fenton's Reagent waste treatment systems will be built in the near future.

To most effectively use the Fenton's Reagent reaction in an actual waste treatment system it will be necessary to thoroughly understand its reaction mechanism and kinetics. Several important questions which can be answered from this type of information include: (1) How much H_2O_2 and Fe^{+2} will be required to oxidize a given amount of waste? (2) Will any potentially hazardous and/or

recalcitrant byproducts be produced? (3) What are the optimal conditions for carrying out the reaction? During the past year we have gained a fundamental understanding of the mechanism and kinetics of the Fenton's Reagent oxidation of CAHs by conducting a series of experiments under conditions relevant to waste treatment systems. These results may also provide information which will improve our ability to predict the mechanisms and rates of CAH degradation in the environment.

a. Background Information on Fenton's Systems.

It is generally accepted that the Fenton's Reagent reaction acts according to the following scheme (9):



Reaction 1 results in the production of OH·, which are consumed by either an organic compound or Fe⁺² in reactions 2 and 3, respectively. Under most conditions reaction 3 is insignificant in the oxidation of aromatic compounds because the rate constant for reaction 2 (k₂) is generally one to two orders of magnitude greater than the rate constant for reaction 3 (k₃) (10,11). The organic radicals produced in reaction 2 can undergo three possible fates: reaction with an oxidant (such as Fe⁺³ or O₂) in reaction 4; dimerization (reaction 5); and bimolecular disproportionation

¹RH represents an organic compound

(reaction 6). It should be noted that when Fe^{+3} acts as the oxidant in reaction 4, Fe^{+2} is regenerated and the catalytic cycle can continue.

The expected reaction pathway for benzene (illustrated in Figure 1) contains several possible pathways through which products may be produced. In addition to the reactions described above, Walling and Johnson (12) hypothesized the existence of a reaction, in which the intermediate hydroxycyclohexadienyl radical (HCD) eliminates water and is reduced by Fe^{+2} , thereby yielding no net oxidation. Conditions such as oxidant concentrations, pH and substrate concentrations will affect the relative importance of each reaction along the branched pathway. A brief review of these factors is presented in the following paragraphs with an emphasis on their effect on product yields and distributions.

The concentrations and strengths of oxidants present in the system alter the importance of reaction 4 relative to reactions 5 and 6. At high oxidant concentrations reaction 4 dominates and HCD is quantitatively oxidized to phenol. This is the most efficient oxidation pathway because only one mole of $\text{OH}\cdot$ is necessary for each mole of product and the loss of H_2O_2 by reaction 7 is minimized. If O_2 acts as the oxidant several additional reactions may occur including: release of hydroperoxy radical ($\text{HO}_2\cdot$) followed by regeneration of H_2O_2 (13,14) or formation of diols (14). At low oxidant concentrations phenol or biphenyl are produced via reactions 5 and 6.

It has been demonstrated that product yields and distributions are also dependent on pH (5,15); however the mechanism through

which this effect occurs has not been fully explained. One possible mechanism for the pH effect is the existence of one or more acid catalyzed reactions. For example, it has been suggested that reaction 7 (12) and reaction 9 (16) are acid catalyzed. A pH dependence for the reaction rate constants would explain both lower overall yields and higher diol production at low pHs.

Another possible explanation for the pH effect is the formation of Fe^{+3} complexes and precipitates (see Figure 2). Assuming that reduction of Fe^{+3} by HCD radicals only occurs when Fe^{+3} is in an uncomplexed form, yields will decrease as pH increases (provided that reaction 4, where Fe^{+3} acts as the oxidant is important). At high pH values all of the Fe^{+3} forms complexes such as $\text{Fe}(\text{OH})^{+2}$, $\text{Fe}_2(\text{OH})_2^{+4}$ or organometallic complexes and at higher pHs $\text{Fe}(\text{OH})_3$ will precipitate.

Consideration of reactions 1-6 also indicates that substrate concentrations (Fe^{+2} , H_2O_2) will affect the relative importance of the various reaction pathways. The concentrations of H_2O_2 and Fe^{+2} control the instantaneous concentration of $\text{OH}\cdot$ produced in reaction 1, which, in turn controls the instantaneous concentration of HCD radicals through reaction 2. Because reaction 4 is first order with respect to HCD radicals (rate expression: $k_4[\text{HCD}]$) and reactions 5 and 6 are second order with respect to HCD radicals (rate expressions: k_5 or $k_6 [\text{HCD}]^2$), the yield of products produced in reactions 5 and 6 (where R can be phenol or biphenyl) will decrease relative to products formed in reaction 4 (phenols) as the value of $[\text{Fe}^{+2}][\text{H}_2\text{O}_2]$ decreases. Thus, addition of all of the H_2O_2 and Fe^{+2} at the beginning of the reaction may be less efficient in terms of

product yield per H_2O_2 oxidized and result in a higher proportion of dimeric products than addition of the same amount of reactants over a longer time period².

b. Experimental Approach and Preliminary Results

1. Solution Reactions

A series of experiments were conducted on the oxidation of chlorobenzene and its oxidation products by Fenton's Reagent to evaluate some of the variables discussed above. Chlorobenzene was selected as a model CAH because it is an EPA priority pollutant and is relatively soluble in water. It is also a good model compound because information such as reaction rate constants and intermediate products for the oxidation of similar compounds (i.e.- benzene, phenol) by $\text{OH}\cdot$ is available in the literature. Finally, we also chose chlorobenzene because one of the dimeric products which could be produced in the reaction is dichlorobiphenyl, which could be more recalcitrant and toxic than chlorobenzene.

The general approach for evaluating the oxidation pathway was to conduct the reaction under controlled conditions and monitor the loss of reactants and/or the formation of products. Intermediate products, identified by GC/MS and/or HPLC, were quantified where possible and pure solutions of those materials were reacted with Fenton's Reagent. Finally, the complete mineralization of chlorobenzene was followed by monitoring concentrations of

²The time required for reaction 1 to go to completion is very fast. For example, in a solution which is 1 mM Fe^{+2} and 1 mM H_2O_2 reaction 1 will be more than 99% complete in 0.1 seconds.

intermediate compounds (identified in previous reactions) and dissolved organic carbon (DOC) during the slow addition of H_2O_2 to a chlorobenzene solution.

Results from oxidation of chlorobenzene in the presence and absence of oxygen are summarized in table 1. In the absence of oxygen the predominant products were the three chlorophenol isomers and several dichlorobiphenyl isomers. The observed chlorophenol isomer distribution (o-58%,m-20%,p-22%) is similar to that observed by Norman and Radda (17) (o-42%,m-29%,p-29%). Dichlorobiphenyl isomers, which accounted for approximately 6% of our total yield, were observed previously in very low quantities when $OH\cdot$ was generated by radiolysis of water (18). This contrasts with results observed for the oxidation of benzene with Fenton's Reagent, in which biphenyl accounted for approximately 50% of the total yield under similar conditions (12).

In addition to these products a group of compounds were formed which were tentatively identified as dihydroxy-dichlorobiphenyls based on similarity to those described by Tulp et al. (19). The formation of similar compounds was hypothesized in the reaction of benzene with $OH\cdot$ generated by pulse radiolysis of water (13).

A mass balance approach was used to determine the most important reaction pathway under these conditions. According to the reaction scheme described in the previous section, one $OH\cdot$ and one Fe^{+3} will be produced each time that reaction 1 occurs. Considering the quantity of Fe^{+3} produced (0.250 mM) we can safely assume that reaction 3 was very slow relative to reaction 2. The total product yields and high Fe^{+3} concentrations indicates that

most of the products were produced via reactions 5 and 6 with a small amount of chlorophenol being produced in reaction 4, where Fe^{+3} acts as the oxidant. The low concentration of dichlorobiphenyls relative to phenols indicates that the rate constant for reaction 6 (k_6) is approximately an order of magnitude greater than the rate constant for reaction 5 (k_5). This estimate helps explain the higher biphenyl yield observed with benzene (12), because measurements of rate constants for the reaction of $\text{OH}\cdot$ with the HCD radical indicate that k_5 and k_6 are approximately equivalent (20).

When chlorobenzene was oxidized by Fenton's Reagent in the presence of O_2 product yields and distributions differed substantially (Table 1). Dichlorobiphenyl was observed at very low concentrations ($<10^{-6}$ mM) and the distribution of para-chlorophenol increased relative to ortho-chlorophenol. Overall product yields were not amenable to analysis with the type of mass balance approach applied previously. We believe that all of these changes can be explained by the reaction of O_2 with HCD radicals. The lower DCB yield occurred because HCD radicals reacted with O_2 much more readily than the HCD radicals could disproportionate or dimerize (reactions 5 and 6). Failure of the mass balance approach to account for all of the H_2O_2 is attributable to several possible events. Formation of diols and regeneration of H_2O_2 may account for some of the discrepancies; however, experiments performed by Kunai et al. (14) suggest that more phenol should be formed than

the amount of H_2O_2 consumed³. This unaccounted product may be related to the formation of polymeric species⁴ which are not amenable to HPLC analysis.

The Fenton's Reagent oxidation of chlorobenzene in the presence of O_2 was repeated at pHs ranging from 1-7 (see Figure 2). Chlorophenol isomer distributions remained constant and DCB concentrations remained below 10^{-6} mM in all experiments. However, overall product yields reached a maxima in the pH range of 2-3. A similar pH dependence was observed by Sudoh et al. (15) for the oxidation of phenol in the electrolytic Fenton's Reagent system. It is difficult to explain our results by employing only the two explanations (acid catalysis and iron speciation) suggested previously because: (1) acid catalysis of reaction 7, which is competing here with the very fast reaction of HCD with O_2 , does not have a drastic effect on overall reaction rates at pH values as low as 1.0 (12); and (2) Fe^{+3} speciation should have little to do with the reaction of chlorobenzene because Fe^{+3} does not play a significant role in the oxidation of HCD radicals in reaction 4 when O_2 is present.

An alternative explanation, which we are currently considering, is the transfer of electrons through some type of complex of Fe^{+3} with the HCD radical and O_2 . The formation of such complexes would undoubtedly be affected by pH and might exhibit behavior similar to the complexation of hydroxylated CAHs with Fe^{+3} ,

³Diols (hydroquinone, catechol, etc.) were not quantified in these experiments.

⁴These polymeric species are discussed in the following paragraphs.

in which maximum complex concentrations occur at pHs in the range of 2-4. This hypothesis is supported by experiments involving organometallic charge transfer complexes containing H_2O_2 and Fe^{+3} (22,23) and evidence of the existence of Cu^+-O_2 complexes (16). Furthermore, the participation of Fe^{+3} in the pH effect is supported by experiments on benzene oxidation in which $\text{OH}\cdot$ generated by irradiation of H_2O_2 with ultraviolet light exhibited a maximum degradation rate at pH 6.8 (24).

Chlorophenol concentrations decreased by between 65 and 75% of the total H_2O_2 added and various diols were observed when Fenton's Reagent was added to separate solutions of each chlorophenol isomer (see Table 2). In addition, Fe^{+2} concentrations did not change significantly over the course of the reaction, implying that Fe^{+3} was reduced by one of the intermediate products.

The intermediate compounds identified included compounds which had undergone dechlorination (i.e.-catechol and benzoquinone), a process not observed in the oxidation reactions with chlorobenzene. Gasowski (25) suggested a mechanism for the dechlorination of chlorobenzene in the pulse radiolysis system in which the quinone radical is formed by loss of HCl . Although this reaction is apparently insignificant in the Fenton's Reagent system the analogous reaction could be important with chlorophenol because the relatively stable semiquinone radical is easily oxidized to quinone by Fe^{+3} (26).

As the oxidation of the chlorophenol isomers proceeded the solutions exhibited an increased absorption of light across the entire visible spectra. In the case of 4-chlorophenol the solution

turned green prior to this broad band absorption. In an attempt to better understand this phenomena we conducted a series of experiments with 4-chlorophenol. In the presence of oxygen and nitrogen (Figure 3) the loss of 4-chlorophenol followed pseudo-first order kinetics⁵ (Figure 4). The pseudo-first order rate constant in the presence of O₂ was approximately twice as large as with N₂, indicating that O₂ is involved in the oxidation of the intermediate radical while two OH· are required to oxidize 4-chlorophenol without O₂.

From these observations we hypothesize the reaction pathway illustrated in Figure 1. The simultaneous presence of hydroquinone and benzoquinone could result in the formation of quinhydrone, a green colored complex of the two compounds. The broad band absorption observed afterward may be attributable to the polymerization of such diols induced by Fe⁺³ and or some radical reaction. The polymerization of diols in radical reactions involving transition metals has been reported previously (23,28,29) and the FTIR spectra of this material demonstrates band broadening characteristic of aromatic rings stabilized by polymerization or complexation with metals (30).

Several preliminary experiments were also conducted on the oxidation of one of the dichlorobiphenyl isomers (4,4'-DCB) observed in our experiments with chlorobenzene (Table 3). At H₂O₂ and Fe⁺² concentrations ranging from 0.04 to 1 mM losses of between

⁵Solving the rate equation for 4-chlorophenol loss by making the appropriate steady-state assumptions yields a pseudo-first order expression with the resulting initial value of k' being a function of the addition rate for H₂O₂ and initial 4-chlorophenol concentration.

77 and 92% of the initial 4,4'-DCB were observed. Because this compound is relatively insoluble in water it was only possible to evaluate the reaction with very low concentrations of 4,4'-DCB. Under these conditions it is difficult to determine the effect of oxidation of Fe^{+2} by $\text{OH}\cdot$ (reaction 3) or sorption of DCBs to the walls of the glass container. The low DCB concentrations also precluded observation of intermediate products, which could be present below detection limits.

Preliminary results from the complete oxidation of chlorobenzene during the slow addition of H_2O_2 is shown in Figure 6. At an addition rate of 5.0 mM/hr almost all of the chlorobenzene was degraded within the first hour. The products which we were able to detect included the three chlorophenol isomers, chlorobenzoinone, at least five DCB isomers, and the compounds tentatively identified as hydroxydichlorobiphenyls. All of these compounds also disappeared after 1.33 hours.

We continued to add hydrogen peroxide to the system for approximately four hours after chlorobenzene and its intermediates disappeared. The reaction mixture continued to exhibit the broad band absorbance described previously for approximately two more hours after which time the reaction mixture cleared to a pale yellow color and Fe^{+2} decreased to less than 0.1 mM. In addition, the acidity of the solution stopped increasing at this time and remained constant. These changes suggest that the reaction had reached completion at this point either because all of the chlorobenzene initially present was completely mineralized or the intermediates present in the system were incapable of reducing Fe^{+3} ,

which would allow for continuation of the catalytic cycle.

c. CONCLUSIONS

Fenton's Reagent effectively oxidizes CAHs in aqueous solutions. Understanding the reaction mechanisms will allow us to control the efficiency and intermediate products formed during the reaction by adjusting conditions such as pH, oxidant concentrations and the rate of H_2O_2 and/or Fe^{+3} addition. Our next step is to continue our evaluation of Fenton's Reagent and develop a better understanding of how to optimize actual systems for treatment of CAH contaminated water and soil.

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Table 1: Products from oxidation of chlorobenzene with Fenton's Reagent

<u>atmosphere</u>	Concentrations ¹ (mM)					<u>total</u>
	<u>Fe⁺³</u>	<u>ortho²</u>	<u>meta</u>	<u>para</u>	<u>DCBs³</u>	
nitrogen	0.250	0.073	0.026	0.028	0.0085	0.1355
air	0.290	0.041	0.023	0.049	< 10 ⁻⁶	0.1110

¹ results shown represent average values of duplicate experiments. Initial conditions (mM): H₂O₂: 0.273; Fe⁺²: 0.452; chlorobenzene: 3.0; pH: 3.0

² chlorophenol isomers

³ total concentrations of dichlorobiphenyl isomers. At least five isomers were observed; with 2,4'; 3,4' and 4,4' accounting for approximately 85% of the total DCB yield.

Table 2: Products from the oxidation of chlorophenol isomers by Fenton's Reagent

<u>Isomer</u>	<u>oxidation¹(mM)</u>	<u>products²</u>
ortho	1.47	ClBq, 3-ClCt, Cat
meta	1.62	ClBq, 3-ClCt, 4-ClCt
para	1.70	Bq, 4-ClCt, ClRes, Hq

¹ mean loss of chlorophenol isomer observed in duplicate experiments under the following conditions: initial chlorophenol isomer concentration: 3.0 mM; Fe⁺²: 0.5 mM; H₂O₂: 2.3 mM

²Qualitative identification of products was performed by comparison of HPLC retention times with those reported by Sehili et al. (24). Abbreviations: ClBq: chlorobenzoquinone; 3-ClCt, 4-ClCt: 3- or 4-chlorocatechol; Cat: catechol; Bq: benzoquinone; Hq:hydroquinone

Table 3: Oxidation of 4,4'-dichlorobiphenyl with Fenton's Reagent

Concentrations¹ (mM)

<u>Experiment #</u>	<u>H₂O₂</u>	<u>Fe⁺²</u>	<u>% DCB degraded</u>
1	1.00	1.00	93
2	0.20	0.20	92
3	0.04	0.04	76

¹ Initial conditions: 4,4'-DCB: 7.06 E⁻⁴ mM; pH: 3.0

Chlorophenol yield (mM)

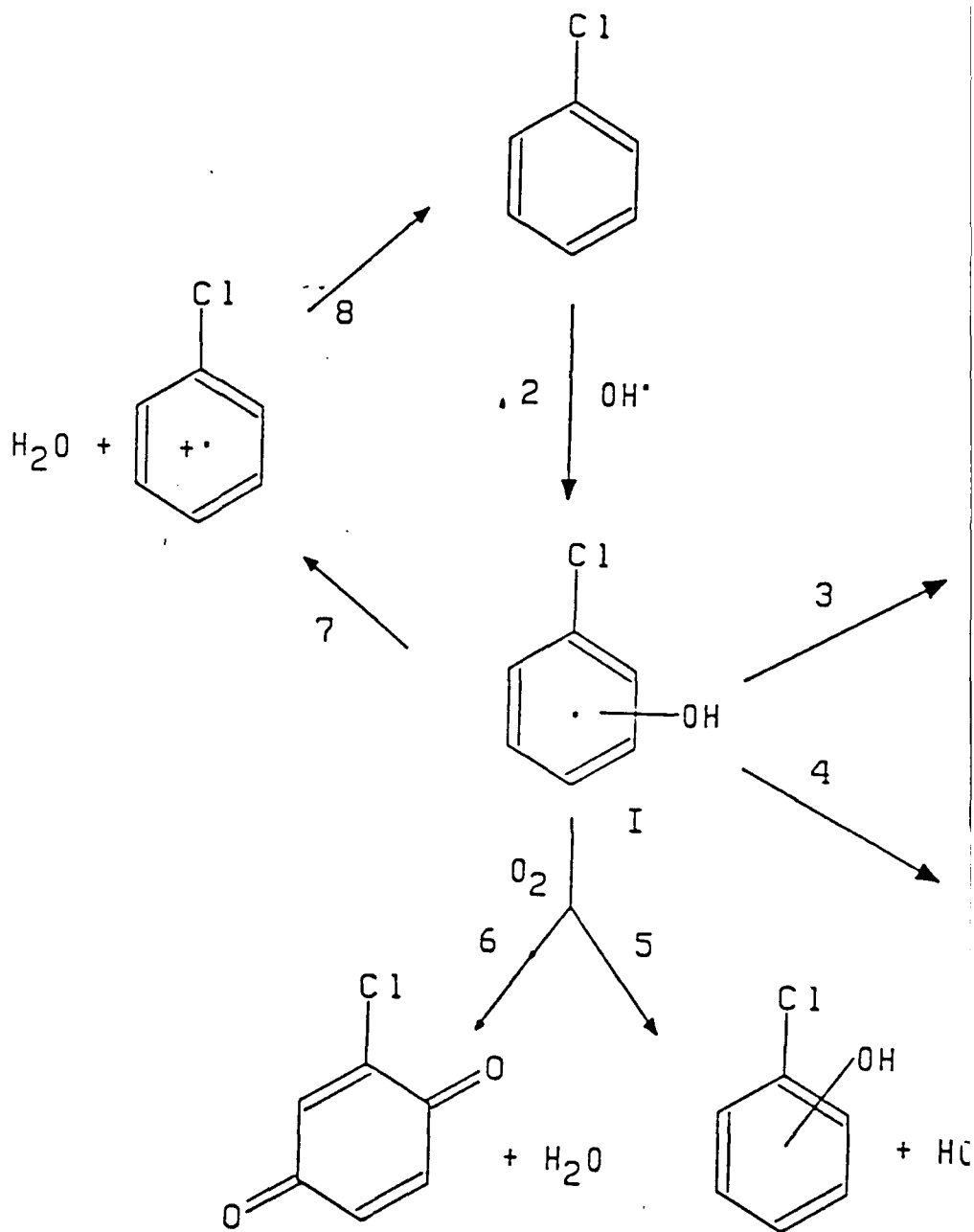
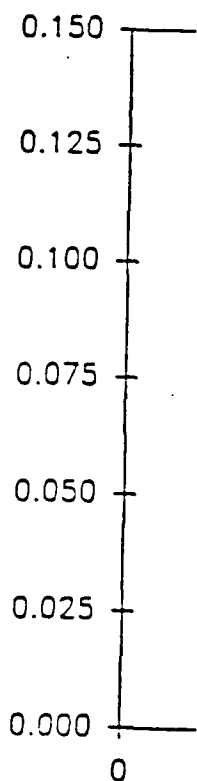


Figure 2 Relatic
 Fe^{2+} , 5.0 mM; H_2O_2
 95% confidence int
 experiments at eac

Figure 1: Proposed reaction pathway for the oxid
 chlorobenzene with Fenton's Reagent.

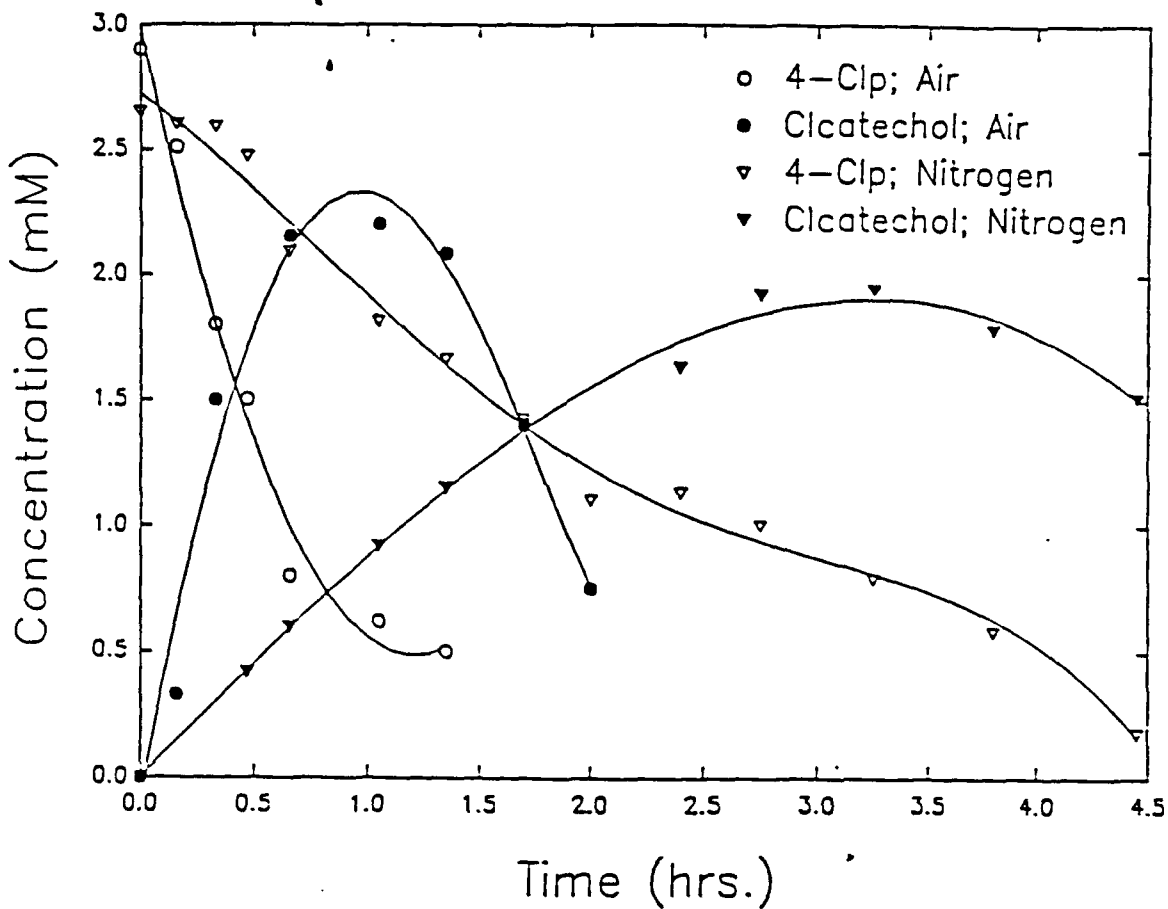


Figure 3 Oxidation of 4-chlorophenol with Fenton's reagent. Initial conditions: Fe^{2+} , 0.5 mM; H_2O_2 addition rate, 3.0 mM/h; pH, 3.0. 4-Chlororesorcinol, hydroquinone and benzoquinone were detected at concentrations less than 0.2 mM.

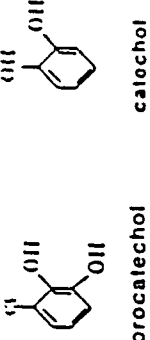
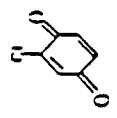
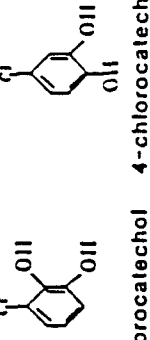
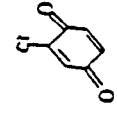
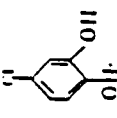
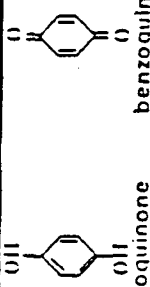
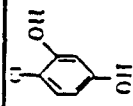
Isomer	products observed		
	ortho	para	meta
2-chlorophenol	 3-chlorocatechol catechol	 chlorobenzoquinone	None detected
3-chlorophenol	 3-chlorocatechol 4-chlorocatechol	 chlorobenzoquinone	None detected
4-chlorophenol	 4-chlorocatechol	 hydroquinone benzoquinone	 4-chlororesorcinol

Figure 4 Products observed from chlorophenol oxidation by Fenton's reagent. Initial conditions: Fe^{+2} , 0.5 mM; pH, 3.0; H_2O_2 , 4.5 mM; chlorophenol isomer, 3.0 mM.

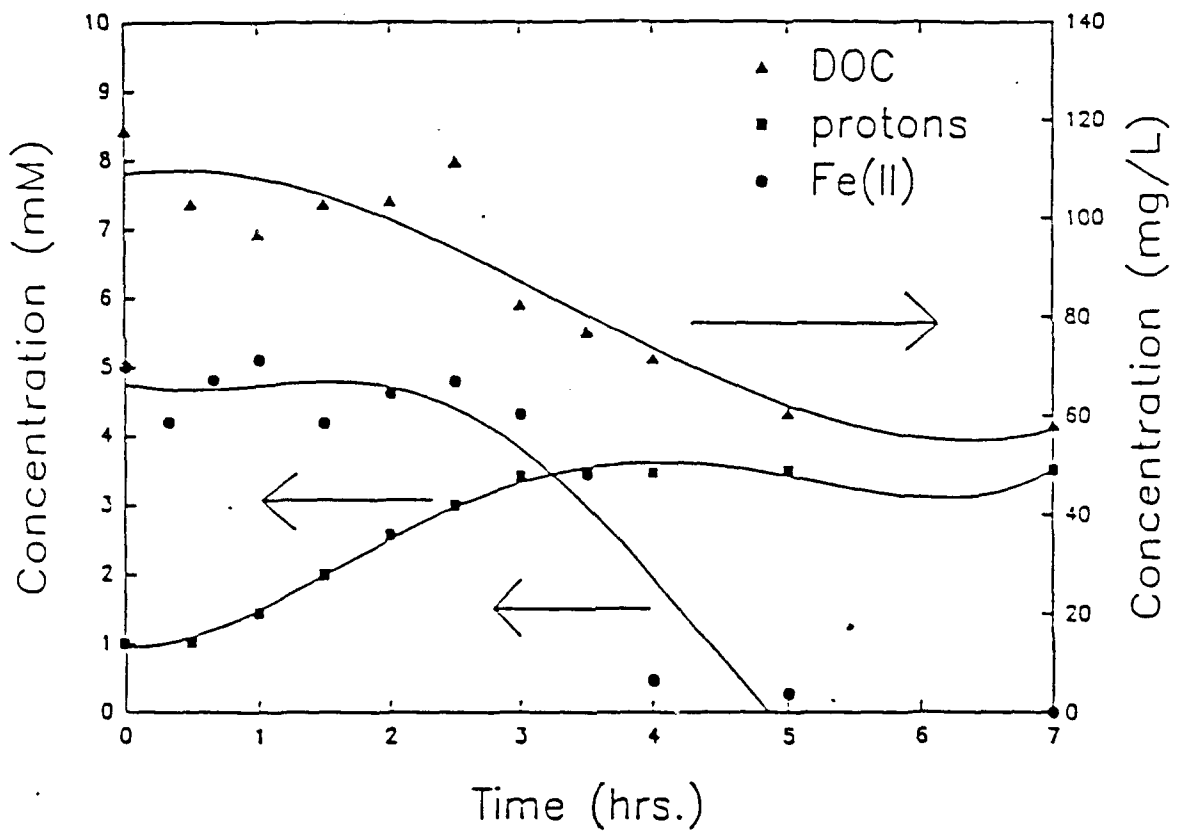


Figure 5 Changes in DOC, pH and Fe²⁺ during oxidation of chlorobenzene with Fenton's reagent.

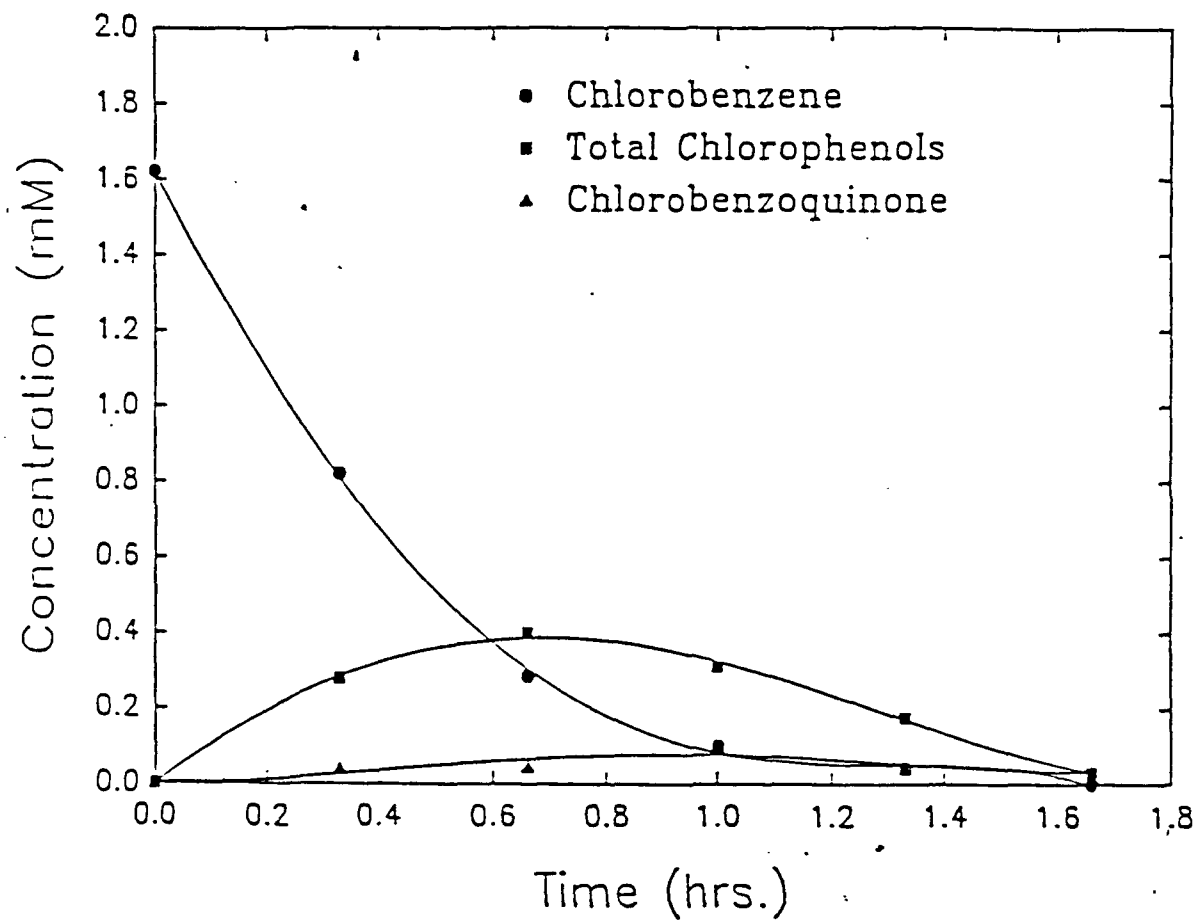


Figure 6 Oxidation of chlorobenzene with Fenton's reagent. Initial conditions: Fe^{2+} , 5.0 mM; pH, 3.0.

Oxidation of Chlorobenzene with Fenton's Reagent

David L. Sedlak and Anders W. Andren*

Water Chemistry Program, University of Wisconsin, Madison, Wisconsin 53706

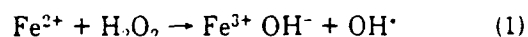
■ The degradation of chlorobenzene and its oxidation products by hydroxyl radicals generated with Fenton's reagent was studied. In the absence of oxygen, chlorophenols, dichlorobiphenyls (DCBs), and phenolic polymers were the predominant initial products. In the presence of oxygen, DCB yields decreased markedly and chlorobenzoquinone was also formed. Chlorophenol isomers were further oxidized by OH's to form chlorinated and non-chlorinated diols. DCBs and the phenolic polymers were also oxidized. The highest yield of product formed per mole of H₂O₂ consumed was observed in the pH range of 2-3. The pH dependence and product distributions suggest that complexes of aromatic intermediate compounds with iron and oxygen may play a role in regulating reaction pathways. At pH 3.0, approximately 5 mol of H₂O₂/mol of chlorobenzene were required to remove all of the aromatic intermediate compounds from solution.

Introduction

Chlorinated aromatic hydrocarbons (CAHs) have been introduced to the environment from a variety of sources. Many of these compounds do not readily degrade and pose a threat to biota and human populations. Concern about the potential hazards associated with these compounds has resulted in laws and policies that require the cleanup of contaminated soil, sediments, surface water, and wastewater (1). Treatment of these wastes necessitates the development of technologies to effectively degrade many types of CAHs.

One potentially important method of destroying CAHs is through chemical oxidation by hydroxyl radicals generated with Fenton's reagent (2, 3). Fenton's reagent is

a mixture of hydrogen peroxide and ferrous iron (Fe²⁺), which produces OH's according to reaction 1 (4):



The OH's produced in reaction 1 are capable of reacting with a variety CAHs (5-7). Preliminary studies for the design of waste treatment systems employing Fenton's reagent (2, 3, 8-10) indicate that the reaction is effective in the degradation of phenols, chlorophenols, formaldehyde, and octachloro-*p*-dioxin. However, none of these studies have focused on either the nature of intermediate products or factors affecting product yields and distributions. Furthermore, mechanistic studies on CAHs are mainly limited to systems in which oxygen is excluded and high H₂O₂ and substrate concentrations are present.

Understanding the reaction mechanism for the oxidation of CAHs under conditions relevant to waste treatment is an essential step in the design of efficient, cost-effective Fenton's reagent treatment systems. These factors are especially important for this oxidation system because product yields and distributions may be drastically affected by environmental conditions such as pH and oxidant concentrations (11, 12). Furthermore, identification and quantification of intermediate products is important because hydroxylated aromatic and dimeric intermediates may be recalcitrant and/or toxic.

In this study we have evaluated reactions of Fenton's reagent with chlorobenzene and its intermediate oxidation products as a function of pH, and in the presence or absence of oxygen. Through determination of intermediate products and the effect of environmental variables on product yields and distributions, we have identified possible reaction mechanisms and optimal conditions for

degrading these compounds. In addition, we have collected data that provide a basis for estimating the quantities of H_2O_2 required to oxidize all of the CAHs and aromatic intermediates.

Materials and Methods

The following chemicals were obtained from Aldrich at the specified purities and were used without further purification: benzoquinone (97%), catechol (99+%), chlorobenzene (99+%), chlorohydroquinone (technical grade), 2-chlorophenol (99+%), 3-chlorophenol (98%), 4-chlorophenol (99+%), 4-chlororesorcinol (98%), hydrogen peroxide (ACS reagent grade, 30% solution), ferric sulfate pentahydrate, ferrous sulfate heptahydrate (99+%), 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) (97%). Dichlorobiphenyl isomers were purchased from Cambridge Isotope Laboratories.

Aqueous solutions of various organic compounds, used for oxidation reactions and as HPLC standards, were prepared with Millipore Milli-Q water. Nitrogen was bubbled through the water for at least 1 h prior to addition of solute for solutions used in reactions conducted in the absence of oxygen. Chlorobenzene solutions were stirred for at least 1 week prior to use. Solutions of chlorophenols and all other standards were prepared by dissolving the appropriate quantity in water and stirring at least 1 h. Chlorobenzoquinone standards were prepared by oxidizing a chlorohydroquinone solution with excess Fe^{3+} . Completion of the reaction was confirmed by the disappearance of the chlorohydroquinone peak on the HPLC chromatogram.

Fenton's reagent reactions were conducted in a 500-mL round-bottom flask. The flask was maintained at 25 °C with a recirculating water bath and shielded from light with aluminum foil. For reactions conducted in the absence of oxygen, a nitrogen atmosphere was maintained over the solution at a slight positive pressure and samples were withdrawn through a sampling port with a syringe. Samples were collected after 1 h unless otherwise noted.

The initial solution pH was adjusted with hydrochloric acid for reactions at pH values up to 3.0. Reactions at pH values of 4.7 and 7.0 were buffered with acetic acid and phosphoric acid buffers, respectively.

Hydrogen peroxide solutions, maintained at 25 °C with a recirculating water bath, were added to the reactor containing the solute and Fe^{2+} either in a total volume of 10 mL at the start of the reaction or at a rate of 5.0 mL/h with a metering pump.

Ferrous iron was quantified by the method of Collins et al. (13), which involves spectrophotometric measurements of the Fe^{2+} /TPTZ complex.

Polar compounds were quantified by HPLC using a 25-cm reverse-phase column (ODS-2; Alltech) and a mobile phase of methanol/water with 0.5 mM acetate buffer. The following gradient was used: 10% methanol (hold 4 min); ramp to 50% methanol by 15 min (hold 6 min). Compounds were detected at 280 nm and quantification was based on comparison with standards, except in the case of 4-chlorocatechol, which was estimated on the basis of the measured extinction coefficient of catechol.

Samples withdrawn from the reactor (5 mL) were also extracted three times with 10 mL of petroleum ether and 0.2 mL of saturated sodium chloride and analyzed for chlorobenzene by GC/MS (Hewlett-Packard 5890/5970). These extracts were then concentrated to 1 mL and analyzed quantitatively for dichlorobiphenyls and qualitatively for other compounds. Dichlorobiphenyls were quantified by using 2,4,5-trichlorobiphenyl as an internal standard. Chromatographic conditions were as follows: 30-m RT_1 -5

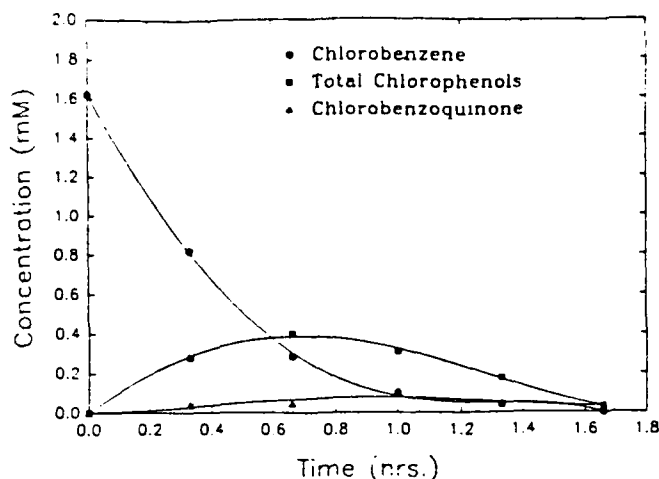


Figure 1. Oxidation of chlorobenzene with Fenton's reagent. Initial conditions: Fe^{2+} , 5.0 mM; pH, 3.0

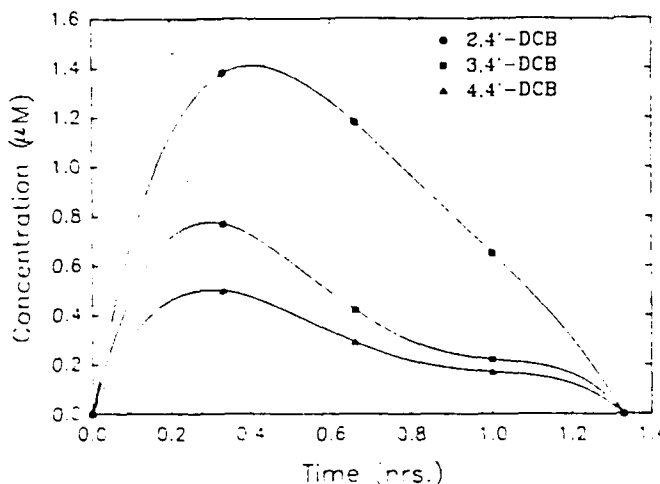


Figure 2. Formation of three dichlorobiphenyl isomers during oxidation of chlorobenzene with Fenton's reagent. 2,2'-DCB, 2,3'-DCB, and 3,3'-DCB are not shown because concentrations were significantly smaller than those observed for the other isomers. Conditions: Fe^{2+} , 5.0 mM; pH, 3.0

capillary column (Restek); oven programmed to start at 50 °C (hold 4 min) then ramp to 280 °C at 5 °C/min; detection with scan mode in the 50–350 mass/charge range.

UV/vis spectrophotometric measurements were performed on a Varian DMS 80 spectrophotometer with a slit width of 3 nm. UV/vis scans were conducted at a scan rate of 100 nm/min.

Dissolved organic carbon (DOC) was analyzed on an automatic TOC analyzer (Model 700, OI Corp.).

Results

Results from the oxidation of chlorobenzene by addition of H_2O_2 at a rate of 5 mM/h at an initial pH of 3.0 are shown in Figures 1 and 2. Chlorobenzene and all intermediate products disappeared within the first 2 h of the reaction. The three chlorophenol isomers, chlorobenzoquinone, and the six dichlorobiphenyl isomers were identified by GC/MS (Table I) and quantified by either GC/MS or HPLC. The mass spectra and retention times for these compounds were identical with those of the standards and the mass spectra closely matched those in the NBS database. A group of compounds with retention times similar to the dichlorobiphenyl isomers were also observed. These peaks were tentatively identified as hydroxymonochlorobiphenyls or hydroxydichlorobiphenyls on the basis of the results of a computerized search of the NBS mass spectral library and similarity of their mass

Table I. Intermediate Compounds Identified from Oxidation of Chlorobenzene with Fenton's Reagent

peak	compound	RT ^a	ID ^b	quant ^c
1	2-chlorophenol	11.9	std	HPLC
2	chlorobenzquinone	10.7	std	HPLC
3	3-chlorophenol	15.9	std ^d	HPLC
4	4-chlorophenol	17.0	std ^d	HPLC
5	2,2'-DCB	21.2	std	GC/MS
6	2,3'-DCB	25.3	std	GC/MS
7	2,4'-DCB	25.8	std	GC/MS
8	3,3'-DCB	28.7	std	GC/MS
9	3,4'-DCB	28.8	std	GC/MS
10	4,4'-DCB	29.4	std	GC/MS
11	MHCIBps	many ^e	NBS	NQ ^f
12	DHCIBps	many ^e	NBS	NQ ^f

^aRetention time in minutes on column used for quantification. ^bMethod of GC/MS identification: std, matched with mass spectra and retention times of standard; NBS, compared with NBS mass spectral database and spectra described by Tulp et al. (14). ^cMethod used for quantification. ^dThese chlorophenol isomers coeluted on GC/MS. Mass spectra showed characteristics of both compounds. ^eFour hydroxymonochlorobiphenyl compounds (RT = 18.5, 22.5, 24.3, and 25.1 min) and four hydroxydichlorobiphenyl compounds (RT = 26.2, 26.9, 27.5, and 27.7 min) were identified. At least 10 additional mono- and dichlorinated hydroxylated biphenyls were also identified between 29 and 31 min but could not be fully separated. ^fNQ, not quantified.

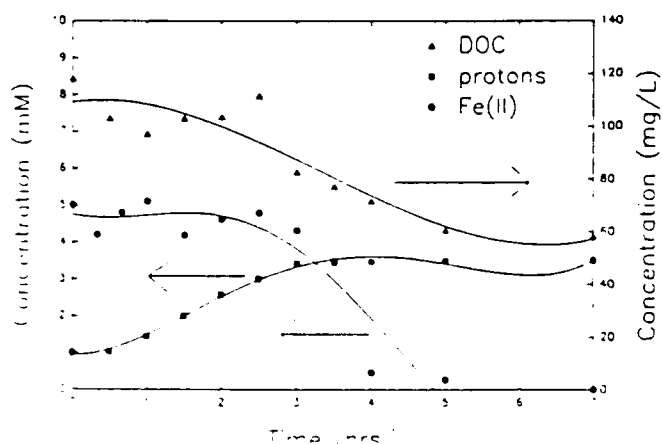


Figure 3. Changes in DOC, pH, and Fe²⁺ during oxidation of chlorobenzene with Fenton's reagent.

spectra to compounds described by Tulp et al. (14). Compounds with identical mass spectra and GC retention times identified in extracts from the oxidation of chlorinated biphenyls with hydroxyl radicals have been identified as hydroxychlorobiphenyls on the basis of comparison with available standards and mass spectra of methylated samples (15).

As the reaction progressed, UV-vis spectrophotometric scans showed a gradual increase in broad-band absorption within the visible spectral region. This increasing absorbance, which was accompanied by a decrease in solution pH, continued until approximately 4 h after the start of the reaction, at which time the solution cleared to a yellow color. Fe²⁺ decreased significantly, and pH stabilized (Figure 3). Dissolved organic carbon decreased by approximately 40% during the reaction and stabilized after approximately 5 h.

A more quantitative understanding of the initial steps of the reaction was achieved by conducting a series of experiments in which a small amount of H₂O₂ (an amount that resulted in the oxidation of less than 10% of the initial chlorobenzene) was added to a solution of chlorobenzene and Fe²⁺ at the start of the reaction (Table II). Reactions in the absence of oxygen yielded much higher concentra-

Table II. Chlorophenol and Dichlorobiphenyl Produced during Oxidation of Chlorobenzene with Fenton's Reagent with and without oxygen

atmos ^a	concn. ^c mM				
	ortho ^b	meta ^b	para ^b	DCBs ^c	total ^d
N ₂	0.073 (53.9)	0.026 (19.2)	0.028 (20.7)	0.0085 (6.3)	0.1355
O ₂	0.041 (36.1)	0.023 (20.3)	0.049 (43.2)	0.0005 (0.4)	0.1135

^aInitial conditions: Fe²⁺, 4.5 mM; pH, 3.0; H₂O₂, 2.7 mM; chlorobenzene, 3.8 mM. Results are average values for two experiments. ^bConcentrations of chlorophenol isomers. ^cTotal concentration of dichlorobiphenyl (DCB) isomers. ^dTotal amount of chlorophenols and DCBs produced. ^eValues in parentheses represent percentage of total.

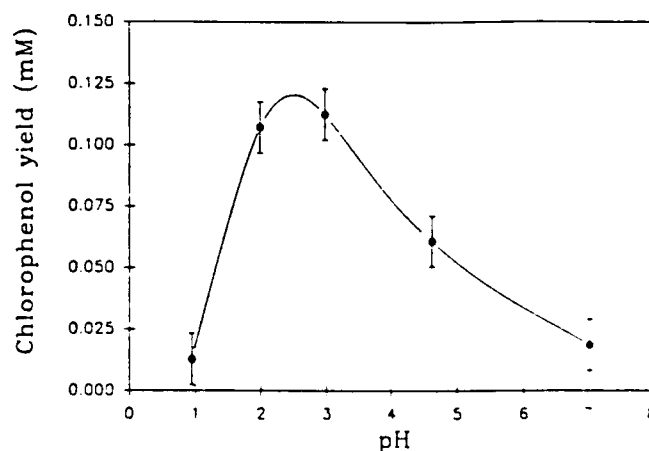









Figure 4. Relationship of total chlorophenol yield and pH. Initial conditions: Fe²⁺, 5.0 mM; H₂O₂, 2.7 mM; chlorobenzene, 3.8 mM. Error bars represent 95% confidence intervals based on pooled variances observed in duplicate experiments at each pH.

tions of dichlorobiphenyls (DCBs) when compared to those in air. Furthermore, chlorophenol isomer distributions under nitrogen contained a higher proportion of *o*-chlorophenol than reactions performed with oxygen. When further experiments were conducted in the presence of oxygen (Figure 4), the highest yield of product formed per mole of H₂O₂ consumed was observed at pH values in the range of 2-3. Chlorophenol isomer distributions remained constant (combining the results of duplicate analyses at each pH the following mean isomer distributions and 95% confidence intervals were calculated: ortho, 35.3 ± 2.1%; meta, 19.7 ± 2.6%; para, 45.0 ± 1.7%) and DCB concentrations remained below 10⁻⁶ M over the entire pH range.

The oxidation of pure solutions of chlorophenol isomers by Fenton's reagent was also qualitatively evaluated (Figure 5). Chlorinated diols resulting from ortho or para substitution accounted for most of the observed products identified by GC/MS. Small quantities of nonchlorinated diols (hydroquinone, catechol, and benzoquinone) were also observed. Reactions with 2-chlorophenol and 3-chlorophenol exhibited the same broad-band absorption observed for chlorobenzene. Reactions with 4-chlorophenol passed through a green-colored stage prior to onset of broad-band absorption.

Oxidation of a 4-chlorophenol solutions was followed quantitatively in the presence and absence of oxygen as depicted in Figure 6. In both cases, 4-chlorocatechol was observed as the predominant product. Compound identification was based upon analysis of mass spectra and comparison with HPLC chromatograms from Sehili et al. (16). Quantification was based upon extinction coefficient measurements for catechol and assumes that the UV

isomer	Products observed		
	ortho ¹	para	meta
2-chlorophenol	 3-chlorocatechol catechol	 chlorobenzoquinone	None detected
3-chlorophenol	 3-chlorocatechol 4-chlorocatechol	 chlorobenzoquinone	None detected
4-chlorophenol	 4-chlorocatechol	 hydroquinone benzoquinone	 4-chlororesorcinol

¹ Location of hydroxyl addition (relative to original OH group on chlorophenol isomer)

Figure 5. Products observed from chlorophenol oxidation by Fenton's reagent. Initial conditions: Fe^{2+} , 0.5 mM; pH, 3.0; H_2O_2 , 4.5 mM; chlorophenol isomer, 3.0 mM.

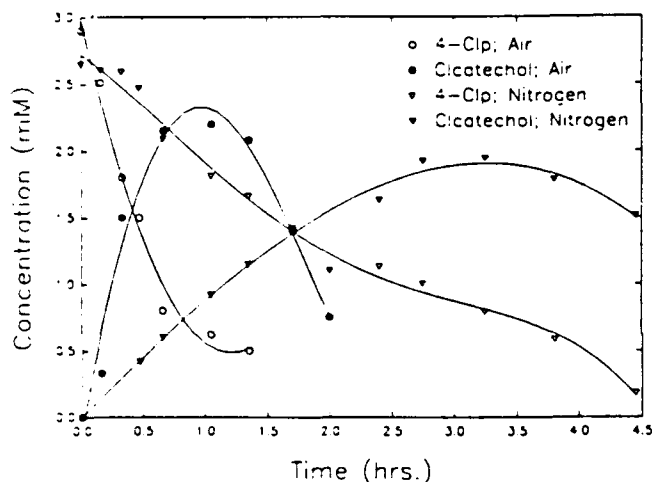


Figure 6. Oxidation of 4-chlorophenol with Fenton's reagent. Initial conditions: Fe^{2+} , 0.5 mM; H_2O_2 addition rate, 3.0 mM/h; pH, 3.0. 4-Chlororesorcinol, hydroquinone, and benzoquinone were detected at concentrations less than 0.2 mM.

spectra of the chlorinated compound is similar to its nonhalogenated parent. Other intermediate compounds were not detected in significant quantities by GC/MS or HPLC. Results from these experiments also illustrate that oxygen almost doubles the rate of disappearance of 4-chlorophenol.

Discussion

The overall results of our experiments indicate that Fenton's reagent can effectively degrade chlorobenzene, chlorophenols, and dichlorobiphenyls. In the presence of oxygen at pH 3.0, approximately 5 mol of H_2O_2 /mol of chlorobenzene is required to completely remove the aromatic intermediates from solution. Results from DOC analysis indicate that the aromatic intermediates undergo ring cleavage prior to mineralization. Cessation of the reaction after approximately 4 h, as evidenced by stabilization of DOC concentrations, pH, and Fe^{2+} , is most likely attributable to the inability of many ring-cleavage intermediates to regenerate Fe^{2+} .

Chlorobenzene Reactions. By analogy to previous work on OH^{\bullet} reactions with aromatic compounds and evaluation of our results, we believe that the oxidation of chlorobenzene by Fenton's reagent (Figure 7) follows a

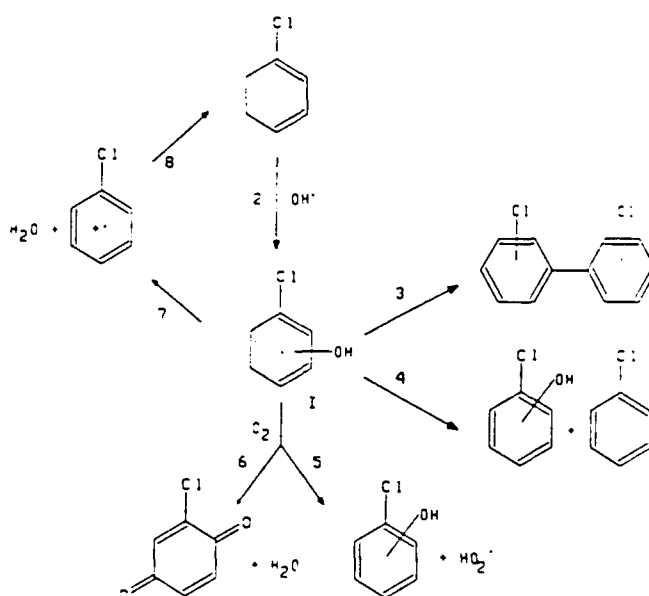


Figure 7. Proposed reaction pathway for oxidation of chlorobenzene with Fenton's reagent.

complicated reaction pathway in which products are formed via several different mechanisms controlled by factors such as oxidant concentrations and pH. The first step in the reaction sequence, OH^{\bullet} attack on chlorobenzene (reaction 2), likely results in the formation of chlorohydroxycyclohexadienyl (CIHCD) radical I (7, 17), which may undergo one of several possible further reactions.

In the absence of oxygen, or other strong oxidants, the two predominant reactions are dimerization to produce dichlorobiphenyls (reaction 3) and bimolecular disproportionation to produce chlorophenol and chlorobenzene (reaction 4). Both of these reactions exhibit an overall stoichiometry of 2 mol of H_2O_2 /mol of chlorobenzene oxidized, which is consistent with our observations (see Table II). A similar stoichiometry has been observed in the oxidation of benzene by Fenton's reagent, but biphenyl yields were as high as 50% (18).

In the presence of oxygen, or other strong oxidants, different product distributions are observed because several additional product reactions contribute to product formation. Reactions of the oxidant (O_2) with the CIHCD radical (reactions 5 and 6) predominate because they are first

reactions 3 and 4 are second order with respect to the radical. Reaction of the ClHCD radical with O_2 results in lower DCB yields, different chlorophenol isomer distributions and higher chlorobenzoquinone yields than reactions under nitrogen. Reactions of ClHCD radicals with O_2 are also important because they could result in the production of hydroperoxy radicals (via reaction 5) or H_2O_2 (19), which could further oxidize CAHs.

The formation of chlorobenzoquinone as a result of oxygen attack on the ClHCD radical in a position para to the initial OH^\bullet addition was expected, based upon previous experimental results with benzene (19, 20). However, the absence of ortho-substituted diols (catechol or chlorocatechol) observed in these reactions is unexpected given the ortho/para directing tendency of hydroxyl groups. One possible explanation is steric hindrance at the ortho position caused by an iron-oxygen complex similar to that observed in the Cu/O_2 analogue of Fenton's reagent (20).

The formation of chlorobenzoquinone by a pathway involving O_2 rather than via a secondary reaction of a chlorophenol isomer is strongly supported by our results. The decreased relative yields of *o*-chlorophenol observed in the presence of oxygen can be explained by a more favorable reaction of O_2 with ortho ClHCD radicals than other ClHCD radicals. Furthermore, catechol and chlorocatechol isomers were produced as primary products in reactions with solutions of the chlorophenol isomers and would presumably be present if chlorobenzoquinone was a secondary reaction product.

Chlorophenol Reactions. Hydroxyl radical attack on the chlorophenol isomers is directed by the position of the hydroxyl group, which is a stronger ortho/para director than chlorine (22) (Figure 5). Reactions performed with each of the chlorophenol isomers resulted almost exclusively in products of OH^\bullet attack at a position ortho or para to the hydroxyl group. Only one product of OH^\bullet attack at a position meta to the hydroxyl group (4-chlororesorcinol) was observed. The formation of nonchlorinated products indicates that the presence of a chlorine group did not prevent OH^\bullet attack on the ring. Hydroxyl radical attack did however occur more readily at positions that were not occupied by chlorine groups because dechlorination occurs via a different reaction mechanism, which is probably not as efficient as reactions not resulting in dechlorination.

The visible light absorption and our inability to account for all of the reaction products [also observed by Kunai et al. (19)] suggest that some compounds are formed that are not amenable to HPLC analysis. The green color observed during the oxidation of 4-chlorophenol is most likely attributable to the formation of a complex of Fe^{2+} with one of the aromatic oxidation products. This green color was also observed when ferric sulfate and catechol were mixed at concentrations comparable to those observed in our experiments. Furthermore, a variety of other colored complexes have been reported when other disubstituted aromatic compounds were mixed with Fe^{3+} (23).

Polymerization Reactions. The broad-band visible light absorption exhibited during the oxidation of chlorobenzene and the chlorophenol isomers, which has been observed previously with benzene and phenol (8, 19), is most likely attributable to the formation of phenolic polymers. Formation of phenolic polymers in reactions involving OH^\bullet was noted by Stein and Weiss (24) and has been implicated in the formation of humic materials (25-27). Hydroxychlorobiphenyls have been identified previously during the radical polymerization of 4-chloro-

(25). The compounds we observed by GC/MS may result from the polymerization of phenoxy radicals or ClHCD radical cations. Alternatively, these compounds may have been produced via a secondary reaction of OH^\bullet with the dichlorobiphenyls, as observed in the oxidation of chlorinated biphenyls by Fenton's reagent (15). Disappearance of the broad-band absorption and the dimers as the reaction progressed suggests that these polymers and dimers are ultimately amenable to oxidation.

pH Dependence. Optimal product yields (in terms of the amount of chlorobenzene oxidized per mole of H_2O_2 consumed) in the pH range of 2-3 have been reported previously for phenol (8). One possible explanation of the pH effect is acid-catalyzed base-catalyzed elimination of water from ClHCD radicals followed by reduction to chlorobenzene (reactions 7 and 8) (18). However, this reaction only contributes to a 50% decrease in product yield for oxidation of benzene in the absence of oxygen at pH 1 (18). In the presence of oxygen, the reaction should exert even less of an effect because the unimolecular elimination of water is competing with the rapid oxidation of ClHCD by O_2 .

Another possible explanation for the pH effect is participation of substrate- $Fe-O_2$ or substrate- $Fe-H_2O_2$ complexes in the reaction. Kinetic results from oxidation of diols in the Fenton's reagent system (28, 29) and in the presence of Mn^{2+}/O_2 (30) do not follow predictions for a radical mechanism, but are better explained by the formation of organometallic ternary complexes. Furthermore, the stability constants for such complexes would likely favor their formation at the pH values where optimal product yields were observed, because ferric complexes with aromatic ligands are most readily formed in the pH range of 2-4 (31). Therefore, higher product yields in this pH range could be explained by a reaction involving the organometallic complex where either H_2O_2 is regenerated (for example, proton abstraction from chlorohydroquinone by O_2) or through increased rates of reactions in which H_2O_2 is wasted.

Conclusions

Fenton's reagent can be employed to effectively degrade recalcitrant CAHs such as chlorobenzene and chlorophenol. The most direct mechanism for CAH degradation proceeds through hydroxylation followed by ring cleavage and mineralization. Another possible reaction pathway involves the formation of dimers (such as chlorinated biphenyls and hydroxychlorobiphenyls) and colored aromatic polymers, which are oxidized by subsequent OH^\bullet attack.

Complete mineralization of organic compounds was not observed because some of the ring-cleavage products were unable to reduce Fe^{3+} . If necessary, these ring-cleavage products could be further oxidized by addition of more Fe^{2+} , as demonstrated in the oxidation of phenol with the electrolytic Fenton's reagent system (8).

Evaluation of factors affecting the reaction mechanism has also helped to define reaction conditions resulting in the greatest loss of CAHs per mole of H_2O_2 consumed. The presence of oxygen or other strong oxidants favors the more direct oxidation pathway and also follows a stoichiometry in which less H_2O_2 is required to degrade the CAHs. The reaction also follows a pH dependence and is most efficient in the pH range of 2-3.

Registry No. 2,2'-DCB, 13029-08-8; 2,3'-DCB, 25569-80-6; 2,4'-DCB, 34883-43-7; 3,3'-DCB, 2050-67-1; 3,4'-DCB, 2974-90-5; 4,4'-DCB, 2050-68-2; chlorobenzene, 108-90-7; 2-chlorophenol, 95-57-8; chlorobenzoquinone, 695-99-8; hydroxymonochlorobiphenyl, 132178-75-7; hydroxydichlorobiphenyl, 53813-74-4; oxygen,

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