PERSULFATE ACTIVATION BY ORGANIC COMPOUNDS

BY

ANA MARIA OCAMPO

A dissertation submitted in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY
Department of Civil and Environmental Engineering

August 2009

To the Faculty of Washington State University:

The members of the committee appointed to examine the dissertation of ANA MARIA OCAMPO find it satisfactory and recommend that it be accepted.

Rick Watts, Ph.D., Chair

Jeremy Rentz, Ph.D.

I. Francis Cheng, Ph.D.

Glen R. Boyd, Ph.D.

ACKNOWLEDGMENTS

I would like to thank my major advisor, Dr. Rick Watts, for his dedication, guidance, and the opportunity that he gave me to study in this program. I wish to express my thanks to my advisory committee, Drs. Glen Boyd, I. Francis Cheng, Jeremy Rentz, and Amy Teel for their help. A special thanks to Dr. Jeremy Rentz for his academic guidance in completing this project. I would like to acknowledge Dr. Amy Teel for her help with proof-reading. And last but not least, Dr. Philip Block, for being so willingness to participate in my defense committee on short notice. The Department of Civil and Environmental Engineering staff, Vicky, Glenda, Lola, and Maureen, all helped ensure the successful completion of this project.

I am grateful to my family for their love, patience, and support help in all aspects of my life outside my home country. Thanks are also extended to my special friends Justin Beaver, Diana Caicedo, Pablo Escobedo, Henry Foust, Olga Lucia Lopez, Helge Reemtsma, and Dennis Fernando Romero.

My special thanks to Scott Economu at the Department of Civil & Environmental Engineering for their guidance with the analytical procedures. I would also like to thank my fellow graduate students at Washington State University. Last but certainly not least, I would have never finished this work without the encouragement and help of my academic mentors Drs. Glen Boyd and Jack Grubbs.

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ABSTRACT

by ANA MARIA OCAMPO, Ph.D.
Washington State University
August 2009

Chair: Richard J. Watts

Activated persulfate is an increasingly popular reagent for the *in situ* chemical oxidation (ISCO) remediation of contaminated soils and groundwater; however most of the investigations conducted to date have been highly empirical. Results for field scale ISCO applications suggest that persulfate is activated by one or more compounds in contaminanted soils.   The purpose of this research was to determine if organic compounds can activate persulfate, and to establish a mechanism of action. This route of activation is very important, since all soils and subsurface solids contain some amount of organic matter.

Laboratory experiments were carried out at alkaline pH to screen different functional groups which include ketone, carboxyl acid, alcohols, aldehyde, and the groups in the Kreb cycle such as keto acids, dicarboxylic acids and alcohol acids. The results of the research demonstrated that ketones, primary alcohols and low carbon chain aldehydes can activate persulfate to generate reactive species, providing enhanced destruction of refractory compounds.

The results also indicated that the ionized form of the organic compound is important to promote the activation of persulfate. Therefore, phenoxides, which are the

salts of phenol and chlorophenols, were selected as the organic compounds for investigating the mechanism of persulfate activation. The results indicate that the activation was via reductive pathway mechanisms, with more rapid activation promoted by the more reduced phenoxides.

The results of this study will enhance the effectiveness of persulfate in field application. Soil organic carbon content should be considered in process screening and treatability testing for persulfate in situ chemical oxidation.

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INTRODUCTION

Soil and groundwater contamination by hazardous chemicals has been a significant concern for the past decades. Hazardous chemicals are released in the environment through spillage or leakage from pipelines, storage tanks, or industrial facilities, and include both highly water soluble, and non-aqueous phase liquid (NAPLs) compounds, which are classified as fluids less dense than water (LNAPLs) or fluids more denser than water (DNAPLs) (Pankow and Cherry, 1996).

In the 1980s, early efforts to remediate contaminated soil and groundwater were typically focused on excavation of the contaminated soil and subsequent off-site treatment, combined with plume or source zone treatment by pumping and treating the contaminated groundwater (EPA, 1996; Pankow and Cherry, 1996). Pump-and-treat was the first technique used to remediate soil and groundwater, but the problem with many pump-and-treat applications was that there was little or no subsequent reduction of the contaminant mass after the initial treatment, and thus pump-and-treat applications required very long periods of time (Pankow and Cherry, 1996; Widemeier et al., 1999).

To overcome the limitations associated with pump-and-treat remediation systems, enhanced pump-and-treat technology was developed as an alternative to *in situ* methods, and is aimed at accelerating contaminant removal by adding chemical additives, such as alcohols or surfactants (Hill et al., 2001; Hofstee et al., 2003; Miller et al., 2000; Roeder et al., 2001). However, these processes require aboveground water treatment and/or off-site disposal; therefore, a promising technology, *in situ* chemical oxidation (ISCO), was

established, with the potential to supplant the more widely used pump-and-treat groundwater remediation technology by remediating groundwater contamination both *in situ*, and faster.

ISCO was established in the 1990s, as a process where strong oxidants are introduced into the subsurface to react with the contaminant of concern and transform groundwater and soil contaminants into less harmful chemical species (Siegrist et al., 2002; Watts and Teel, 2005). ISCO represents a series of chemical oxidation technologies which includes oxidants species such as ozone (O_3), permanganate (MnO_4^-) and catalyzed hydrogen peroxide (H_2O_2) propagations (CHP) (Watts and Teel, 2006).

CHP is the most often used ISCO process. Ozone is sparged into wells, where it reacts directly with organic contaminants or decomposes into hydroxyl radicals. Permanganate reacts primarily by direct contaminant oxidation. It is a relatively selective oxidant, being most reactive with alkenes, so it has been used primarily for aquifers contaminated with trichloroethene (TCE), perchloroethene (PCE), and, 1,1,1-trichloroethane (Amarante, 2000; Liang et al., 2003).

Although many ISCO processes have a high degree of potential for destroying hydrophobic and bio-refractory compounds in the soil and the subsurface, none are ideal under full-scale field conditions. Each of these oxidants has its limitations in the remediation matrix. Ozone is limited by its short retention time in the subsurface because it reacts rapidly with a wide range or naturally occurring non-target chemical species such as reduced minerals and organic matter and hydroxide ions. Also, ozone has a relatively low solubility in water and is highly vulnerable to hydraulic short-circuiting as a gas in the unsaturated zone (EPA, 1996). Permanganate is characterized as having a

very low reactivity with many contaminants, and by the formation of manganese oxide precipitates which may clog subsurface pores. Permanganate also reacts preferentially with organic matter and inorganic constituents in the soil, which limits its effectiveness (Mumford et al., 2005). Also, MnO_2^-, which is the main reaction byproduct, has the tendency to accumulate near the injection well or at the DNAPL interface resulting in mass transfer limitations (EPA, 2006). Modified Fenton's reagent is unstable in the presence of subsurface solids, particularly those containing high concentrations of manganese oxides (Watts et al., 2005).

The persistence of the oxidant in the subsurface plays an important role since this affects the contact time for advective and diffusive transport and ultimately the delivery of oxidant to targeted zones. Therefore, new oxidant agents were added to the list of possible oxidants for the use within ISCO processes (Liang et al., 2007). The newest ISCO agent was persulfate ($S_2O_8^{-2}$), which has become an increasingly popular oxidant that is more stable in the subsurface as compared to H_2O_2 and O_3 (Huang et al., 2002), and can persist in the subsurface for weeks, suggesting that the natural oxidant demand (NOD) for persulfate is low (Droste et al., 2002). However, persulfate must be activated to oxidize contaminants of concern. Moreover, the reported investigations using persulfate were highly empirical and consequently a fundamental study of persulfate activation in soils and groundwater would greatly enhance its effectiveness in the field.

Persulfate Chemistry

Persulfate, known also as peroxydisulfate or peroxodisulfate, is a sulfate peroxide with the chemical structure $[O_3S-O-O-SO_3]^{2-}$ (Ahmad, 2008; House, 1962; Liang et al.,

2004). Persulfate has been used as an agent in a number of industrial applications such as an initiator for olefin polymerization in aqueous systems, as a micro-etchant for printed circuit boards, for leaching of textiles, and in studies related to industrial wastewater treatment (Killian et al., 2007).

There are three possible salts of persulfate: potassium, ammonia and sodium. The solubility of potassium persulfate is very low for environmental applications, and the reaction of ammonium persulfate results in an ammonia residual, which is an undesirable reaction product. Therefore, sodium persulfate ($Na_2S_2O_8$) is the most common and feasible form used to date in ISCO, with a high solubility (73 g/100 g H_2O at $25^{o}C$) (Behrman and Dean, 1999; EPA, 2006; FMC, 1998).

Persulfate salts are dissociated in water to the persulfate anion ($S_2O_8^{-2}$) which, despite having a strong oxidation potential ($E^{o} = 2.01$ V), is kinetically slow to react with many organic compounds. Studies have indicated that persulfate anions can be activated to generate sulfate radicals ($SO_4^{\bullet-}$), which are stronger oxidants compared to the persulfate anion ($E^{o} = 2.6$ V) (Liang et al., 2007; Watts and Teel, 2006).

Conventional oxidants can accept electrons from persulfate ions to form the sulfate anion radical, but the reaction rate is extremely slow. Therefore, the oxidation of target contaminants by this oxidant has to be accelerated by activation of persulfate, thus increasing the rate persulfate decomposition and the rate of sulfate free radical formation (Liang et al., 2007; Todres, 2003).

To the date, the methods that have been extensively used for the activation of persulfate include heat, light, gamma radiation, and transition metals (Anipsitakis and

Dionysiou, 2004; Liang et al., 2007; Waldemer et al., 2007). Their initiation reactions, which result in the formation of sulfate radicals, are:

$$S_2O_8{}^{2-} \xrightarrow{\text{Heat, h}\nu\text{ activation}} 2\,SO_4{}^{2-} \hspace{4cm} [1.1]$$

$$S_2O_8{}^{2-} + M^{n+} \xrightarrow{\text{metal activation}} SO_4{}^{\bullet-} + SO_4{}^{2-} + M^{+(n+1)} \hspace{2cm} [1.2]$$

Another common approach to activate the generation of sulfate radicals is the use of base (Liang et al., 2007). Recent studies have demonstrated the influence of pH on the generation of reactive oxygen species in base-activated persulfate systems (Corbin, 2008). Under these conditions most sulfate radicals are converted to hydroxyl radicals ($OH^\bullet$) (equations 1.3 to 1.9), which can proceed through propagation reactions to give the same reactive species (hydroxyl radicals, hydroperoxide, superoxide, and hydrogen peroxide) as those that are found in CHP systems (Gonzalez and Martire, 1997; Dogliotti and Hayon, 1967; Liang et al., 2007). Therefore, the reactive species formed in neutral and alkaline conditions are:

$$SO_4{}^{\bullet-} + OH^- \rightarrow OH^\bullet + SO_4{}^{-2} \hspace{4cm} [1.3]$$

$$SO_4{}^{\bullet-} + H_2O \rightarrow HSO_4{}^- + OH^\bullet \hspace{4cm} [1.4]$$

$$OH^\bullet + OH^\bullet \rightarrow H_2O + \frac{1}{2}O_2 \hspace{4cm} [1.5]$$

$$S_2O_8{}^{2-} + OH^\bullet \rightarrow HSO_4{}^- + SO_4{}^{\bullet-} + \frac{1}{2}O_2 \hspace{3cm} [1.6]$$

$$S_2O_8{}^{2-} + OH^{\bullet} \rightarrow S_2O_8{}^{-} + OH^{-} \qquad [1.7]$$

$$SO_4{}^{\bullet-} + OH^{\bullet} \rightarrow SO_4{}^{2-} + \frac{1}{2}O_2 \qquad [1.8]$$

$$SO_4{}^{\bullet-} + S_2O_8{}^{2-} \rightarrow SO_4{}^{2-} + S_2O_8{}^{-} \qquad [1.9]$$
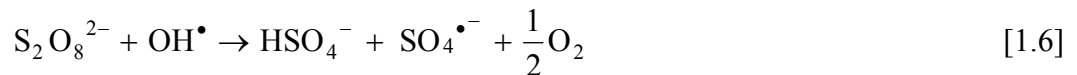
However, this mechanism implies that the initial step to generate sulfate radicals is carried out by heat or *UV* (Equation 1.1).

Persulfate Activation by Organic Compounds

Sulfate and hydroxyl radicals are formed during the activation pathways of persulfate. Sulfate radicals and hydroxyl radicals are very strong oxidants that potentially oxidize common groundwater contaminants. The hydroxyl radical is a non-specific oxidant that reacts with most organic compounds, and chlorinated contaminants such as TCE and PCE (Haag and Yao, 1992). Sulfate radicals, like hydroxyl radical, are strong oxidants and oxidize organic contaminants through three mechanisms: 1) hydrogen abstraction; 2) addition and substitution reactions with alkenes and aromatic compounds; and 3) electron transfer from carboxylate groups (Liang et al., 2003; Todre, 2003).

Studies developed by Neta et al. (1977) indicate that with many organic compounds $SO_4{}^{\bullet-}$ reacts as a more effective oxidant than $OH^{\bullet}$ because it is more selective to oxidation while $OH^{\bullet}$ may react rapidly by hydrogen abstraction or addition (Neta et al., 1988). The sulfate free radicals, $SO_4{}^{\bullet-}$, have been shown to react with several aromatic and benzene derivatives by electron transfer (Neta et al., 1977). Also, sulfate radicals have the ability to react with alcohols, hydrocarbons and ether compounds through

hydrogen (H) abstraction by breaking the C-H bond (Elbenberger et al., 1978; George et al., 2001). The reactions of aliphatic acids with sulfate radicals usually lead to carboxylations, but reactions with hydroxyl radical do not. Therefore, the reactions with sulfate radicals involve electron transfer for the —COO^- group, whereas hydroxyl radical abstracts hydrogen atoms from an aliphatic C—H bond. The reaction rate constants of the hydroxyl radical and sulfate radicals with some aromatic and aliphatic compounds are shown in Table 1.1 (Buxton et al., 1987; Neta et al., 1977).

Elbs (1893) reported the oxidation of *o*-nitrophenol to nitroquinol by reaction with ammonium persulfate in the presence of alkali. Elbs persulfate oxidation involves nucleophilic displacement where the nucleophile is a phenolate anion and the main reaction product is an aromatic sulfate with a *para* orientation relative to the phenolic group (Behrman, 2006). Baker and Brown (1948) suggested that during the Elbs persulfate oxidation of phenols, resonance hybrids of the phenoxide ion may be involved.

Fenton initiation reaction and sodium hydroxide activation likely proceeds through the base activated hydrolysis of persulfate. Other mechanisms of persulfate activation likely occur, but have received little attention to date. Work conducted in Dr. Rick Watt's laboratory at Washington State University indicated that persulfate is activated by one or more compounds in the contaminated soils. Minerals, soluble metals, and organic matter have all been implicated, but it is unclear how much each of these components contributes to the activation. The activation of persulfate by organic compounds that may exists as contaminants and those that can be produce by native microbes is examined in details in Chapters 2 and 3.

Project Objectives

The focus of this dissertation is:

- Study the activation of persulfate by an array of different organic compounds that may exists as contaminants in the subsurface and those that can be produce by native microbes. The organic compounds include carboxyl acids, alcohols, aldehydes, and the groups in the Krebs cycle such as ketoacids, dicarboxylic acids, and alcohol acids.

- Evaluate the activation of persulfate by phenoxides, the basic form of phenols.

- Determine the mechanism of phenoxide activated persulfate systems at basic pH.

The results from this research are important to determine the pathway for contaminant degradation in ISCO applications.

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Table 1.1: Rate Constants for Reactions of Hydroxyl Radicals and Sulfate Radicals with Aliphatic and Aromatic Compounds (Buxton et al., 1987; Neta et al., 1977).

Aliphatic/Aromatic Compounds	Rate Constants	
	$k_{OH\cdot}$, M^{-1} s^{-1}	$k_{SO4\cdot}$, M^{-1} s^{-1}
Methanol	8.0×10^8	1.0×10^7
Ethanol	1.8×10^9	4.3×10^7
2-Propanol	2.0×10^9	8.2×10^7
t-Butyl alcohol	5.2×10^8	$\leq 10^6$
1-Hexanol	5.2×10^9	1.6×10^8
Anisole	6.0×10^9	4.9×10^9
Benzene	7.8×10^9	3.0×10^9
Benzoic acid	4.0×10^9	1.2×10^9
Nitrobenzene	3.9×10^9	$< 10^6$

CHAPTER 2
PERSULFATE ACTIVATION BY ALCOHOLS, ALDEHYDES, KETONES, ORGANIC ACIDS, AND KETO ACIDS

ABSTRACT

Activated persulfate is an increasingly popular reagent for the *in situ* chemical oxidation (ISCO) remediation of contaminated soils and groundwater. Persulfate appears to directly oxidize highly reduced compounds, such as benzene derivatives with ring activating groups; however, persulfate must be activated to oxidize most other contaminants of concern. Minerals, soluble metals, and organic matter have all been implicated in the activation, but it remains unclear how much each of these components contributes to the activation. The activation of persulfate by organic compounds was investigated as a basis for understanding its interaction with persulfate in the subsurface. Reactions were conducted at basic pH (>12) with 0.5 M persulfate using nitrobenzene as a hydroxyl radical probe and hexachloroethane as a reductant probe, using as organic activators different functional groups including ketones, carboxyl acids, alcohols, aldehydes, and the groups in the Krebs cycle such as keto acids, dicarboxylic acids, and alcohol acids. The results demonstrated that all of the four classes of organic compounds activated persulfate at high pH. However, the degree of activation was related to the functional group in the organic compound and its position within the structure. Keto acid was the most effective activator by degrading the hydroxyl radical probe nitrobenzene, and the reductant probe hexachloroethane. Dicarboxylic acid and ternary alcohols did not effectively promote the generation of hydroxyl radicals or reductants. The results also

indicated that the ionized form of the organic compound is important to promote the activation of persulfate. The results of this research suggest that some organic contaminants or their degradation products may activate persulfate, providing enhanced destruction of refractory contaminants.

INTRODUCTION

The quality of groundwater resources is an extremely important issue. Innovative and effective strategies for the remediation of groundwater contaminated with organic chemicals are needed to ensure the quality of the resource. Organic compounds that contaminate groundwater include both highly water soluble and non-aqueous phase liquids (NAPLs), which are classified as fluids less dense than water (LNAPLs) or more dense than water (DNAPLs) (Pankow and Cherry, 1996).

A common technique used to remediate contaminated soil and groundwater is *in situ* chemical oxidation (ISCO), in which strong oxidants are introduced into the subsurface to react with contaminants of concern and transform them into less harmful chemical species (Watts and Teel, 2005; Siegrist et al., 2002). ISCO encompasses a series of chemical oxidation technologies, including major oxidants such as ozone (O_3), permanganate (MnO_4^-) and catalyzed hydrogen peroxide (H_2O_2) propagations (CHP) (Watts and Teel, 2006) (Table 2.1). However, each of these oxidants has limitations in the remediation matrix.

To overcome these limitations, activated persulfate has become an increasingly popular reagent for ISCO technology. Sodium persulfate ($Na_2S_2O_8$) is used as a persulfate source because of its high water solubility (73g/100g water) and stability in the

subsurface (Liang et al., 2007). It is a more stable oxidant source than hydrogen peroxide and provides greater potential for transport from the point of injection to the contaminants in lower permeability regions of the subsurface. Persulfate anion ($S_2O_8^{-2}$) is a strong oxidant ($E^o = 2.01$ V), and appears to oxidize highly reduced compounds, such as benzene derivatives with ring activating groups, but reacts slowly with most contaminants of concern. However, persulfate must be activated to oxidize most other contaminants of concern, such as trichloroethene (TCE), perchloroethene (PCE), and, 1,1,1-trichloroethane. The activation of persulfate generates the reactive oxygen species sulfate radical ($SO_4^{\bullet-}$), a more effective oxidizing agent than persulfate ($E^o = 2.6$ V).

The activation is usually accomplished using base, transition metals, heat, light, or gamma radiation (Anipsitakis and Dionysiou, 2004; Liang et al., 2007; Waldemer et al., 2007). Sodium hydroxide most likely activates persulfate through base catalyzed hydrolysis. Recent studies have demonstrated the influence of pH on the generation of reactive oxygen species in base-activated persulfate systems (Corbin, 2008). Under these conditions most sulfate radicals are converted to hydroxyl radicals ($OH^{\bullet}$), which can proceed through propagation reactions to give the same reactive species as those that are found in CHP systems (Dogliotti and Hayon, 1967). In the case of transition metals, persulfate is activated by an electron transfer similar to the Fenton initiation reaction (Watts and Teel, 2005). The sulfate radicals generated during heat activation can initiate a series of radical chain reactions, which results in the degradation of organic compounds (Huang et al., 2002).

Persulfate use for field scale ISCO applications has increased in recent years, and results from these studies suggest that persulfate is activated by one or more compounds

in the contaminated soils. Minerals, soluble metals, and organic matter have all been implicated, but it is unclear how much each of these components contributes to the activation (Ahmad, 2008).

Organic matter is divided into two basic categories: nonhumic and humic materials. Nonhumic materials include amino acids, carbohydrates, fats, and other biochemicals that occur in the soil as a result of the metabolism of living organisms. Humic substances are present in soil, water and sediments. These substances are derived from plant, algal and microbial material (Scott et al., 1998) and are associated with functional structures such as aromatic carboxyl groups, ketones, esters, ethers, and hydroxyl structures. Some of these compounds found in living organisms are components of the Krebs cycle. Other investigators (David-Gara et al., 2008) have studied the interaction between humic substances and sulfate radicals ($SO_4^{\bullet -}$) with organic contaminants in water and soil. They emphasized that the presence of humic substances can decrease the effectiveness of oxidants, since these compounds could scavenge sulfate radicals. However, it is also possible that some humic substances could increase the effectiveness of oxidants, such as Krebs cycle compounds that have the potential to activate persulfate in high pH systems.

Some investigators also have evaluated the interaction of sulfate radicals generated by flash photolysis with humic substances and the organic contaminants (David-Gara et al., 2007). These results indicated that the initial step of reaction mechanism involves the reversible binding of the sulfate radicals by the humic substances. Both the bound and the sulfate radicals then decay to oxidized products. Additionally, Caregnato et al. (2008) performed a mechanistic investigation of the

reaction of sulfate radicals with gallic acid, a low molecular weight humic substance. The flash photolysis experiments performed with this system showed the formation of phenoxyl radicals of the organic substrate as reaction intermediates, which supports the H-abstraction by the sulfate radical from gallic acid.

This research focused on organic compounds that may exist as contaminants and those that can be produced by native microbes, since analyzing the interaction of living microorganisms with persulfate as an oxidant is important. Recent studies have demonstrated that phenolic compounds activate persulfate, providing enhanced destruction of refractory contaminants (Ocampo et al., 2007). The objective of this study was to investigate the activation of persulfate by an array of different organic compounds at alkaline pH. A study was undertaken to screen different functional groups including ketones, carboxyl acids, alcohols, aldehydes, and the groups in the Krebs cycle such as ketoacids, dicarboxylic acids, and alcohol acids, for their ability to activate persulfate. The organic-activated persulfate reactions were evaluated through the use of reaction-specific probe compounds.

MATERIALS AND METHODS

Chemicals. Sodium hydroxide (reagent grade, 98%), sodium bicarbonate, nitrobenzene, potato starch, and hexane (>98%) were obtained from J.T. Baker (Phillipsburg, NJ). Sodium persulfate ($Na_2S_2O_8$) (reagent grade, >98%), magnesium chloride ($MgCl_2$) (99.6%), and hexachloroethane (HCA) (99%) were purchased from Sigma Aldrich (St. Louis, MO). A purified solution of sodium hydroxide was prepared by adding 5–10 mM of $MgCl_2$ to 1 L of 8 M NaOH, which was then stirred for a minimum 8

hours and passed through a 0.45 μM membrane filter. Sodium thiosulfate (99%), potassium iodide, methylene chloride, and mixed hexanes were purchased from Fisher Scientific (Fair Lawn, NJ). Deionized water was purified to >18 MΩ•cm with a Barnstead Nanopure II ultrapure system (Dubuque, Iowa).

Potential Persulfate Activators. Different classes of organic compounds were evaluated for their potential to activate persulfate under basic conditions. Acetone, sodium pyruvate, pyruvate acid, citrate, 1-propanol (>99%), 2-propanol (>99%), *t*-butyl alcohol (>99%), and formaldehyde were obtained from J.T. Baker (Phillipsburg, NJ).2-Butanone (>99%), 2-pentanone (>99%), 2-heptanone (99%), oxalic acid, acetoacetic acid (98%), L(-) malic acid disodium, succinic acid, 1-pentanol (>99%), 2-pentanol (98%), 3-pentanol (98%), acetaldehyde (99%), propionaldehyde (97%), and butyraldehyde (>99%) were purchased from Sigma Aldrich (St. Louis, MO). Levulinic acid (98%) and isobutanol (>99%) were obtained from Alfa Aesar (Ward Hill, MA). sec-Butanol (>99%) was obtained from Acros Organics (Morris Plains, NJ).

Probe Compounds and Scavengers. Nitrobenzene, which has a high reactivity with hydroxyl radicals ($k_{OH•} = 3.9 \times 10^9$ $M^{-1}s^{-1}$) and negligible reactivity with sulfate radicals ($k_{SO4•-} = \leq 10^6$ $M^{-1}s^{-1}$), was used to detect hydroxyl radicals (Neta et al., 1977; Buxton et al., 1987; Clifton and Huie, 1989). HCA was used as a reductant probe because it is not oxidized by hydroxyl radicals ($k_{OH•} = < 1 \times 10^6$ $M^{-1}s^-$) (Haag and Yao, 1992). *t*-Butyl alcohol was used to scavenge hydroxyl radicals ($k_{OH•} = 5.2 \times 10^8$ M^{-1} s^{-1}) without scavenging sulfate radicals ($k_{SO4•-} =< 1 \times 10^6$ M^{-1} s^{-1}) (Buxton et al., 1987). The scavenger: probe molar ratio used was 1000:1.

General Reaction Procedures. All reactions were conducted in 20 mL borosilicate vials capped with polytetrafluoroethylene (PTFE) lined septa. Each reaction vial contained 0.5 M sodium persulfate, 2M NaOH, 10 mM of the organic compound used as an activator, and the selected probe (1 mM of nitrobenzene or 2 μM of hexachloroethane). At selected time points, sodium persulfate was measured using iodometric titrations, and the residual probe concentration was analyzed with gas chromatography (GC) after extracting the contents of the reactor with hexane. All reactions were performed in triplicate, and the data were reported as the mean of the three replicates. The standard error of the mean was calculated and included as error bars for each data point. All reactions were conducted at a temperature of ± 20 °C. Triplicate control systems for each organic system were evaluated in parallel at a pH above 12 using deionized water in place of the organic activator solution. Solution pH was monitored by using a Fisher Accumet pH meter 900 (Fisher Scientific, Hampton, NH).

Analytical Procedures. Hexane extracts were analyzed for nitrobenzene using a Hewlett Packard Series 5890 GC with a 0.53 mm (i.d) x 15 mSPB-5 capillary column and flame ionization detector (FID). Chromatographic parameters included an injector temperature of 200 °C, detector temperature of 250 °C, initial oven temperature of 60 °C, program rate of 30 °C/min, and a final temperature of 180 °C. Hexane extracts were analyzed for HCA using a Hewlett Packard Series 5890 GC with electron capture detector (ECD) by performing splitless injections onto a 0.53 mm (i.d.) x 30 m Equity-5 capillary column. Chromatographic parameters included an injector temperature of 220 °C, detector temperature of 270 °C, initial oven temperature of 100 °C, program rate of

30 °C/min, and a final temperature of 240 °C. A 6-point calibration curve was developed using known concentrations of nitrobenzene or hexachloroethane solutions respectively.

Sodium persulfate concentrations were determined by iodometric titration with 0.01 N sodium thiosulfate (Kolthoff and Stenger, 1947). The Statistical Analysis System package SAS 9.1.3 was used to calculate the variances between the experimental data sets and 95% confidence intervals for rate constants.

RESULTS AND DISCUSSIONS

Ketones. The potential of ketones to activate persulfate was studied by using acetone, 2-butanone, 2-pentanone, and 2-heptanone. Hexachloroethane was used as a probe compound to evaluate the generation of reductants in the high pH persulfate systems. The relative generation rates of reductants by ketone-activated persulfate over 3 hr are shown in Figure 2.1. Hexachloroethane was degraded most rapidly with acetone as the activator, with >99% degradation, compared with 20% degradation when 2-heptanone was the activator. In the control system, the approximately 8% loss of hexachloroethane was likely due to volatilization. The results demonstrate that ketones activate persulfate, and that the relative generation of reductants in ketone-activated persulfate systems decreased as the number of carbons that are bound to the carbonyl group (C=O) of the ketone increased.

Hydroxyl radical generation in the high pH ketone-activated persulfate systems was studied by using nitrobenzene as a probe (Figure 2.2). The destruction of nitrobenzene over time exhibited a similar pattern to the hexachloroethane results for all ketones. Acetone was the most effective activator of persulfate with 93% nitrobenzene

loss over 3 hr, while 2-heptanone was the least effective activator with 20% nitrobenzene loss. In the control systems containing no ketones, no measurable loss of nitrobenzene was observed during the 3 hr experiment.

The behavior of acetone indicates that the two methyl substituents next to the ketone group increased the reactivity of persulfate activation for that group. The degradation rate of both probes, hexachloroethane and nitrobenzene, was inversely proportional to the size of the substituents linked to the carbonyl group of the ketone. For example, 2-heptanone activation of persulfate resulted in less probe degradation compared to 2-butanone. In 2-heptanone has methyl and pentyl groups bonded to the carbonyl group, while 2-butanone has methyl and ethyl groups. Therefore, the size of the relative substituent to the ketone group affects the activation rate. These results are similar to the study of the ketone-catalyzed decomposition of peroxomonosulfate (SO_5^{2-}) in aqueous alkaline medium (Selvararani et al., 2005). In that case, the nucleophilic addition of SO_5^{2-} ion at the carbonyl carbon in the ketone leads to the formation of the oxirane, and the rate constant of that reaction is inversely proportional to the size of the substituents of the carbonyl group.

Krebs Cycle Compounds. The Krebs cycle compounds were classified into three categories: keto acids, alcohol acids, and dicarboxylic acids. The keto acids included pyruvic acid, the main substrate for the Krebs cycle, acetoacetic, and levulinic acid. Alcohol acids included malic and citric acid. Dicarboxylic acids were represented by oxalic acid and succinic acid. The relative proportion of the acid form and the ionized salt for the Krebs cycle compounds, as a function of pH, is shown in Table 2.2. Persulfate

activation by these organic compounds was studied in a basic environment at a pH above 12; therefore, all the Krebs cycle compounds used were in their ionized form.

The generation of reductants in the high pH Krebs cycle compounds-activated persulfate systems is shown in Figure 2.3. The most rapid degradation of hexachloroethane was accomplished by the keto acids (Figure 2.3a). In particular, levulinic acid, which has the ketone group located at the third carbon from the carboxylic acid (Table 2.1), was the compound that most effectively activated persulfate to generate reductants. Conversely, in the presence of alcohol acids (Figure 2.3b) complete degradation of hexachloroethane was achieved but at a slower rate compared with the keto acids. Greater than 99% hexachloroethane degradation was accomplished in just 0.4 hours when keto acids were the activators in the persulfate system, compared to 1 hour when alcoholic acids were the selected organic activators. Dicarboxylic acids (Figure 2.3c) showed the smallest degradation of hexachloroethane (< 20%) of all the Krebs cycle compounds evaluated.

The generation of hydroxyl radicals in the high pH Krebs intermediates-activated persulfate systems is shown in Figure 2.4. After the 2 hr reaction time, total degradation of nitrobenzene was not achieved in the alcohol acids system (Figure 2.4b), but >99% degradation occurred in the presence of keto acids (Figure 2.4a). For the two alcohol acids used as activators, the nitrobenzene degradation was 80% in the presence of malic acid and 40% in the presence of citric acid, which could be attributed to citric acid being a ternary alcohol and malic acid a secondary alcohol, thereby increasing its reactivity and potential as an activator for persulfate (Bernthsen, 1933). In the other hand, both

dicarboxylic acids used, oxalic acid and succinic acid, showed minimal nitrobenzene degradation (< 10%) during the reaction period of 2 hr (Figure 2.4c).

Moreover, dicarboxylic acids did not promote either reductant or hydroxyl radical generation. The presence of organic compounds with two carboxyl groups may scavenge the hydroxyl radical or inhibit hydroxyl radical generation. It may also promote minimal generation of reductants such as superoxide radicals.

In general, these data show that in high pH systems, Krebs cycle keto acids are the compounds with the greatest persulfate activation. Therefore, a ketone functional group results in more activation of persulfate to generate hydroxyl radicals and reductants in the system compared to a carboxylic acid group. It also shows that when the organic compound contains a carboxylic group in its structure the activation of persulfate is slow or insignificant. A possible explanation for this behavior is that an electron is generally needed to activate persulfate, and the activation is coming from the oxidation of a reduced organic compound, therefore a ketone group can activate persulfate much more effectively than a carboxylic group.

Alcohols. This research focused on the activation of persulfate by primary, secondary, and ternary alcohols. The isomers of the alcohols used are listed in Table 2.3. The pK_a values of these alcohols range from 15 to 17 (Perrin et al., 1981); consequently they could not be 100% ionized at the pH of the experiments.

Different isomers of alcohol were screened to determine their effectiveness for activating persulfate based on the position of the hydroxyl group in the structure. Maruthamuthu and Neta (1977) reported the rate constant for the reaction between sulfate radicals and some alcohols such as methanol, ethanol, 2-propanol and *t*-butyl alcohol.

Their results indicated that the rate constant values for the primary and secondary alcohols are the same order of magnitude, but the rate constant values for the ternary alcohols are two orders of magnitude smaller.

Relative rates of reductant generation, as measured through the oxidation of hexachloroethane, over a 9 h period in a high pH persulfate system in the presence of alcohols, are shown in Figure 2.5. The highest relative rates of reductant generation occurred in the presence of the three primary alcohols: *n*-propanol, *n*-butanol and *n*-pentanol (>99%).The slowest rate generation of reductants was found with the ternary alcohol *t*-butyl, which had a 20% degradation of hexachloroethane. Alcohol-free controls showed no degradation of hexachloroethane.

Relative rates of hydroxyl radical generation, measured through the degradation of nitrobenzene, over a 9 h period in high pH systems in the presence of alcohols are shown in Figure 2.6. The behavior of the alcohols in the generation of hydroxyl radicals is similar to the results for the generation of reductants. Based on batch experimental results, the alcohol with the fastest degradation rate for nitrobenzene was *n*-propanol (>99%). Only minimal nitrobenzene degradation (< 16 %) was observed for the three ternary alcohols: neopentyl, *t*-butyl and 3-pentanol.

The results of Figures 2.5 and 2.6 indicate that the position of the OH group in the chemical structure of the alcohol plays an important role in its reactivity with persulfate. The alcohols with the greatest persulfate activation were the primary alcohols, and the ones with the least activation capacity were the ternary alcohols. Additionally, the number of carbons in the chain is important in determining the percentage of the persulfate activation. For example, in the case of the primary alcohols, the alcohol with the lowest

number of carbons in the chain was *n*-propanol (Figure 2.6a), which also produced the most degradation of nitrobenzene. However, as the total number of carbons increased, the degradation of nitrobenzene was slower, as illustrated by *n*-pentanol. The same effect is observed in the case of the secondary alcohols (Figure 2.6b), where the alcohol with the least activation of persulfate was 3-methyl-2-butanol, which also had the slowest degradation rate for nitrobenzene.

In general, the potential of primary alcohols to activate persulfate is lower compared with other potential activators such as acetone or ketoacids. The primary alcohols required 9 hours to degrade both probe compounds, nitrobenzene or hexachloroethane, compared with 3 hours for the acetone and only 1 hr for the keto acid compounds.

Aldehydes. Formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde were used in order to identify the potential for an aldehyde functional group to active persulfate. The pK_a value of these aldehydes is 17 (Perrin et al., 1981); consequently they could not be 100% ionized at the pH of the experiments.

The loss of hexachloroethane in aldehyde activated persulfate systems at basic pH is show in Figure 2.7. This figure illustrates the generation of reductants as a result of propagation reactions from persulfate activation. The data demonstrate that all the aldehydes used in this study activate persulfate. However, the rate of degradation differed depending on the structure of the radical group attached to the aldehyde group. For example, the use of propionaldehyde as the organic activator resulted in a > 99 % loss of hexachloroethane in 3 hours, compared to 30% when formaldehyde was used. In the

control system, without aldehydes, the degradation of hexachloroethane was insignificant and likely due to volatilization.

Nitrobenzene degradation was measured to evaluate the generation of hydroxyl radicals during persulfate activation by aldehydes. The loss of nitrobenzene in aldehyde activated persulfate systems at basic pH is shown in Figure 2.8. The data indicate that persulfate activation using most of the aldehydes investigated generates hydroxyl radicals, but at a relatively slower rate than for reductants. For example, in propionaldehyde activated persulfate systems, hexachloroethane degradation was near-complete in 3 h, compared with the 9 h that were needed for the nitrobenzene degradation.

The pattern between the different aldehydes was not the same for hexachloroethane and nitrobenzene as it was for other functional groups such as ketones and alcohols. Acetaldehyde, for example, was one of the fastest activators during hexachloroethane degradation, but fairly slow for nitrobenzene. Nitrobenzene and hexachloroethane react at completely different rates with hydroxyl radicals and reductants/superoxides, respectively. However, the principal use of the probe compounds is to compare relative rates for a given species (such as the hydroxyl radical) rather than to compare rates between hydroxyl radicals and reductants/superoxides.

Scavenging of Hydroxyl Radicals. An excess of *t*-butyl alcohol was added to scavenge hydroxyl radicals (Anipsitakis et al., 2004). The organic compounds used to evaluate the degradation of nitrobenzene in the presence of the hydroxyl radical scavenger *t*-butyl alcohol were acetone, pyruvic acid, *n*-propanol, and propionaldehyde. These four compounds were used because they presented the greatest activation of

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persulfate in each functional group evaluated. A common characteristic of these compounds is that they have a similar molecular formula, with 3 carbons in the main chain. In the absence of the scavenger, >99% of the nitrobenzene was lost with acetone, pyruvic acid, *n*-propanol, and propionaldehyde activation. Nitrobenzene was extensively degraded due to the ready availability of hydroxyl radicals (Figure 2.9). However, on the same figure it becomes apparent that when *t*-butyl alcohol was added, nitrobenzene was not significantly degraded by persulfate activation through addition of acetone, pyruvic acid, and *n*-propanol. For propionaldehyde the degradation was less than 40%. Therefore, the hydroxyl radical is the dominant oxidant in persulfate systems at pH 12 when the activation is carried out by organic compounds such as ketones, alcohols, aldehydes, and Krebs cycle compounds.

CONCLUSIONS

The results of this study demonstrate that organic compounds similar to those present in soil organic matter promote persulfate activation at basic pH. These organic compounds may exist as contaminants, or as compounds that can be produced by native microbes. All of the four classes of organic compounds that were selected for this study activated persulfate at pH > 12. The organic groups included ketones, Krebs cycle compounds, alcohols, and aldehydes.

However, the degree of activation was related to the functional group in the organic compound and its position in the structure. For example, results indicated that when carboxylic acids were the only functional group in the structure of the organic compound, the activation of persulfate was insignificant, as was the case with oxalic and succinic acid. In contrast, when carboxylic acid was combined with other functional

group such as an alcohol, the rate of persulfate activation increased as with malic and citric acid. The reactivity of the carboxylic acids also increased when a ketone was present in the structure of the organic compound as was the case with keto acids. Similarly, the alcohol group plays an important role in alcohol activation of persulfate. However, the degree of activation depends on the orientation of the OH group in the structure. For example, primary alcohols were more effective activators compared with the ternary alcohols.

Ketones, alcohols and aldehydes were not completely in their ionized form during the experiments, since their pKa values were above 12. The only group that was fully ionized during the experiments were the Kreb cycle compounds, with pKa values ranging from one to six. The results indicate that the organic group with the greatest degree of persulfate activation was the ketoacid, which suggests that the ionized forms of the organic compounds are important to promote the activation of persulfate. Further studies of the importance of ionization will be evaluated in the the chapter on *Persulfate Activation by Phenoxide Derivatives* (Chapter 3).

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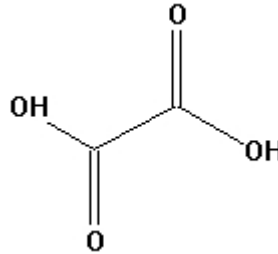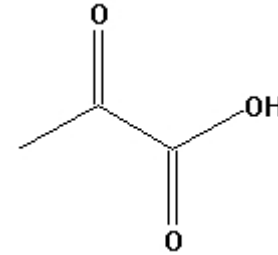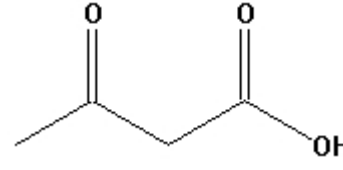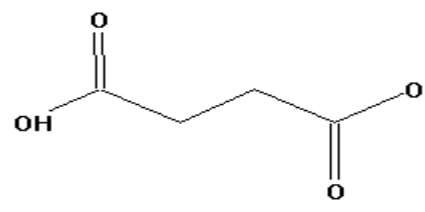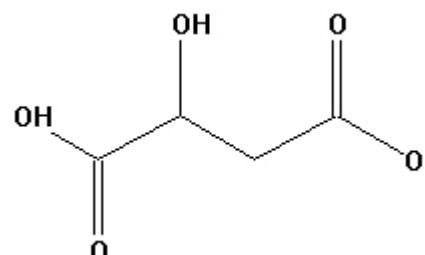
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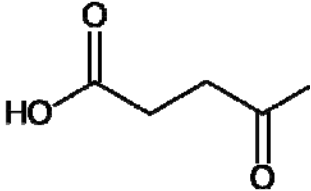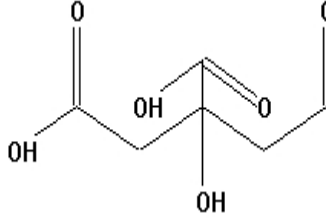**Table 2.1:** In situ Chemical Oxidation (ISCO) Technologies.

Oxidant	Amenable Contaminants of Concern	Oxidation Potential	Oxidant Stability	By-products
Modified Fenton's Reagent	TCA, PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, MTBE, *tert*-butyl alcohol (TBA), high explosives	2.80 V	Low	Fe(III) O_2 H_2O
Ozone	PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, MTBE, TBA, high explosives	2.07 V	Low	O_2
Permanganate (K/Na)	PCE, TCE, DCE, VC, BTEX, PAHs, phenols, high explosives	1.70 V	High	Mn_{aq} MnO_2 potential metals
Activated Sodium Persulfate	PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, 1,4-dioxane, MTBE, TBA	2.60 V	High	SO_4^{2-}

Table 2.2: Values of pK$_a$ for Ketones and Krebs Cycle Compounds.

Compound	Molecular Formula	Chemical Structure	Step of the Dissociation Constant	pK$_a$
Oxalic Acid	C$_2$H$_2$O$_4$		1	1.25[1]
			2	3.81[1]
Pyruvic Acid	C$_3$H$_4$O$_3$			2.39[1]
Acetoacetic Acid	C$_4$H$_6$O$_3$			3.6[1]
Succinic Acid	C$_4$H$_6$O$_4$		1	4.21[1]
			2	5.64[1]
Malic Acid	C$_4$H$_6$O$_5$		1	3.40[1]
			2	5.11[1]

[1]Lide, 2008-2009.

Table 2.2: continued

Compound	Molecular Formula	Chemical Structure	Step of the Dissociation Constant	pKa
Levulinic Acid	$C_5H_8O_3$			4.62
Citric Acid	$C_6H_8O_7$		1	3.13[1]
			2	4.76[1]
			3	6.40[1]

[1]Lide, 2008-2009.

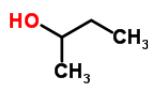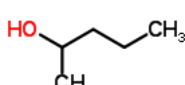**Table 2.3:** Isomers of the Alcohols Used in the Study to Activate Persulfate.
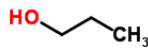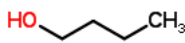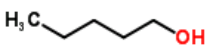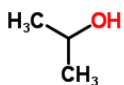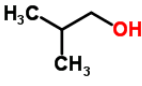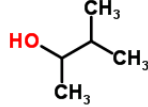
Position Isomer	Alcohol Compound	Molecular Formula	Chemical Structure
Primary Alcohols	n-propanol	C_3H_8O	
	n-butanol	$C_4H_{10}O$	
	n-pentanol	$C_5H_{12}O$	
Secondary Alcohols (Straight chain)	sec-butanol	$C_4H_{10}O$	
	2-pentanol	$C_5H_{12}O$	
Secondary Alcohols (Isomers)	2-propanol	C_3H_8O	
	isobutanol	$C_4H_{10}O$	
	3-methyl-2-butanol	$C_5H_{12}O$	

Table 2.3: continued

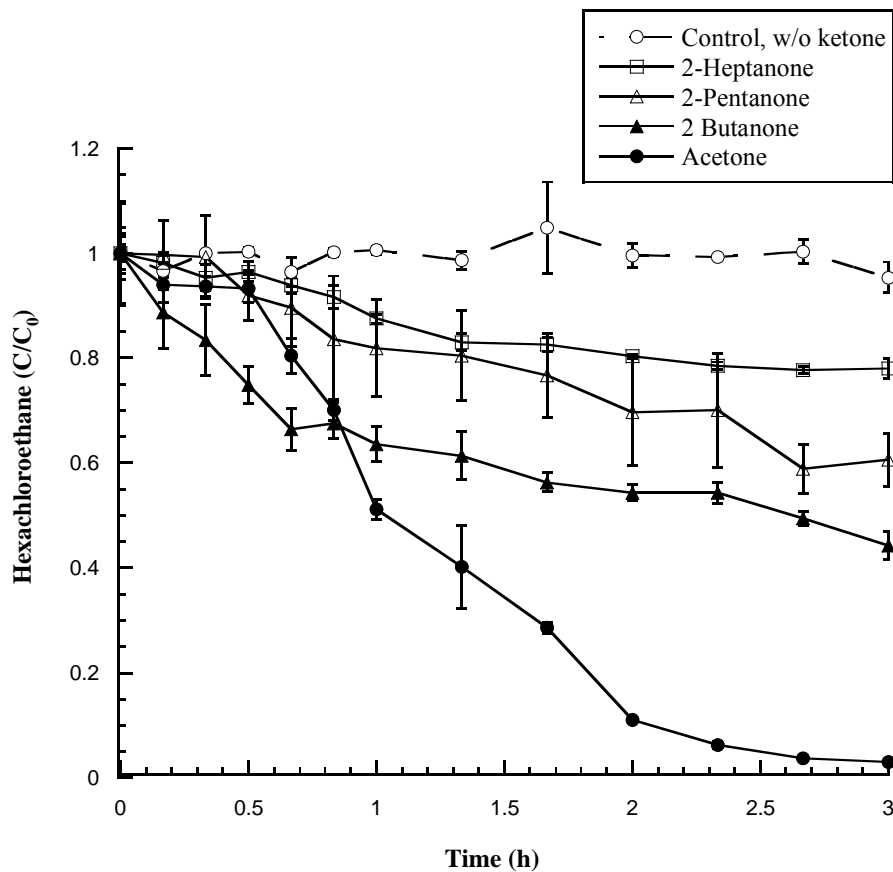| Position Isomer	Alcohol Compound	Molecular Formula	Chemical Structure
Ternary Alcohols	*t*-butyl alcohol	$C_4H_{10}O$	
	neopentyl alcohol	$C_5H_{12}O$	
	3-pentanol	$C_5H_{12}O$	

Figure 2.1: Degradation of hexachloroethane in ketones activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM ketone, and 2 μM hexachloroethane; 20 mL total volume. Error bars represent the standard error of the mean for three replicates.
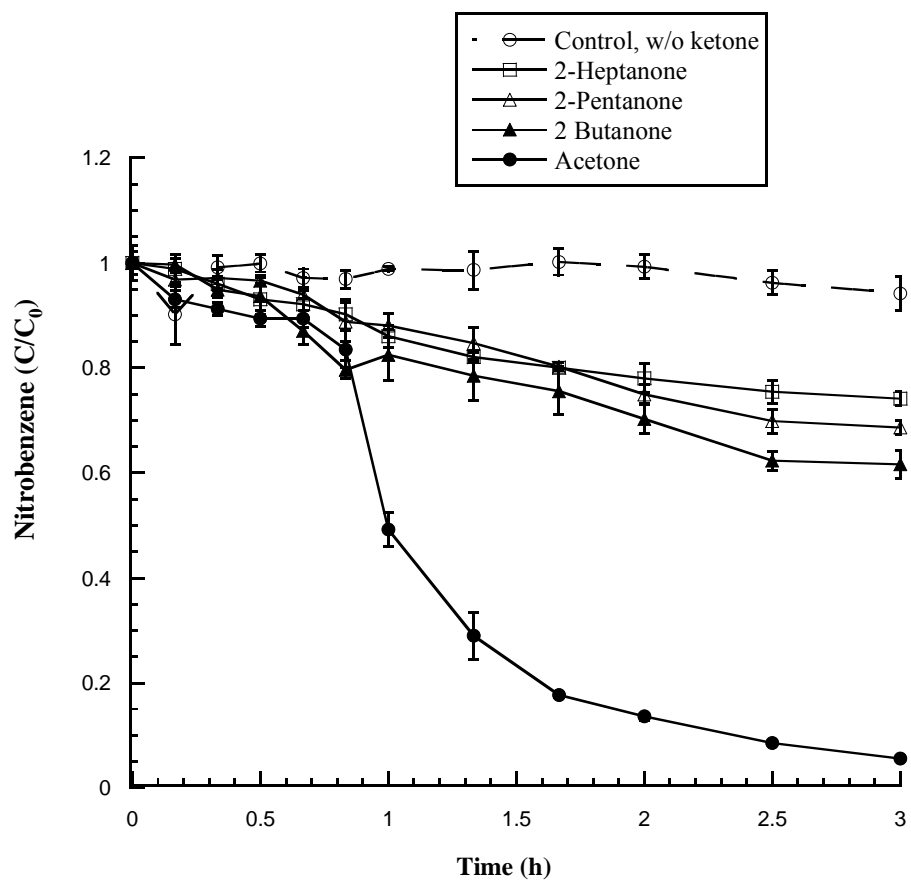
Figure 2.2: Degradation of nitrobenzene in ketones activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM ketone, and 1 mM nitrobenzene; 15 mL total volume. Error bars represent the standard error of the mean for three replicates.
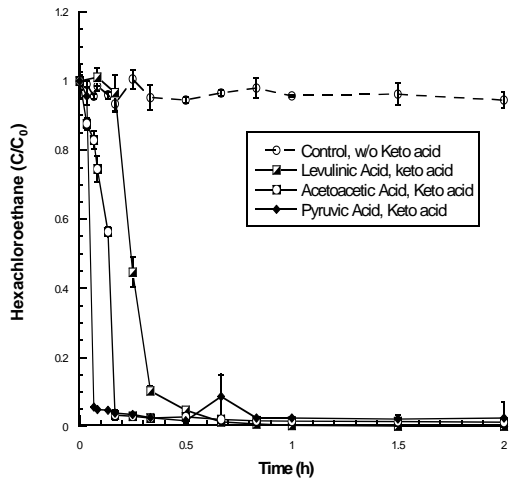
a.
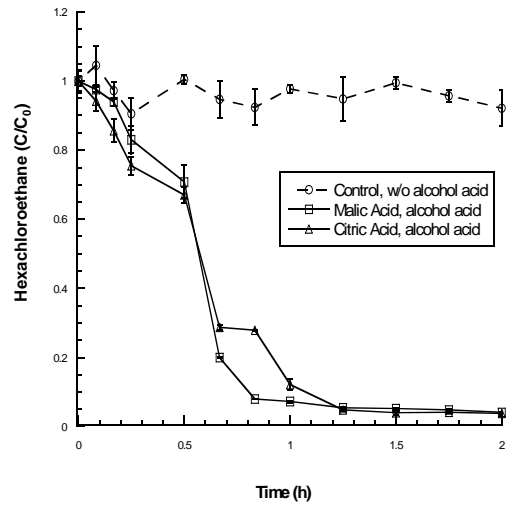
b.
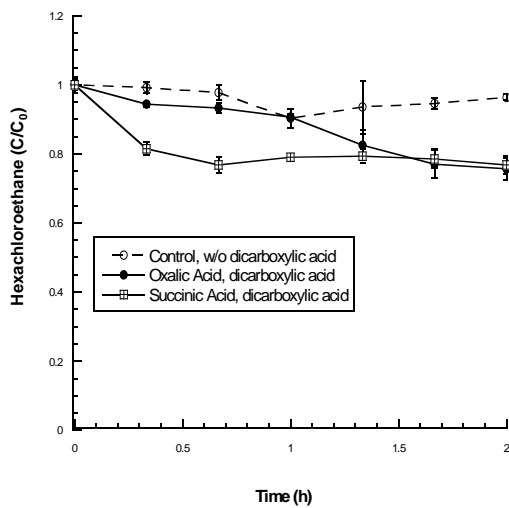
c.

Figure 2.3: Degradation of hexachloroethane in Krebs cycle-activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM Krebs cycle compound, and 2 μM hexachloroethane; 20 mL total volume. Error bars represent the standard error of the mean for three replicates. **(a)** Keto acids **(b)** Alcohol acids **(c)** Dicarboxylic acids.

a.

b.

c.

Figure 2.4: Degradation of nitrobenzene in Krebs cycle-activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM Krebs cycle compound, and 1 mM nitrobenzene; 15 mL total volume. Error bars represent the standard error of the mean for three replicates. **(a)** Keto acids **(b)** Alcohol acids **(c)** Dicarboxylic acids.

a.

b.

c.

Figure 2.5: Degradation of hexachloroethane in alcohols activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM alcohol, and 2 μM hexachloroethane; 20 mL total volume. Error bars represent the standard error of the mean for three replicates. **(a)** Primary alcohols **(b)** Secondary alcohols **(c)** Ternary alcohols.
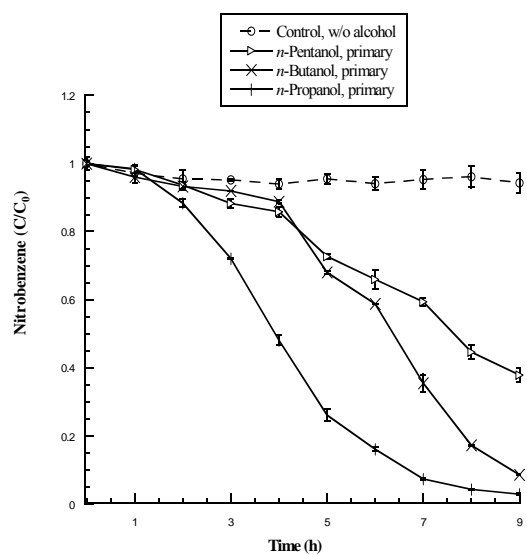
a.
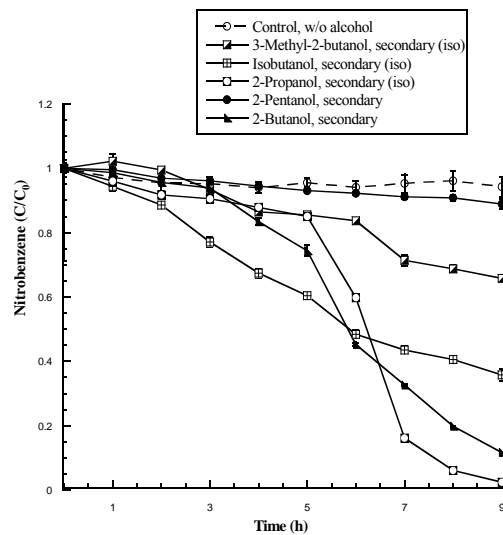
b.
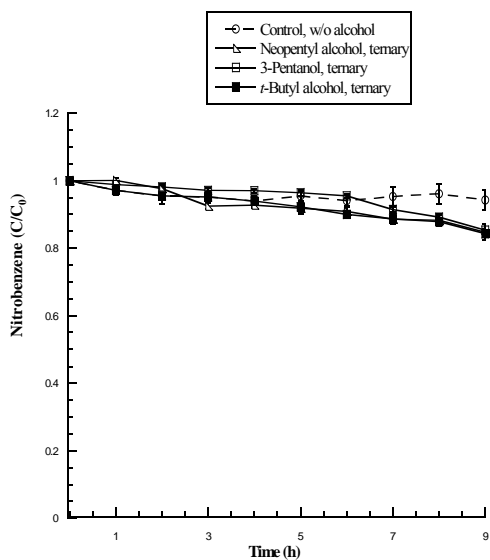
c.

Figure 2.6: Degradation of nitrobenzene in alcohols activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM alcohol, and 1 mM nitrobenzene; 15 mL total volume. Error bars represent the standard error of the mean for three replicates.
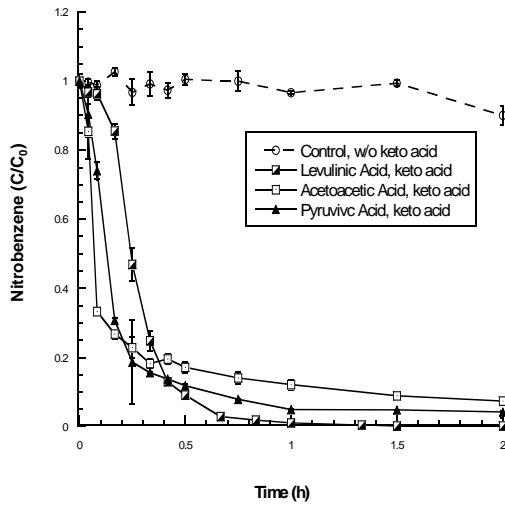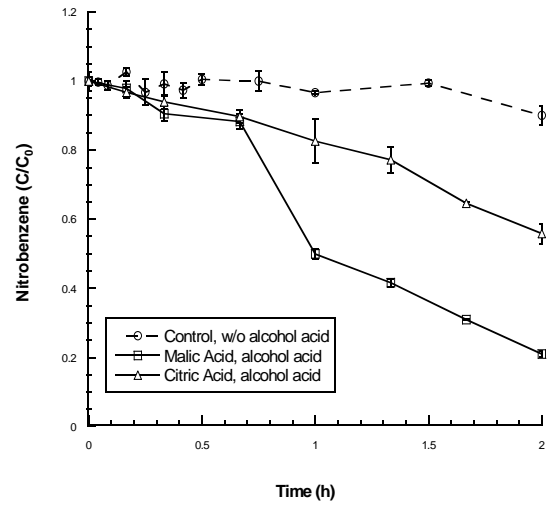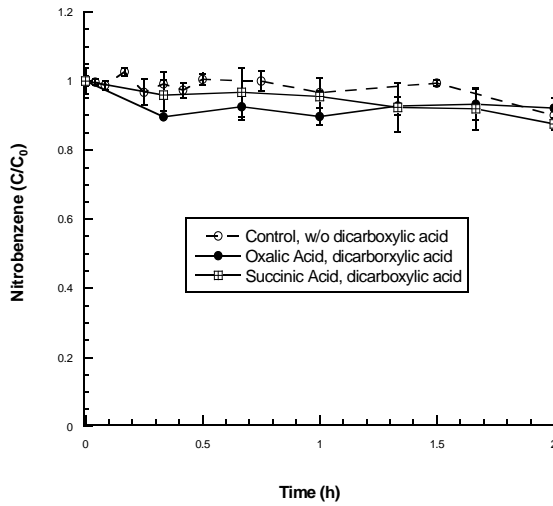**(a)** Primary alcohols **(b)** Secondary alcohols **(c)** Ternary alcohols.
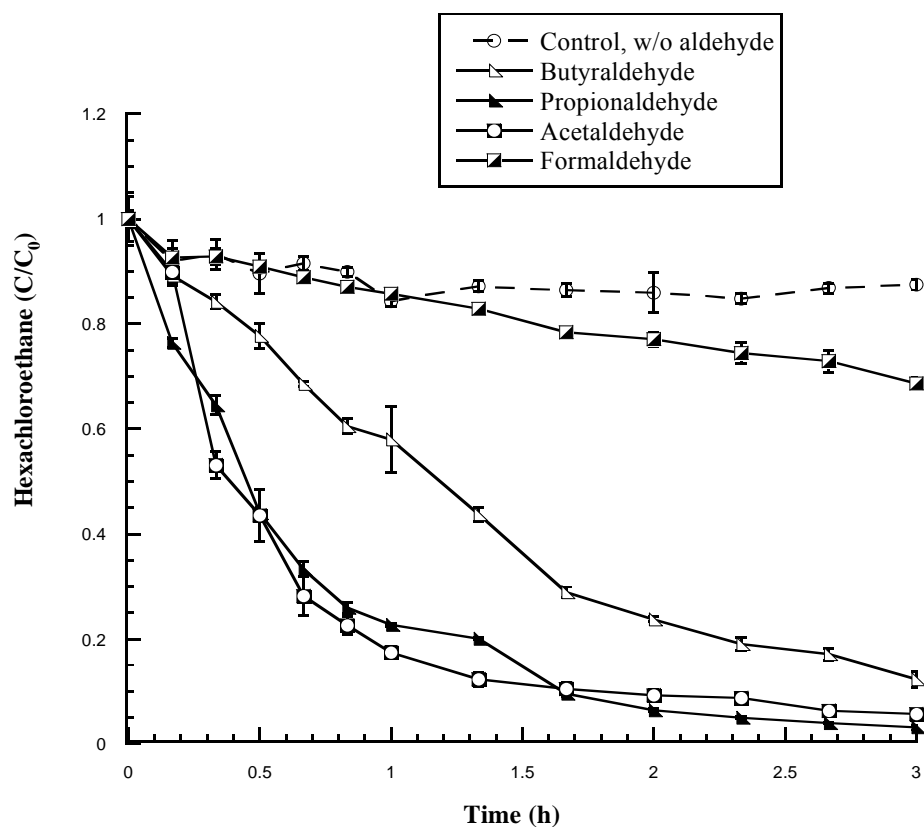
Figure 2.7: Degradation of hexachloroethane in aldehydes activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM aldehyde, and 2 μM hexachloroethane; 20 mL total volume. Error bars represent the standard error of the mean for three replicates.
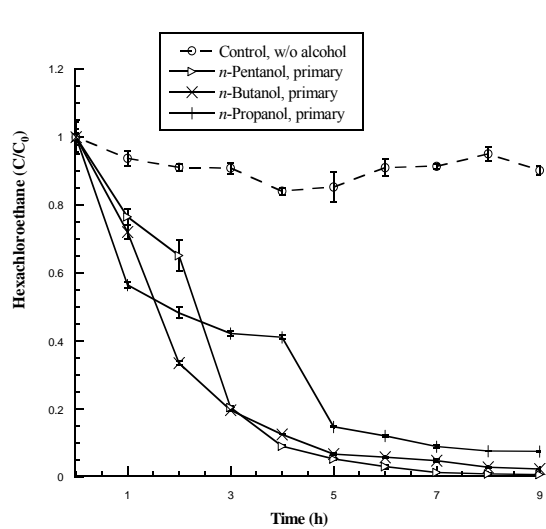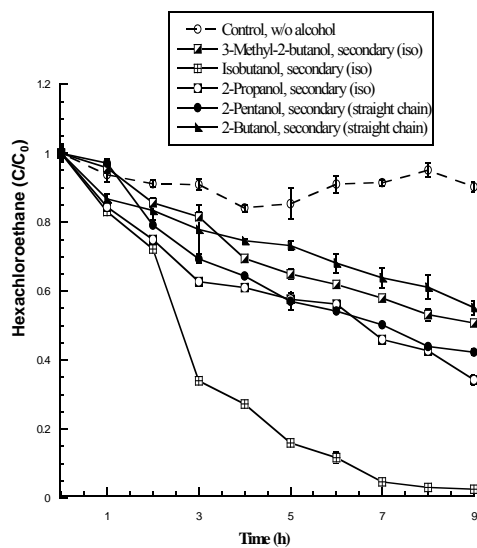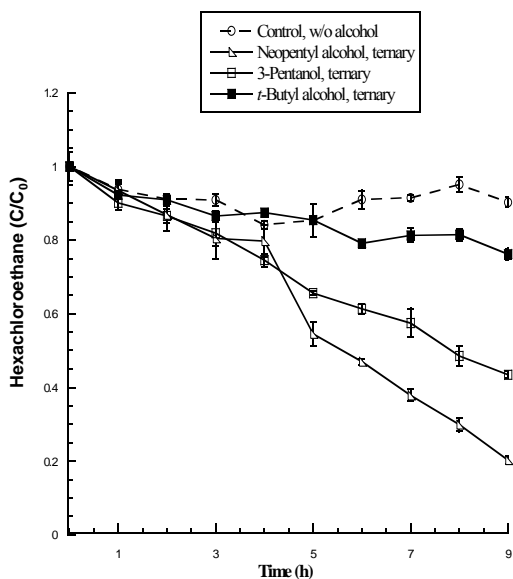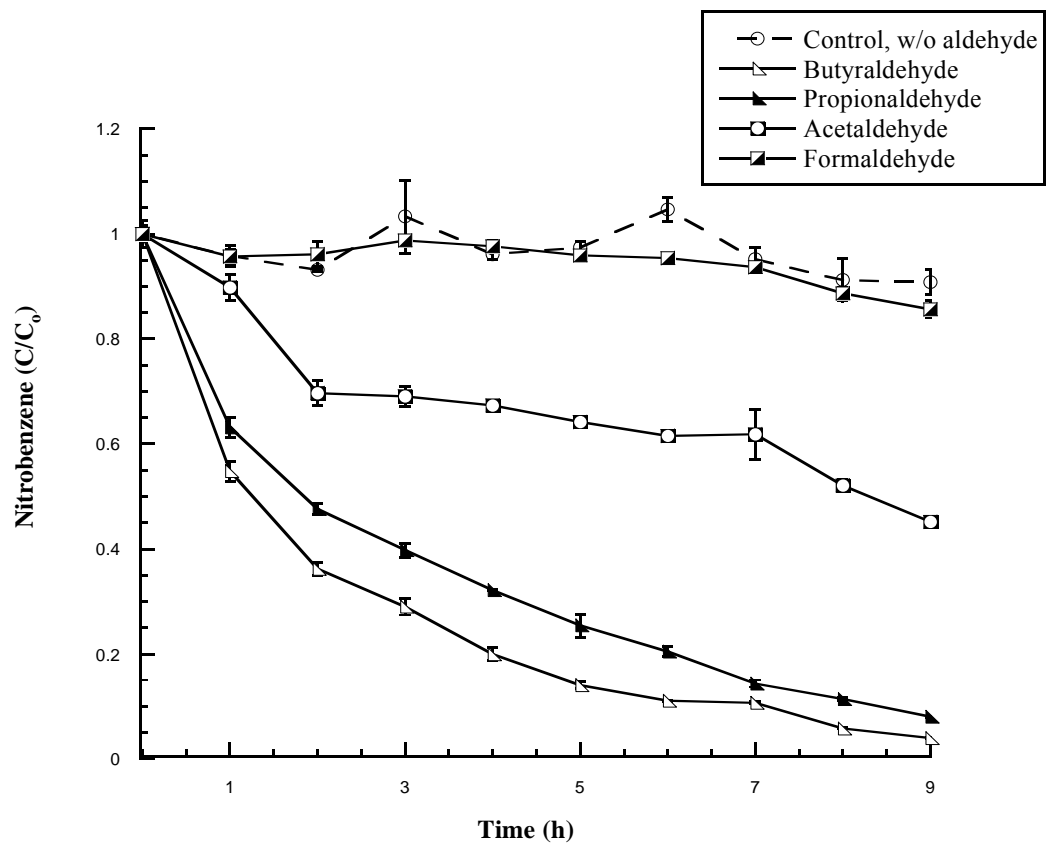
Figure 2.8: Degradation of nitrobenzene in aldehydes activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 10 mM aldehyde, and 1 mM nitrobenzene; 15 mL total volume. Error bars represent the standard error of the mean for three replicates.

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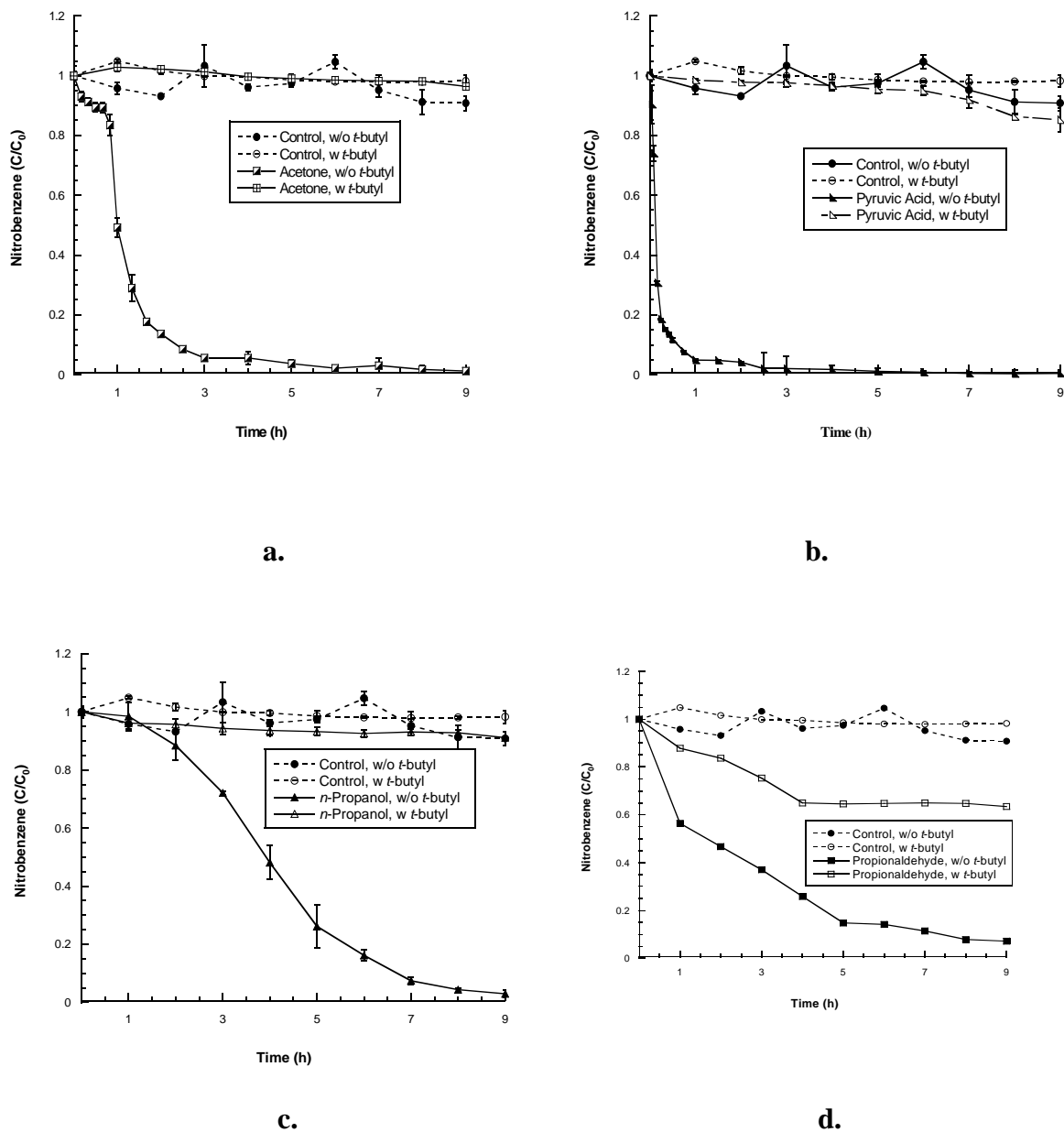
Figure 2.9: Scavenging of hydroxyl radicals in persulfate activation by selected organic compounds: 0.5 M sodium persulfate, 2 M NaOH, 10 mM organic compound, and 1 mM nitrobenzene; 15 mL total volume; the molar ratio of nitrobenzene to *t*-butyl alcohol was 1:1000. Error bars represent the standard error of the mean for three replicates. **(a)** acetone (C_3H_6O) **(b)** pyruvic acid ($C_3H_4O_3$) **(c)** *n*-propanol (C_3H_8O) **(d)** propionaldehyde (C_3H_6O).

CHAPTER 3
PERSULFATE ACTIVATION BY PHENOXIDE DERIVATIVES

ABSTRACT

The activation of persulfate by numerous substituted phenoxides (the basic form of phenols) was investigated at alkaline pH. Relative rates of hydroxyl radical generation, quantified using the hydroxyl radical probe nitrobenzene, were inversely proportional to the degree of chlorine substitution on the phenoxide ring. Similarly, relative rates of reductant/superoxide generation were inversely proportional to the degree of chlorine substitution. All of the phenoxides were found to activate persulfate, with more rapid activation promoted by the more reduced phenoxides. Batch experiments were conducted at various pH regimes to study the effects of pH on persulfate activation by the phenoxides. The anionic form of phenols (phenoxide) is the activating species in persulfate systems. Results showed that the activation of persulfate is being accomplished primarily by the phenoxide ion. Pentachlorophenol at pH 8 was used to evaluate the mechanism of persulfate activation by phenoxides, as it discerns between reductive and nucleophilic activation. The results obtained are in agreement with a reductive pathway. GC/MS confirmed that hydroquinones are formed as the pentachlorophenol was degraded. The results of this research suggest that some organic contaminants or their degradation products may activate persulfate, providing enhanced destruction of refractory contaminants.

INTRODUCTION

In situ chemical oxidation (ISCO) was established in the 1990s as a process in which strong oxidants are introduced into the subsurface to transform groundwater and soil contaminants into less harmful products (Siegrist et al., 2002; Watts and Teel, 2005). The newest and least explored ISCO agent is persulfate ($S_2O_8^{-2}$). Persulfate is more stable in the subsurface than hydrogen peroxide or ozone (Huang et al., 2002) and can persist for weeks, suggesting that the natural oxidant demand for persulfate is low (Droste et al., 2002).

Persulfate salts readily dissociate in water to form the persulfate anion ($S_2O_8^{-2}$), which has a strong oxidation potential (E^o = 2.01 V) but reacts slowly with most contaminants of concern. Persulfate is usually chemically or thermally activated to generate the reactive oxygen species sulfate radical ($SO_4^{\bullet-}$), a more effective oxidizing agent than persulfate (E^o = 2.6 V) (Watts and Teel, 2006; Liang et al., 2007). Sulfate radical reacts with water or hydroxide to generate another effective oxidizing species, hydroxyl radical ($OH^{\bullet}$) (Watts and Teel, 2006). Both sulfate and hydroxyl radicals are strong oxidants. The traditional persulfate activation processes are well established. For example, sulfate radicals generated during heat activation can initiate a series of radical chain reactions in which organic compounds are degraded (Huang et al., 2002; Waldemer et al., 2007). Other approaches for generating sulfate radicals include elevated pH (Liang et al., 2007) and activation with transition metals (Liang et al., 2004; Huang et al., 2005; Watts and Teel, 2006).

Recent studies indicate that persulfate activation may also be accomplished using minerals and organic matter (Ahmad, 2008). An electron is generally needed to activate

persulfate. Therefore, activation may be coupled to the oxidation of a reduced organic compound. Neta et al. (1977) suggested that for many organic compounds, $SO_4^{•-}$ is a more effective oxidant than $OH^•$. This is most likely because $SO_4^{•-}$ operates primarily via oxidation, while $OH^•$ may also act by hydrogen abstraction or addition (Neta et al., 1988).

Sulfate radicals have, however, been shown to react with several aromatics and benzene derivatives by electron transfer (Neta et al., 1977). The high redox potential of $SO_4^{•-}$ (Todres, 2003) enables sulfate radicals to engage in electron-transfer processes with several classes of organic compounds. $SO_4^{•-}$ is highly electrophilic, which promotes addition reactions (Davies et al., 1985); studies have demonstrated its reaction with alcohols and bicarbonate through hydrogen atom abstraction by breaking the C-H bond (Dogliotti and Hayon, 1967; Elbenberger et al., 1978; Elbenberger et al., 1978; George et al., 2001). Minisci et al. (1983) showed that oxidation of nucleophilic radicals ($R^•$) can induced a series of chain processes that generate sulfate radicals.

Elbs (1893) reported the oxidation of *o*-nitrophenol to nitroquinol by reaction with ammonium persulfate in the presence of alkali. In this type of reaction, hydroxyphenyl alkali sulfate was formed as an intermediate product, which was then hydrolyzed in acid solution to quinol. Elbs persulfate oxidation involves nucleophilic displacement where the nucleophile is a phenolate anion and the main reaction product is an aromatic sulfate with a *para* orientation relative to the phenolic group (Behrman, 2006). Baker and Brown (1948) suggested that during the Elbs persulfate oxidation of phenols, resonance hybrids of the phenoxide ion may be involved.

Merz and Waters (1949) studied the oxidation of aromatic compounds by hydrogen peroxide in the presence of ferrous salts, where the reaction mechanism was a

free-radical. The oxidation converted benzene to phenol and biphenyl. It has been suggested that substituted benzenes react with sulfate radicals either by electron transfer from the aromatic ring to sulfate radicals or by addition/elimination (Rosso et al., 1999).

The proposed mechanism for base activation of persulfate includes the two initial steps (Furman et al., 2009):

$$^-O_3S-O-O-SO_3^- + 2OH^- + \rightarrow HO_2^- + SO_4^{2-} + HSO_4^-$$ [3.1]

$$HO_2^- + {}^-O_3S-O-O-SO_3^- \rightarrow SO_4^{\bullet-} + HSO_4^{2-} + O_2^{\bullet-}$$ [3.2]
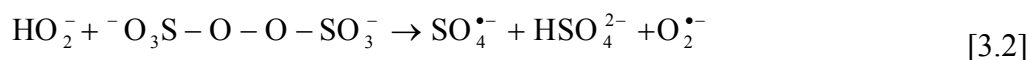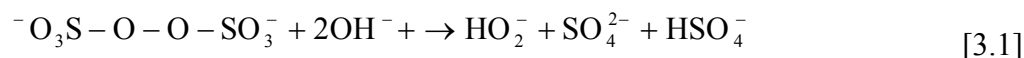
The study of the mechanism for base activation of persulfate shows that hydroperoxide anion (HO$_2^-$) is important in the generation of SO$_4^{-2}$, O$_2^{\bullet-}$, and OH$^\bullet$ radicals from persulfate activation (Furman et al., 2009):

$$HOO^- + {}^-O_3S-O-O-SO_3^- \rightarrow HSO_4^{2-} + SO_4^{\bullet-} + O_2^{\bullet-}$$ [3.3]

$$2O_2^{\bullet-} \rightarrow O_2 + OH^- + HO_2^-$$ [3.4]

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^\bullet$$ [3.5]

Other mechanisms of persulfate activation likely occur, but have received little attention to date. Recent observations in Dr. Watts' laboratory at Washington State University provide evidence that some organic compounds may activate persulfate.

Persulfate activation by organic compounds is an important mechanism given that all soils and sediments contain some amount of organic matter. Phenoxides, which are the salts of phenol and chlorophenols, were the selected organic compounds used to accomplish the study of persulfate activation at alkaline pH. The hypothesized mechanism for persulfate activation by phenoxides included a nucleophilic or reductive pathway.

If phenoxides react with persulfate by nucleophilic attack, sulfate radicals and hydroperoxide can be generated for further chain reactions.

$$PhO^- + {}^-O_3S-O-O-SO_3^- \rightarrow HO_2^- + 2SO_4^{2-} + \text{Phenoxides products} \qquad [3.6]$$
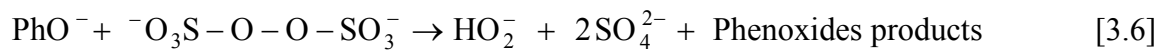
If persulfate activation by phenoxides follows a reductive mechanism, phenoxyl radicals are generated:

$$PhO^- + {}^-O_3S-O-O-SO_3^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + PhO^\bullet \qquad [3.7]$$

The formation of phenoxyl radicals, a product from equation 3.7, should be confirmated by the generation of hydroquinones as degradation byproducts (Equation 3.5) (Sethna, 1951). If the reductive pathway is parallel to the base-activation pathway, the oxidation of phenolates to hydroquinones is achieved based on the production of hydroxyl radicals from Equations 3.3 to 3.5:

$$PhO^{\bullet} + OH^{\bullet} \longrightarrow \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad [3.8]$$
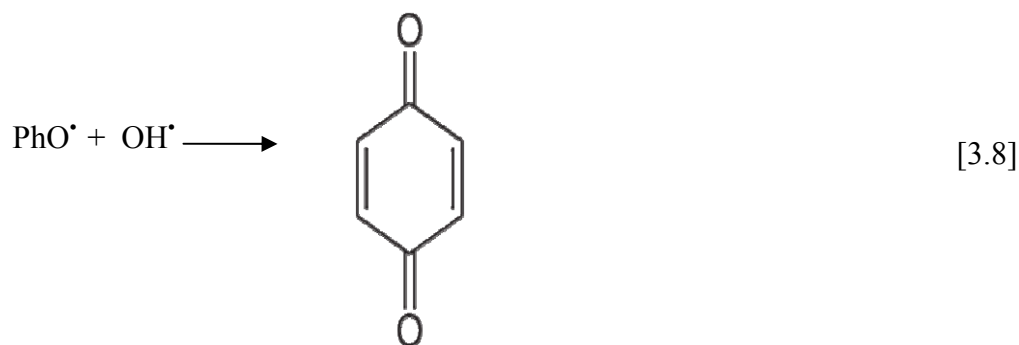
It is hypothesized that reduced organic compounds such as glucose, fatty acids, anisole, ketones, and phenols may activate persulfate, unlike oxidized organic compounds (i.e., chlorobenzenes). Therefore, the objective of this study was to evaluate the activation of persulfate by phenoxides (salts of phenol and chlorophenols) and determine the mechanism of action.

MATERIALS AND METHODS

Materials. Sodium hydroxide (reagent grade, 98%), sulfuric acid, sodium bicarbonate, nitrobenzene, isopropanol (>99%), *t*-butyl alcohol, potato starch, sodium phosphate dibasic, and hexane (>98%) were obtained from J.T. Baker (Phillipsburg, NJ). Sodium persulfate ($Na_2S_2O_8$) (reagent grade, >98%), magnesium chloride ($MgCl_2$) (99.6%), methyl formate (97%), sodium phosphate monobasic monohydrate (98.0–102.0%), xylenes, toluene, aniline (99.5%), and hexachloroethane (HCA) (99%) were purchased from Sigma Aldrich (St. Louis, MO). Carbon adsorbent tubes (ORBO-32) were obtained from Supelco (St. Louis, MO). A purified solution of sodium hydroxide was prepared by adding 10 mM of $MgCl_2$ to 1 L of the 8 M NaOH solution, which was

then stirred for a minimum 8 hours and passed through a 0.45 μM membrane filter. Sodium thiosulfate (99%), potassium iodide, and methylene chloride were purchased from Fisher Scientific (Fair Lawn, NJ). Deionized water was purified to > 18 MΩ•cm with a Barnstead Nanopure II ultrapure system (Dubuque, Iowa).

Potential Persulfate Activators. Phenol (C_6H_5OH) (89.6%) was obtained from J.T. Baker. (Phillipsburg, NJ). Catechol ($C_6H_6O_2$) (98%), 2-chlorophenol (C_6H_5ClO) (>99%), 2,3-dichlorophenol ($C_6H_4Cl_2O$) (98%), 2,4,6-trichlorophenol ($C_6H_3Cl_3O$) (98%), 2,3,4,6-tetrachlorophenol ($C_6H_2Cl_4O$) (>99%), and pentachlorophenol (C_6HCl_5O) (98%) were purchased from Sigma-Aldrich (St. Louis, MO).

Probe Compounds and Scavengers. Nitrobenzene was used as a hydroxyl radical probe due to its high reactivity with hydroxyl radicals ($k_{OH\bullet} = 3.9$ x 10^9 $M^{-1}s^{-1}$) and negligible reactivity with sulfate radicals ($k_{SO4\bullet-} = \leq 10^6$ $M^{-1}s^{-1}$) (Neta et al., 1977; Buxton et al., 1987; Clifton and Huie, 1989). HCA was used as a reductant probe because it is unreactive with hydroxyl and sulfate radicals ($k_{OH\bullet} = < 1$ x 10^6 $M^{-1}s^{-1}$) (Haag and Yao, 1992), but is readily reduced. Hydroxyl radicals were scavenged from the system using *t*-butyl alcohol ($k_{OH\bullet} = 5.2$ x 10^8 M^{-1} s^{-1}), which is unreactive with sulfate radicals ($k_{SO4\bullet-} \leq 1$ x 10^6 M^{-1} s^{-1}) (Neta et al, 1977; Buxton et al, 1987). The scavenger:probe molar ratio was 1000:1. Sulfate radicals and hydroxyl radicals were scavenged from the system using isopropanol ($k_{OH\bullet} = 8.2$ x 10^7 M^{-1} s^{-1}) (Clifton and Huie, 1989; Buxton et al, 1987). The scavenger: probe molar ratio was 1000:1.

General Reaction Procedures. All reactions were conducted in 20 mL borosilicate vials capped with polytetrafluoroethylene (PTFE) lined septa. Each reaction vial contained 0.5 M sodium persulfate and 2 M NaOH in a persulfate to NaOH molar

ratio of 1:4, 2 mM phenoxide, and 1 mM of nitrobenzene or 2 μM of HCA. At several times during the course of the reactions, sodium persulfate was measured by iodometric titration and probe concentrations were analyzed by gas chromatography (GC) after extracting the contents of the reactors with hexane. All reactions were performed in triplicate, and the data were reported as the mean of the three replicates. The standard error of the mean was calculated and included as error bars for each data point. All reactions were conducted at a temperature of ± 20 °C. Triplicate control systems for each phenoxide system were evaluated in parallel at a pH above 12 using deionized water instead of the phenoxide solution. Solution pH was monitored using a Fisher Accumet pH meter 900 (Fisher Scientific, Hampton, NH).

Detection of the Dominant Radical Oxidant. *t*-Butyl alcohol was used as a hydroxyl scavenger to distinguish between hydroxyl radical and sulfate radical. Reactions consisted of a 15 mL solution of 2 mM phenoxide, 0.5 M sodium persulfate, 1 mM nitrobenzene, a molar ratio of sodium persulfate to NaOH of 1:4, and a molar ratio of nitrobenzene to *t*-butyl alcohol of 1:1000. Control reactions were conducted in parallel using double-deionized water in place of phenoxide.

Effect of pH on Persulfate Activation by Phenoxides. Persulfate activation was studied at various pH regimes. The characteristics of the organic compounds used in this study are highly pH dependent; therefore experiments were run from a pH starting at 12 and going down to a pH below the pK_a of the corresponding phenoxide. Vials were filled with 15 mL of a solution containing 2 mM phenol, 0.5 M sodium persulfate, and 1 mM nitrobenzene. The initial pH was adjusted with a 0.1 M phosphate buffer (a mixture of monosodium and disodium phosphate). As the reaction proceeded, the pH was monitored

and sulfuric acid (0.1 N) and sodium hydroxide (0.1 N, 1 N and 4 N) were used to maintain the pH close to the initial value. Control reactions were conducted in parallel using double-deionized water in place of phenol. Also, a catechol-activated system was studied at 2 pH values above and below the pK_a of catechol to observe the degradation rates of nitrobenzene and hexachloroethane.

Mechanisms for Phenoxide-Persulfate Activation. Reductive and nucleophilic mechanisms were studied as possible mechanisms in phenoxide-persulfate activation. Pentachlorophenol was used in this study as the selected phenoxide. Experiments were conducted at a pH 8.0. Vials were filled with 15 mL of the following solution: 2 mM pentachlorophenol, 0.5 M sodium persulfate, and either 1 mM of nitrobenzene or 2 μM HCA. The initial pH was adjusted with a 0.1 M phosphate buffer. As the reaction proceeded, the pH was monitored and sulfuric acid (0.1 N) and sodium hydroxide (0.1 N, 1 N and 4 N) were used to maintain the pH close to 8. Control reactions were conducted in parallel using double-deionized water in place of pentachlorophenol. At several times during the course of the reactions, hydrogen peroxide was measured by spectrometry, and nitrobenzene or HCA concentrations were analyzed by GC after extracting the contents of the reactors with hexane. Pentachlorophenol and their derivatives were analyzed by GC/MS after extracting the contents of the reactors with methylene chloride.

Measurement of Hydrogen Peroxide Concentrations. Hydrogen peroxide was measured by the reaction between titanium sulfate and H_2O_2 (Cohen and Purcell, 1967). The absorbance at 407 nm was read on a Spectronic 20 Genesys spectrophotometer.

Analytical Procedures. Hexane extracts were analyzed for nitrobenzene using a Hewlett Packard Series 5890 GC with a 0.53 mm (i.d) x 15 m SPB-5 capillary column

and flame ionization detector (FID). Chromatographic parameters included an injector temperature of 200 °C, detector temperature of 250 °C, initial oven temperature of 60 °C, program rate of 30 °C/min, and a final temperature of 180 °C. Hexane extracts were analyzed for HCA using a Hewlett Packard Series 5890 GC with electron capture detector (ECD) by performing splitless injections onto a 0.53 mm (i.d.) x 30 m Equity-5 capillary column. Chromatographic parameters included an injector temperature of 220 °C, detector temperature of 270 °C, initial oven temperature of 100 °C, program rate of 30 °C/min, and a final temperature of 240 °C. Six-point calibration curves were developed using solutions of known concentrations of nitrobenzene and HCA.

Phenolic compounds and their derivatives were analyzed on a Hewlett-Packard model 7890A GC/5975C mass spectrometer. Samples were acidified to a pH of 1–2 with sulfuric acid, followed by extraction with methylene chloride. Methylene chloride extracts were analyzed by GC/MS. Chromatographic parameters included an injector in splitless mode and maintained at 250 °C; an initial oven temperature of 40 °C for 2 min, then programmed at a rate of 40 °C/min to 100 °C and held for 0.5 min, and finally raised to 300 °C at a rate of 10 °C/min and held for 3 min. The column used was a 30 m MDB-5ms Agilent column (Santa Clara, CA) with a 0.5 μm i.d. and 250 μm film thickness. Helium was used as the carrier gas at a constant flow rate of 1.5 ml/min. The temperature of the transfer line was maintained at 320 °C.

Sodium persulfate concentrations were determined by iodometric titration with 0.01 N sodium thiosulfate (Kolthoff and Stenfer, 1947). The Statistical Analysis System package S.A.S version 9.1 was used to calculate the variances between the experimental data sets and 95% confidence intervals for rate constants.

RESULTS AND DISCUSSION

Detection of Hydroxyl and Sulfate Radicals. For all experiments using different phenoxides to activate persulfate, the change in persulfate concentration over time was negligible ($\alpha = 0.05$) (Figure 3.1). This may reflect the fact that only a small amount of persulfate is needed to promote the generation of reactive species.

The loss of hexachloroethane in phenoxides activated persulfate systems at basic pH is shown in Figure 3.2. Loss of hexachlroethane indicates the generation of reductants as a result of propagation reactions from persulfate activation. The data clearly demonstrate that all the phenoxides used in this study activate persulfate. Furthermore, a more reduced compound such as phenol activates persulfate more effectively than a highly chlorinated or more highly oxidized compound, such as pentachlorophenol. Activation using pentachlorophenol resulted in a 40% loss of hexachloroethane in 4 hours, compared with > 99.9% when phenol was used. Hexachloroethane was degraded most quickly when catechol was used as the activator, with > 99.9% Hexachloroethane loss in less than an hour. This is likely due to catechol being a stronger reducing agent than phenol. Controls without added phenoxide showed no degradation of hexachloroethane. When hexachloroethane was used as a probe, the results show that persulfate activation by phenoxides in a basic environment generates primarily reductants. Experimental results also demonstrate that without phenoxide in the system, no degradation of hexachloroethane was observed.

Nitrobenzene degradation was measured to indicate the generation of hydroxyl radicals during persulfate activation. As with hexachloroethane experiments, the persulfate concentrations remained relatively constant during the course of the reaction (α

= 0.05) (Figure 3.3). The loss of nitrobenzene in phenoxide activated persulfate systems at basic pH, shown in Figure 3.4, indicates that persulfate activation using phenoxides generates hydroxyl radicals. The relative capacities of the phenoxides to activate persulfate were similar to that seen with hexachloroethane, with pentachlorophenol promoting a slower degradation rate and the more reduced compounds (e.g., catechol, phenol) causing faster nitrobenzene degradation.

Scavenging of Hydroxyl Radicals. An excess of *t*-butyl alcohol was added to scavenge hydroxyl radicals (Anipsitakis et al., 2004). Nitrobenzene analyses show a loss of approximately 40% with activation by phenol, 2-dichlorophenol, and 2,3-dichlorophenol (Figure 3.5). However, nitrobenzene degradation in the presence of the other phenoxides was < 10% , and did not vary significantly from the degradation achieved in the control system containing persulfate without phenoxides ($\alpha = 0.05$). These data contrast strongly with the scavenger-free system shown in Figure 3.4, where nitrobenzene was extensively degraded due to the ready availability of hydroxyl radicals.

Influence of pH. The anionic (i.e. phenoxide) form of phenols is likely the activating species in persulfate systems; therefore, it was important to evaluate the effects of pH on persulfate activation by the phenoxides. The effectiveness of phenoxides in activating persulfate is expected to decrease with increasing acidity of the solution. The degradation of nitrobenzene by phenol-activated persulfate at pH values ranging from 7 to 13 over 2 hr is shown in Figure 3.6. These results indicate that when phenol was primarily in the ionized form (PhO^-) (pH above its pK_a of 9.8) (Watts, 1998), the degree of persulfate activation increased. Minimal nitrobenzene degradation was observed at pH 8 and 9, indicating less activation of persulfate and subsequent formation of hydroxyl

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radicals. These data are consistent with the activation of persulfate being accomplished primarily by the phenoxide ion. Furthermore, the above results indicate the importance of hydroxyl radicals in a system where persulfate is activated by organic compounds. Lipczynska-Kochany (1992) found that neutral forms of phenols are more susceptible to the electrophilic attack from hydroxyl radicals than the phenolate forms.

Figure 3.7 shows the effects of pH during the activation of persulfate by catechol (pK_a = 9.34) (Linde, 2009), another reduced compound. As with phenol, the rates of nitrobenzene degradation were markedly greater at higher pH (Figure 3.7a), achieving near complete loss at a pH of 12.96. HCA loss exhibited a similar pattern (Figure 3.7b), suggesting that a similar reaction pathway is involved in both oxidant and reductant generation.

Effects of Phenol Concentrations. Persulfate activation was tested at several phenol concentrations (0.01 to 10 mM) with a fixed persulfate:NaOH molar ratio of 1:4. The reactions were conducted at pH > 12, which is 2 pH units greater than the pK_a of phenol; therefore > 99% of the phenol is in the phenoxide form. Figure 3.8 shows that the rates of hydroxyl radical generation as indicated by nitrobenzene loss are faster as the phenol concentration increases. These results suggest a zero order phenomenon in hydroxyl radical generation with respect to phenoxide concentration.

Mechanism of Persulfate Activation. The mechanism of base-activation of persulfate by phenoxides could occur through two possible pathways: (1) nucleophilic or (2) reductive. The nucleophilic vs. reductive mechanisms were tested by using pentachlorophenol as an activator at pH 8. At this pH, pentachlorophenol (pK_a = 4.75) is fully ionized (Watts, 1998), and hydroperoxide anion is > 99.9% protonated (pK_a =

11.62) (Linde, 2009). By conducting the reaction at pH 8 activation by a phenoxide can be separated from activation by hydroperoxide anion.

HCA concentrations as a function of time in a pentachlorophenolate activated persulfate systems at pH 8 are shown in Figure 3.9. HCA degradation in the system was insignificant from the degradation achieved in the control system containing persulfate without pentachlorophenol ($\alpha=0.05$). Although no HCA was degraded, GC/MS analysis showed the generation of tetrachlorohydroquinone as the reaction proceeded; i.e., pentachlorophenol was oxidized to tetrachlorohydroquinone during the activation of persulfate:

$$^-SO_3\text{-O-O-}SO_3^- + \text{[structure]} \longrightarrow SO_4^{\cdot-} + SO_4^{-2} + \text{[structure]} \qquad [3.9]$$
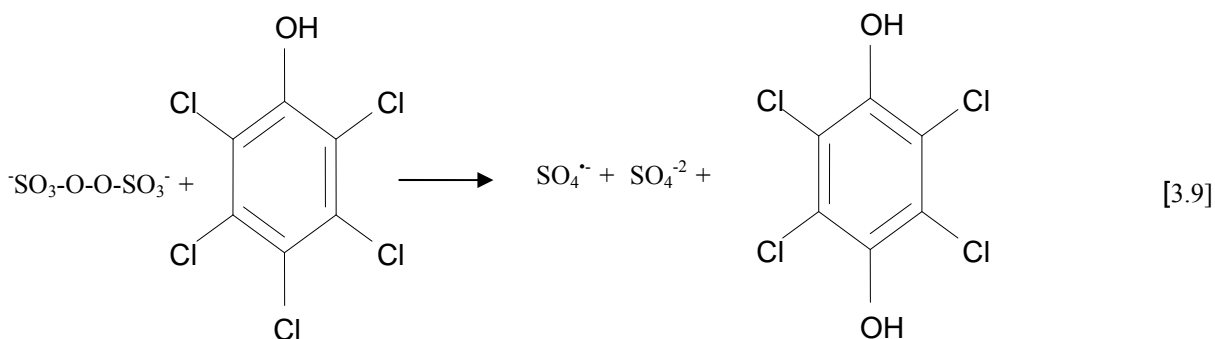
HO$_2^-$ or H$_2$O$_2$ was not detected during the pentachlorophenoxide activation of persulfate, indicating that persulfate was not attacked in a **nucleophilic** manner, which would have resulted in the generation of hydroperoxide. The concentration of H$_2$O$_2$ was measured over time by spectrometry. H$_2$O$_2$ was expected to accumulate as the reaction proceeded as the result of propagation reactions that form SO$_4^{\cdot-}$, OH$^\cdot$, and O$_2^{\cdot-}$ radicals. However, H$_2$O$_2$ was not detected at any time as the pentachlorophenol was consumed.

Relative hydroxyl radical generation rates in a parallel system, as quantified by the degradation of nitrobenzene, are shown in Figure 3.10. Nitrobenzene was degraded by 50% in the pentachlorophenoxide system, but was not degraded in the control system. Furthermore, pentachlorophenoxide loss exceeded 99% during the 2 hr reaction time. Degradation of pentachlorophenoxide generated hydroquinone byproducts, as predicted by the oxidation of pentachlorophenol (Merz and Waters, 1949). The most relevant compounds produced were tetrachloride-hydroquinone, 3,4,6-trichloro-pyrocatechol, and 3,4-dichloro-2,5-furandione. These hydroquinone products have primarily *ortho* and *para* orientation of the OH groups, which is typical of electrophilic substitution in benzene rings (Metelitsa, 1971). The formation of furandione may indicate the production of chlorophenoxyl radicals (Sommeling et al., 1993).

CONCLUSIONS

The results of the study demonstrate that phenoxides promote persulfate oxidation at basic pH, resulting in the rapid oxidation of the hydroxyl radical probe nitrobenzene and loss of the reductant probe hexachloroethane. Phenoxides decomposed along with the probe compound. Rates of loss of both nitrobenzene and hexachloroethane were inversely proportional to the degree of chlorine substitution on the phenol used for activation.

Reactions conducted at different pH regimes confirmed that only the phenoxide forms of the phenols promote the activation of persulfate.

Because persulfate can be activated by both hydroperoxide and phenoxides at pH > 12, the activation of persulfate by a phenoxide was evaluated using pentachlorophenol at pH 8, a pH regime at which hyroperoxide existed in the protonated form of hydrogen

peroxide. The results obtained are in agreement with a reductive pathway in the activation of persulfate by phenoxides.

The results of this research suggest that when persulfate is used in the presence of phenols, such as these present in soil organic matter, persulfate activation by organic compounds can be a significant pathway for contaminant degradation. Therefore, the soil organic carbon content should be considered in process screening and treatability testing for persulfate ISCO.

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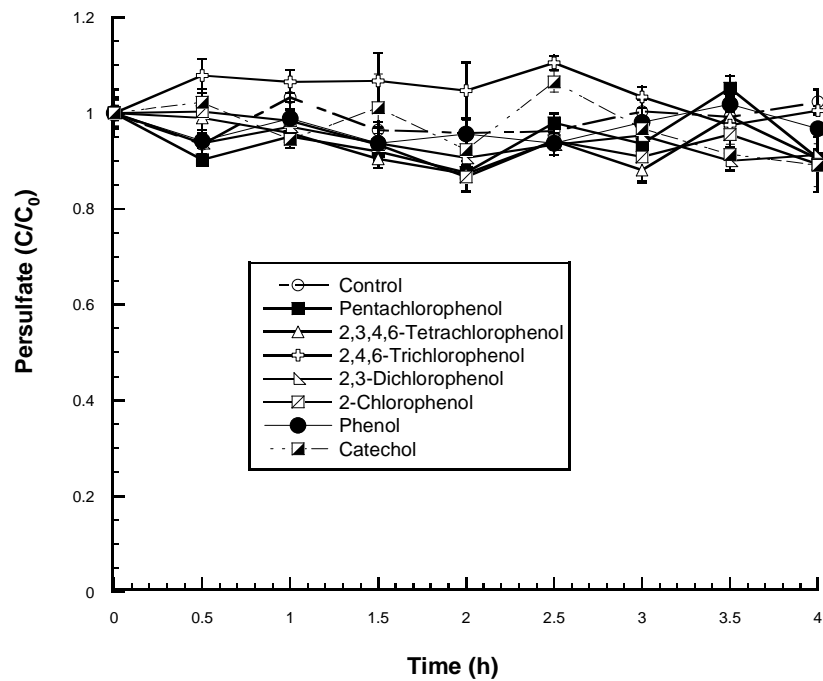
Figure 3.1: Persulfate decomposition in phenoxides activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2M NaOH, 2 mM phenoxide, and 2 μM hexachloroethane; 20 mL total volume. Error bars represent the standard error of the mean for three replicates.
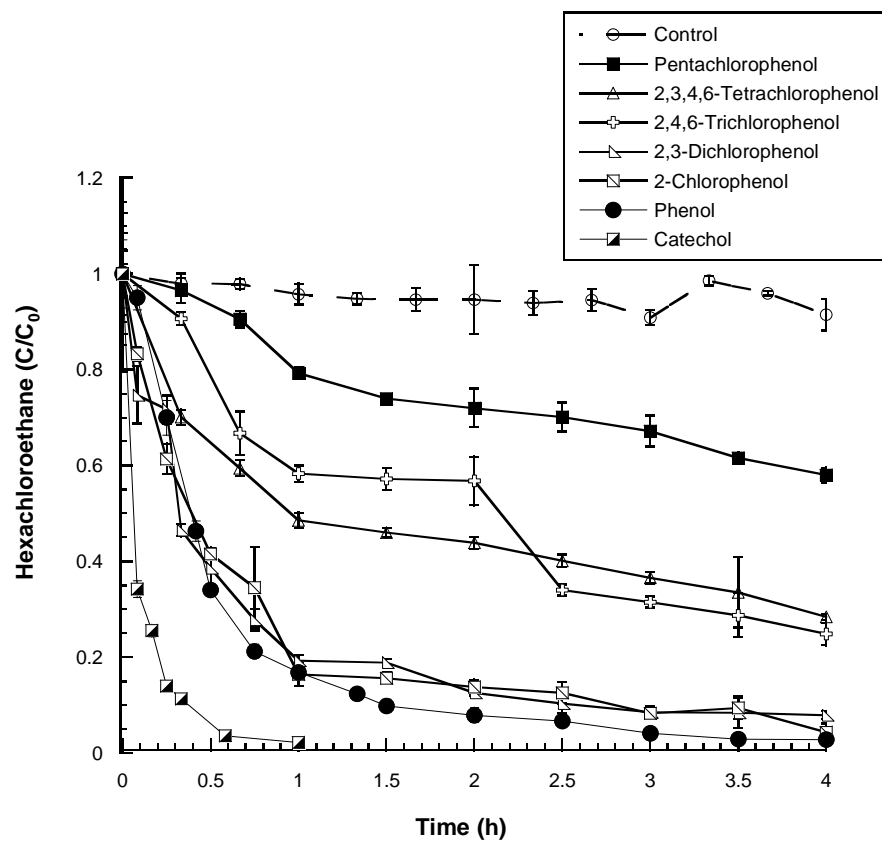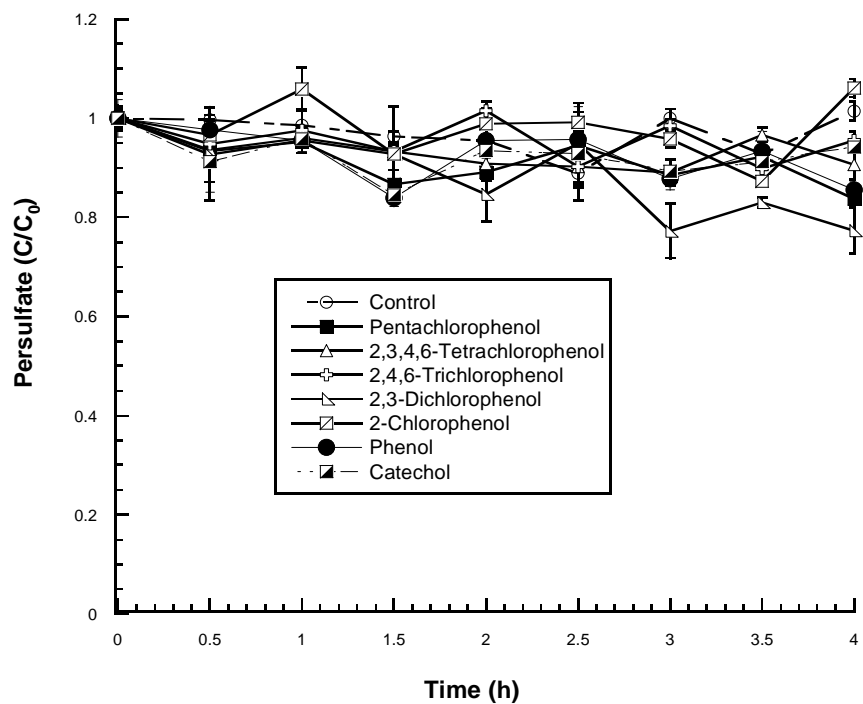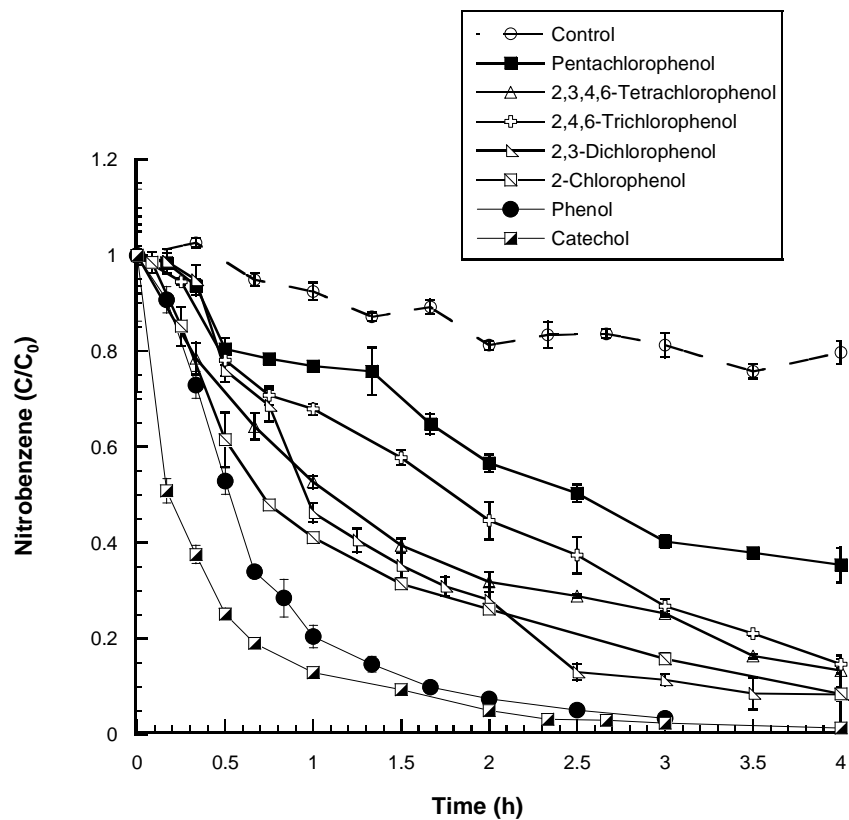
Figure 3.2: Degradation of hexachloroethane in phenoxides activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2M NaOH, 2 mM phenoxide, and 2 μM hexachloroethane; 20 mL total volume. Error bars represent the standard error of the mean for three replicates.
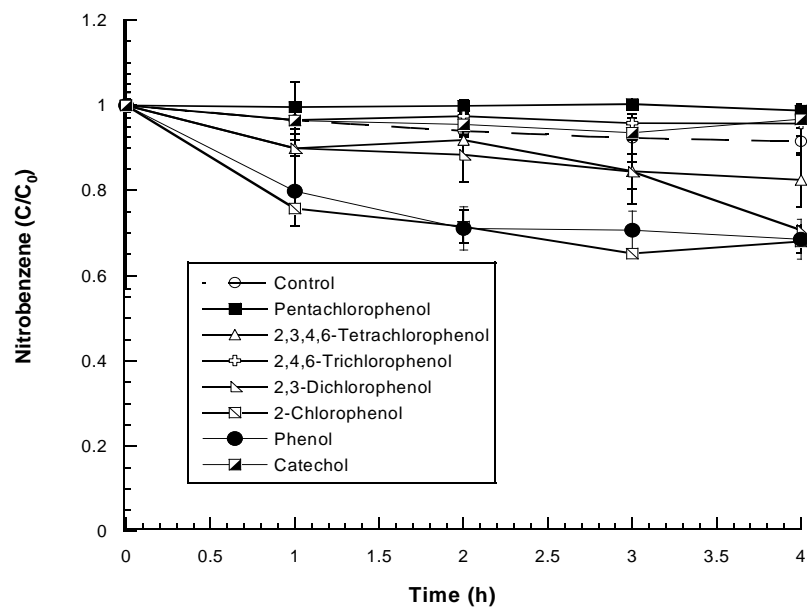
Figure 3.3: Persulfate decomposition in phenoxides activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 2 mM phenoxide, and 1 mM nitrobenzene; 15 mL total volume. Error bars represent the standard error of the mean for three replicates.

Figure 3.4: Degradation of nitrobenzene in phenoxides activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 2 mM phenoxide, and 1 mM nitrobenzene; 15 mL total volume. Error bars represent the standard error of the mean for three replicates.

Figure 3.5: Scavenging of hydroxyl radicals in phenoxides activated persulfate systems at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 2 mM phenoxide, and 1 mM nitrobenzene; 15 mL total volume, the molar ratio of nitrobenzene to *t*-butyl alcohol was 1:1000. Error bars represent the standard error of the mean for three replicates.
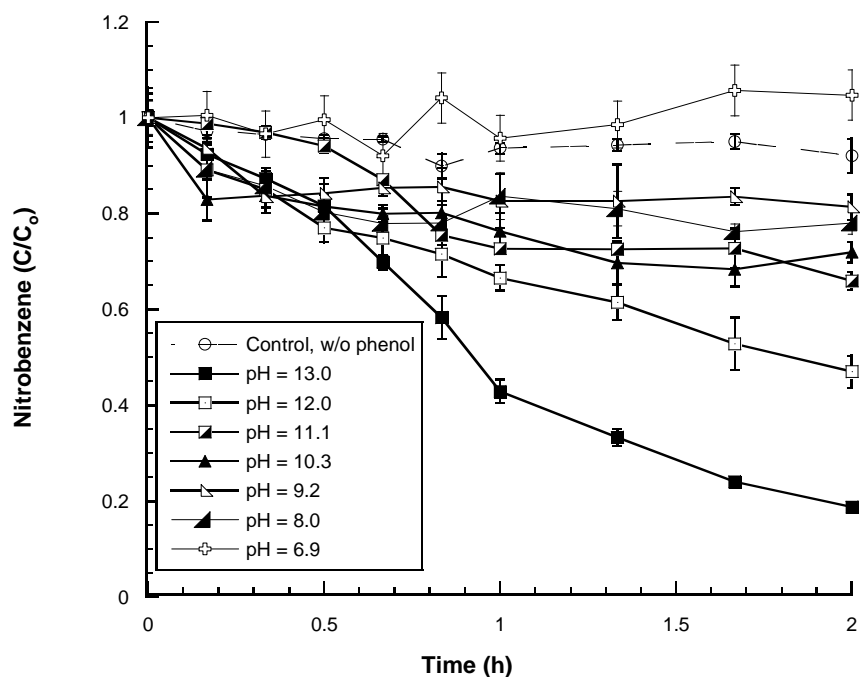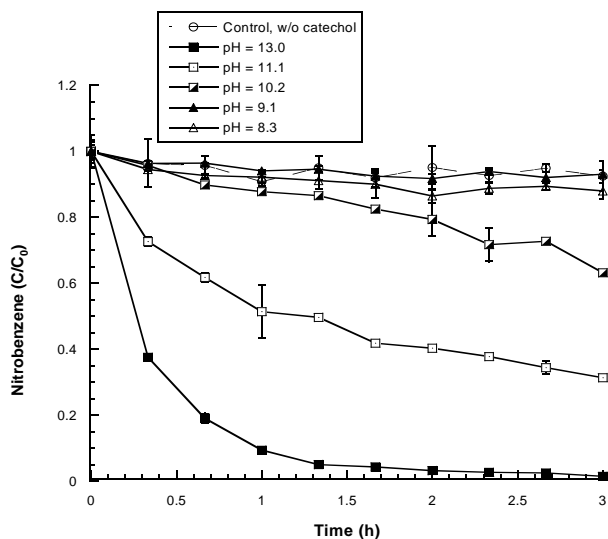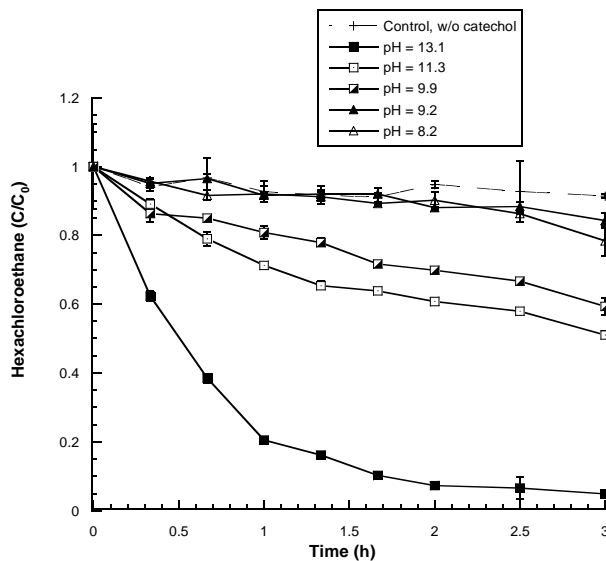
Figure 3.6: Degradation of nitrobenzene in phenol activated persulfate system at different pH regimes: 0.5 M sodium persulfate, 2 mM phenol, and 1 mM nitrobenzene; 15 mL total volume at 7, 8, 9, 10, 11, and 12 pH values. Error bars represent the standard error of the mean for three replicates.

Figure 3.7: Degradation of probe compounds in catechol activated persulfate system at different pH regimes: 0.5 M sodium persulfate, 2 mM catechol, at 8, 9, 10, 11, and 13 pH values. Error bars represent the standard error of the mean for three replicates (a) Degradation of nitrobenzene (1 mM nitrobenzene, 15 mL total volume) (b) Degradation of hexachloroethane (2 μM HCA, 20 mL total volume).
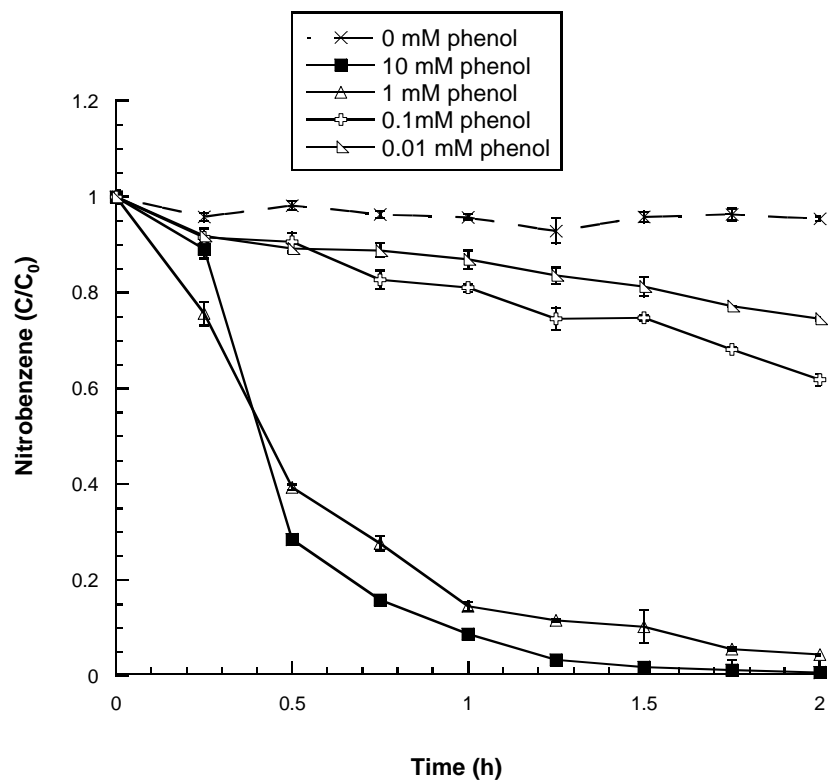
Figure 3.8: Degradation of nitrobenzene in phenol activated persulfate system at basic pH: 0.5 M sodium persulfate, 2 M NaOH, 1 mM nitrobenzene, and different phenol concentrations ranging from 0.01 to 10 mM; 15 mL total volume. Error bars represent the standard error of the mean for three replicates.
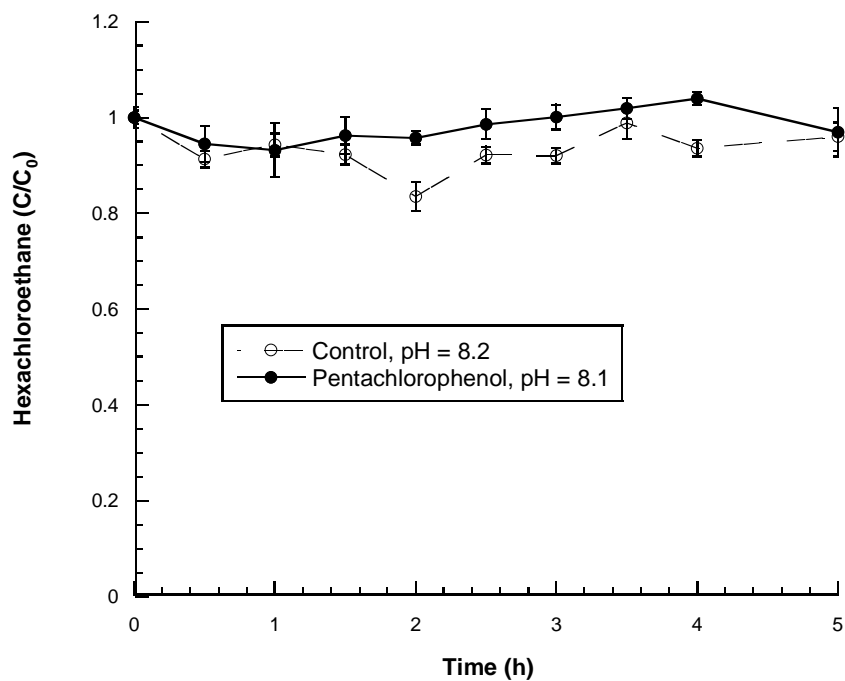
Figure 3.9: Degradation of hexachloroethane in pentachlorophenolate activated persulfate system at pH 8: 0.5 M sodium persulfate, 2 mM pentachlorophenol, and 2 μM hexachloroethane; 20 mL total volume. Error bars represent the standard error of the mean for three replicates.
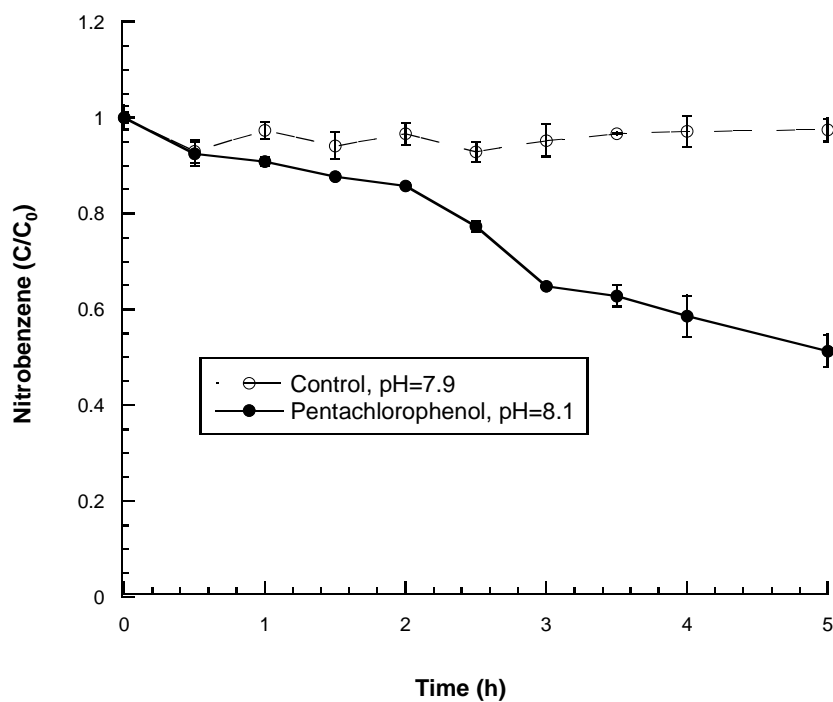
Figure 3.10: Degradation of nitrobenzene in pentachlorophenolate activated persulfate system at pH 8.0: 0.5 M sodium persulfate, 2 mM pentachlorophenol and 1 mM nitrobenzene; 15 mL total volume. Error bars represent the standard error of the mean for three replicates.