

Metal Organic Interactions at Hydrothermal Conditions:  
Useful Transformations Through Geomimicry

by

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A Thesis Presented in Partial Fulfillment  
of the Requirements for the Degree  
Master of Science

Approved April 2020 by the  
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May 2020

## ABSTRACT

Organic compounds are influenced by hydrothermal conditions in both marine and terrestrial environments. Sedimentary organic reservoirs make up the largest share of organic carbon in the carbon cycle, leading to petroleum generation and to chemoautotrophic microbial communities. There have been numerous studies on the reactivity of organic compounds in water at elevated temperatures, but these studies rarely explore the consequences of inorganic solutes in hydrothermal fluids. The experiments in this thesis explore new reaction pathways of organic compounds mediated by aqueous and solid phase metals, mainly Earth-abundant copper. These experiments show that copper species have the potential to oxidize benzene and toluene, which are typically viewed as unreactive. These pathways add to the growing list of known organic transformations that are possible in natural hydrothermal systems. In addition to the characterization of reactions in natural systems, there has been recent interest in using hydrothermal conditions to facilitate organic transformations that would be useful in an applied, industrial or synthetic setting. This thesis identifies two sets of conditions that may serve as alternatives to commonplace industrial processes. The first process is the oxidation of benzene with copper to form phenol and chlorobenzene. The second is the copper mediated dehalogenation of aryl halides. Both of these processes apply the concepts of geomimicry by carrying out organic reactions under Earth-like conditions. Only water and copper are needed to implement these processes and there is no need for exotic catalysts or toxic reagents.

## ACKNOWLEDGEMENTS

I thank my advisor, Dr. Everett Shock for taking me on as a graduate student and exposing me to countless new topics and ideas. The things I have learned in his group have been instrumental in my development as a geochemist. I could not have come this far without his guidance. I must thank the other members of my committee, Dr. Hilariy Hartnett, and Dr. Ian Gould for their suggestions and guidance. I thank the rest of the Hydrothermal Organic Geochemistry group, Dr Lynda Williams, Dr Kirt Robinson, Dr. Kris Fecteau, Garrett Shaver, and Zhen Holmes for help in the lab and for facilitating constructive discussions at weekly meetings. The input I received in these meetings was key in developing these projects.

On a personal note I would like to thank my family, Brad and Amy Loescher, for their support throughout my academic career and for encouraging me to follow my interests. I greatly appreciate all you have done for me.

Lastly, I would like to thank my friends that supported me throughout the process. Thanks to Jon Bayne, Owen Loughlin, and Kyle Border were always there to talk. Thanks to Danika Marzillier, who was greatly supportive in this endeavor. Thanks to friends in the GEOPIG lab and Lauren Heald who made me feel at home in Arizona.

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## 1. INTRODUCTION

### **Overview**

Many experimental hydrothermal investigations have been carried out in water with no added solids. The water only experiments provide the fundamental understanding of organic reactivity in aqueous solutions at elevated temperatures and pressures. To date, the reactivity and reaction pathways of many geochemically relevant functional groups have been studied and characterized to some degree (Bell and Palmer, 1994; Seewald et al., 2006; Yang et al., 2012; Shipp et al., 2013; Bockisch et al., 2018; Fecteau et al., 2018; Robinson et al., 2019; Glein et al., 2020). In addition to water only experiments, minerals are common additions to hydrothermal experiments proving to be catalytic (Shipp et al., 2014; Venturi et al., 2017; Bockisch et al., 2019) and used as redox buffers to maintain the oxidation environment in experimental systems (Seewald, 1994; Seewald 1996; McCollom, 2013). The experiments in my thesis were centered around expanding the conditions under which hydrothermal chemistry is performed by introducing copper in both aqueous and native mineral forms. Copper is present in many natural waters and mineral deposits (Raymont & Shields, 1963; McMillan & Panteleyev, 1980). These experiments show the reactive potential of copper with organics in high temperature aqueous systems. Copper species can oxidize and reduce organic compounds that are resistant to functional group transformations in water alone.

### **Hydrothermal Organic Geochemistry**

The vast majority of organic carbon on the Earth is in the form of kerogen and coal, located in sedimentary basin and is subjected to conditions entirely different than the

typical laboratory i.e., 25°C and 1 bar (Falkowski et al., 2000; Houghton, 2007). These systems are dominated by high temperatures and pressures and are greatly influenced by the presence of water (Philippi, 1965). As temperatures increase, the properties of water typically are significantly different than they are at room temperature and pressure. At high temperature, the dissociation constant for water ( $K_w$ ) increases making both protons and hydroxide ions more abundant, which influences the kinetics of acid-promoted and base-promoted reactions. The dielectric constant drops and the hydrogen bonds become weaker (Owen et al., 1961). These properties influence the intermolecular forces in aqueous solutions and are associated with increased solubility of organic compounds.

Hydrothermal conditions lead to reaction pathways that are markedly different than what is expected at room temperature. Recently, there has been an effort to understand organic functional group transformations in these systems (Shipp et al., 2013; Bockisch et al., 2018; Fecteau et al., 2018; Robinson et al., 2019). This elucidates reaction pathways from one functional group to another and helps us to understand the reactivity of organic carbon in hydrothermal systems. These transformations play an important role in oil and gas resources, microbial ecology, and the carbon cycle. Hydrothermal transformations of organic compounds produce petroleum (Simoneit & Lonsdale, 1982) as well as generate organic compounds that are consumed by microbial heterotrophs (Dombrowski et al., 2018). Lastly, the transformation of organic carbon in sedimentary basins has implications for the carbon cycle, functional group transformations can lead to increased aqueous solubility and the partition of organic molecules from organic phases to aqueous phases.

## **Geomimicry**

In addition to expanding our understanding of natural systems, hydrothermal organic geochemistry has also been used to promote organic transformations that are useful in industrial settings (Yang et al., 2015; Bockish et al., 2018). Elevated temperatures facilitate useful transformations that cannot be carried out at typical laboratory conditions. These previous studies and the experiments in this thesis adhere to the principles of geomimicry by carrying out useful reactions in a way that is similar to what happens in natural geologic systems. Geomimicry in hydrothermal experiments has applications in green chemistry. The experiments are environmentally friendly because they contain earth abundant reagents and use only water as a solvent. This leads to little production of unwanted waste products.

## **Subjects of Study**

Oxidation-reduction reactions are central to all of the experiments presented here. Industrial oxidation processes are often carried out with toxic reagents, including oxidized metals and halogen gases. There has been considerable interest in phasing out these types of reactions in favor of processes with more benign reagents (Peng et al., 2003; Boltz et al., 2012). This study outlines a new set of conditions to oxidize benzene using relatively benign reagents. These new, single-step oxidation pathways are alternatives to the current industrial process and could be implemented to avoid hazardous reagents and multi-step processes. In addition to oxidative reactions in industry, an aim of this thesis was to better understand organic transformations in natural hydrothermal systems. I describe reactions that may be possible in natural systems but are not previously characterized in experimental

studies. The oxidation of benzene and toluene by aqueous copper can aid in our understanding of natural hydrothermal systems. These previously uncharacterized reactions are possible since the reactants can be present in natural systems. The oxidations performed in these experiments demonstrate a plausible pathway for the oxidation of common compounds found in natural sources of organic carbon. Lastly this thesis expands well known reactions such as the Ullmann and Birch Reactions to hydrothermal conditions. Copper-mediated nucleophilic aromatic substitution and the reduction of aromatic compounds with metal electron donors are two processes that are not typically carried out at hydrothermal conditions. My results show that reactions that are common in the organic chemistry laboratory can readily be performed in aqueous solutions at elevated temperatures. In these reactions, aryl halides, which are widely associated with anthropogenic pollutants, are shown to be degraded.

My experiments outline organic transformations that are carried out under novel conditions. These hydrothermal reactions shed light on organic reactions in natural systems and provide new ways to promote transformations that may be useful in an applied industrial or laboratory setting.

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## 2. METHODS

This chapter outlines the general procedure for conducting the hydrothermal experiments in this thesis as well as information on the different procedures used in each chapter.

### **Hydrothermal Reaction Vessels**

All hydrothermal experiments were carried out in fused silica glass tubes supplied by Technical Glass Products. Tubing had an inner diameter of 2 mm and an outer diameter of 6mm. The tubes were cut to 8-inch lengths and sealed to close one end. After sealing, the tubes were annealed overnight at 1140 °C.

All reaction vessels were loaded with 300  $\mu\text{L}$  of water measured by Hamilton gastight syringes. Deionized water with a resistance of 18.2  $\text{M}\Omega$  was obtained from a Barnstead Diamond Ultrapure water system. To remove oxygen from the experiments all water was sparged with ultra-high purity argon for at least one hour before being loaded into tubes. Organic reagents were added by volume using a 10  $\mu\text{L}$  gastight Hamilton syringe. The organic concentration was varied to fit the needs of the experiment. Experiments in Chapter 3 used 8 $\mu\text{L}$  of benzene. Experiments in Chapter used 4  $\mu\text{L}$  of toluene. Experiments in Chapter 5 used 8  $\mu\text{L}$  of chlorobenzene in the experiments comparing effects of copper added, and 5 $\mu\text{L}$  of respective organic in the experiments comparing the effects of different functional groups. All organic reagents were selected to be the highest possible purity. After the tubes were loaded with reagents and water, they



were immediately frozen in liquid nitrogen to prevent the evaporation of the organic compound.

The inorganic reagents used in these experiments were  $\text{CuCl}_2$ ,  $\text{CuSO}_4$ , and 23  $\mu\text{m}$  grain size Cu powder. For experiments in chapters 3 and 5 the copper salt and the copper powder were measured by mass and added directly to the tube. High concentration salt solutions were not added directly to the tubes because of difficulty of freezing and sealing. Solutions with high salt concentrations tended to shatter the tubes as they thawed. In the lower concentration experiments in chapter 4, a  $\text{CuCl}_2$  solution was used in place of water. The copper solutions received the same treatment as the pure water experiments.

The tubes were submerged in liquid nitrogen so that the reactants were all frozen just below the surface of the liquid nitrogen. The tubes were then evacuated with a rough pump to  $<80$  mTorr to remove air from the reaction vessel. While under vacuum the tubes were flame sealed using a hydrogen torch. The seal was made directly above the reagents to minimize headspace in the reaction vessels.

### **Reaction Conditions**

The glass reaction vessels were placed in stainless steel tubes to contain the glass in the event of shattering. The reaction vessels were heated to the desired temperature in Gas Chromatography (GC) ovens. The temperature used in the experiments was  $250^\circ\text{C}$  and the duration ranged from 0.5 to 144 hours. The temperature was monitored by the GC oven and monitored by a thermocouple. After the desired experimental duration, the tubes were taken out of the GC oven and quenched in room temperature water. Experiments were then analyzed or frozen for later analysis.

## **Sample Processing**

Once cooled to ambient temperature, approximately 25°C, the reaction vessels were scored and broken with a pipe cutter near the middle of the tube so that approximately half of the liquid was in each half of the tube segments. The liquid was removed with a Pasteur pipet and transferred to a 4 mL silanized glass vial. All experiments were extracted by adding 3 mL dichloromethane (DCM) with dodecane as an internal standard. The vials were lightly shaken for at least 10 minutes to extract all of the organic material. Lastly, an aliquot of the DCM containing the sample was pipetted into a 1.5 mL Agilent trace clean amber autosampler vial.

## **Gas Chromatography Analysis**

The products and reactants were quantified using a Bruker-Scion 456 gas chromatograph with an autosampler. The GC system used a Supelco Equity-5 column and a flame ionization detector. The autosampler was configured to inject 1  $\mu$ L of sample. The injector temperature was 275 °C. The flow rate of the helium carrier gas was 1ml/min. The detector was set to 300 °C. The temperature rates programed into the GC method are given in Table 1.

The mass balance of these experiments was determined by quantifying total molality of organic at the end of the experiments and comparing it to the starting concentration. The reagents are used in trace quantities and the presence of inorganic solids introduces a surface that organic reagents and products tend to stick to. This makes it difficult to fully extract the organic products to achieve complete mass balance.

Table 1. GC Temperature Program Parameters

Rate (°C/min)	Temperature (°C)	Time (min)	Total Time (min)
Initial	40	0	0
10	140	0	10
5	220	0	26
20	300	15	45

### CuSO<sub>4</sub> Thermodynamic Parameters Calculation

No thermodynamic data existed for CuSO<sub>4</sub> (aq) at the temperatures used in these experiments, so the parameters were estimated using the Helgeson-Kirkham-Flowers (HKF) model (Helgeson et al., 1981). Parameters for the reference temperature and pressure of 25°C and 1 bar were compiled used. Complete thermodynamic data for Cu<sup>+2</sup> and SO<sub>4</sub><sup>+2</sup> was acquired from Shock et al. (1997). The volume change for the association of copper and sulfate ions ( $\Delta_r \bar{V}^\circ$ ) at reference conditions is reported to be 10.66 cm<sup>3</sup> mol<sup>-1</sup> (Hamann 1974). With this value, I calculated the volume of the complex at reference to be -0.06 cm<sup>3</sup> mol<sup>-1</sup> using equation 1.

$$\bar{V}^\circ_{CuSO_4} = \Delta_r \bar{V}^\circ + \bar{V}^\circ_{Cu^{+2}} + \bar{V}^\circ_{SO_4^{-2}} \quad (1)$$

The change in entropy for the association reaction at reference conditions ( $\Delta_r \bar{S}^\circ$ ) is 18 cal mol<sup>-1</sup> K<sup>-1</sup> (Smith & Martel 1976). To determine  $\bar{S}^\circ_{CuSO_4}$  I used equation 2 and the entropy values of the ions and determined the entropy of the complex at reference conditions was -0.7 cal mol<sup>-1</sup> K<sup>-1</sup>.

$$\bar{S}^{\circ}_{CuSO_4} = \Delta_r \bar{S}^{\circ} + \bar{S}^{\circ}_{Cu^{+2}} + \bar{S}^{\circ}_{SO_4^{-2}} \quad (2)$$

Heat capacity for  $CuSO_4$  at reference conditions was estimated using the methods described in St. Clair et al. (2019). The  $\Delta_r \bar{C}_p^{\circ}$  for divalent cation association with sulfate is estimated to be  $47.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Using equation 3 gives  $CuSO_4$  a reference conditions heat capacity ( $\bar{C}_p^{\circ}_{CuSO_4}$ ) of  $-22.7 \text{ cal mol}^{-1} \text{ K}^{-1}$ .

$$\bar{C}_p^{\circ}_{CuSO_4} = \Delta_r \bar{C}_p^{\circ} + \bar{C}_p^{\circ}_{Cu^{+2}} + \bar{C}_p^{\circ}_{SO_4^{-2}} \quad (3)$$

The equilibrium constant of association (K) at reference conditions is  $10^{2.35}$  (Powell et al., 2015). This constant is used to calculate the change in Gibbs energy for the formation of  $CuSO_4$  at reference conditions. The Gibbs energy of formation for the formation of copper sulfate from the elemental species ( $\Delta_f \bar{G}^{\circ}_{CuSO_4}$ ) is calculated using equation 4.

$$\Delta_f \bar{G}^{\circ}_{CuSO_4} = -RT \ln K + \Delta_f \bar{G}^{\circ}_{Cu^{+2}} + \Delta_f \bar{G}^{\circ}_{SO_4^{-2}} \quad (4)$$

The thermodynamic parameters of  $CuSO_{4(aq)}$  were expanded to  $1000^{\circ}\text{C}$  and  $5\text{kb}$  using the revised HKF model in a way that was consistent with Sverjensky et al., (1997).

## Geochemical Modeling

The figures in Chapter 4 were based on equilibrium constants generated using the CHNOSZ geochemical modeling package (Dick, 2019). Relative ratios based on equilibrium constants were used to create relative abundance plots. The pe-pH diagrams

include lines of equal activity for aqueous species and stability fields for crystalline minerals generated from the equilibrium constants of the reactions listed in the text.

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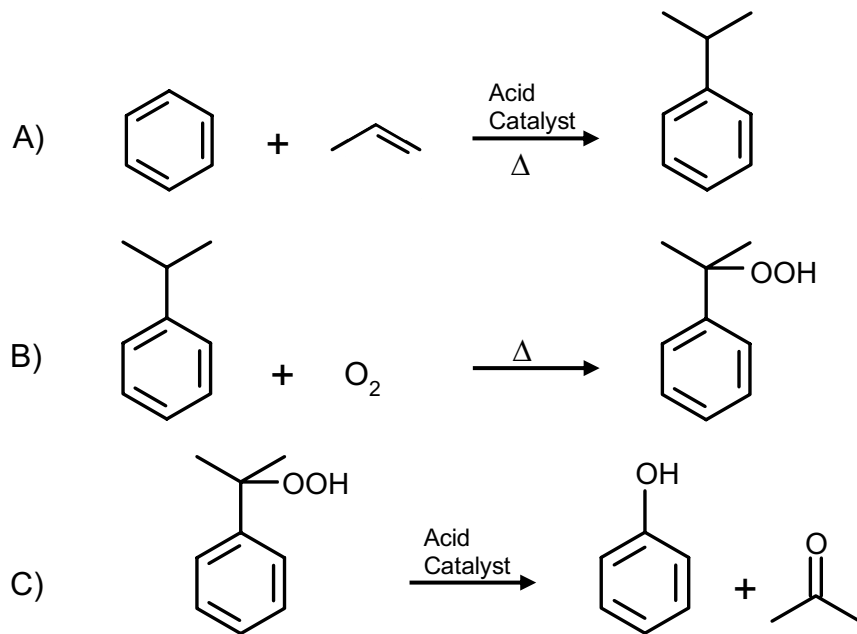
### 3. BENZENE OXIDATION WITH Cu(II)

#### **Abstract**

Many industrial chemicals utilize oxidized benzene derivatives. Benzene is typically oxidized by multi-step processes or by using toxic reagents. The experiments reported here are simple, one-step syntheses of phenol and chlorobenzene from benzene using only copper salts and water under hydrothermal conditions. These reactions utilize the principles of geomimicry, using Earth-abundant materials and conditions analogous to natural systems. Consequently, the experiments performed here are examples of relatively green alternatives to the current methods for industrial synthesis of phenol and chlorobenzene. The experiments also show the importance of inorganic speciation of the metal oxidants. The speciation of the copper salts in these experiments is also characterized showing that variations in the composition of aqueous solutions can lead to different organic and inorganic products.

#### **Introduction**

Benzene oxidation is an important synthetic step in the manufacture of many chemicals and materials. However, its aromatic stability leads to generally low reactivity making oxidation challenging. Many of the traditional oxidants employed in organic chemistry such as halogen gases, and chromium (VI) are toxic or hazardous (Norseth, 1981; Winder, 2001). Benzene oxidation, in particular, is typically performed using multi-step syntheses such as the cumene process to yield phenol or by halogen gases to produce halogenated benzenes.



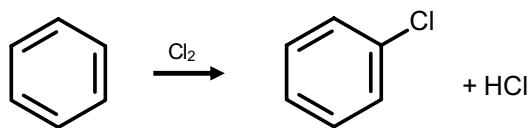
**Figure 1:** The three steps used in the production of phenol by the cumene process. A) The alkylation of benzene with propene to form cumene. B) The oxidation of cumene to form cumene hydroperoxide. C) The Hock rearrangement to yield phenol and acetone.

Phenol is an intermediate in the synthesis of polymers such as bisphenol A and phenolic resins. To meet the demands for these materials, more than 6 million metric tons of phenol are produced every year making phenol an important commodity chemical. Industrially, 95% of phenol production is carried out through the three-step cumene process (Molinari & Poerio, 2010) summarized in Figure 1. First, benzene is alkylated in the gas phase over an acid catalyst such as phosphoric acid with propene at temperatures of  $\sim 250^{\circ}\text{C}$  to form cumene. Next, cumene is oxidized with atmospheric oxygen to form cumene hydroperoxide. Finally, cumene hydroperoxide is thermally decomposed to form phenol and acetone. The cumene process has low overall yields and produces unwanted side products such as poly-alkylated benzenes (Niwa et al., 2002; Yang et al., 2013). Because



of the importance of phenol as a chemical intermediate, there have been numerous efforts to develop a single step process that converts benzene to phenol. These methods employ a variety of oxidants including  $N_2O$ ,  $O_2$ , and  $H_2O_2$  (Panov et al., 1992; Balducci et al., 2003; Kuznetsova et al., 2005). Recent developments in phenol production typically involve exotic catalysts, such as carbon nanoparticles (Chen et al., 2009, Yang et al., 2013), platinum and palladium (Ehrich et al., 2002), or palladium membranes (Niwa et al., 2002). A simple, economical alternative to these pathways is highly desirable (Plotkin, 2016).

Chlorinated aromatic compounds such as chlorobenzene have uses including high boiling point solvents and chemical intermediates. In contrast to phenol, chlorobenzene is produced through the simple process shown in Figure 2. In this process, benzene undergoes radical halogenation with chlorine radicals created through ultraviolet radiation (Sokolov et al., 1998). The chlorine radicals are derived from chlorine gas that is both hazardous and poisonous (Withers and Lees, 1985; Das & Blanc, 1993). Oxidative halogenation of aromatic compounds has been demonstrated with metal chlorides (Kovacic & Brace, 1954), but without an aqueous solution present the inorganic products are not dissolved and the reaction produces gaseous HCl.



**Figure 2:** The typical halogenation reaction for producing chlorobenzene from benzene in industrial settings,

To reduce the need for hazardous materials and reagents while at the same time avoiding exotic and expensive catalysts, we can apply the principles of geomimicry by looking to natural systems to see how hydrocarbons are oxidized with Earth-abundant materials. Most of Earth's organic carbon is found in underground reservoirs (Falkowski et al., 2000, Houghton, 2007), where the oxidation state of the system is controlled by organic species or by Earth-abundant redox sensitive metals in inorganic mineral assemblages (Helgeson et al., 1993; Shock, 1994; Seewald, 1994). My goal in this study is to employ these Earth-like conditions to develop new pathways for organic transformations. Previous work in this field has shown that oxygen-bearing organic compounds can be selectively oxidized with relatively benign and Earth-abundant copper salts under hydrothermal conditions (Yang et al., 2015; Fu et al., 2020). The experiments in this investigation extend these conditions to the oxidation of benzene, with the goal of producing industrially desirable products. I found that under hydrothermal conditions copper salts can oxidize benzene via a simple, one-pot synthesis to produce phenol and/or chlorobenzene. These pathways represent green alternatives to the current synthetic pathways used to produce phenol and chlorobenzene.

## **Results**

### *Oxidation of Aromatic Compounds with Cu(II) Salts*

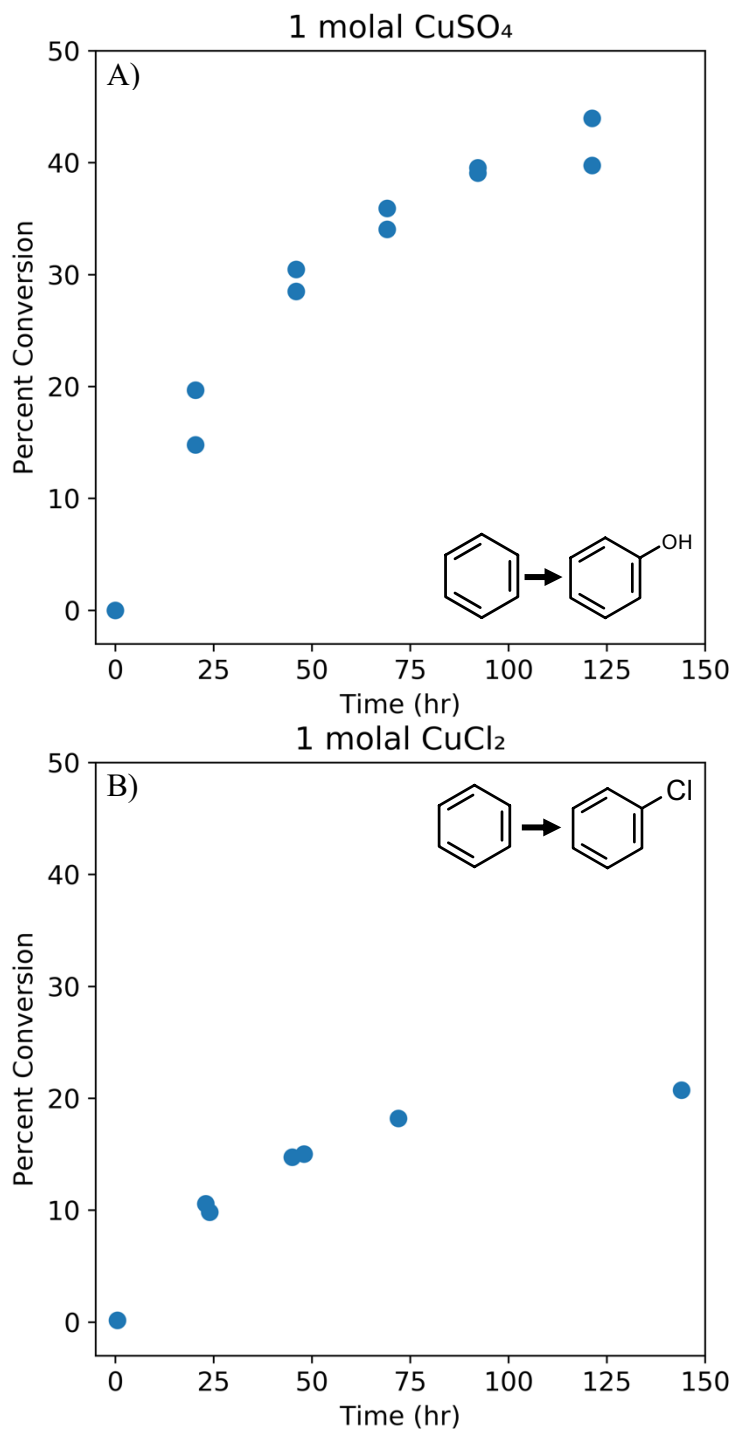
Benzene was oxidized using both  $\text{CuCl}_2$  and  $\text{CuSO}_4$  to produce substituted aromatic molecules. In the  $\text{CuCl}_2$  experiments, the product was chlorobenzene. In the  $\text{CuSO}_4$  experiments, the product was phenol. The reduced form of copper produced in the experiments is also different depending on which copper salt was used. When  $\text{CuCl}_2$  is used

the copper turns to a white, acid-soluble solid with the appearance of  $\text{CuCl}_{(s)}$ , consistent with results reported in Yang et al. (2015) and in Greenwood and Earnshaw (1997). In the experiments using  $\text{CuSO}_4$ , the precipitate appeared to be  $\text{Cu}(0)$  based on its color and metallic luster.

### *Reaction Time Series*

Time-series data are presented in Table 1 and the oxidation of benzene by  $\text{CuSO}_4$  and by  $\text{CuCl}_2$  are illustrated in Figure 3. All experiments were conducted at  $250^\circ\text{C}$  under anoxic conditions in fused silica tubes, using the general experimental procedures and analyses outlined in Chapter 2. When  $\text{CuSO}_4$  was used as the oxidant (Fig 3a), conversion was  $\sim 40\%$  after 121 hours with no other major products. When  $\text{CuCl}_2$  was used as the oxidant (Fig 3b), conversion was comparatively slower, only  $\sim 20\%$  after 141 hours. The experiments involving copper sulfate were performed in duplicate to confirm the replicability of this experimental process. Two sets of close time points in the copper chloride experiments had similar conversion, confirming reasonable replicability.

$\text{FeCl}_3$  also oxidized benzene to chlorobenzene, Similar to the Cu (II) experiments. This oxidation was much slower and only achieved 2% conversion after 9 days at  $250^\circ\text{C}$ . Although this small conversion is less appealing for synthetic applications it demonstrates that these oxidations are possible with other Earth-abundant oxidants.



**Figure 3:** Percent conversion as a function of time for the conversion of benzene to A) phenol using CuSO<sub>4</sub> and B) chlorobenzene using CuCl<sub>2</sub> in the hydrothermal experiments.

**Table 2:** Conversion and molar concentration of organic compounds from hydrothermal experiments. The first set of experiments used CuSO<sub>4</sub> as an oxidant. The second set of experiments used CuCl<sub>2</sub> as an oxidant.

Time (hr)	Conversion (%)	Benzene (mm)	Phenol (mm)	Mass Balance (%)
20.4	19.7	179	43.9	77
20.4	14.8	245	42.4	99
46.0	28.5	197	78.3	95
46.0	30.5	133	58.2	66
69.2	34.1	151	78.1	79
69.2	35.9	153	85.6	82
92.2	39.1	129	82.9	73
92.2	39.6	120	78.7	69
121.3	44.0	114	89.5	70
121.3	39.8	115	76.0	66
Time (hr)	Conversion (%)	Benzene (mm)	Chlorobenzene (mm)	Mass Balance (%)
0.5	0.2	188	0.3	65
23	10.6	200	23.6	77
24	9.8	250	27.2	96
45	14.7	203	35.0	82
48	15.0	228	40.2	92
72	18.2	209	46.4	88
144	20.7	228	59.5	99

## Discussion

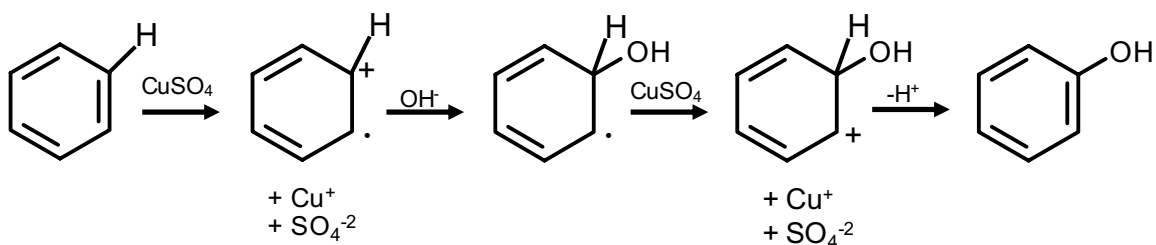
Both of the oxidations reported here represent unconventional pathways to the respective products. For oxidations with copper salts, Cu(II) is the oxidant and the anions

have no involvement in oxidizing organic compounds (Fu et al., 2020). However, the anions strongly influence the products of each oxidation reaction. If Cu(II) was the reagent and  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were simply spectator ions we expect both salts would yield the same products and have similar kinetics. However, these experiments reveal two different substituents on the oxidized benzene and two different reduced inorganic products. When  $\text{CuSO}_4$  is used as an oxidant, benzene is oxidized to phenol and the remaining inorganic material appears to be metallic Cu. When  $\text{CuCl}_2$  is the oxidant, benzene is oxidized to chlorobenzene and the inorganic precipitate appears to be  $\text{CuCl}_{(s)}$ . The inorganic products suggest that  $\text{CuCl}_2$  favors a single electron transfer as implied by the conversion of Cu(II) into a Cu(I) species. The oxidation with  $\text{CuSO}_4$  follows a different reaction mechanism. Since the Cu(II) is fully reduced to Cu(0), it is not entirely clear if the oxidation proceeds through a single or double electron transfer. The proposed mechanisms for the observed reactions are guided by the speciation of Cu in solution and previous observations from experiments using Cu(II) as an oxidant.

#### *Phenol Reaction Pathway and Sulfate Speciation*

The proposed mechanism for benzene oxidation with  $\text{CuSO}_4$ , depicted in Figure 4, is similar to the mechanism outlined by Yang et al. (2015). In the first step, Cu(II) accepts a single electron from benzene and becomes Cu(I). The occurrence of single-electron transfers is common in organic oxidations via metals oxidant (Mijs and Jonge, 2013). In the case of these specific reactants, Cu(II) in mineral form has been shown to complex with benzene (Doner & Mortland, 1969) disrupting the aromaticity of benzene (Pinnavaia & Mortland, 1971) implying the formation of a benzene radical cation (Rupert, 1972). A

benzene radical cation would be the result of a single electron transfer from benzene to Cu(II). Yang et al. (2015) note substituent effects for benzyl alcohol oxidation with Cu(II) associated with a mechanism involving a positive charge on the ring. A positive charge on the ring is consistent with a mechanism involving a single electron transfer. The observations from these previous studies suggest that the radical cation is an intermediate in the oxidation of aromatic compounds with Cu(II). Thus, the first step shown in Figure 4 is the single electron transfer from benzene to Cu(II). In the second step, after the radical cation is formed, a hydroxide ion or water molecule acts as a nucleophile and bonds to the positive charge. This forms a neutral radical compound which is oxidized by another Cu(II) in step three, turning the radical cation into a carbocation. In the final step the molecule can deprotonate at the site of the hydroxide and the electrons of the deprotonated C-H bond form a pi bond and restore aromaticity.



**Figure 4:** Reaction pathway for the oxidation of benzene with copper sulfate.

The mechanism proposed here leads to the formation of two Cu(I) molecules from two separate single-electron transfers. In this case, the reaction of benzene and Cu(II) is not responsible for the production of metallic Cu observed in the experiments. If Cu(II) is only oxidized to Cu(I), a disproportionation would be responsible for the metallic Cu. This is supported by observations in which  $\text{Cu}_2\text{SO}_4$  rapidly disproportionates to form Cu(0) and

CuSO<sub>4</sub> in presence of water (Van & Habashi, 1972). In aqueous solutions, disproportionation largely favors the Cu(II) and Cu(0) oxidation states over Cu(I) because of the increased ability for these species to interact with water molecules. There is more energy released in the hydration of Cu(II) than Cu(I) e.g., Moen & Nicholson, (1995), suggesting that it is energetically favorable for Cu to be in the +2 oxidation state. The disproportionation of copper is thought to be controlled by the properties of the solution it is dissolved in, suggesting that intermolecular forces between the solvent and the copper species determine the equilibria between the redox states of copper species (Persson et al., 1993). It is possible that complexation of copper with other ions in solution influences the extent of disproportionation. Anions that strongly associate with Cu<sup>+2</sup> or Cu<sup>+</sup> may influence the concentration of species that participate in the disproportionation. It is possible Cu(I) and Cu(II) complexes influence the equilibrium of the disproportionation reaction:

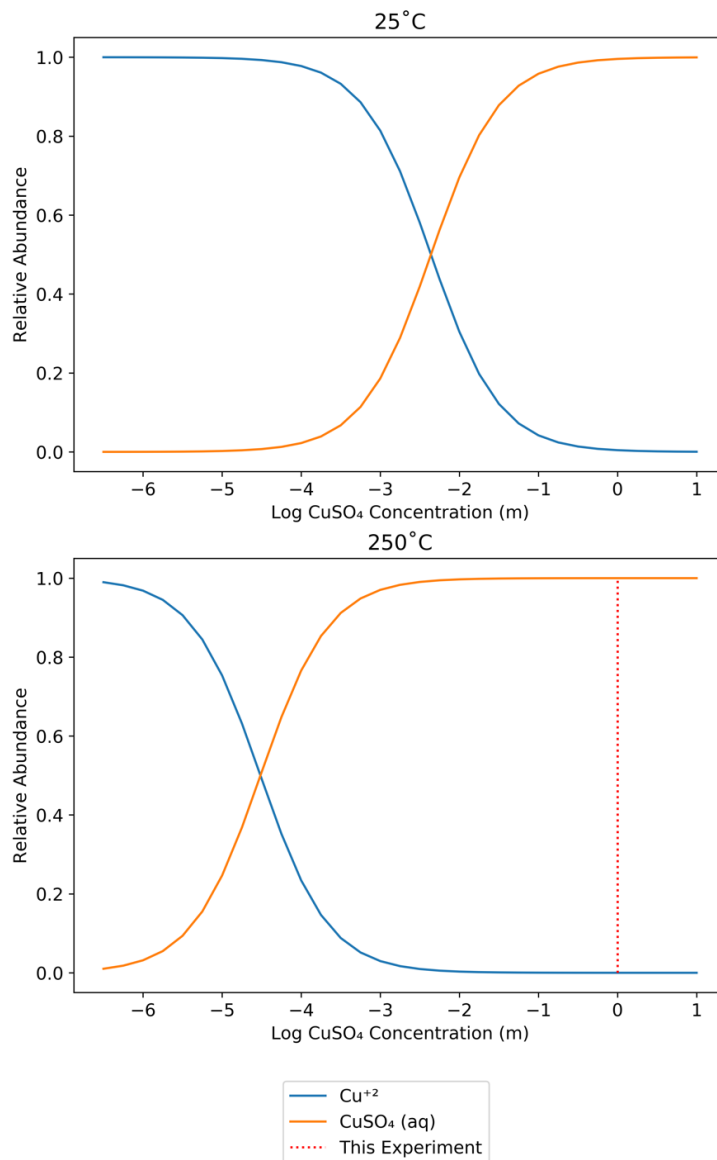


Complexes influence the activity of free ions and could shift the equilibrium of the disproportionation reaction. Cu(I) complexes could consume Cu<sup>+</sup> ions, shifting the equation to the left favoring reactants. Cu(II) complexes could consume Cu<sup>+2</sup> ions and shift the reaction to the right to favor more products.

To investigate the strengths of the aqueous CuSO<sub>4</sub> complexes, I estimated the thermodynamic properties of CuSO<sub>4(aq)</sub> to find the dominant form of Cu(II) over a range of CuSO<sub>4</sub> concentrations. Estimation methods are described in detail in Chapter 2. Speciation calculations at 25°C and 250°C for these data are shown in Figure 5. The speciation of CuSO<sub>4</sub> goes against the traditional notion that salts generally dissociate in water. At the 1 molal concentration of CuSO<sub>4</sub> used in these experiments, the copper in



solution is speciated almost entirely as the aqueous neutral species. Ionic species are prevalent only when  $\text{CuSO}_4$  concentration is less than 0.001 molal at  $25^\circ\text{C}$  and less than 0.1 millimolal concentrations at  $250^\circ\text{C}$ . The  $\text{CuSO}_4$  complex appears to have an effect on the fate of the copper and the benzene. The presence of sulfate leads to phenol and metallic Cu while  $\text{CuCl}_2$  leads to an entirely different set of products.



**Figure 5:**  $\text{CuSO}_4$  speciation at  $25^\circ\text{C}$  and 1 bar and at  $250^\circ\text{C}$  and 37.9 bar, the conditions of this experiment.

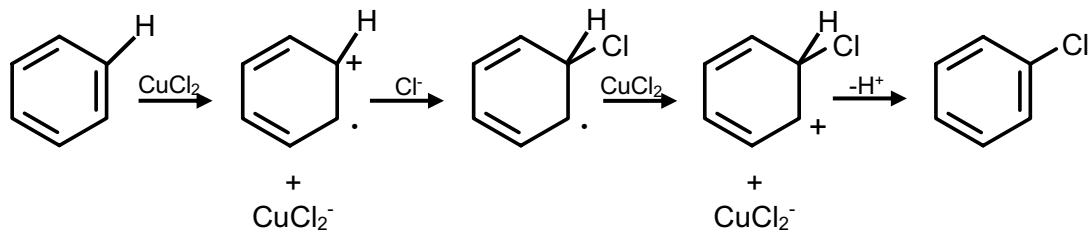
The thermodynamic properties of Cu(I)-sulfate species are uncharacterized at these conditions, but the rapid disproportionation of  $\text{Cu}_2\text{SO}_4$  in water described by Van and Habashi (1972) implies there are no stable complexes of Cu(I) and  $\text{SO}_4^{2-}$ . If rapid disproportionation is due to stable complexes with Cu(II) and its surroundings, it follows that the even higher formation constant for the aqueous  $\text{CuSO}_4$  complex at hydrothermal temperatures would lead to even more disproportionation than at room temperature. The metallic copper observed at the end of the experiments can be explained by the powerful sulfate complexation leading to Cu(I) disproportionation.

#### *Chloride Pathway and Speciation*

The mechanism for chlorinating benzene with  $\text{CuCl}_2$  shown in Figure 6 proceeds similarly to the oxidation of benzene to phenol discussed previously. The initial step is a single-electron transfer from a pi bond of the benzene ring yielding a Cu (I) complex and a benzene radical cation. In the second step, the cation is attacked by a chloride ion from solution or by the adjacent copper chloride complex leaving a neutral radical compound. In the third step, the radical undergoes another single-electron transfer leaving a cation. Finally, the molecule deprotonates at the position of the chloride bond. The electrons from the broken C-H bond restore aromaticity to the system by forming a  $\pi$ -bond. The resulting product is chlorobenzene.

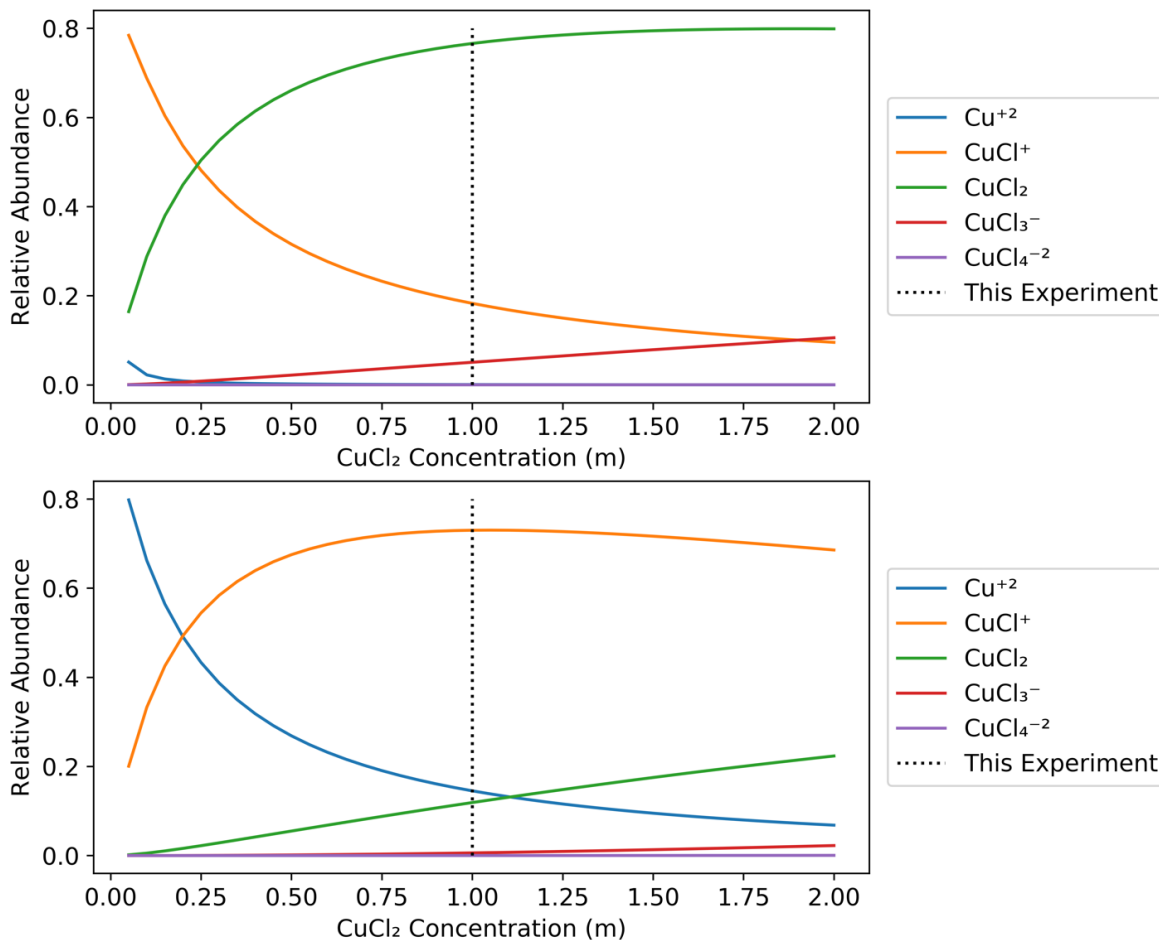
The evidence for single-electron transfer is much more straightforward in this reaction scheme than in the  $\text{CuSO}_4$  oxidation. Because the inorganic precipitate appears to

be  $\text{CuCl}_{(s)}$  and no metallic Cu is formed, the copper products are only reduced by one electron rather than two.



**Figure 6:** Reaction mechanism for the chlorination of benzene with copper chloride. A variety of copper chloride complexes are present in solution. This reaction is not limited to  $\text{CuCl}_2$  and  $\text{CuCl}_2^-$ , these are the dominant species of each oxidation state.

Since water is a much more abundant nucleophile than chloride in these experiments, it is surprising that experiments using  $\text{CuCl}_2$  produce no phenol. However, the calculated speciation of copper in solution shows that the majority of chloride in solution is in the form of copper complexes. At the experimental conditions, 93% of the chloride is in copper complexes. At higher temperatures, aqueous complexes between metals and ligands become increasingly favorable. The relative abundance of copper species is shown in in Figure 7. The majority of copper and chloride ions are speciated as copper complexes rather than as free ions as the concentration increases and the temperature is increased toward hydrothermal conditions. Aqueous  $\text{CuCl}_2$  is the dominant species at  $250^\circ\text{C}$  and  $\text{CuCl}^+$  is the dominant species at  $25^\circ\text{C}$ . Lower temperatures and concentrations are required for Cu(II) to be predominately speciated as  $\text{Cu}^{+2}$ . At the conditions used in my experiments, these abundant copper chloride complexes position chloride-bearing molecules directly adjacent to the cation that forms when the benzene ring



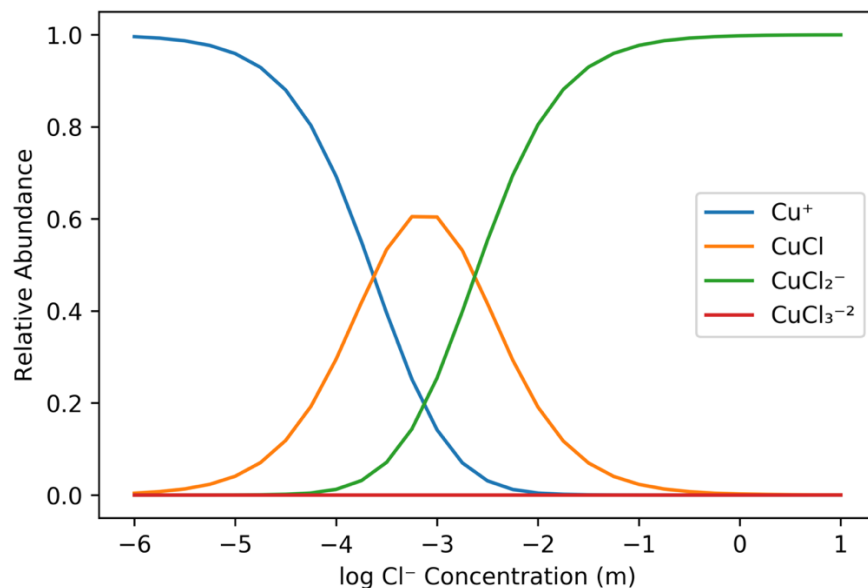
**Figure 7:** Copper chloride speciation at A) 250°C, the conditions of this experiment and at B) 25°C, room temperature. The relative abundances are calculated by the methods described in chapter 2.

is oxidized. The proximity of chloride to the carbocation may create conditions where chloride is the better nucleophile while water or hydroxide are close enough to react with the cation.

The speciation of  $\text{Cu(II)}$  complexes and  $\text{Cl}^-$  ions accounts for the production of chlorobenzene rather than phenol when benzene is oxidized through the proposed mechanism, but it does not explain the differences observed in inorganic products. I

attributed metallic copper in the  $\text{CuSO}_4$  experiments to the disproportionation of  $\text{Cu(I)}$  once it is reduced. This reaction should be enhanced by the overwhelmingly stable aqueous  $\text{CuSO}_4$  complex and the generally more favorable intermolecular forces between water and  $\text{Cu(II)}$ . In the experiments using  $\text{CuCl}_2$ , however, metallic  $\text{Cu(0)}$  is not an observed product meaning there was no disproportionation. Since the disproportionation is controlled by intermolecular forces between the copper and the solution (Persson et al., 1993) the added chloride is likely stabilizing the  $\text{Cu(I)}$  and inhibiting the disproportionation reaction. The lack of disproportionation can be attributed to the stability of  $\text{Cu(I)}$  complexes formed when  $\text{Cl}^-$  ions are present. The  $\text{Cl}^-$  complexes are the most abundant species at  $250^\circ\text{C}$  when  $\text{Cl}^-$  is present at millimolar concentrations which is the case for these experiments. The speciation of  $\text{Cu(I)}$  over different chloride concentrations is shown in Figure 8. At the concentrations used in these experiments there is a strong drive to form complexes. The stability of these  $\text{Cu(I)}$  complexes is likely responsible for the difference in reaction between the  $\text{CuCl}_2$  and  $\text{CuSO}_4$ . The different inorganic products resulting from the different anions suggest  $\text{Cu(I)}$  is much less likely to disproportionate if there are  $\text{Cl}^-$  ions in the system to interact with. When chloride is absent, the disproportionation to two lower energy oxidation states can occur.

The lack of disproportionation is also consistent with the conversions shown in Figure 3. Since the reduction of  $\text{CuCl}_2$  stops at  $\text{Cu(I)}$ , while the  $\text{CuSO}_4$  can be fully reduced to metallic  $\text{Cu}$ , the experiments using  $\text{CuCl}_2$  effectively have fewer electron acceptors because the copper species only accepts one electron instead of two.



**Figure 8:** The speciation of Cu(I) with Cl<sup>-</sup> ions over a range of Cl<sup>-</sup> concentrations.

## Conclusions

The mechanisms shown in these experiments are novel pathways for aromatic oxidation. The reactions illustrated in this investigation show that aromatic hydrocarbons can be oxidized with aqueous metal species. The reactions shown here are simple, one-pot syntheses of industrially significant compounds using relatively benign, Earth-abundant materials. While the temperature needed for hydrothermal reaction conditions are high, traditional aromatic oxidations, such as the cumene process, also utilize high reaction temperatures. These hydrothermal oxidations serve as a geomimetic alternative for the current industrial methods. In addition to the novel pathways, these experiments also demonstrate the importance of metal speciation in oxidation reactions. Metal speciation can lead to different organic and inorganic products. This suggests that the reaction can be tuned to produce desired products by adjusting the solution composition and the metal speciation. A significant upside of the reaction of benzene with copper sulfate is that it

produces metallic copper in addition to phenol. The reaction is a value-added process for both the oxidant and the reductant. These pathways represent a new approach to functional group transformation in the relatively unreactive class of aromatic hydrocarbons.

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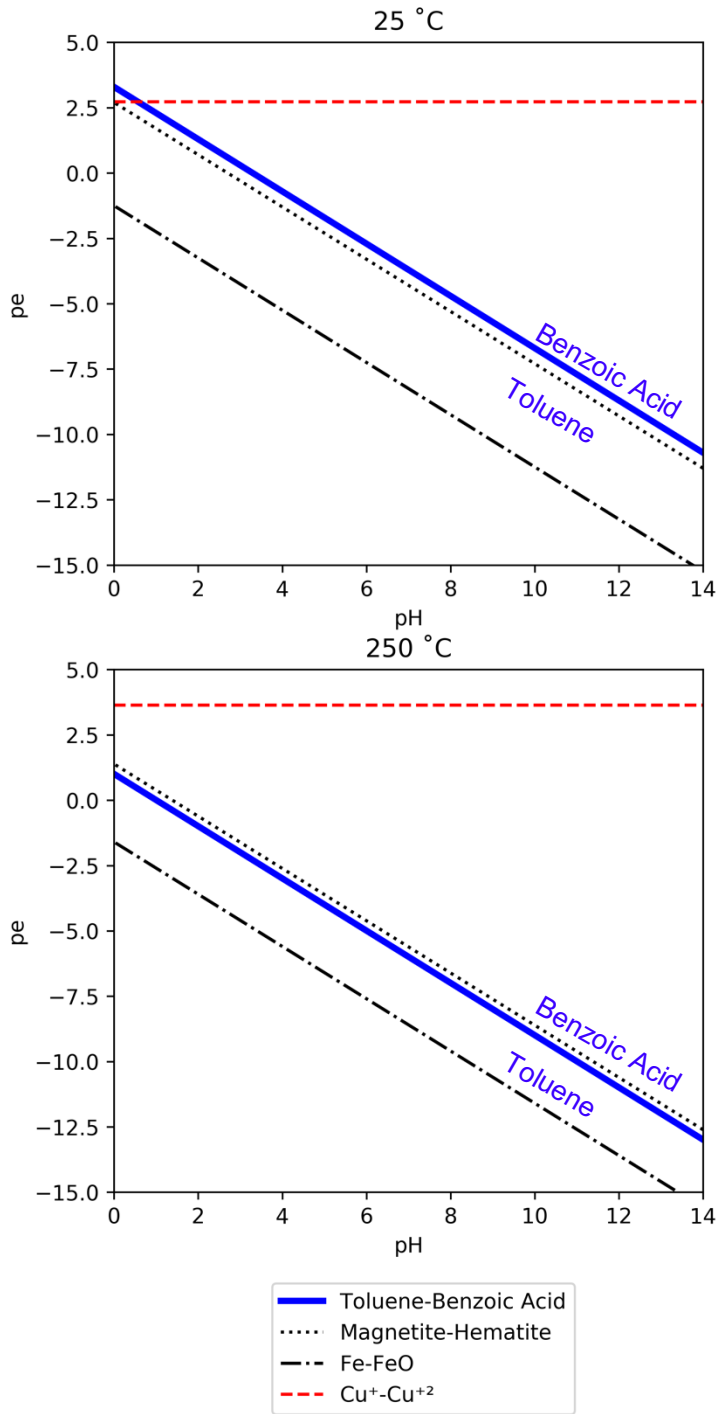
#### 4. TOLUENE OXIDATION WITH Cu(II)

##### **Abstract**

Aromatic hydrocarbons, such as toluene, are thought to be recalcitrant compounds in hydrothermal systems. In this experimental investigation toluene was oxidized with aqueous Cu(II) to form a suite of aromatic compounds with oxygen-bearing functional groups. Organic products are soluble compounds that are reactive at hydrothermal conditions. These results show that toluene can undergo redox-sensitive transformations through metal mediated reaction pathways. The results demonstrate the role aqueous metals play in organic transformation in natural systems.

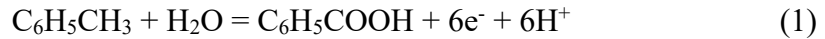
##### **Introduction**

Toluene is present in sedimentary basins, sedimented hydrothermal vent systems, and volcanic fumaroles associated with hydrothermal circulation (Cruse & Seewald 2006; Vaselli et al., 2006; Konn et al., 2009; Cruse & Seewald 2010). Its persistence in these settings and the traditional assumption of aromatic stability suggest it is very unreactive (McCollom et al., 2001). However, the general fate of toluene under hydrothermal conditions in natural systems is not fully characterized. In water alone, toluene has been shown to have very little reactivity over 144 hours, with less than 1% conversion to benzene (Shipp et al. 2013). Toluene's lack of reactivity makes it essentially an end product in experiments containing only water and toluene. In experiments with redox-sensitive minerals toluene is thought to equilibrate with benzene through oxidative decarboxylation

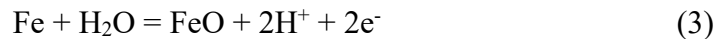


**Figure 9:** Relative stability fields in pe vs pH space for aqueous toluene and benzoic acid based on equation 1. Common redox buffers and aqueous copper species are plotted to the context for redox conditions. The lines for aqueous species denote equal concentrations of the two redox sensitive species. Methods for calculation are described in Chapter 2.

over long timescales (McCollom et al., 2001). However, coupled redox systems of toluene and oxidized aqueous inorganic species have not been explored at hydrothermal conditions. The relative stability fields in pe/pH space for toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) and benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH) are shown in Figure 9 at 25°C and 250°C for reaction 1.



This relationship shows that acidic and reduced conditions favor toluene, while oxidized and basic conditions favor benzoic acid. Figure 9 also includes the mineral redox equilibrium for magnetite-hematite (reaction 2) and Fe-FeO (reaction 3).



Magnetite-Hematite is a more oxidized mineral assemblage and commonly used reference state for oxidized geochemical conditions (Seewald, 2001). Iron-Wustite (Fe-FeO), is a reduced assemblage commonly used for context in very reduced systems (Jakobsson & Holloway, 1986). The two bracket a range of redox conditions that encompass many hydrothermal systems. The line of equivalence between toluene and benzoic acid shifts below the hematite-magnetite buffer and closer to the Fe-FeO buffer at high temperature, making the oxidation of toluene more favorable. Thus, a system where the redox conditions are controlled by magnetite-hematite at 250°C favors benzoic acid. At lower temperatures toluene-benzoic acid equivalency is above the magnetite-hematite signifying that toluene

is the favored organic species. The oxidation state set by the mineral assemblages does not appear to strongly favor the oxidation of toluene. In contrast, the line of equal activity for Cu(II) and Cu(I) (reaction 4) falls at more oxidized conditions, as shown in Figure 9. The equilibrium between the two copper ions appears to strongly favor the oxidation of toluene since the copper line is well above the organic line.



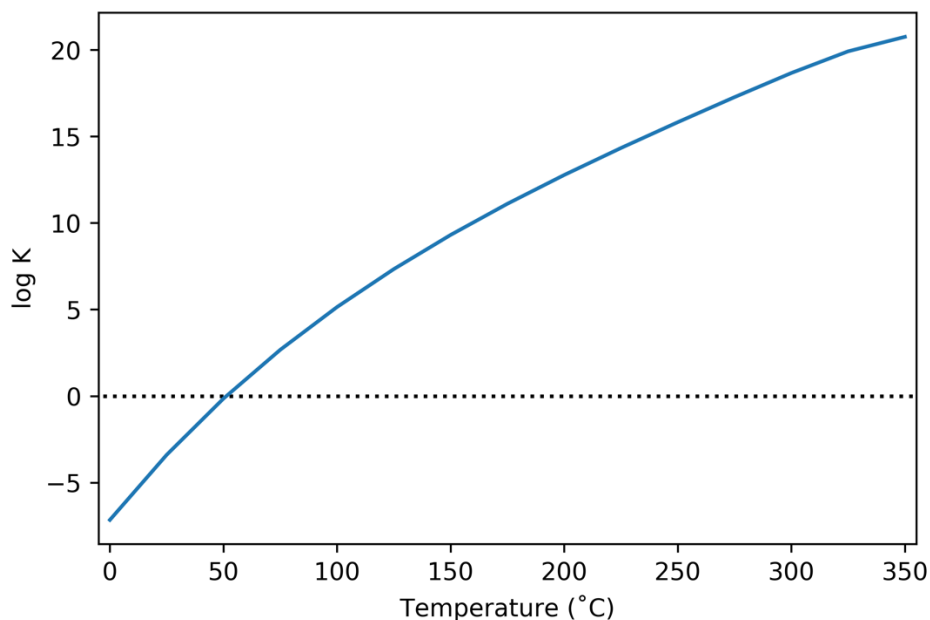
Aqueous copper is prevalent in many hydrothermal systems (Elderfield & Schultz, 1996) and, therefore, has the potential to act as a reactive species in natural systems. Coupling the copper half reaction and the organic half reaction yields reaction 5.



The calculated equilibrium constant for this reaction as a function of temperature is shown in Figure 10. There is a thermodynamic drive to oxidize toluene in a solution containing aqueous Cu(II). The experiments conducted here assess the mechanism of reaction for the oxidation of toluene with Cu(II).

Oxidized toluene derivatives such as benzyl alcohol and benzaldehyde have been previously studied under hydrothermal conditions. At hydrothermal conditions benzyl alcohol is rapidly oxidized by Cu(II) to form benzaldehyde (Yang et al., 2015). Benzaldehyde under hydrothermal conditions undergoes a disproportionation to form benzoic acid and benzyl alcohol through a hydride transfer. These products further react to

form a suite of products resulting from electrophilic aromatic substitution (EAS); (Fecteau et al., 2019). The reactivity of these oxidized toluene derivatives suggests that the oxidation of toluene promotes other organic transformations by producing these reactive compounds.



**Figure 10:** Equilibrium constant for the oxidation of toluene to benzoic acid with  $\text{Cu}^{+2}$  as an oxidant (reaction 5) from 0 to 350°C. Calculation methods are described in chapter 2.

Reactions of toluene are important to characterize as toluene is a component of oil and it is used in gasoline, solvents, and as a chemical intermediate (Karl-Heinz & Stokholm, 2010). The products of toluene oxidation have implications for natural systems as well. All oxidized products that contain oxygen-bearing functional groups have increased aqueous solubility and they may be present in circulating brines and hydrothermal fluids. Benzoic acid is highly water soluble and may act as an organic ligand to stabilize metal cations and promote metal mobility in aqueous environments. The EAS

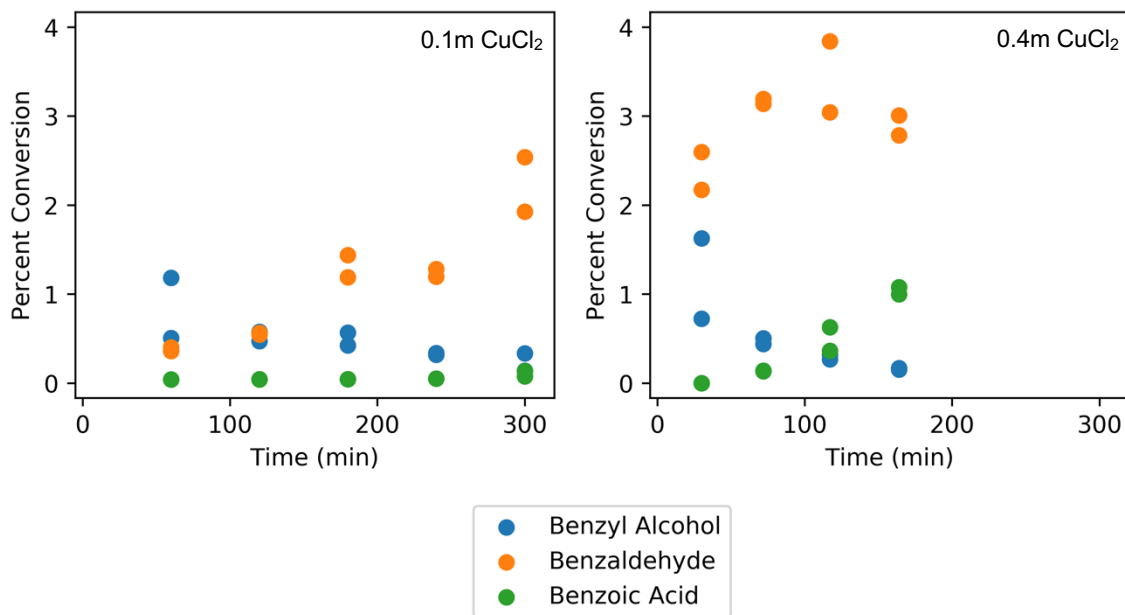
reactions of benzaldehyde and benzyl alcohol lead to increasingly aromatic products with multiple rings and lower C:H ratios. When aromatic compounds react to form polycyclic molecules, they release H<sub>2</sub> that can participate in other hydrothermal organic reactions (Bockisch et al., 2019, Venturi et al., 2017) or that can be metabolized by a variety of microorganisms (Shock, 2009).

## Results

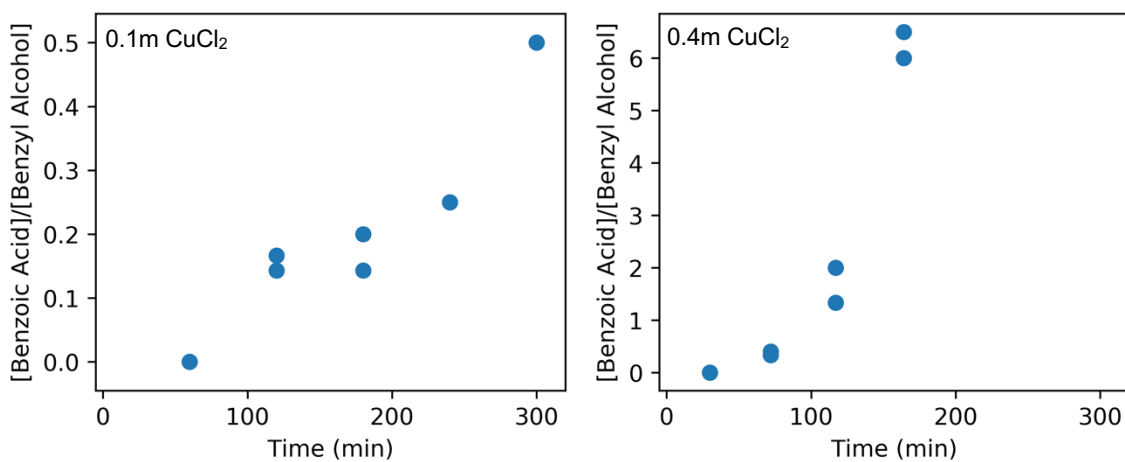
Experimental hydrothermal reactions with toluene and CuCl<sub>2</sub> produced benzyl alcohol, benzaldehyde, and benzoic acid (Figure 11 and Table 3). Overall conversion is greater with higher concentrations of CuCl<sub>2</sub>, however, the same products form at both concentrations. The results show decreasing concentrations of benzyl alcohol over time, consistent with the changing acid to alcohol ratio shown in Figure 12. This is consistent with a reaction scheme in which benzyl alcohol forms first and is reacting to produce different organic products. Benzaldehyde concentration increases at longer time scales signifying that it is the product of benzyl alcohol oxidation. This is in agreement with a previous study that shows oxidation of benzyl alcohol with CuCl<sub>2</sub> to form benzaldehyde (Yang et al., 2015). Benzoic acid concentration increases over time at the same time that benzaldehyde concentration begins to level out. The stepwise oxidation from the most reduced compound, toluene, to the most oxidized compound, benzoic acid is demonstrated by the increasing benzoic acid to benzyl alcohol ratio shown in Figure 4.

The reaction of toluene and Cu(II) also leads to the production of multi-ring EAS products consistent with benzyl toluene isomers. Figure 21 in Appendix A shows the three peaks of the high molecular weight compounds that I attribute to EAS products. The





**Figure 11:** Percent conversion to benzyl alcohol, benzaldehyde, and benzoic acid as a function of time for experiments with 0.12 molal toluene and 0.1m (left) or 0.4m CuCl<sub>2</sub> (right).



**Figure 12:** The acid to alcohol ratio over time for the time series presented in figure 11.

**Table 3:** Experimental data and products from experiments.

Time (min)	Starting CuCl <sub>2</sub> (mm)	Toluene (mm)	Benzaldehyde (mm)	Benzyl Alcohol (mm)	Benzoic Acid (mm)	2 Ring Products (mm)	Mass Balance (%)
30	400	85.8	3.1	2.0	bdl	2.5	78
30	400	87.9	2.6	0.9	bdl	2.3	78
72	400	106.8	3.8	0.6	0.2	3.4	96
72	400	109.4	3.8	0.5	0.2	3.4	98
117	400	81.8	4.6	0.4	0.8	3.6	76
117	400	105.7	3.6	0.3	0.4	3.4	95
164	400	98.8	3.3	0.2	1.2	3.2	89
164	400	86.6	3.6	0.2	1.3	2.9	79
60	100	83.6	0.5	1.4	bdl	0.2	71
60	100	90.1	0.4	0.6	bdl	0.1	76
120	100	90.0	0.7	0.7	0.1	1.0	77
120	100	82.1	0.7	0.6	0.1	1.0	70
180	100	85.8	1.7	0.5	0.1	1.2	74
180	100	86.0	1.4	0.7	0.1	1.3	75
240	100	85.7	1.4	0.4	0.1	1.9	75
240	100	91.9	1.5	0.4	0.1	2.5	80
300	100	75.5	2.3	0.2	0.1	2.8	67
300	100	90.4	3.0	0.4	0.2	2.3	80

reaction to form benzyltoluene through EAS is presented in Fecteau et al. (2019). Three closely spaced peaks are associated with ortho-, meta-, and para- isomers, and the retention times are characteristic of a 2-ring hydrocarbon. The EAS products are also reactive and lead to higher molecular weight compounds, increasing complexity, and multiple side products. The experiments were kept to durations under 5 hours to avoid the production of high molecular weight compounds.

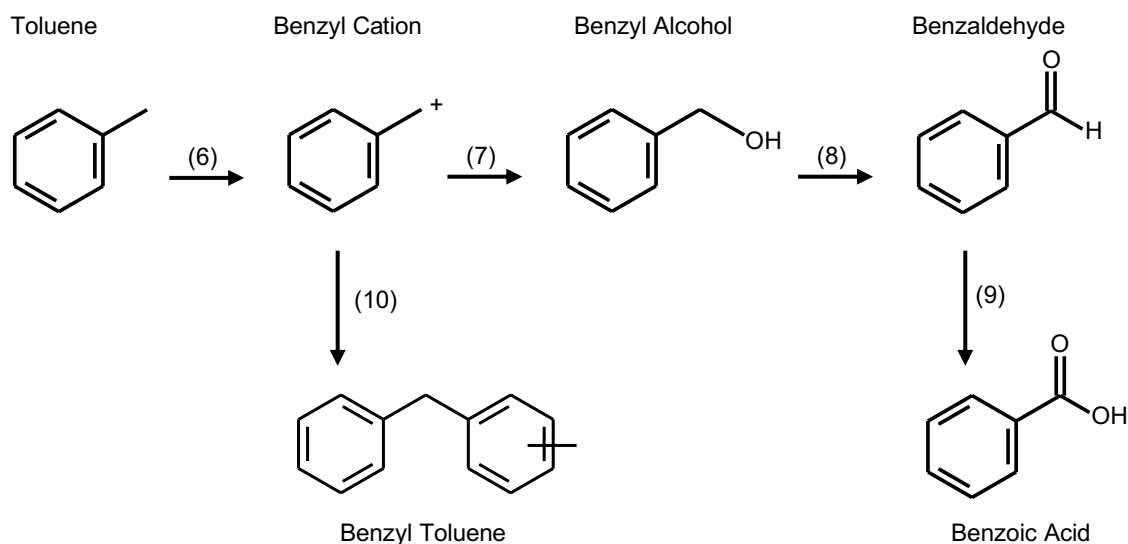
## **Discussion**

### *Reaction Pathway*

The oxidation of toluene is notably different from the oxidation of benzene presented in Chapter 3. In contrast to the oxidation of benzene that leads to a hydroxyl group on the ring, the main products of toluene oxidation involve the methyl group. If the reaction pathways were the same, cresols would be the expected products of toluene. The different interactions of aromatic hydrocarbons and Cu(II) in spectroscopic studies further demonstrate this different behavior. Cu(II) in minerals has been shown to complex with benzene (Doner & Mortland 1969). Spectroscopic investigations of interactions between aromatic compounds and Cu(II) suggest that two different types of complexes form, one complex where aromaticity is maintained and another where the aromaticity is disturbed (Mortland & Pinnavaia, 1971). Toluene does not form the complexes associated with disrupted aromaticity (Pinnavaia, & Mortland 1971). Electron spin resonance shows that the disturbed resonance is characteristic of a radical cation through a single electron transfer (Rupert, 1973). Since toluene does not form complexes associated with radical cation formation, the positive charge on the methyl group is likely formed through a

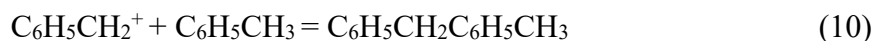
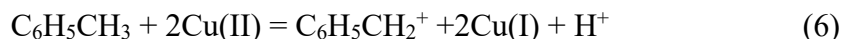
different pathway. A plausible mechanism is the complexation of toluene with two Cu(II) molecules that do not disrupt the aromaticity of toluene but rather act as electron withdrawing groups. The methyl group then deprotonates and transfers the  $\sigma$  electrons of the C-H bond into the  $\pi$  aromatic system to form a benzyl cation. The cation then reacts with a hydroxide molecule to form benzyl alcohol.

Once produced, benzyl alcohol can be further oxidized to benzaldehyde and benzoic acid. The oxidation of benzyl alcohol with copper to produce benzaldehyde and benzoic acid is described in detail by Yang et al. (2015); they propose that benzyl alcohol goes through two single-electron transfers and two deprotonations via a radical cation intermediate to yield benzaldehyde. After benzaldehyde is produced, it can be hydrolyzed, oxidized by Cu(II), and deprotonated to yield benzoic acid.



**Figure 13:** Proposed reaction scheme of reactions 6-10 for the oxidation of toluene with  $\text{CuCl}_2$ . This pathway includes the major organic transformations consistent the products observed in the experiments.

Figure 13 summarizes the proposed reaction scheme for the oxidation of toluene by Cu(II). The balanced reactions for this scheme are shown in equations 6-10. Cu(II) and Cu(I) exist as a variety of chloride complexes. The copper in these experiments is not simply  $\text{Cu}^{+2}$  and  $\text{Cu}^+$ ; Chapter 3 outlines the copper speciation encountered in these experiments in detail. No chlorinated organic products were detected so chloride does not seem to participate in these reactions. In the first step of the reaction scheme proposed in Figure 13, toluene is oxidized by Cu(II) to form a benzyl cation. The benzyl cation reacts with a hydroxide ion to yield benzyl alcohol through reaction 7. Benzyl alcohol is then oxidized by Cu(II) through a series of single electron transfers to yield benzaldehyde and two protons through reaction 8 (Yang et al., 2015). Finally, benzaldehyde is oxidized by Cu(II) via two single electron transfers and hydrated with a water molecule to form benzoic acid and two protons.



The benzyl cation also undergoes electrophilic aromatic substitution (reaction 10) where toluene acts as the nucleophile. The products in these experiments are multi-ring compounds with three isomers, consistent with benzyl toluene formation. These would

occur when the  $\pi$ -electrons in a toluene molecule act as a nucleophile and react with the benzyl cation. The experiments produced no bibenzyl which further supports the absence of a radical mechanism. If the benzyl cation was formed through a benzyl radical intermediate, bibenzyl would be the expected product of the termination of the two radicals. The multi-ring products here are not reported by Yang et al. (2015) but those experiments started with phenylacetic acid and were carried out on short time scales of 30 and 60 minutes, allowing less time for the EAS reaction. Additionally, in the experiments conducted by Yang et al., benzyl alcohol or benzaldehyde would have to serve as the nucleophile rather than toluene. The substituent in benzaldehyde has an inductive electron withdrawing effect that would hinder EAS while benzyl alcohol has no inductive effect (Hansch & Taft, 1991). Toluene, on the other hand, has a methyl group that acts as an electron donating substituent and increases the likelihood for EAS.

The general scheme shown in Figure 13 is consistent with the data outlined in the time series (Figures 11 and 12). In both cases benzyl alcohol concentration appears to reach a maximum early in the experiments and decreases as benzaldehyde and EAS products form. Benzoic acid is produced slowly and only appears as benzaldehyde has higher concentrations. As shown in Figure 11, benzaldehyde concentration decreases as benzoic acid concentration increases. This is consistent with benzaldehyde being an intermediate in the production of benzoic acid.

### *Toluene Oxidation in Natural Systems*

In the laboratory, toluene oxidation is typically accomplished using  $O_2$ , peroxides, or radical halogenation (Anderson et al., 1953; Barnard & Ibberson, 1965; Tanermura et

al., 2003; Guo et al 2005; Kesavan et al. 2011; Silva et al., 2017). Metals such as chromate and permanganate can also be used to oxidize toluene (Cullis & Ladbury, 1955; Necsoiu et al., 1963) but these oxidants are not found in environmental systems where natural organic transformations take place. The oxidants prepared for these applications are not stable in natural systems and are not available to carry out these transformations outside of the laboratory. Copper, however, is present in natural waters and available to oxidize organics such as toluene.

Prior to these experiments the oxidation of toluene in natural hydrothermal systems was not well established. Hydrothermal experiments with toluene alone and toluene with minerals yielded no measurable benzyl alcohol or benzaldehyde (McCollom et al., 2001; Shipp et al., 2013) while they are major products in experiments with dissolved  $\text{CuCl}_2$ . Even in a natural hydrothermal system where copper species do not control the redox state of the system, the copper-mediated pathway shown in these experiments may be present. The presence of aqueous copper ions allows for mechanisms that are not possible in water alone. These pathways expand the knowledge of possible fates of toluene in natural systems.

The high concentrations of copper in the experiments reported here are not likely in natural systems but the mechanisms may still be possible at lower concentration if there is a sufficient thermodynamic drive. Copper deposits are known to be associated with organic-rich rocks in sedimentary basins (Wang et al., 2006; Ho & Mauk, 1996). It is plausible that the reduction of copper by organic matter over geologic time proceeds through mechanisms similar to those described here. It is also worth noting that many of the oxidation products of toluene have oxygen bearing functional groups and some are

capable of hydrogen bonding. This greatly increases the solubility of the organic compounds and makes them more likely to partition from organic phases into the aqueous phases. These experiments help to constrain the possible reaction pathways that lead to oxidized organics observed in hydrothermal fluid samples.

## **Conclusions**

Many of the experiments to assess organic reactivity in hydrothermal systems are conducted in pure water. The experiments described here show that Earth-abundant inorganic compounds can be responsible for mechanisms that do not occur in water alone. Though these experiments were specific to copper, it would be useful to explore this reaction with other Earth-abundant metals. In these experiments, a common, seemingly unreactive compound like toluene can undergo redox transformations when oxidized copper is present in solution. The reactions outlined in these experiments highlight the need to include inorganic components in hydrothermal experiments to fully characterize natural system organic transformations. Gaining an understanding of the interactions of organic compounds and aqueous inorganic species at high temperature is a step towards fully characterizing the processes occurring in natural hydrothermal systems.



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## 5. AROMATIC DEHALOGENATION

### **Abstract**

Aryl halides are known to be hazardous to humans and the environment. This experimental study outlines a copper-mediated process for removing the halogen and replacing it with a hydrogen or a hydroxyl group. Aryl halides react under hydrothermal conditions to produce an alcohol or a hydrocarbon. These transformations are the result of reduction and substitution reactions. Metallic copper increases overall conversion and acts as a reductant. Pathways for the major products are proposed.

### **Introduction**

Halogenated aromatic organic compounds include polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and many pesticides that are known to be hazardous to human health and to the environment (Nicholson & Landrigan, 1994; Van de Plassche & Schwegler, 2002). Many of these compounds contaminate soils and sediments; they are persistent organic pollutants that bioaccumulate (Gomes et al. 2013). Halogenated aromatic compounds have been shown to accumulate in fauna of the deepest ocean trenches (Jamieson et al., 2017). The hazardous nature of halogenated organic compounds has led to extensive study of their remediation including biological methods (Abramowicz, 1995; Aken & Schnoor, 2010; Sudharshan et al., 2012), high temperature incineration (Hutzinger et al., 1985; Diot & Young 1991), and chemical oxidation and reduction (Rahuman et al., 2000; Alonso et al., 2002).

While incineration is the most common form of disposal, there are merits to recycling halogenated aromatics rather than combusting them. These hazardous materials

can be repurposed and turned into less harmful chemicals. Reductive processes are often explored because they have the potential to return halogenated compounds back into simple hydrocarbons that can be repurposed (Alonso et al., 2002). Additionally, nucleophilic aromatic substitution has been studied for its potential to replace halogen functional groups with hydroxyl groups in order to make the compounds more easily extractable (Brunelle et al., 1985). The experiments performed here demonstrate the effect of metallic copper on the reactivity of halogenated aromatic compounds in hydrothermal solutions. The products show a reductive pathway and a substitution pathway mediated by copper.

The experiments reported here represent geomimetic pathways in hydrothermal chemistry. Both of the pathways described here are named reactions, but these reactions are seldom carried out with water as the solvent. These experiments demonstrate an Ullmann reaction in which the aryl halogen undergoes a copper mediated substitution. Additionally, I observe a reductive mechanism in which halogenated aromatics undergo a Birch-type reduction to yield a simple hydrocarbon. The processes outlined here represent useful pathways in hydrothermal chemistry with potential applications to the recycling and management of halogenated aromatic compounds.

## **Results**

Two sets of experiments are presented in this chapter. All experiments were conducted at 250 °C with >20 μm copper powder. In the first set of experiments, 8 μL of chlorobenzene, a concentration of 0.26 m, reacted with copper in 300 μL of water with variable amounts of copper to show the relationship between copper and overall conversion. In the second set of experiments, 5 μL of chlorobenzene, chlorotoluene, and

chloronaphthalene were used with 300  $\mu$ L water and 0.07 g of copper. The initial organic concentrations were 0.16m, 0.14m, and 0.12m for chlorobenzene, chlorotoluene, and chloronaphthalene respectively. These compounds were chosen to see the effects of different functional groups while only using a single chloride group to limit the number of products.

**Table 4:** Reaction parameters and results of hydrothermal experiments reported in this study.

Time (hr)	Cu Powder (g)	Initial Cl-Benzene ( $\mu$ L)	Cl-Benzene (mol %)	Benzene (mol %)	Phenol (mol %)	Mass Balance (%)
42	0	5.0	99.1	nd	0.9	96
42	0	5.0	98.9	nd	1.1	99
42	0.07	5.0	42.1	4.9	53.0	77
42	0.07	5.0	33.7	3.4	62.9	85
47	0.08	8.0	16.4	5.3	78.3	76
47	0.04	8.0	57.1	2.6	40.3	96
47	0.02	8.0	72.8	2.9	24.3	92
47	0.01	8.0	91.1	0.4	8.4	97

Time (hr)	Cu Powder (g)	Initial Cl-Toluene ( $\mu$ L)	Cl-Toluene (mol %)	Toluene (mol %)	Cresol (mol %)	Mass Balance (%)
42	0	5.0	99.2	nd	0.8	97
42	0	5.0	99.2	nd	0.8	99
42	0.07	5.0	68.9	2.4	28.7	72
42	0.07	5.0	47.1	3.5	49.4	69

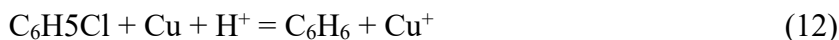
  

Time (hr)	Cu Powder (g)	Initial Cl-Naphthalene ( $\mu$ L)	Cl-Naphthalene (mol %)	Naphthalene (mol %)	Naphthol (mol %)	Mass Balance (%)
42	0	5.0	99.1	nd	0.9	98
42	0	5.0	99.1	nd	0.9	98
42	0.07	5.0	64.4	11.7	23.9	71
42	0.07	5.0	72.4	10.5	17.1	79

There are two predominant products when chlorobenzene is subject to hydrothermal conditions in the presence of copper, as shown in Table 4 and Figure 14. The main product is phenol which is the result of a substitution. There is no oxidation or reduction in the substitution pathway and copper is not consumed in the reaction. The reaction is summarized for chlorobenzene:



The other main product is benzene. The presence of benzene in these experiments must be the result of chlorobenzene reduction, meaning that copper is acting as a reductant. This reaction is:

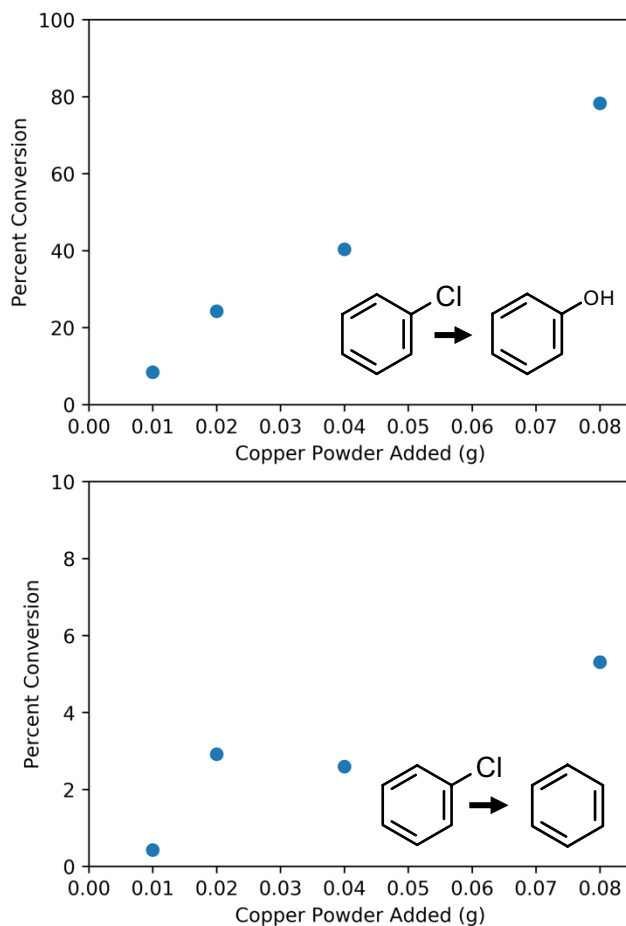
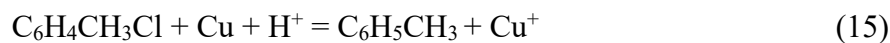


The amount of copper added to the experiments influences the conversion to phenol and benzene, as shown in Figure 14, which compares the amount of copper added and the percent of chlorobenzene converted over 47 hours. In these experiments, conversion is over 80% in experiments containing 0.08 g of copper powder, while experiments with 0.01 g of copper exhibit conversions of around 10%.

Chlorotoluene and chloronaphthalene were also dehalogenated in similar experiments shown in Figure 15. In all cases the chlorinated aromatic compound reacted to form the alcohol that resulted from a substitution of the halogen group with a hydroxyl group. The corresponding reactions are given by:



Additionally, these experiments produced hydrocarbons that resulted from the reductive substitution of the chlorine with hydrogen given by:

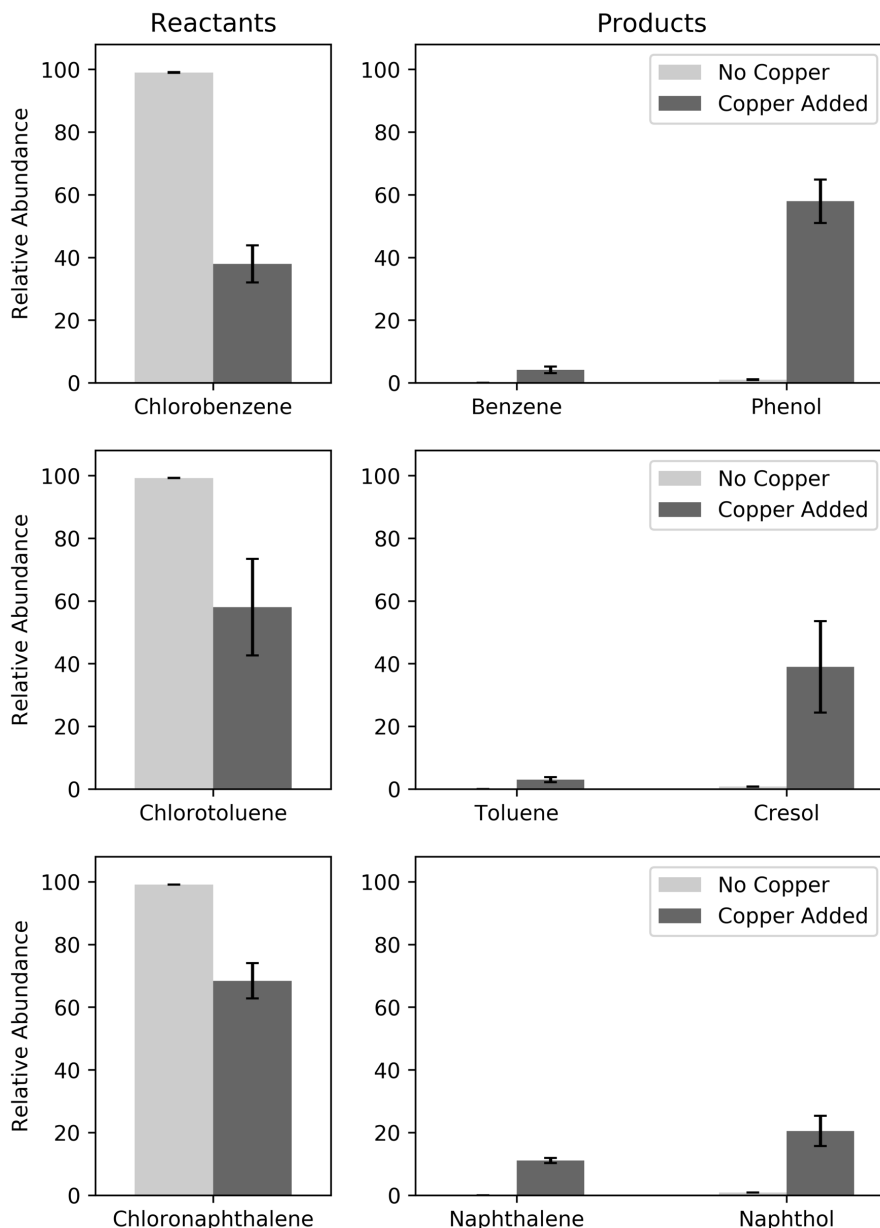


**Figure 14:** Percent conversion of chlorobenzene to phenol (top) and benzene (bottom) over 47 hours under hydrothermal conditions using an initial volume of 8  $\mu\text{L}$  chlorobenzene and the indicated amounts of copper powder.

The results of a functional group comparison are shown in figure 15. Multiple halogenated aromatic compounds were reacted in order to determine the influence of addition functional groups on the ring. In all cases, there was greater conversion to dehalogenated products when copper was added to the experiments. When no copper was present the reaction was slow and more than 98% of the aryl halide remained in solution



after the experiment. When copper was added to the solution there was more than 10x higher conversion to the dehalogenated products. The alcohol to hydrocarbon ratio is highest in the chlorobenzene experiments and lowest in the chloronaphthalene experiments.

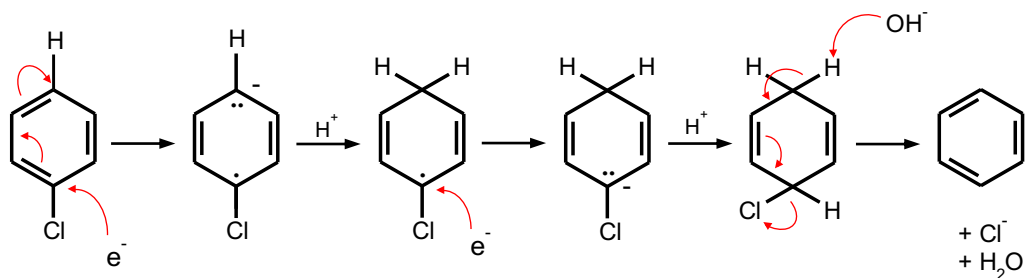


**Figure 15:** Relative abundance of organic compounds after 42 hours at 250°C with an initial chlorobenzene volume of 5  $\mu$ L. Experiments were performed in duplicate, with and without 0.07 g copper. The values on the graph represent the mean of duplicates and the error bars are one standard deviation.

## Discussion

### *Reduction Reaction Pathway*

To produce the hydrocarbons observed in these experiments, chlorobenzene must be reduced by copper since copper is the only reductant present in the system. The proposed reduction mechanism is carried out through a series of single-electron transfers. Copper species are known to readily participate in these redox reactions (Zhang et al., 2012). The reaction is similar to the Birch reaction mechanism in which benzene and halogenated benzene derivatives are reduced (Birch et al., 1980). The purpose of the Birch reaction is to partially oxidize aromatic compounds to form dienes; it is typically carried out in liquid ammonia with metallic sodium or lithium (Birch, 1944). The general mechanism is extended to hydrothermal conditions in Figure 16 to explain the production of hydrocarbons from the reduction of aryl halides.



**Figure 16:** The proposed mechanism for the reduction of an aromatic halogen. The pathway is the same for all organic compounds in this study. The mechanism is similar to the well-characterized Birch reduction.

The proposed mechanism can be generalized to all of the aryl halides reported here. The reaction begins with a single electron transfer from the copper metal to the aromatic system. This extra electron causes the aromatic system to be disrupted and a pair of

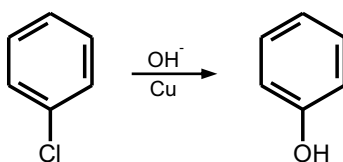
electrons shifts to a single carbon producing a radical anion. The radical anion bonds with a proton in solution, leaving a diene radical. The molecule gains another single electron from the copper and becomes an anion with a lone pair of electrons. At this point, the anion bonds with another proton and forms a halogenated cyclohexadiene. This would typically be the stopping point of a Birch reduction under traditional conditions as the goal of Birch reductions are dienes. However, halides on  $Sp^3$  carbons are increasingly reactive at higher temperatures in aqueous solutions (Mabey & Mill, 1978). The chloride acts as a leaving group and the compound becomes a diene cation. Diene cations are known to deprotonate and transfer electrons that formerly made up the C-H bond into the pi bond system to restore aromaticity (Olah, 1971). This results in the dehalogenation of the original compound, effectively replacing the halogen with a hydrogen.

### *Substitution Reaction Pathway*

The path from chlorobenzene to phenol, shown in Figure 17, is a simple substitution reaction in which a halogen group is replaced by a hydroxyl group. This substitution is well known; in fact, one of the primary means of phenol synthesis before the widespread use of the cumene method was base-catalyzed hydrolysis of chlorobenzene (Richle, 1970). While this substitution proceeded in all experiments, the most notable aspect of these experiments is the influence of the copper on the overall conversion. The effect of copper on this type of reaction makes it similar to Ullmann-type reactions.

Ullmann-type reactions are copper-mediated aromatic substitutions in which an aryl halide is substituted with another nucleophile. The Ullmann reaction was first described in 1903 and is still not well understood. There are four classes of mechanisms

proposed in the literature. These mechanisms include Cu(I) complexes that increase the electrophilicity of the aromatic system, single-electron-transfer mechanisms, mechanisms assuming that copper-halogen complexes make the halogen a better leaving group, and finally mechanisms involving oxidative-reductive cycles with Cu(III) intermediates (Sambiagio et al., 2014).



**Figure 17:** Pathway for the substitution of a halogen with a hydroxyl group. This pathway is generally referred to as an Ullmann reaction.

The form of copper in the Ullmann reaction is not as simple as the metallic powder that is added to the experiments. In Ullmann-type reactions using, the catalyst was found to have a layer of Cu<sub>2</sub>O surrounding the metal (Paine, 1987). It is possible that the experiments reported here contain copper at a variety of oxidation states, although no measurements were conducted to test this hypothesis. The oxidation of copper is possible through the reduction of organic compounds. The pathway that describes the halide reduction in Figure 16 presents a mechanism that produces Cu(I). Reduced organic products are observed in these experiments and it is likely that there is a coupled redox reaction between copper and aqueous organic compounds. Because there may be many forms of copper in the experiments, the form of copper that exhibits catalytic behavior is inconclusive. Given the ambiguity surrounding the Ullmann reaction mechanism and the uncertainty associated with these experiments, the absolute mechanism through which

copper mediates these transformations is beyond the scope of this experimental investigation. The notable finding of this study is that under hydrothermal conditions halogenated aromatic compounds undergo Ullmann-type reactions where water acts as the nucleophile.

### *Functional Group Comparison*

Overall conversion is highest for chlorobenzene, lowest for chloronaphthalene, and chlorotoluene conversion is intermediate. Although, there are slight differences in starting concentration of the organic compounds that likely influence overall reaction rates. The trend of conversion can be anticipated from a comparison of Hammett constants that denote the extent of electron-donating effects for each substituent group. Hammett constants are ordered; naphthyl > methyl > H (Hansch & Taft, 1991). The differences in the conversion among these three chlorinated aromatic compounds is consistent with the notion that substituents with higher electron-donating potential decrease the relative rate of substitution (Bunnet et al., 1957). This suggests, as expected, substituents on the benzene ring have an influence on the overall conversion for the substitution reaction. This is useful in developing expectations for aryl halides that are untested in this reaction. The hydrocarbon to alcohol ratio also follows the trend naphthyl > methyl > H. This suggests that the substituents also affect the reductive pathway.

### *Applications*

The dehalogenation of chlorinated aromatics is widely studied in the field of environmental science. Both hydrolysis and reduction pathways are the subject of

extensive study (Gomes et al., 2013). Since the alcohols are the major products of dehalogenation, aryl halide hydrolysis has the most applicability to remediation practices. Hydrolysis is a popular method for PCB remediation and has been implemented in U.S. superfund sites (Benoit et al., 1997). This technology is commonly carried out in the presence of a base-catalyst to promote the reaction and under an inert atmosphere such as N<sub>2</sub> to prevent dioxin formation (Taniguchi et al., 1998). My findings suggest that copper could be incorporated into these remediation technologies to promote the dehalogenation reaction. The dehalogenation-promoting potential of various metals has been noted previously (Kubátová et al., 2003). Remediation studies, however, generally focus more on overall PCB removal than on the underlying mechanism and products. The experiments presented here are centered around simple, single compounds to show the products of dehalogenation reactions and shed light on the mechanism.

## **Conclusion**

The reaction conditions explored in this study have practical value in the dehalogenation of aryl halides. The knowledge that copper promotes dehalogenation can be implemented in the field of remediation to increase the efficacy of PCB-hydrolysis and reductive dehalogenation. The products of my experiments suggest the main pathway for dehalogenation is through copper-mediated hydrolysis to form alcohols via an Ullmann-type reaction. Ullmann reactions are typically not carried out in water because hydroxide is often not the desired nucleophile in laboratory organic synthesis. Since there is a wealth of knowledge on the details of the Ullmann reaction, an understanding that this dehalogenation is similar to an Ullmann reaction will be instrumental in implementing

copper in existing technologies. Similarly, I propose that the reductive pathway is similar to a well-known reaction. This reduction vastly expands the conditions of the Birch reduction. At hydrothermal conditions this reduction can be carried out with a traditionally weak reductant such as copper instead of explosive sodium metal. The desired diene products of Birch reductions are not stable under hydrothermal conditions; this allows the reaction to continue to the alcohol and expands our general understanding of the mechanisms of metal-organic interactions at hydrothermal conditions.

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## 6. CONCLUDING REMARKS

The reactions characterized in this thesis represent new pathways for organic reactions at hydrothermal conditions. The experiments here have direct applications to the understanding of natural systems. Chapter 4 focuses on the oxidation of toluene by copper in natural systems but the relevance to natural systems extends to the oxidation of benzene. These transformations are not previously demonstrated in experimental studies. The experiments use 1 molal concentrations of copper salts which is far greater than the amount of aqueous copper found in hydrothermal systems. This is not inherently problematic for understanding natural systems, however. Even at lower concentrations, the reactions may still be favorable in natural systems, but the kinetics will likely be much slower. Organic compounds in natural systems react over geological timescales in contrast to the hours to days in the laboratory, so even at lower metal and organic concentrations, these mechanisms will likely have an effect on the organic reservoirs. These mechanisms account for pathways to phenol, chlorobenzene, benzaldehyde, benzyl alcohol, benzoic acid, and to multi-ring compounds which are all observed in natural systems influenced by hydrothermal processes (Kawka & Simoneit, 1990; Tassi et al., 2012). Oxidation with Cu(II) is only a starting point for characterizing metal-organic redox reactions. Future work should focus on characterizing organic reactions with different geochemically relevant metals. Similar oxidations have also been carried out with Fe(III) salts in preliminary experiments. The pathways observed deepen our understanding of organic reactions in organic carbon reservoirs.

The reactions described in Chapter 5 outlining the dehalogenation of aromatic compounds with copper are less likely to occur in natural systems. Native copper is known to exist in organic rich sediments (Cornwall, 1956) and the experiments in Chapter 3 show that organic compounds are capable of reducing copper to its metallic state. However, native copper is far less abundant than copper in the +2 state and halogenated organic compound have only trace concentrations in natural systems. This makes the Birch-type reduction pathway of chlorobenzene less relevant in these environments. The Ullman reaction, on the other hand, can proceed with copper in the more oxidized +1 state. It is plausible that this form of copper could mediate nucleophilic aromatic substitutions in natural systems and lead to different functional groups on aromatic rings.

These experimental results highlight the importance of inorganic speciation on metal-organic reactions. It is notable that the different copper salts lead to different organic products and different overall conversions. In natural systems the inorganic fluid composition will certainly play a role in the oxidation of benzene and toluene, among other organic compounds. A study that outlines the relationship between organic products and the inorganic fluid composition would be advantageous in future work. There is substantial knowledge of fluid compositions for marine and terrestrial hydrothermal systems with diverse geochemical conditions. Experiments can be designed in conjunction with geochemical modeling that speciates metals accordingly. This could be used to better understand these oxidations outside of a laboratory setting and to better constrain which species are most active in metal-organic reactions. The experiments presented in this thesis were focused on organic transformations, but it would also be useful to fully characterize

the inorganic products in these experiments in future studies to conclusively determine the inorganic portion of these reactions.

In addition to the characterization of organic transformations in natural hydrothermal systems, using hydrothermal geochemistry to develop industrially useful processes was a central goal of these experiments. Producing phenol by oxidizing benzene with copper sulfate has the most potential for use in an applied setting. The conversion is relatively high, and the process is selective. These aspects make the hydrothermal processes an attractive alternative to the widely used cumene method. A potential drawback of using the process described here is the amount of copper it would take to implement on a large scale. Copper is an Earth-abundant metal but its recyclability for this process has not been investigated. However, copper is mainly mined in the +2 oxidation state through the leaching of ores (Wang, 2005). This creates a copper rich solution that must be electrochemically reduced usually through electrowinning to form the desired metallic copper. If the solution was instead used in a hydrothermal reaction with benzene, the product would be metallic copper and phenol, thus creating two more valuable products from two less valuable reactants. This process would require an evaluation of the economics and engineering before it could be implemented, but the production of copper metal and phenol from benzene and copper ions seems to be a promising application of hydrothermal geochemistry in an industrial setting.

Similarly, the hydrothermal reactions outlined in chapter 3 are alternatives to the oxidative chlorination of benzene with chlorine gas. The hydrothermal process does not have the hazards associated with chlorine gas. The reaction appears to be related to the speciation of copper in solution since the main form of copper in these reactions is aqueous

CuCl<sub>2</sub>. It is possible to speciate the copper to the desired form by adding a simple chloride salt like sodium chloride. This new process may also limit the polychlorinated products associated with free radical chlorination because none were observed in these experiments. Again, the viability of this oxidation as an industrial process is dependent on the ability to design a suitable reactor and the recyclability of the copper species.

The dehalogenation process outlined in chapter 5 has direct application to methods that are currently used in the remediation of hazardous compounds. Hydrolysis is already employed in the degradation of halogenated organic pollutants such as PCBs (Benoit et al., 1997). Copper improves the conversion of aryl halides to alcohols and provides a reductive pathway to hydrocarbons. In cases where hydrolysis is already being used, copper can be included in the reaction vessel as a catalyst to aid the dehalogenation. Since the chloride is substituted by water, it may also be useful to explore the effect of adding other nucleophiles to the solution. If effective nucleophiles are added, it is possible that halogen groups can be substituted by functional groups other than hydroxyls. The reductive pathway presents a method to transform aryl halides into potentially useful compounds. If there was an electrochemical way to keep copper in its reduced, metallic state, this could be a promising method for reductive dehalogenation. Electrochemistry at hydrothermal conditions is not yet explored, however. The experiments in Chapters 3 and 4 involve oxidation and Chapter 5 involve reduction. Future work should focus on combining oxidative and reductive reactions in a cyclical process so that as much material can be recycled as possible.

Lastly, benzyl alcohol and benzaldehyde are desirable products as chemical intermediates, but the low conversion and ample side products observed in Chapter 4 make this method less useful in the synthesis of benzyl alcohol and benzaldehyde. The

experiments in Chapter 4 were initially designed to produce cresols through the same oxidative mechanism described in Chapter 3. However, the results demonstrate that copper will oxidize the methyl group, rather than oxidizing the ring. Despite limited synthetic potential, the oxidation of toluene with copper informs our understanding of organic transformations in natural systems.

These experiments bring together the fields of geology and chemistry. Geological studies typically ignore the industrial applicability of Earth system processes and synthetic chemistry studies often use complicated or expensive processes. My results highlight the need to bring geochemistry outside of natural system research and the need to explore synthetic processes that use Earth-abundant materials. The pathways developed here provide alternatives and improvements to industrial processes and further the understanding of organic behavior in natural systems . Ideally the processes shown here could be extended to various metals and different speciation. This is one step towards a more complete understanding of organic transformations in hydrothermal solutions.

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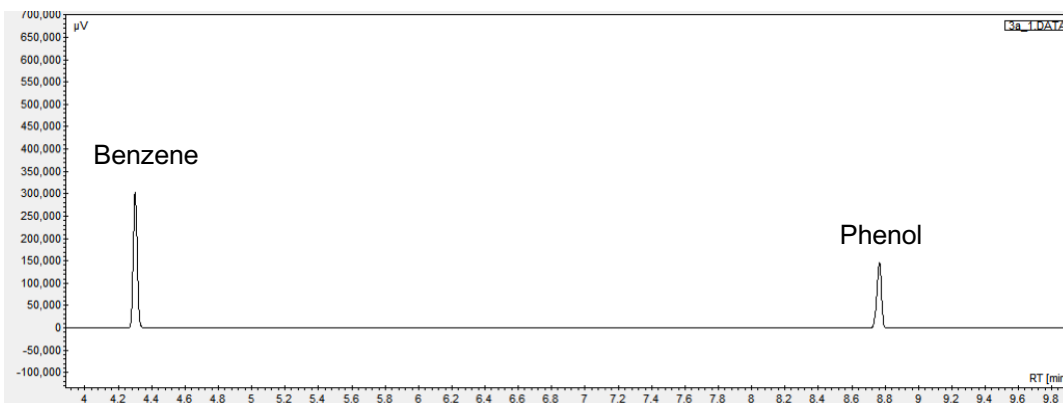
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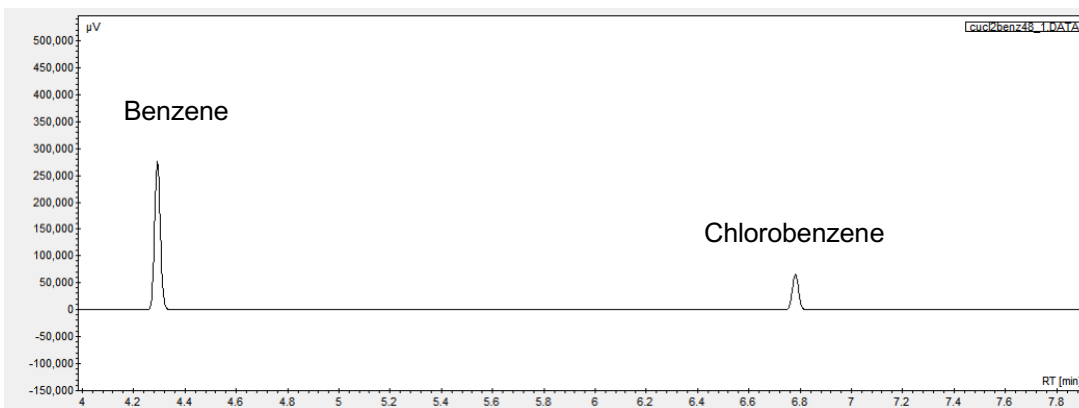
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APPENDIX A  
GAS CHROMATOGRAPHY

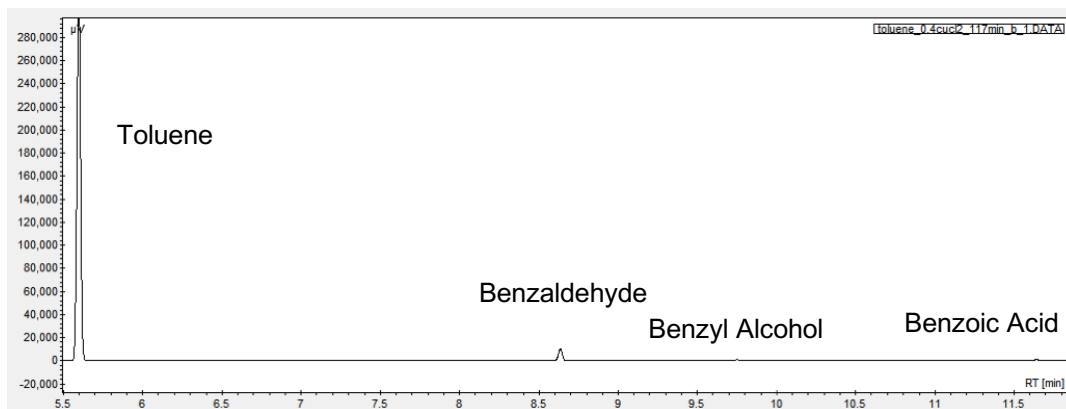
The following figures are chromatograms from experimental extractions. All products were identified using reference standards.



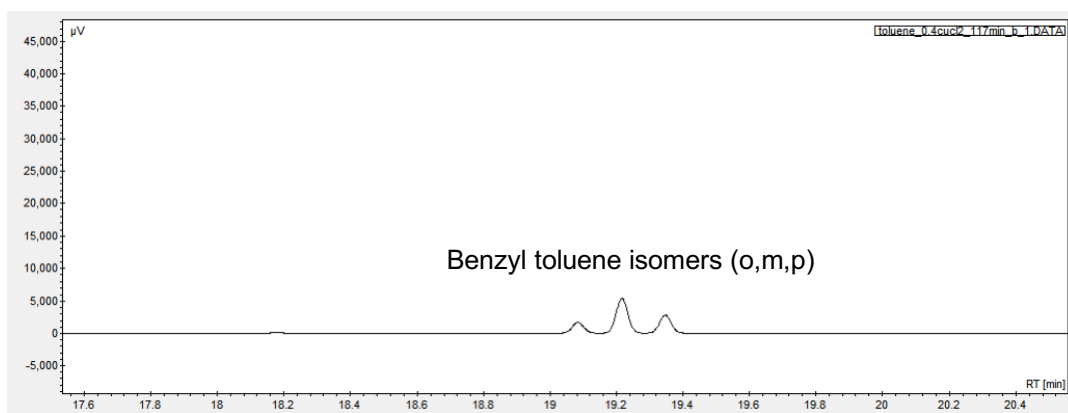
**Figure 18:** Chromatogram for experiment in which benzene was oxidized with  $\text{CuSO}_4$ . Peaks of the product and the reactant are shown.



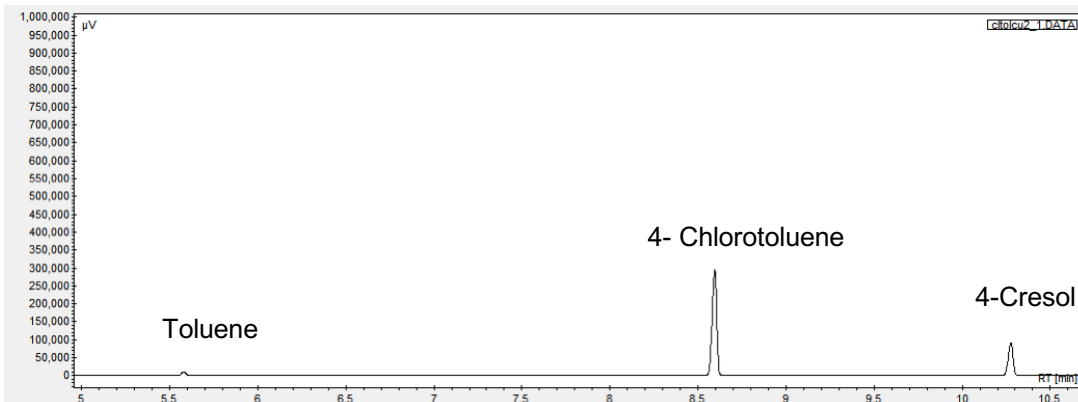
**Figure 19:** Chromatogram for experiment in which benzene was oxidized with  $\text{CuCl}_2$ . Peaks of the product and the reactant are shown.



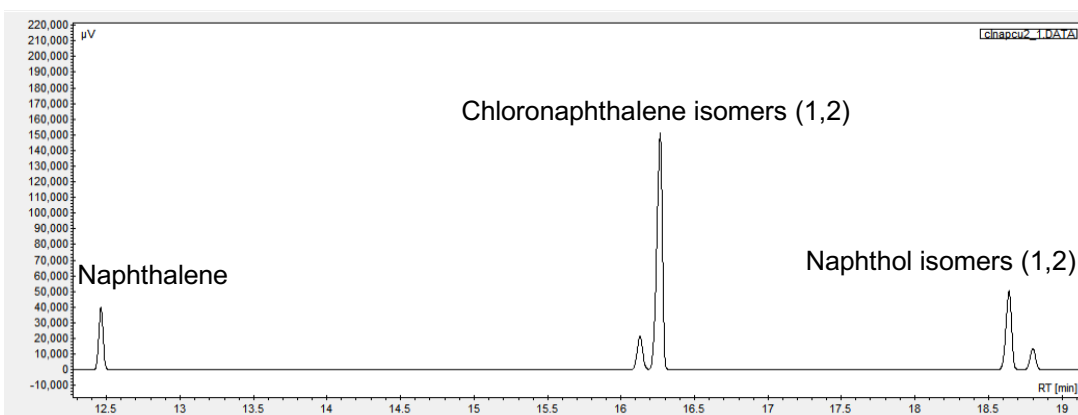
**Figure 20:** Chromatogram for experiment in which toluene was oxidized with  $\text{CuCl}_2$ . Peaks of the product and the reactants are shown.



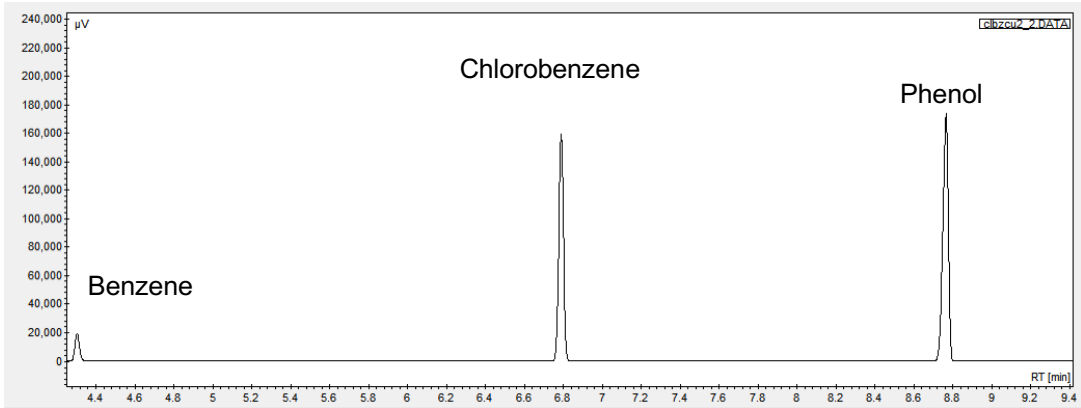
**Figure 21:** Chromatogram for experiment in which toluene was oxidized with  $\text{CuCl}_2$ . Peaks of the high molecular weight products are shown.



**Figure 22:** Chromatogram for dehalogenation of chlorotoluene. Peaks of the products and the reactant are shown.



**Figure 23:** Chromatogram for dehalogenation of chloronaphthalene. Peaks of the products and the reactant are shown.



**Figure 24:** Chromatogram for dehalogenation of chlorobenzene. Peaks of products and reactant are shown.