INVESTIGATION OF DIFFERENT ORGANIC FUNCTIONAL GROUPS TRANSFORMATIONS IN LABORATORY-SIMULATED HYDROTHERMAL SYSTEMS

by

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To my mother and father

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PREFACE

Organic transformation located at hydrothermal hosted area draw attention recent year due to its tight connection to origin of life in and beyond Earth. The presence of minerals and salts in real geological set-ups have been found effecting these processes with great potential. This dissertation firstly discussed the role of copper and iron salts on the pathway of alcohol hydrothermal conversions and found their oxidative role in anaerobic hydrothermal conditions. This second investigation on aldehydes hydrothermal oxidation also revealed good tolerance of ferric nitrate on functionalized compounds with different structures. In another 2 chapters, kinetical mechanisms of amines with different ring structures have been studied at elevated temperature and different pH conditions. The presence of minerals and dissolvable salts also exhibited their special work in hydrothermal deamination. Finally, findings from this dissertation highlights the importance of hydrothermal transformation on the exploration on prebiotic evolution on Earth and other solar system, offering our more insights into benign and green oxidation on industrial productions.

ABSTRACT

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The study of organic reactions within natural hydrothermal environments is significant for our understanding of the profound carbon and nitrogen cycles, the life dynamics of deep microbial populations, and possibly, life's origins. Numerous reaction routes that involve organic compounds under geochemically pertinent hydrothermal conditions have been identified. However, the underlying mechanisms of these reactions, particularly those associated with inorganic substances, remain largely unexplored. This research aims to demystify these mechanisms to enable the development of predictive reactivity models and the investigation of potential applications of these reactions beyond the field of geochemistry. The focus of this dissertation is the mechanisms of interconversion of alcohols, aldehydes, amines with and without the presence of metal ions. Dehydration is always the primary pathway for alcohols in the hydrothermal fluids. However, in the presence of copper(II) or iron(III) salts, the oxidation of alcohols is greatly promoted and becomes a competitive pathway to form aldehydes and carboxylic acids as the major products. Inspired by the role of iron ions, we reported the first

examples of oxidation of aldehydes with $Fe(NO_3)_3$ in water under anaerobic hydrothermal conditions in green and relatively clean way, with relatively high yields of carboxylic acids achieved within hours. A framework was investigated for selecting amines as geochemical tracers based on kinetic modeling. Even though the catalysis from minerals can be neglectable, the presence of metal ions altered the pathway by aerobic oxidation reaction. The geomimetic reactions discussed in this dissertation could potentially be employed in biomass oxidation to yield beneficial fuels and other high-value chemicals. Leveraging plentifully available metal ions and water as the solvent, these reactions offer a sustainable alternative to the existing biomass oxidation methods. The latter often involve the use of rare, exotic metal catalysts and organic solvents, presenting an environmental challenge. Thus, the exploration of these environmentally friendly reactions provides a greener approach to pollutants oxidation.

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CHAPTER ONE

INTRODUCTION

1.1 Overview

The research elaborated in this dissertation encompasses a blend of hydrothermally observed organic reactions, mechanistic organic studies, and exploration of the breadth of anaerobic oxidation with metal salts in solution under hydrothermal conditions. This project diverges from conventional organic chemistry research norms, as standard organic chemistry textbooks seldom address reactions occurring in high-temperature water; the majority of discussed reactions are typically confined to ambient temperature and pressure. Conventional organic chemistry reagents are typically toxic, hazardous, exotic, and absent from natural systems. Take thionyl chloride ($SOCl_2$), a standard organic chemistry reagent known for its toxicity and hazard, as an example. Its high reactivity and corrosiveness make it an excellent candidate for converting alcohols to alkyl chlorides. Nonetheless, its potential to cause severe burns and respiratory irritation mandates careful handling, a quality seldom found in natural environments.[1-2] Another example is mercury (II) acetate ($Hg(OAc)_2$), which is used in organic synthesis as an oxidizing agent. As it is well known, Mercury is a highly toxic heavy metal that can cause serious health problems such as kidney damage and neurological disorders but is not found in natural systems in significant quantities.[3] Furthermore, organic chemistry reactions have been conducted on the Earth for millions of years in natural geochemical processes and none of the traditional toxic reagents are used in the process. In particular, buried organic carbon in geological areas experiences high temperatures and pressures, a

variety of inorganic materials, and is surrounded by water, which all help to facilitate the natural transformation of carbon.

Over the last 30 years, more details have been revealed about these types of organic reactions that can happen in high temperature water and various schemes of pathways have been proposed.[4] The reaction pathways have been observed in natural hydrothermal systems, but the specific processes of different compounds are not clear and the effects from the surrounding inorganic material are still a mystery. These changes would not only alter the direction of natural organic transformation, but they promisingly could influence the primitive synthesis of peptides and prebiotic life. Another area of interest is how these reactions can be utilized and improved upon real industrial processes. Indeed, many pathways are possible, but increasing the kinetics and selectivity of these reactions is necessary for them to have any application in organic synthesis. In this project, both carbon and nitrogen transformations were investigated. To illustrate, mechanistic pathways of alcohols and aldehydes in the presence of metal ions under hydrothermal conditions have been addressed. Hydrothermal kinetics of decomposition of amines have been found and role of minerals and metal ions on such reactions were discussed in the perspective of greener oxidation methods.

1.2 Introduction to Hydrothermal Conditions

Rather than ambient conditions in surface areas which are at 25℃ and 1 atm, most of the organic reactions occurring on earth are happening in extreme environments which are in the deep ocean. 99.99% of Earth's abiotic organic carbon is buried under ground, undergoing processes and transformations that are not fully understood.[5-6] The reaction conditions encountered there are significantly different than those in the typical

laboratory - high temperatures and pressures, in the presence of water rather than an organic solvent, and occasionally with extremes in pH and salinity.[7-9] Hydrothermal systems are one of such reservoirs on earth containing organic reactions, where the temperatures range between 200-400 ℃ and the pressure ranges from 2-100 MPa.[8-9] In such areas, the water under high temperatures and pressures would play a much different role from what we observe at ambient conditions, where a multitude of organic reaction pathways become favorable.

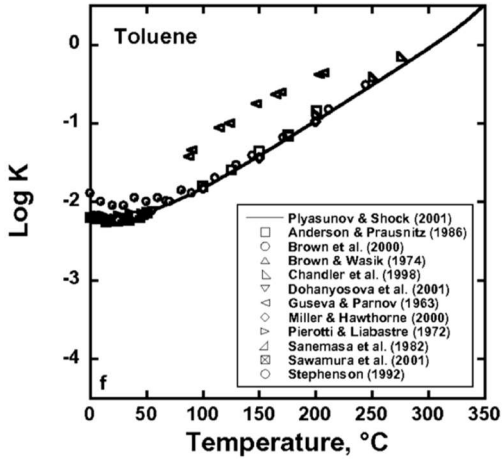


Figure 1. Log K of solubility of toluene in water with increasing temperature. The curve is an adaptation of theoretical thermodynamic calculations made by Plyasunov et al.[6] A review by Shock et al compiled experimental data from various sources, all of which agree strongly with the curve.[13]

Hydrothermal water's behavior differs from liquid water at ambient conditions. With the increasing activity of hydronium ions and decreasing dielectric constant, non-polar compounds are able to dissolve more easily in the water.[10-11] For example, the solubility of toluene in water increases more than an order of magnitude from 25-300°C, which is supported by both experimental and theoretical data (Figure 1).[10,12] At 250°C,

water has a dielectric constant that is comparable to organic reagents like acetone, and a pH of 5.6 (Figure 2).[12] Heating water in a closed system will increase the water vapor saturation pressure (Figure 3), so the evaporation of water could be controlled by high pressure even under high temperature. In this case, water can work as a tunable solvent.[13]

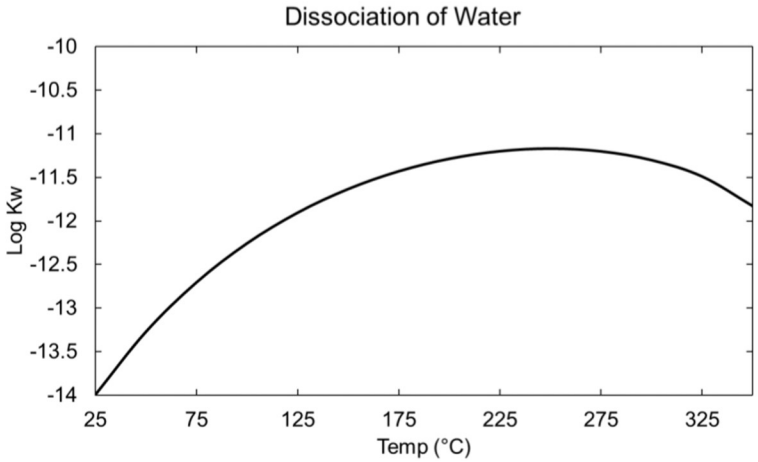


Figure 2. The water autoionization constant, Kw, as a function of temperature. These values were calculated using the revised Helgeson-Kirkham-Flowers (HKF) equation of state, using data and parameters from Shock and Helgeson. [12]

Numerous properties of water can be regulated by varying the temperature and pressure. Even though the density of water increases with increasing pressure and decreasing temperature, the viscosity of water also increases with increasing pressure and temperature, which can affect the transport of solutes and the rates of chemical reactions.[14] The dielectric constant of water decreases under hydrothermal conditions, which can affect the solubility of polar and ionic solutes.[15] The hydrogen-bonding network of water is weakened under hydrothermal conditions, resulting with moderately strong acids like HCl becoming weaker[16]. With increased solubility of organic molecules,

a lower pH, higher pressure, and inherently high thermal energy, many organic synthesis applications occur in hydrothermal water.[12]

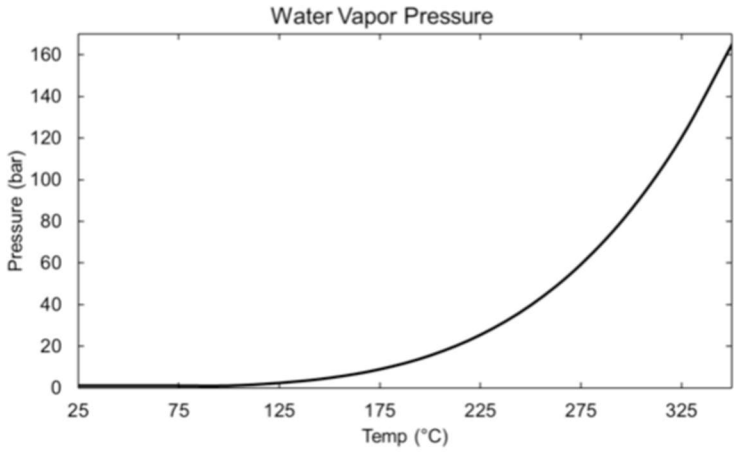


Figure 3. Water vapor saturation pressure as a function of temperature.[13]

Ions in dissociated forms become less favorable in hydrothermal water due to the weakened hydrogen-bonding by water, but the associated, neutral, forms of ionic compounds become the more stable species (Figure 4). For example, bicarbonate (HCO^{3-}) is favored over carbonate (CO_3^{2-}) due to the reduced solubility of CO_3^{2-} in hydrothermal fluids.[17] This results in the precipitation of calcium carbonate ($CaCO_3$) minerals in hydrothermal systems, rather than the dissociated forms of the bicarbonate and calcium ions. In hydrothermal fluids, chloride (Cl^-) can occur in a variety of forms, including free chloride ions and complexed species such as chlorides of metals like iron, copper, and zinc.[18] The relative abundance of these species depends on factors such as temperature, pressure, and pH. Thus, it is essential to consider the speciation of dissolved ionic compounds in hydrothermal water, as it can often be complex.[19]

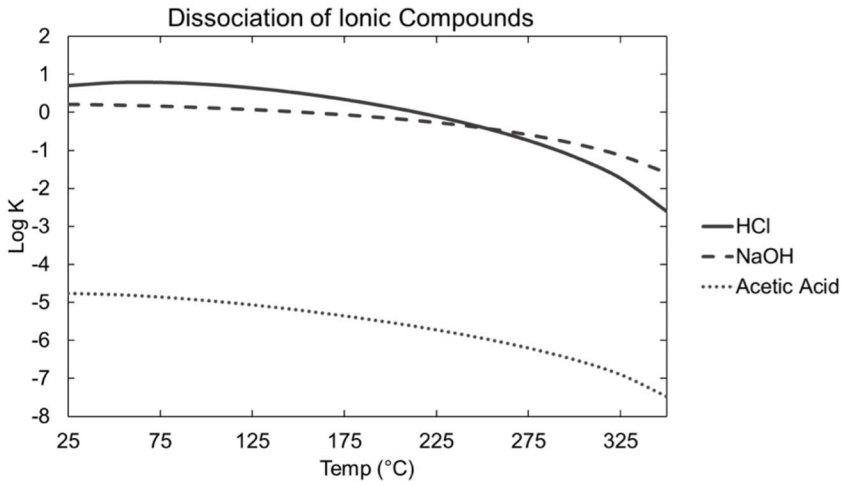
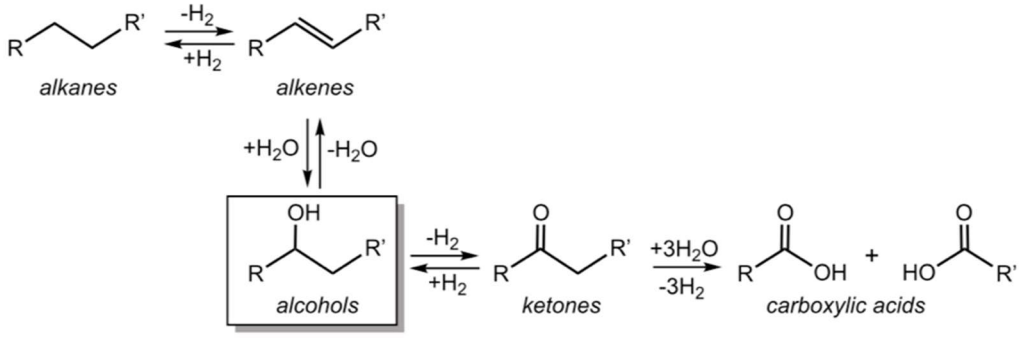


Figure 4. The temperature dependence log K values for the dissociation of hydrochloric acid, sodium hydroxide, and acetic acid in water, obtained using HKF.[13, 16, 17] This resulted in a tendency for ionic species to remain associated at higher temperatures. Strong acids become weak, and weak acids become weaker.

1.3 Hydrothermal Organic Geochemistry

Hydrothermal conditions are created in a variety of geological locations, including volcanic zones, terrestrial sedimentary basins, and mid-ocean ridges beneath the seafloor. These conditions are often found around black smoker hydrothermal vents. As previously mentioned, these systems are characterized by high temperatures and pressures. For instance, the Guayamas Basin, a mid-ocean ridge located in the Gulf of California, demonstrates this with temperatures ranging from 350 to 400°C and pressures from 200 to 300 bar.[20] The temperature of Juan de Fuca Ridge located at Lost City is in the range of 2-385°C.[21] Organic materials can be introduced into these systems and subsequently undergo transformations. It's projected that at least once every 10 million years, the entirety of the ocean's volume is processed through hydrothermal vents. This extensive

cycling highlights the significant potential for organic matter transformation under hydrothermal conditions.[22] The organic compounds that emerge from hydrothermal vents can provide energy and nutrients for microbial communities at the sea floor.[23] In addition to the direct influence of hydrothermal systems on organic matter cycling, there are also indirect effects related to the alteration of oceanic crust and the formation of mineral deposits. Hydrothermal systems can alter the chemistry of the surrounding rock, releasing nutrients and trace elements into the ocean that can support the growth of phytoplankton and other organisms. The formation of mineral deposits can also sequester carbon and other elements from the ocean, potentially affecting global biogeochemical cycles.[24] Organic compounds commonly found in hydrothermal systems include hydrocarbons from reduced carbon, such as methane and ethane, as well as oxidized carbon in the form of carboxylic acids, alcohols, and aldehydes. These compounds can be generated by a variety of processes, including abiotic reactions between carbon dioxide and hydrogen, as well as by microbial activity.[25]



Scheme 1. The organic reaction pathway of alkanes to acids in hydrothermal conditions. This model was first proposed by Seewald. [4]

Instead of considering microbial transformation processes, an abiotic redox pathway from alkanes to carboxylic acids has been proposed by Seewald and experimentally observed for organic transformations in hydrothermal systems. In this process, oxidation and reduction occur reversibly between alkenes and alkanes; alkenes are hydrated to alcohols, and alcohols are dehydrated to alkenes; alcohols are oxidized to ketones, and ketones are reduced to alcohols; Some oxidation pathways result in carboxylic acids, that can undergo decarboxylation to alkanes (Scheme 1).[4] These essential organic chemistry reactions, which are regularly featured in organic chemistry textbooks, have been conducted and characterized through laboratory experiments for more than a hundred years. This solidifies their fundamental role in the field of organic chemistry. However, the hydrothermal pathways of these functional groups are still much less understood. For example, reagents like $KMnO_4$ (potassium permanganate), CrO_3 (chromium trioxide), HIO_4 (periodic acid) and NBS (N-bromosuccinimide) are used to oxidize alkanes to alkenes in industry, considering these reagents are strong oxidizing agents.[26-27] Strong acids such as concentrated sulfuric acid have classically been used to dehydrate an alcohol,[28] and oxymercuration-demercuration, which uses mercury to hydrate an alkene.[29] To oxidize alcohols to ketones, Jones reagent is commonly used to oxidize primary and secondary alcohols to their corresponding ketones and aldehydes, respectively.[30] PCC and Dess-Martin periodinane are milder reagents that are commonly used for the oxidation of primary alcohols to ketones.[31] The Swern oxidation is a two-step process that involves the conversion of the alcohol to an intermediate sulfonium ion, which is then oxidized to the ketone by a strong base.[32] Hazardous metals such as chromium(VI) are also commonly used to oxidize alcohols to ketones and carboxylic acids.[33]

Nevertheless, these typical organic chemistry reagents and catalysts are applied in lab and are obviously not used by the Earth in these reactions. In simpler terms, the Earth does not utilize these harsh, toxic, and costly reagents. Almost all the reactions depicted in Figure 5 have been experimentally shown to happen reversibly, solely in high-temperature water, demonstrating nature's efficiency and inherent environmental respect.[34-35]

Nonetheless, our understanding of hydrothermal organic reactions remains incomplete. Although some pathways have been partially identified, most of the mechanisms remain a mystery. The notion that life may have originated in hydrothermal systems has been proposed, further underscoring the importance of expanding our knowledge in this area.[36-37] Gaining a deeper understanding of these mechanisms can aid in forecasting the behavior and fate of organic molecules within specific hydrothermal systems. This knowledge can be instrumental in further exploring the interactions and transformations of organic compounds in these environments. Additionally we can recognize how organic matter formed and interconverted, ultimately forming prehistoric organisms. In contrast to the reducing conditions found in serpentinizing systems—which experiments have demonstrated to stabilize biologically derived compounds—oxidizing environments cause the breakdown of organic compounds. This process results in the production of simpler products, highlighting the diverse impact of different hydrothermal conditions on the transformation of organic matter.[38-39] The available thermal energy may have also allowed critical organic transformations to occur under hydrothermal temperatures.[40] Although some argue that organic molecules are simply degraded into simpler structures under hydrothermal conditions, thereby making a hydrothermal origin

of life implausible, mounting evidence suggests otherwise. This ongoing debate highlights the need for further research into the complex transformations of organic compounds under hydrothermal conditions and their potential implications for the origins of life. Our previous research suggested the amides can be synthesized from amines in pure-water hydrothermal conditions, meaning there is potential to subsequently produce peptides and proteins.[41] Experimental characterizations have identified processes such as radical couplings and electrophilic aromatic substitution reactions that lead to the formation of multi-ring structures. This demonstrates the diverse range of reactions and potential complex compounds that can be generated under these conditions.[42-43] Research has also shown that minerals can act as catalysts, promoting the transformation of smaller, simpler organic structures into larger and more complex ones. This emphasizes the critical role of minerals in the complex processes of organic synthesis under hydrothermal conditions.[44-45] Understanding the mechanisms of organic reactions in these systems can provide constraints on system behavior, and potentially offer insights into the range of chemical reactions that may have been possible, as well as their implications during life's evolution on prebiotic Earth. This knowledge can provide invaluable context for our understanding of life's origin and early development.

The dehydration of alcohols in a pure water environment and the oxidation of alcohols, aldehydes and amines in the presence of minerals and dissolved metal ions were investigated here. While mechanistic studies of dehydration of alcohols and amines have been already released in pure water hydrothermal systems,[46-47] there are few reports on how minerals or surrounding ions influence these processes. The oxidation of alcohols is hard to occur during hydrothermal reactions due to the lack of oxidizing power. The

dehydration and oxidation of primary alcohols, like 2-phenylethanol we used as model compound, is unfavorable at the hydrothermal condition of 200℃ for 2h reaction. However, the addition of copper(II) and iron(III) ions significantly alter the dominant reaction to oxidation in the same hydrothermal condition as the pure-water experiments, then the serial oxidation from alcohols to aldehydes and carboxylic acids was observed. With optimized metal ions-oxidation method, different structure of aldehydes can be oxidized in anaerobic water environment efficiently. In this reaction, water served as both catalyst and solvent, it on one hand chelated with the subsistent ions resulting to the oxidants, on the other hand provides the acid-base catalysis improve both dehydration and oxidation. The point deserving attention is that there is rarely dissolved air abundant in deep-ocean floor, and the presence of ions can proceed the oxidation without oxygen. In this case, investigating the mechanism that metal ions on the anaerobic oxidation not would only help us realize the oxidation method in oxygen-absent water environments, and it is also able to offer plausible optimized approach for specific application.

1.4 Role of Minerals and Dissolvable Salts in Hydrothermal System

Geochemical processes involving organic compounds occur not only in an aqueous medium but also in environments rich with gases, electrolytes, variable pH levels, and critically, inorganic substances such as minerals, clay substrates, and ions dissolved from these solids. These diverse conditions contribute to the complexity of the reactions and the potential for a wide array of organic transformations. For example, iron ions can be released from minerals such as pyrite (FeS_2) and magnetite (Fe_3O_4) during hydrothermal alteration.[48] Copper (Cu^{2+}), Zinc (Zn^{2+}), and Lead (Pb^{2+}) ions can be released from sulfide minerals like chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS) in

hydrothermal ore deposits.[49] The exploration of hydrothermal organic-mineral interactions and mineral-driven organic reactivity could hold significant interest across numerous scientific disciplines such as geochemistry, mineralogy, organic catalysis, petrology, and astrobiology. Suggestions that minerals might affect organic hydrothermal transformations have been proposed for decades, stemming from observations of abundant hydrothermal organic compounds in association with various minerals. This potential intersection of mineralogy and organic chemistry in hydrothermal environments presents an exciting frontier for multidisciplinary scientific research.[50-54] Moreover, there have been some remarkable studies highlighting how naturally occurring inorganic substrates can affect the stability of organic structures under lab-simulated hydrothermal conditions. These findings suggest a compelling interplay between inorganic substrates and organic structures in these extreme environments.[55-58] For instance, The production of decanoic acid and organosulfur compounds from nonanethiol is encouraged in the presence of iron sulfide and CO. This suggests a catalytic effect from iron sulfide minerals and the potential creation of organometallic species under hydrothermal conditions. Carboxylations and carbonyl insertions have also been extensively documented for alkylthiol compounds in the presence of transition metal sulfides, such as FeS, NiS, and CoS. The concept of heterogeneous catalysis on the mineral surface was proposed by Huber and Wächtershäuser, further supporting the idea of mineral involvement in these complex reactions.[59-60]

Numerous studies investigating hydrothermal organic reactions have been conducted using mineral assemblages to manage experimental variables like oxidation state, pH, and dissolved sulfur species. This method of incorporating mineral assemblages helps

simulate more realistic hydrothermal conditions, providing valuable insights into the actual mechanisms at play in nature. [53,54,58,61] For example, Seewald documented that mineral assemblages consisting of pyrite-pyrrhotite-magnetite, hematite-magnetite, and hematite-magnetite-pyrite were capable of controlling the activities of dissolved H_2 and H_2S in hydrothermal solutions, illustrating the active role of mineral assemblies in modulating the chemical behavior in hydrothermal environments.[53] These iron-bearing minerals have been discovered to play diverse roles in organic hydrothermal reactions. These roles include promoting bond cleavage processes on the mineral surface and altering solution properties such as ionic strength, pH, and the levels of dissolved metals and sulfur compounds. This underscores the complex influence of minerals in the chemical transformations happening in these environments.[4] In recent studies, a pyrite-pyrrhotite-magnetite assemblage has been used to create a redox-buffered hydrothermal environment for C_1-C_5 n-alkanes at 323°C and 350 bar. This experiment observed extensive and reversible incorporation of water-derived hydrogen into the alkanes. However, comparatively minimal exchange was noted for CH_4, indicating that isotopic exchange likely takes place within the reversible equilibration between the alkane and its corresponding alkene. This insight can help refine our understanding of the complex reactions happening within these hydrothermal systems.[61] A study conducted by McCollom on the impact of iron oxide and sulfide minerals on the hydrothermal decomposition of amino acids like norvaline and alanine found that both amino acids decomposed more quickly and with different product distributions in the presence of minerals compared to water alone. This implies that the effects of the minerals were due to both surface catalysis and alterations in the chemical species in the solution phase.

This research further underscores the crucial role of minerals in altering the course and rate of hydrothermal reactions.[62] There are also studies that have emphasized the presence of individual minerals, rather than a mineral-assemblage, that distinguished the role of each mineral in the hydrothermal interconversions of organic functional groups resulted from surface catalysis, pH controlling or redox state changing. Yang et al. (2012) examined the effect of iron-containing minerals, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), and troilite (synthetic FeS) on hydrothermal dibenzylketone (DBK) conversion and found that they accelerated the reaction of DBK by up to an order of magnitude. Fragmentation products, such as toluene and bibenzyl, dominated in the presence of hematite or magnetite, while use of troilite gave primarily the reduction products, suggesting that the reactions catalyzed by iron oxides (hematite and magnetite) are promoted mainly by the mineral surfaces, whereas the sulfide mineral (troilite) facilitated the reduction of ketones in the reaction solution.

Rather than using mineral assemblages, here we examined the role of isolated minerals on the transformation of amines under hydrothermal conditions to determine the stability of amines on minerals. Different structures of amines and minerals with diverse surface areas will be used to understand their effects on the stability of amines in hydrothermal systems. Compared to cyclohexylamine and cyclohexanemethylamine which were relatively inert, benzylamine converted rapidly in buffered hydrothermal water. Similar to the ketone experiments conducted by Yang et. al (2012), the presence of iron-containing minerals accelerated the condensation reaction slightly; while pyrrhotite significantly facilitated the condensation reaction, hematite and magnetite enhanced the formation of dehydration and oxidation products. Although the majority of the

applications of corundum (Al_2O_3) are in industrial processes (like the dehydration of alcohols or the dehydrogenation of hydrocarbons), it's possible that it could similarly catalyze certain organic reactions under hydrothermal conditions.[63] With a large surface area, it can adsorb various chemical species. Such property could influence organic reactions by concentrating reactants on the mineral surface, potentially enhancing reaction rates or favoring certain reaction pathways.[64] Here, Al_2O_3 slightly enhanced the conversion by promoting the dehydration pathway to form benzyl alcohol. Additionally, it was suggested that gibbsite ($Al(OH)_3$) could potentially act as catalysts or platforms for various reactions, where it could provide a surface for adsorption, potentially facilitating some organic reactions. However, there are limited studies that investigated this observation.[65] Our amine conversion study found that it accelerated the conversion of benzylamine and cyclohexanemethylamine by improving both deaminization and condensation pathways. Brucite ($Mg(OH)_2$) is another important mineral in natural hydrothermal systems because its dissolution can lead to an increase in the pH of the surrounding solution due to the release of hydroxide ions (OH^-), but the influence of brucite on hydrothermal transformations have been rarely studied. This highly alkaline environment can plausibly influence organic reactions by enhancing the nucleophilic character of certain organic compounds or by promoting hydrolysis reactions.[66] Similar to gibbsite, brucite enhances the conversion of amines, but it also promoted the yield of oxidation products, which may be attributed to the Lewis acids formed from the releasing Mg^{2+} in buffered hydrothermal water. Investigation of each mineral on hydrothermal amine reactions would show the stability of different structure of amines on diverse surface of minerals. Like the role of the three iron-containing minerals discussed above,

this study would also elucidate if the role is inherently due to the surface adsorption and catalysis, so we can understand the abiotic evolution of N-cycling on hydrothermal rock surfaces.

Another property of all minerals above is that they release metal ions after undergoing alteration, which could also affect organic functional groups transformations under hydrothermal conditions. It is well known that ocean water is not only composed of deionized water, thus laboratory simulated experiments should consider the occurrence of ions. There are several reports that have shown that mineral-facilitated hydrothermal reactions are potentially attributed to their dissolved ions.[4] For example, even though copper(II) was thought to be toxic to organisms in the deep ocean, low concentrations of copper can act as a mediator in the interaction between amino acids and gibbsite's surface. The formation of a ternary complex between glycine, Cu^{2+}, and Al oxyhydroxide surfaces (Figure 5) has been proposed in an early paper of McBride (1985) on the basis of EPR spectroscopy. Cody et al. discovered that iron ions (Fe^{2+}/Fe^{3+}) can catalyze reactions such as Fischer-Tropsch synthesis, potentially leading to the generation of hydrocarbons from carbon monoxide and hydrogen.[44] Additionally, iron(III) can undergo redox reactions, influencing the oxidation state of organic molecules and their surrounding fluids. [67] In addition to iron, our previous research also found copper(II) can be another oxidant under hydrothermal conditions, which significantly altered the reaction pathways of phenylacetic acid from dehydration to oxidative decomposition. Herein, the oxidative role of both copper(II) and iron(III) were performed on the different structure alcohols and functionalized aldehydes. The presence of copper and iron ions changed the pathway distribution, favoring oxidation as the dominant pathway rather than dehydration, which

was the only reaction observed in the pure-water environment. The efficient oxidation method also offers new sights into industrial oxidation, meeting the requirements of green chemistry using Earth-abundant materials, where expensive and toxic oxidants and organic solvents would not be required. Easy-obtained metal solutions would significantly reduce the cost of large-range synthesis or pollutant treatments. In summary, utilizing geochemical methods that already occur in real-world environments based on the understanding of hydrothermal organic-inorganic interactions have the potential to improve on industrial application in recent years.

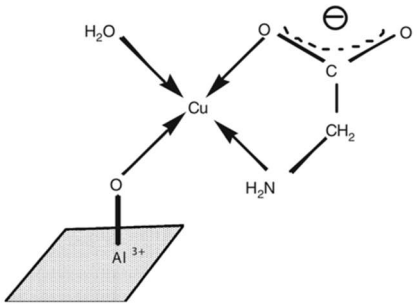


Figure 5. Specific adsorption of glycine on Al oxyhydroxides through the formation of a ternary coordination complex

1.5 Geomimicry

While many hydrothermal organic transformations can happen in water alone, not all reactions are selective, and the timing can be on geologic timescales.[68-69] For instance, 2-phenylethanol exhibited very low reactivity in 200°C hydrothermal water even after 24hr. The multitude of research highlighted here predominantly involves geomimicry - the application of hydrothermal reactions, which have been fine-tuned for particular objectives. The term "geomimicry" or "geomimetic" is typically used to refer to the

creation of minerals or materials resembling minerals, specifically designed for certain uses.[19,70,71] Numerous hydrothermal organic reactions that have been conducted also meet these criteria - being natural processes that have been adopted or optimized. The objective of our geomimetic experiments was not solely to decipher the reactions and the resulting product quantities in natural hydrothermal systems. Rather, we intended to enhance established hydrothermal reactions, with the ultimate goal of paving the way for invention of new methods in organic synthesis.

A prior research indicated that the mineral Sphalerite (ZnS) demonstrated the ability to selectively activate C-H bonds in 1,2-dimethylcyclohexanes when exposed to hydrothermal conditions.[72] It has been proven that Copper (II) chloride serves as a selective oxidant, specifically enabling the transformation of alcohols into aldehydes.[19] Copper(II) was also found to oxidatively decarboxylate phenylacetic acid to benzyl alcohol, subsequently oxidizing the alcohol to benzaldehyde and benzoic acids without other byproducts.[71] These studies all show that an increase in thermal energy does not inevitably lead to a loss of selectivity or complete breakdown of the organic starting material, a notion that is often assumed.[73] Like copper salts, iron(III) nitrate also inhibited the dehydration pathway of primary, secondary, and tertiary aromatic alcohols, but promoted the oxidation of alcohols to benzoic acids.[74] Research with functionalized aldehydes as the substrate also revealed the high selectivity and relatively high efficiency on oxidation of aldehydes.[75] The one-electron transfer oxidation was also proposed for the reaction of hydrocinnamic acid on the surface of hematite and magnetite, although it had a complex product distribution.[76] Since plentiful copper and iron-containing minerals were observed in hydrothermal areas with recorded concentrations of Cu(II), Fe(II), and

Fe(III),[77] these ions displayed great potential to control the organic groups transformations, nutrients formation, and energy cycling of ecosystems in hydrothermal areas. If the origin of life indeed stemmed from a hot spring or hydrothermal system, it's plausible that these soluble salts could have played a part in the synthesis of essential organic compounds.[25,52] It was found that oxidation of ketones cannot occur without the presence of an external oxidizing power in hydrothermal conditions, and the reduction to alkenes was more favorable.[69] However, the appearance of carboxylic acids in geological areas suggest the natural transformation of ketones is possible to be facilitated by surrounding abiotic material. Our research on 2-phenyl-2-proponal hydrothermal conversion observed the oxidation from alcohols to ketones and subsequently to benzoic acid by iron(III) nitrate, which indicated the excellent activity on oxidative scope of metal salts. Nevertheless, current metal ions-participating studies are limited to special structure compounds such as aromatics for quantification convenience and are mainly focused on carbon cycle as Seewald proposed.[4] Therefore, their function in reactions involving more complex compounds, such as those in the nitrogen cycle, remains ambiguous as either a reagent or a catalyst, and it varies depending on the different substrates involved.

Another aim of this study is to determine the scope and applicability of copper(II) and iron(III) salts as Earth-abundant oxidants and catalysts, so it can be used in future green chemistry applications such as biomass oxidation or water waste degradation. Present techniques for biomass or waste oxidative degradation predominantly fall into two categories - catalytic conversion and hydrothermal processing. Hydrothermal processing, while beneficial in certain respects, lacks the necessary redox propensity towards more oxidized materials. Moreover, it tends to be chemically and/or

energetically inefficient, exhibiting a lack of selectivity in the resulting products.[78] Typical oxidation catalysts are rare metals and metal oxides, such as palladium (Pt), platinum (Pd), vanadium oxide (V_2O_5), tungsten oxide (WO_3), and molybdenum oxide (MoO_3), but the conditions always require supercritical water which causes severe reactions.[79] Moreover, although catalysts are recyclable, all catalysts inevitably deteriorate, suffer from poisoning, or experience reduction in surface area over time. Given these limitations, it would be more advantageous to utilize inexpensive, easily accessible materials for catalysis in large-scale productions.[80]

The methods detailed in this study, employing water as a harmless solvent, present significant potential for more secure and ecologically responsible industrial processes. Upon cooling the reaction, the organic products naturally segregate from the water solvent, thereby streamlining the post-reaction cleanup process. Using iron(III), copper(II) or other geological-existing salts, this work combines the examination of the oxidative effects on carbon cycle and nitrogen cycle to selectively generate acids from original organics by observing hydrothermal processing and optimizing geomimicry approaches without the use of expensive metals. Given that petroleum is a finite resource, there will inevitably come a time when we need to explore alternative sources for its derivative chemical products, including solvents, synthetic starting materials, and oils. Current methods of converting biomass or waste often need to overcome their high-water content, hence wet waste and biomass feedstock with high moisture still require substantial pre-treatment.[81-82] However, the use of hydrothermal conversion methods can advantageously utilize this water as the solvent for the reaction. Moreover, the water pollutants, such as PAHs (polycyclic aromatic hydrocarbons), which have troubled

humanity for many years, can be degraded and transformed into valuable chemicals through oxidation, which inspired us to study the function of hydrothermal oxidation on these pollutants.[83] Thus, it is ideal to develop a process that involves starting with high-moisture biomass and PAHs, using affordable and safe reagents, and fully enhancing the efficiency of these reactions. The investigations presented in this document signify a step towards this objective.

CHAPTER TWO

HYDROTHERMAL TRANSFORMATIONS OF ALCOHOLS WITH COPPER(II) AND IRON(III) SALTS

2.1 Introduction

The changes that organic matter undergoes in Earth's hydrothermal systems hold relevance to several key geological phenomena, such as the creation of crude oil and petroleum, the transportation and deposition of sedimentary organics, and the cycling of deep carbon within the ocean crust.[84-85]The breaking down of pre-existing organic material and the production of new organic molecules in hydrothermal conditions could potentially act as a source of nutrition and energy for life forms residing deep within the Earth.[4,86,87] Astonishing and unforeseen methods of generating precursors to biomolecules, like peptides and amides, in hydrothermal fluids have been observed.[88 ,89,60] These could hold significance for the synthesis of prebiotic elements and processes pertaining to the origin of life on Earth and potentially other planets with suitable living conditions.[90] Within these organic transformations under hydrothermal conditions, the reciprocal changes that connect alkanes to carboxylic acids through alkenes, alcohols, and ketones/aldehydes are of specific interest.[69,24,61] Consequently, revealing the pathways and mechanisms of these organic interconversions in hydrothermal conditions is vital to comprehend the origin and eventual destination of organic compounds within the deep subsurface.

Numerous comprehensive studies have delved into the dynamics, balance, routes, and mechanisms of organic functional group transformations under hydrothermal

conditions. These include the equilibrium between alkanes and alkenes, the dehydration of alcohols, the redox conversion of ketones and aldehydes, and the decarboxylation of carboxylic acids.[62,47,91-93] While these distinctive transformations of organic functional groups can naturally occur in pure water under high temperatures and pressures, organic compounds in natural hydrothermal systems are bound to interact with surrounding inorganic materials, such as minerals and dissolved metals. Recent studies propose that the presence of commonly found minerals and metal ions can significantly impact the reactivity of organic functional groups in hydrothermal conditions and the course of their reaction pathways.[94,70,57,71] For instance, natural iron and nickel have the ability to selectively reduce alkenes to alkanes; iron sulfide minerals can aid in the reduction of ketones; copper salts can introduce new oxidative decarboxylation pathways for organic acids; and iron oxide minerals can foster the transformation of carboxylic acids into ketones. These remarkable interactions between organic and inorganic substances not only highlight the crucial roles of minerals and metal ions in the transformations of organic geochemical components within hydrothermal systems, but they also connect geochemistry with green chemistry in the emerging field of 'geomimicry'.

Alcohols play a pivotal role in the interconversion of organic functional groups. Past research has suggested that alcohols tend to dehydrate under hydrothermal conditions, and the transformation of alcohols into alkenes can occur swiftly within a temperature range of 200 - 350 °C, happening in just a matter of hours.[47,95,96] The mechanisms of alcohol dehydration under hydrothermal conditions have been extensively studied and are generally attributed to homogeneous Brønsted acid-catalyzed water elimination processes. For instance, Bockisch and his team examined the hydrothermal dehydration

mechanisms of secondary alcohols through kinetic and stereoelectronic effect studies in pure water, discovering that the E1 elimination mechanism took precedence over the corresponding E2 mechanism under their experimental conditions. Nonetheless, there is a scarcity of research on the hydrothermal interactions between alcohols and inorganic materials, and in particular, the way in which abundant earth metals and minerals influence alcohol reaction pathways is not well-understood. Therefore, this study's primary objective is to investigate the effects of dissolved metals, such as copper and iron, on hydrothermal transformations of alcohols. Copper and iron salts are selected for the study due to their widespread distribution in seawater and seafloor hydrothermal vents.[97-99] For instance, minerals rich in iron and copper, such as pyrrhotite and chalcopyrite, are frequently found in deep-ocean hydrothermal systems. There, they can dissolve to form metal ions combined with a variety of anions in the surrounding seawater. Additionally, our recent studies indicate that copper(II) salts can serve as an oxidant, triggering unique pathways for organic acids (e.g., oxidative decarboxylation). We hypothesize that copper(II) and iron(III) could potentially exert a similar oxidizing effect on hydrothermal reactions involving alcohols.[19,71] In this study, we explore the impacts of various copper(II) and iron(III) salts on three representative alcohol compounds, namely 1-phenylethanol, 2-phenylethanol, and 2-phenyl-2-propanol. These model compounds are chosen as they represent primary, secondary, and tertiary alcohols. Moreover, the benzyl group in their structures permits straightforward reactions and relatively simple product extraction and analysis, which aids in identifying the reaction pathways and mechanisms. By examining the interaction between alcohols and metal ions under hydrothermal conditions, this study aims to unearth new insights and

mechanistic understanding of alcohol transformations in natural hydrothermal environments.

2.2 Experimental Procedures

2.2.1 Materials

Primary, secondary, and tertiary alcohol compounds, including 1-phenylethanol (98%), 2-phenylethanol (99%), and 2-phenyl-2-propanol (99%), were procured from Sigma-Aldrich. Metal salts such as cupric nitrate (99%), ferric nitrate (99%), sodium nitrate (99%), cupric chloride (99%), ferric chloride (99%), cupric sulfate (99%), and ferric sulfate (99%) were all sourced from Sigma-Aldrich. Other compounds including Styrene (99%), α−methylstyrene (99%), acetophenone (99%), diphenylmethanol (99%), benzophenone (99%), benzaldehyde (99%), and benzoic acid (99%) were also supplied by Sigma-Aldrich and used as received. Dichloromethane (DCM, 99.9%) was acquired from VWR and utilized as the organic extraction solvent. Decane (⩾99%) was bought from Sigma-Aldrich and employed as the internal standard for gas chromatography (GC). Deionized water (18.2 MΩ·cm), used for the hydrothermal experiments, was procured from a Barnstead Nanopure system.

2.2.2 Methods

The hydrothermal experiments were performed adhering to the protocols established in previous studies.[71,41,100] In brief, liquid alcohols were introduced into fused-silica glass tubes (6 mm OD and 2 mm ID) using a gas-tight microsyringe, followed by the addition of 0.3 mL of either copper or iron salt solution (0.2 molal in deoxygenated, deionized water). The final alcohol concentration in the solution was maintained at 0.1 molal. These initial organic and inorganic concentrations were consistent with those used in our

previous copper salt studies.[71] After the initial materials were introduced, the oxygen and air inside the tubes were eliminated by three freeze-pump-thaw cycles before the tubes were sealed under vacuum with an oxyhydrogen flame. The tubes were sealed while the solution was frozen using liquid nitrogen. These sealed tubes were then heated in a pre-heated GC oven at 200 °C for either 2 or 24 hours. The internal water vapor pressure within the tube at 200 °C was estimated to be around 15 bar.[101] The relatively brief reaction time of 2 hours was selected primarily to investigate the initial products of alcohols and to minimize the formation of secondary or complex by-products.

Upon completing the hydrothermal experiment, the silica tubes were quenched by immersion in a cold water bath. The reaction products were then extracted using the previously established methods.[19] In brief, the organic products were extracted using 3.0 mL of DCM, with 8.8 mM decane serving as the GC internal standard. The solution mixtures were then separated further by sonication and centrifugation, after which they were transferred to GC vials. The organic products were analyzed and quantified using an Agilent 7820A GC equipped with a polycapillary column and a flame-ionization detector. The structures of the dimers were also identified using high-resolution gas chromatography-mass spectrometry (GC-MS, Agilent 7890A/5975C), based on fragmentation pattern analysis and database matching.

Thermodynamic calculations concerning the aqueous properties of alcohol reactions were performed utilizing the revised Helgeson-Kirkham-Flowers equation of state, implemented through the SUPCRT92 software,[101] similar to previous studies.[90] Equilibrium reaction constants (log K_{eq}) were calculated for both alcohol dehydration and oxidation reactions within a temperature range of 0 to 300 °C at P_{sat}. Thermodynamic

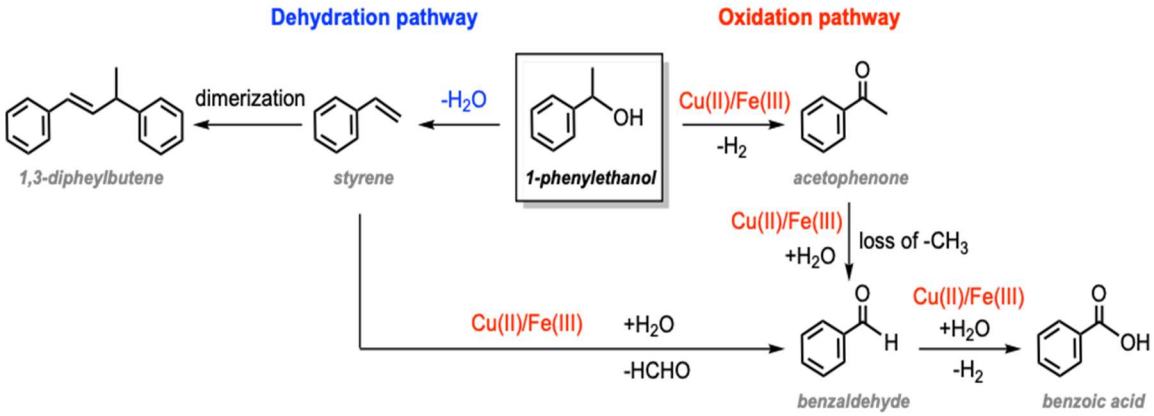
modeling of reactions converting alcohol to alkene and alcohol to aldehyde was performed using basic alcohol structures available in the database. Detailed information on these specific reactions and calculations will be depicted in subsequent sections, with the resulting data presented in the figures.

2.3 Results and Discussion

2.3.1 Hydrothermal Reactions of 1-Phenylethanol

Under our experimental conditions of 200 °C and 15 bar (P_{sat}), we observed two main reaction pathways for 1-phenylethanol (Scheme 2). The first pathway involves alcohol dehydration, resulting in the formation of styrene as the primary product. The second pathway entails oxidation, wherein 1-phenylethanol is converted into acetophenone, alongside the formation of other oxidized products including benzaldehyde and benzoic acid. Both observed pathways align with the functional group interconversions depicted in Figure 6, as established in previous studies.[4,68,69] However, according to the results of this study, the two pathways aren't equally represented. To identify the differences between these pathways, we calculated and compared the percentage contribution of each pathway (Table 1). Specifically, the percentage of the dehydration pathway is calculated by dividing the total amount of dehydration products (e.g., styrene and its dimers) by the initial alcohol concentration (0.1 molal), while the percentage of the oxidation pathway is determined by dividing the total amount of oxidation products (e.g., acetophenone, benzaldehyde, and benzoic acid) by the initial alcohol concentration. In the absence of metal salts, 1-phenylethanol primarily follows the dehydration pathway (49.7% after 2 hours), with styrene as the main product, whereas the oxidation pathway accounts for only 2.9%, producing acetophenone and

benzaldehyde as minor products (Table 1; Figure 6). The results suggest that dehydration is the principal pathway for 1-phenylethanol in pure hydrothermal water, a finding that aligns well with the hydrothermal dehydration of other secondary alcohols such as cyclohexanols under similar experimental conditions (e.g., 250 °C and 40 bar).[47]



Scheme 2. Hydrothermal reaction pathways of 1-phenylethanol (as a representative secondary alcohol) in the presence of copper/iron salts.

Table 1. Hydrothermal reactions between 1-phenylethanol and iron/copper salts in H_2O at 200 °C, 15 bar after 2 h. The starting concentration of the alcohol was 0.1 molal; the starting concentrations of the iron/copper salts were either 0.1 or 0.2 molal, making the total metal concentrations consistent (0.2 molal). The dimer represents 1,3-diphenylbutene. b.d. means below detection.

Reactant	Iron/copper salt(molal)	Methyl styrene (mmolal)	Benzaldehyde (mmolal)	Benzoic acid (mmolal)	Acetophenone (mmolal)	Dimers (mmolal)	Alcohol conv. (%)	Dehydration pathway(%)	Oxidation pathway (%)
alcohol	0	89.1±4.3	b.d.	b.d.	5.4±2.0	b.d.	94.4±2.3	89.1	5.4
alcohol+ $FeCl_3$	0.2	25.7±2.2	3.1±0.1	4.0±0.1	3.5±1.0	22.9±2.4	82.2±1.8	71.5	10.6

Table 1. Hydrothermal reactions between 1-phenylethanol and iron/copper salts in H_2O at 200 ℃, 15 bar after 2 h. The starting concentration of the alcohol was 0.1 molal; the starting concentrations of the iron/copper salts were either 0.1 or 0.2 molal, making the total metal concentrations consistent (0.2 molal). The dimer represents 1,3-diphenylbutene. b.d. means below detection.(Continued)

Reactant	Iron/copper salt(molal)	Methyl styrene (mmolal)	Benzaldehyde (mmolal)	Benzoic acid (mmolal)	Acetophenone (mmolal)	Dimers (mmolal)	Alcohol conv. (%)	Dehydration pathway(%)	Oxidation pathway (%)
alcohol+ $Fe_2(SO_4)_3$	0.1	28.1±1.2	0.6±0.1	b.d.	1.9±0.3	32.0±1.4	94.5±1.3	92.1	2.5
alcohol+ $Fe(NO_3)_3$	0.2	19.4±0.7	2.2±0.1	37.6±1.1	18.7±1.0	b.d.	77.8±0.8	19.4	58.5
alcohol+ $CuCl_2$	0.2	24.7±0.7	2.3±0.2	3.9±0.2	1.7±0.9	27.0±1.3	86.2±2.9	78.3	7.9

In the presence of copper(II) or iron(III) salts, however, the pathway distribution of 1-phenylethanol is evidently altered. For example, compared to the pure-water experiments with no added metals, the addition of copper(II) or iron(III) chloride increases the oxidation pathway% from 2.9% to 10.3% and 11.4%, respectively, although the dehydration pathway% remains nearly unchanged (44.7−52.4%) (Table 1; Figure 6). The enhanced oxidation pathway% is mainly due to the increased production of acetophenone and benzaldehyde, which suggests an oxidative role of copper(II) and iron(III) in alcohol hydrothermal transformations. This finding is not surprising, considering that previous studies showed that copper(II) salts can facilitate organic

hydrothermal oxidations, such as oxidative decarboxylation of carboxylic acids and oxidation of alcohols to aldehydes and organic acids, and our results further indicate that iron(III) can also serve as an oxidant with a similar effect to copper(II). However, the formation of benzaldehyde from 1-phenylethanol does not look straightforward, since the direct oxidation of 1-phenyl- ethanol should form acetophenone rather than benzaldehyde, which would involve the loss of a carbon (Scheme 2). To figure out how benzaldehyde is formed, experiments starting with acetophenone (0.1 molal) were conducted in the absence and presence of copper(II) and iron(III) at 200 °C and 2 h. Results show that acetophenone is unreactive (<5%) in pure water, whereas the addition of copper(II)/iron(III) enables more than 50% conversion of the ketone to benzaldehyde and benzoic acid as the major products. For example, in the presence of $Cu(NO_3)_2$, 0.1 molal acetophenone yields ∼0.02 molal benzaldehyde and ∼0.03 molal benzoic acid at 200 °C after 2 h. Although the form of the lost methyl group from acetophenone has not been identified, the result suggests that acetophenone can serve as an intermediate from 1-phenyl- ethanol to benzaldehyde (Scheme 2). In addition, experiments starting with styrene also demonstrate that styrene can be readily oxidized to benzaldehyde and benzoic acid (as major products) by copper(II) or iron(III) at 200 °C within 2 h, which suggests another pathway to benzaldehyde via the oxidation of styrene (Scheme 2). Although the reaction mechanisms are not clear yet, it is likely that an ozonolysis-like oxidative alkene cleavage could occur involving water and copper(II)/iron(III) under the experimental conditions.

Copper(II) or iron(III) chloride does not seem to greatly influence the dehydration pathway% of 1-phenylethanol (Table 1; Figure 6), but the major dehydration product is

changed from styrene to 1,3-diphenylbutene, a dimer that is expected to form from the dimerization of styrene. Compared to the pure-water experiments, the dimer's concentration increases substantially when metal salts are added, from <1.0 mmolal in pure water to 19.5 and 23.8 mmolal with copper(II) and iron(III) chloride, respectively (Table 1), suggesting that both copper and iron salts can facilitate the dimerization of alkenes under hydrothermal conditions. It is likely that copper(II)/iron(III) chloride potentially acts as Lewis acid to catalyze the reaction.[102-103]

The 1-phenylethanol experiments with copper(II)/iron(III) sulfate under the same hydrothermal conditions (200 °C, 15 bar, and 2 h) share a similar pathway distribution to the copper(II)/iron(III) chloride experiments, although the dehydration pathway is more dominating (Figure 1). Both copper(II) sulfate and iron(III) sulfate also increase the production of benzaldehyde compared to pure-water experiments, but their oxidations (reflected by the oxidation pathway %) are less prominent than those with the chlorides (Figure 6; Table 1). However, the sulfates significantly increase the dehydration pathway% (sum of styrene concentration and twice of the dimer concentration), from 44.7−52.4% (with chlorides) to 68.4−69.9% (with sulfates), with the dimer produced as the major product (Table 1). This difference may be explained by the hydrothermal solution pH change caused by the metal salts, since alcohol dehydration usually occurs through an acid-catalyzed mechanism.[47,96,104] Although the exact pH under hydrothermal conditions is unknown (not measured), the pH of the starting metal solutions at room temperature is measured between 2 and 4, lower than that of the metal-free solution (~5.7), suggesting that the copper(II)/ iron(III) solution could be more favorable for acid-catalyzed dehydration and dimerization. However, the actual pH under the experimental

conditions is expected to be even lower due to the increased ionic product of water at higher temperatures,[47] and it may also be dependent on the type of metal− anion complexes formed in the hydrothermal solution.[19]

In contrast to the dehydration-dominated pathway with the chlorides and sulfates, copper(II)/iron(III) nitrate exhibits a distinct pathway pattern for 1-phenylethanol. As shown in Figure 6, oxidation becomes the most pronounced pathway with the nitrates, which is indicated by the increased alcohol oxidation pathway% from 2.9% (in pure water) to 60.4% and 49.7% in the presence of copper(II) and iron(III) nitrate, respectively (Table 1). The strong oxidative effect of the nitrates is also evidenced by the product distribution in which benzoic acid is formed in much larger amounts than benzaldehyde or acetophenone. Since formation of benzoic acid requires an even further oxidation step from benzaldehyde (Scheme 2), this result demonstrates a much stronger oxidizing role of copper(II)/iron(III) nitrate than the other metal salts in the alcohol hydrothermal reactions. This finding is also consistent with the previous study, in which copper(II) nitrate performs a much higher oxidative power than copper(II) chloride/sulfate in decomposing and oxidizing phenylacetic acid in hydrothermal solutions.[71] In that study, benzaldehyde and benzoic acid were also formed as the major oxidation products, and the highest benzoic acid/benzaldehyde ratio was observed with copper(II) nitrate. In the present study, a similar mechanism could apply to the oxidation of 1- phenylethanol, where the high yield of benzoic acid is most likely due to the strong oxidation of nitrates.[105]

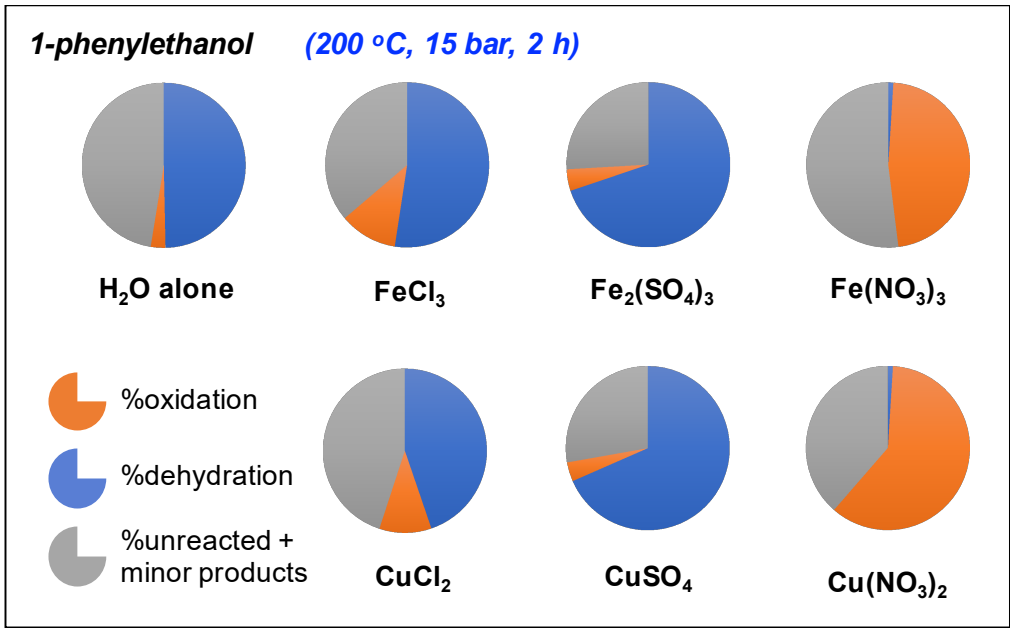
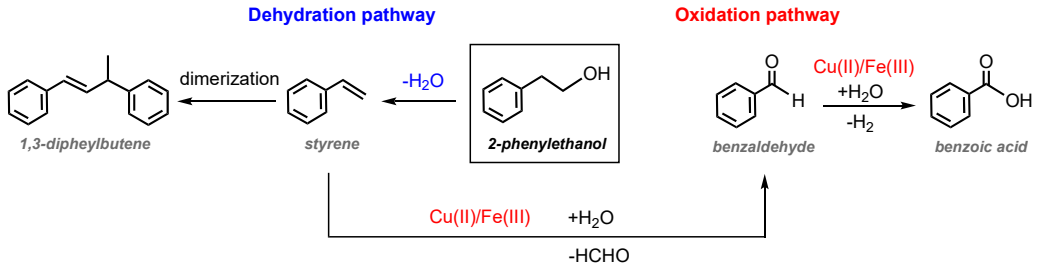


Figure 6. Hydrothermal reaction pathway distributions of 1- phenylethanol in the absence and presence of iron(III) or copper(II) salts in H_2O at 200 °C and 15 bar after 2 h. The %dehydration (blue) and %oxidation (orange) pathways were calculated based on the products formed through the dehydration pathway and the oxidation pathway (Scheme 2; Table 1), respectively. The %unreacted + minor products pathway (gray) indicates the percentage of unreacted alcohol and undetected minor products after the hydrothermal reaction.



Scheme 3. Hydrothermal reaction pathways of 2-phenylethanol (as a representative primary alcohol) in the presence of copper/iron salts.

Hydrothermal experiments with another secondary alcohol compound, diphenylmethanol, were also conducted in the presence of copper(II)/iron(III) nitrate under the same experimental condition (200 °C and 15 bar), where >90% of diphenylmethanol is oxidized to diphenylketone after 2 h (data not shown). This result further corroborates that these metal nitrates are highly oxidizing in hydrothermal solutions. The relatively clean reaction and high yield of ketone can be explained by the fact that diphenylmethanol is unable to dehydrate, which forces the only oxidation pathway to occur for the secondary alcohol. In comparison, 1-phenylethanol can dehydrate, but interestingly, the styrene and dimer concentrations are both below the detection limit in the copper(II)/ iron(III) nitrate experiments (Table 1), indicating a minimal alcohol dehydration pathway. However, this does not mean that 1-phenylethanol cannot dehydrate in the presence of the nitrates, since its dehydration product styrene can also be quickly oxidized to benzaldehyde and benzoic acid by copper(II)/iron(III) (Scheme 2). Taken together, these results highlight that copper(II)/iron(III) nitrate can efficiently and selectively control the secondary alcohol hydrothermal trans- formations, by highly promoting the oxidation pathway and suppressing the formation of dehydration products.

2.3.2 Hydrothermal Reactions of 2-Phenylethanol

A primary alcohol model compound, 2-phenylethanol, is studied under the same hydrothermal conditions of 200 °C and 15 bar. The reaction products of 2-phenylethanol are found to be quite similar to those of 1-phenylethanol, including styrene and its dimer as the dehydration products and benzaldehyde and benzoic acid as the oxidation products (Scheme 3). However, the hydrothermal reactivity of 2-phenylethanol is much lower than

that of 1-phenylethanol, and the corresponding aldehyde (phenylacetaldehyde) or acetophenone is not observed. In pure-water experiments, the dehydration and oxidation path- way% are both <1% for 2-phenylethanol after 2 h (Table 2; Figure 7). Styrene and its dimer are not detected in the 2 h experiment, which indicates that dehydration is negligible for 2-phenylethanol during the short reaction time. However, at longer reaction times (e.g., 24 h), both styrene and the dimer are generated (1.9 and 5.9 mmolal, respectively, data not shown), suggesting that the dehydration pathway does occur for 2-phenylethanol. The dramatically different reactivities between 2-phenylethanol and 1-phenylethanol suggest that these two alcohol compounds may have separate reaction mechanisms. Indeed, primary alcohols are usually expected to undergo dehydration through an E2 mechanism, while secondary alcohols could dehydrate via either the E1 or E2 mechanisms.[47,106,107] The main difference between the E1 and E2 mechanisms is that the E1 mechanism involves a carbocation intermediate that can rearrange, whereas the E2 mechanism is a one-step reaction and does not involve an intermediate. Bockisch et al.[47] conducted a detailed kinetic and mechanistic study on dehydration of secondary alcohols, where they found a dominating E1 mechanism over the E2 mechanism for most secondary alcohols under similar hydrothermal conditions. Although the present study lacks of solid evidence for the specific mechanisms, the faster degradation of 1-phenylethanol than 2-phenylethanol seems to suggest that both alcohols may proceed through an E1 mechanism, since substituted alcohols (e.g., secondary alcohols) are expected to have a higher E1 reaction rate than primary alcohols.

Table 2. Hydrothermal reactions between 2-phenylethanol and iron/copper salts in H2O at 200 ℃, 15 bar after 2 h. The starting concentration of the alcohol was 0.1 molal; the starting concentrations of the iron/copper salts were either 0.1 or 0.2 molal, making the total metal concentrations consistent (0.2 molal). The dimer represents 1,3-diphenylbutene. b.d. means below detection.

Reactant	Iron/copper salt(molal)	Styrene (mmolal)	Benzaldehyde (mmolal)	Benzoic acid (mmolal)	Dimer (mmolal)	Alcohol conv.(%)	Dehydration pathway(%)	Oxidation pathway (%)
alcohol	0	b.d.	0.8±0.2	b.d.	b.d.	0.8±0.2	0	0.8
alcohol+ $FeCl_3$	0.2	b.d.	3.6±0.5	b.d.	b.d.	3.6±0.5	0	3.6
alcohol+ $Fe_2(SO_4)_3$	0.1	b.d.	1.3±0.1	b.d.	b.d.	1.3±0.1	0	1.3
alcohol+ $Fe(NO_3)_3$	0.2	b.d.	5.5±0.3	9.1±0.4	b.d.	14.6±0.3	0	14.6
alcohol+ $CuCl_2$	0.2	b.d.	1.3±0.1	b.d.	b.d.	1.3±0.1	0	1.3
alcohol+ $CuSO_4$	0.2	b.d.	0.9±0.2	b.d.	b.d.	0.9±0.2	0	0.9
alcohol+ $Cu(NO_3)_2$	0.2	b.d.	3.7±0.1	10.9±0.1	b.d.	14.7±0.1	0	14.7

The addition of the copper(II) and iron(III) salts also influences the reactivity and pathways of 2-phenylethanol but to various extents. For example, the oxidation pathway% of 2- phenylethanol increases from 0.8% (in pure water) to 3.6% with iron chloride, 1.3% with copper chloride, 1.3% with iron sulfate, and 0.9% with copper sulfate (Table 2; Figure 7). These increases suggest that the chloride and sulfate salts have a

weak but still noticeable effect on the hydrothermal reactivity of 2-phenylethanol under the experimental conditions. The increased oxidation pathway% is mainly due to the increased yield of benzaldehyde (Table 2), whereas the dehydration pathway is still negligible (<1%), suggesting that these copper(II)/iron(III) salts do not promote the dehydration reaction and only play a minor role in oxidizing the primary alcohol. The nitrate salts, however, significantly facilitate the oxidation of 2-phenylethanol, with the oxidation pathway% increasing from 0.8% to 14.7% and 14.6% in the presence of copper(II) and iron(III) nitrate, respectively (Table 2; Figure 7). Consistent with the results from 1-phenylethanol, the nitrate oxidation of 2-phenylethanol also produces more benzoic acid than benzaldehyde (Table 2), which again demonstrates a strong oxidizing role of copper(II)/iron(III) nitrate in alcohol hydrothermal reactions. Benzaldehyde and benzoic acid are also expected to form through the oxidation of styrene by copper(II)/iron(III) (Scheme 3), following a similar scheme to 1-phenylethanol (Scheme 2). Nevertheless, the absence of phenylacetaldehyde and acetophenone in the 2-phenylethanol experiments indicates that the direct oxidation of this primary alcohol is limited even when copper(II)/ iron(III) nitrate is present (Table 2; Scheme 3). These results further suggest that copper(II)/iron(III) nitrate can drive the hydrothermal oxidation of both primary and secondary alcohols, but the effect is much higher on secondary alcohols.

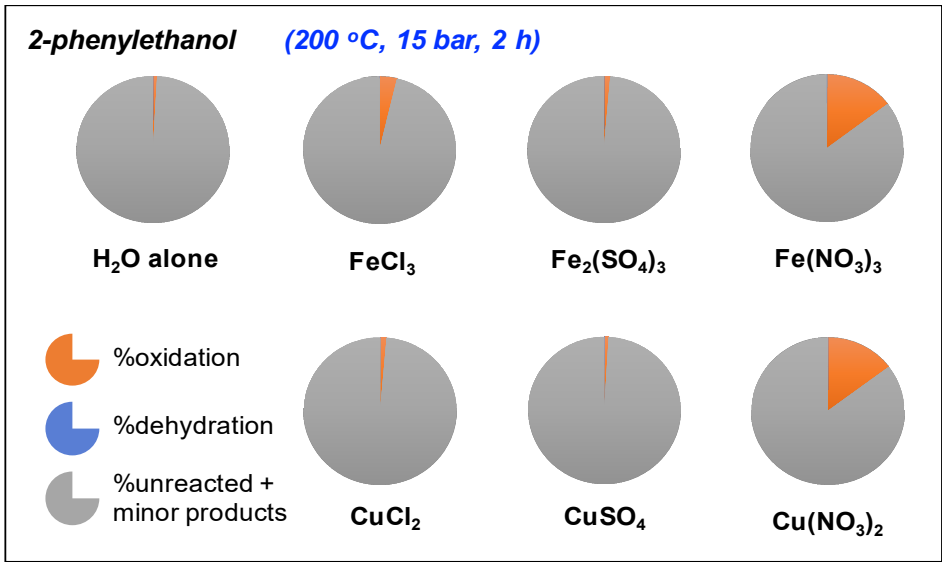


Figure 7. Hydrothermal reaction pathway distributions of 2- phenylethanol in the absence and presence of iron(III) or copper(II) salts in H_2O at 200 °C and 15 bar after 2 h. The %dehydration (blue) and %oxidation (orange) pathways were calculated based on the products formed through the dehydration pathway and the oxidation pathway (Scheme 3; Table 2), respectively. The %unreacted + minor products pathway (gray) indicates the percentage of unreacted alcohol and undetected minor products after the hydrothermal reaction.

Table 3. Hydrothermal reactions between 2-phenyl-2-propanol and iron/copper salts in H2O at 200 ℃, 15 bar after 2 h. The starting concentration of the alcohol was 0.1 molal; the starting concentrations of the iron/copper salts were either 0.1 or 0.2 molal, making the total metal concentrations consistent (0.2 molal). The dimers include methylstyrene dimer and its isomers. b.d. means below detection.

Reactant	Iron/copper salt(molal)	Styrene (mmolal)	Benzaldehyde (mmolal)	Benzoic acid (mmolal)	Dimer (mmolal)	Alcohol conv.(%)	Dehydration pathway(%)	Oxidation pathway (%)
alcohol	0	49.7±1.6	0.9±0.2	b.d.	b.d.	50.6±1.8	49.7	0.9
alcohol+ FeCl3	0.2	4.8±0.6	7.9±0.7	b.d.	23.8±1.7	60.4±4.6	53.4	7.9

Table 3. Hydrothermal reactions between 2-phenyl-2-propanol and iron/copper salts in H2O at 200 ℃, 15 bar after 2 h. The starting concentration of the alcohol was 0.1 molal; the starting concentrations of the iron/copper salts were either 0.1 or 0.2 molal, making the total metal concentrations consistent (0.2 molal). The dimers include methylstyrene dimer and its isomers. b.d. means below detection.(Continued)

Reactant	Iron/copper salt(molal)	Styrene (mmolal)	Benzaldehyde (mmolal)	Benzoic acid (mmolal)	Dimer (mmolal)	Alcohol conv.(%)	Dehydration pathway(%)	Oxidation pathway (%)
alcohol+ $Fe_2(SO_4)_3$	0.1	5.1±0.4	3.5±0.4	b.d.	32.4±0.2	73.5±1.2	70.0	3.5
alcohol+ $Fe(NO_3)_3$	0.2	b.d.	2.2±0.2	44.8±1.7	b.d.	47.0±1.9	0	47.0
alcohol+ $CuCl_2$	0.2	5.7±2.0	9.1±2.0	b.d.	19.5±0.3	53.8±0.5	44.7	9.1
alcohol+ $CuSO_4$	0.2	17.0±1.1	2.1±0.5	b.d.	25.7±2.0	70.5±3.3	68.4	2.1
alcohol+ $Cu(NO_3)_2$	0.2	b.d.	5.0±1.8	51.2±1.0	b.d.	56.2±2.8	0	56.2

2.3.3 Hydrothermal Reactions of 2-Phenyl-2-propanol

To examine the effects of copper(II) and iron(III) salts on tertiary alcohols, a third model compound, 2-phenyl-2- propanol, is also investigated under the same experimental conditions. Compared to 1-phenylethanol and 2-phenyl- ethanol, 2-phenyl-2-propanol also undergoes the dehydration and oxidation pathways (Scheme 4) but with the highest reactivity and degradation rate. Specifically, in pure water at 200 °C and 15 bar, 89.1% of

2-phenyl-2-propanol undergoes the dehydration pathway after 2 h, while 5.4% reacts toward the oxidation pathway (Table 3; Figure 8). The product distribution of 2-phenyl-2-propanol is also different. The dehydration pathway forms methylstyrene and two dimers (methylstyrene dimer and its isomer), while the oxidation pathway generates acetophenone, benzaldehyde, and benzoic acid (Scheme 4). The formation of methylstyrene could follow the same dehydration path of 1-phenylethanol and 2-phenylethanol in which the alkene forms directly from water elimination of the alcohol. As a tertiary alcohol, 2-phenyl-2- propanol is unable to be oxidized to ketone, but its dehydration product methylstyrene can be potentially oxidized. In fact, methylstyrene experiments at 200 °C show that ∼3% of methylstyrene is oxidized to acetophenone in pure water after 2 h, while more than 60% of methylstyrene can be oxidized to acetophenone, benzaldehyde, and benzoic acid when copper- (II) or iron(III) is present (data not shown). In addition, as described earlier, since acetophenone is a precursor to benzaldehyde and benzoic acid in the reaction scheme of 1- phenylethanol (Scheme 2), the same pathway scheme can be shared with 2-phenyl-2-propanol (Scheme 4). Although the specific oxidation mechanisms are not very clear, previous studies have shown that acetophenone could be generated from 2-phenyl-2-propanol with the aid of Fenton's reagent through a radical mechanism.[108] Future detailed kinetics study on the alkene and ketone intermediates may help to reveal how these oxidation reactions occur under the hydrothermal conditions.

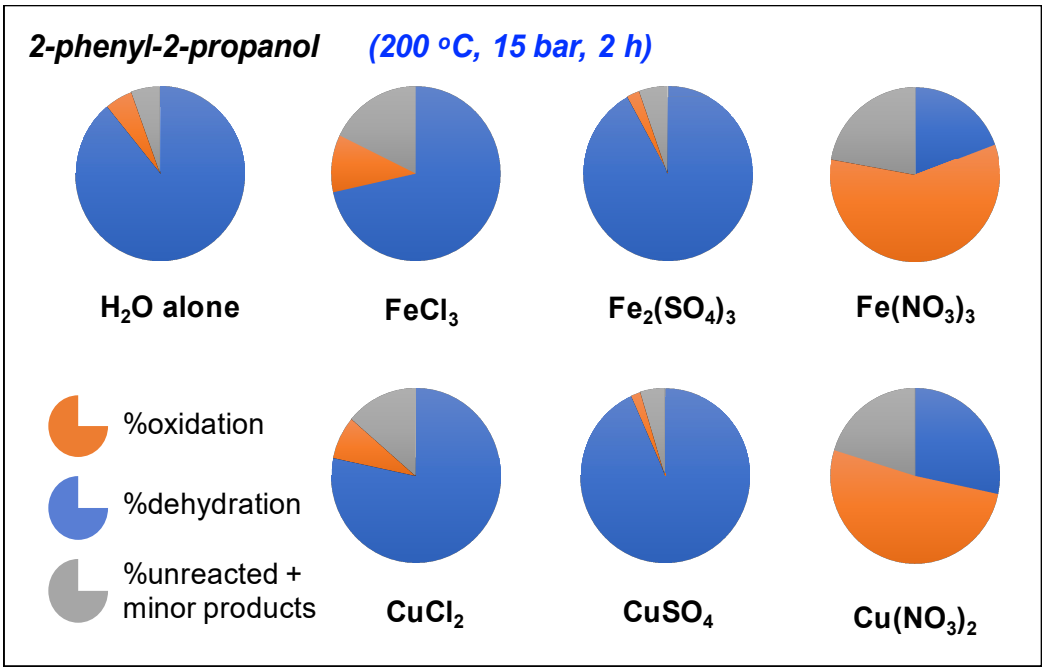


Figure 8. Hydrothermal reaction pathway distributions of 2-phenyl-2- propanol in the absence and presence of iron(III) or copper(II) salts in H_2O at 200 °C and 15 bar after 2 h. The %dehydration (blue) and %oxidation (orange) pathways were calculated based on the products formed through the dehydration pathway and the oxidation pathway (Scheme 4; Table 8), respectively. The %unreacted + minor products pathway (gray) indicates the percentage of unreacted alcohol and undetected minor products after the hydrothermal reaction.

The reaction pathways of 2-phenyl-2-propanol are also influenced by the presence of the copper(II)/iron(III) salts. In experiments with copper(II) and iron(III) chloride, the oxidation pathway% increases from 5.4% (in pure water) to 7.9% and 10.6%, respectively (Table 3; Figure 8), suggesting a mild oxidation effect of the chloride, similar to that on 1- phenylethanol (Figure 6). The chloride salts also significantly change the dehydration product distribution of 2-phenyl-2- propanol. Compared to the methylstyrene-dominated dehydration in pure water, copper(II)/iron(III) chloride greatly

promotes the dimerization reaction (Scheme 4), yielding a much higher concentration of the dimers (Table 3). This observation is in line with the trend observed in the 1-phenylethanol experiments in which copper(II)/iron(III) chloride also facilitates the hydrothermal dimerization of styrene (Table 1). In the presence of copper(II)/iron(III) sulfate, the pathway distribution of 2-phenyl-2-propanol looks very similar to that in pure water (Figure 8). The sulfates do not promote the oxidation of alcohol but instead change the product distribution in the dehydration pathway, making both methylstyrene and the dimers the major products (Table 3), similar to the chloride salts. In contrast to the chlorides and sulfates, the presence of copper(II) and iron(III) nitrate substantially elevates the oxidation pathway% of 2-phenyl-2- propanol, from 5.4% (pure water) to 51.4% and 58.5%, respectively (Table 3), with benzoic acid formed as the major product. Meanwhile, the dehydration pathway% is reduced from 89.1% (pure water) to 28.3% (copper nitrate) and 19.4% (iron nitrate), with no dimers formed (Table 3). These results, again, are consistent with the trends observed for 1- phenylethanol (Figure 6; Table 1). The similar trends between 2-phenyl-2-propanol and 1-phenylethanol suggest that the copper(II) and iron(III) salts may exhibit predictable effects on reactions of different alcohols under hydrothermal conditions.

2.3.4 Relative Alcohol Reactivity under Hydrothermal Conditions

The reactivity of the three studied alcohols follows the trend of 2-phenyl-2-propanol>1-phenylethanol>2- phenylethanol at 200 °C and 15 bar (Figures 6, 7, 8). The difference in alcohol reactivity should be dependent on their structures and the associated reaction pathways and mechanisms. As described earlier, it is likely that an E1 mechanism is associated with the hydrothermal degradation of these alcohols, since the

degradation rate follows as tertiary>secondary>primary; however, the E2 mechanism still cannot be ruled out, as primary alcohols tend to favor E2 over E1 eliminations.[47] Although dehydration is usually considered a dominating hydrothermal pathway for alcohols,[13,47] it may not be a major pathway for certain primary alcohols such as 2-phenylethanol. This could be explained by the much less facile formation of the primary carbocation intermediate (e.g., from 2-phenylethanol) than that of the tertiary intermediate (e.g., from 2-phenyl-2-propanol), which can be stabilized by the more substituted carbocation through the E1 mechanism.[109-110] The reactivity of primary alcohol 2-phenylethanol at a higher temperature (250 °C, 40 bar) and a longer reaction time (24 h) is also investigated, but only ∼17.6% of the alcohol reacts (data not shown), still considerably lower than that of 1- phenylethanol (∼52.6%) and 2-phenyl-2-propanol (∼94.5%) at 200 °C after 2 h (Tables 1 and 2). These results suggest that primary alcohols may have a longer lifetime than secondary or tertiary alcohols in natural hydrothermal fluids, which would allow oxidized products such as aldehydes and carboxylic acids to form in a more competitive way toward supporting the deep biosphere.[111-114]

2.3.5 Control of Copper and Iron Salts on Alcohol Hydrothermal Transformations

The influence of copper- (II) and iron(III) salts on hydrothermal transformation of alcohols are twofold: (1) they affect the alcohol reactivity and reaction rate, and (2) they alter the reaction pathways and product distributions. Among the studied salts, for example, copper(II)/iron(III) sulfate increases the reactivity of 1- phenylethanol and accelerates the alcohol decomposition rate (Figure 6), whereas copper(II)/iron(III) nitrate enables the highest conversion for 2-phenylethanol (Figure 7). The copper/iron-promoted

reactions are also associated with the alteration of alcohol reaction pathways. For example, copper- (II)/iron(III) sulfate tends to facilitate the dehydration pathway for 1-phenylethanol and 2-phenyl-2-propanol, while copper(II)/iron(III) nitrate exhibits the strongest oxidizing power and makes the oxidation pathway dominant for all three alcohols (Figures 6,7,8). This particular and highly oxidizing effect of nitrates has also been shown in the previous study, where cupric nitrate is effective in oxidizing aldehydes to carboxylic acids under similar hydrothermal conditions.[71] In the present study, alcohol experiments with another nitrate salt, sodium nitrate ($NaNO_3$), were also conducted at 200 °C for 2 h. However, interestingly, the oxidation pathway% of 1- phenylethanol, 2-phenylethanol, and 2-phenyl-2-propanol are all found to be very low (<5%), which are nearly identical to those in pure water under the same experimental conditions (Tables 1, 2, 3). This finding demonstrates that nitrate ions alone are incapable of driving the oxidation pathway of alcohols, and both copper(II)/iron(III) and nitrate ions are required to trigger the reaction. It is likely that copper/iron ions serve not only as an oxidant but also as a catalyst, and the formation of metal−nitrate complexes is essential for the oxidation to occur. In addition, the present study shows that the copper(II) and iron(III) salts with the same anions have quite similar effects on both alcohol conversion and pathway% changes (Figures 6, 7, 8), suggesting a more important role of the metal−anion complexes in these alcohol hydrothermal transformations.

The presence of copper and iron salts also changes the solution pH for the alcohol reactions. The measured pH in the copper(II)/iron(III) solutions (2−4) is significantly lower than that in nonmetal solutions (∼5.7) at room temperature, which likely makes the acid-catalyzed dehydration and dimerization more favorable under hydrothermal

conditions.[70,96,104] However, since the conducted hydrothermal experiments are not pH-buffered, the actual solution pH can be quite different under the experimental conditions (e.g., water dissociation constant K_w increases more than two orders of magnitude from 25 to 200 °C). Furthermore, the metal salts are expected to form various types of metal−anion complex species as a function of the solution oxidation state,[19] which could also influence the pH of the hydrothermal solution. In addition, the dehydration and oxidation reactions can be associated with pH changes and potentially influence the rate of each other. For example, oxidation of alcohol to aldehyde by copper(II) or iron(III) may result in the production of H^+ (see eq 5 below as an example), which would affect the rates of dehydration and dimerization. Our experimental results show that in the presence of copper(II)/iron(III) sulfate, the total concentrations of the dehydration products including styrene, methylstyrene, and their dimers are more accumulated for 1-phenylethanol and 2-phenyl-2-propanol than those in pure water (Tables 1 and 3). However, this acid-catalyzed dehydration pathway is not accelerated by the chloride or nitrate, which could be best explained by the increased formation of oxidized products that makes the oxidation pathway more competitive (Figures 6,7,8). These findings suggest that the promoted alcohol dehydration could be partially attributed to the change of pH in the copper and iron solutions, but the pathway may also be limited due to the increased oxidation of alcohols by the dissolved copper(II) and iron(III).

2.3.6 Geochemical Calculations and Implications

$$\mathrm{CH_3(CH_2)_nOH_{(aq)} \rightleftarrows C_{n+1}H_{2n+2(aq)} + H_2O} \quad (1)$$

$$k_{eq} = \frac{a(alkene_{(aq)})a\mathrm{H_2O}}{a(alcohol_{(aq)})} \quad (2)$$

Because of the central position that alcohols occupy in the organic functional group interconversions (Scheme 1), their transformations are important to drive the formation of other organic structures in the organic carbon pool. For example, dehydration of alcohols widely occurs in hydrothermal systems and is a feasible way to produce alkene structures. Alcohol dehydration is favored under hydrothermal conditions because the entropy effect could be more important than the enthalpy effect at elevated temperatures.[13,70] Thermodynamic calculations show that the equilibrium constant (K_{eq}) for alcohol dehydration is sensitive with temperature changes, and the log K_{eq} becomes more positive with increasing temperature. As an example, the generic reaction for alcohols to form alkenes through dehydration can be written as follows (eq 1). where n ($\geqslant$ 0) represents the number of $-CH_2$ groups in the alcohol structure. The equilibrium constant for this reaction can be given by eq 2. where aH_2O can be assumed $\approx$ 1 in deionized water, and K_{eq} is thus equivalent to the activity ratio of the alkene to the alcohol. As shown in Figure 9, the calculated log K_{eq} for the dehydration of 1-propanol, 1-butanol, and 1-pentanol all increases with temperature at water saturation pressure (P_{sat}), and for 1-propanol and 1-butanol, the log K_{eq} shifts from negative to positive at temperature around 200 °C.[101] A positive log K_{eq} means that the reaction is prone to the direction of forming alkene and water, which is consistent with what we observed in the alcohol hydrothermal experiments. However, the log K_{eq} for 1-pentanol is still negative even at 300 °C (Figure 9), suggesting that the equilibrium constants should be dependent on the alcohol structure, and not all of the alcohol compounds can favor the dehydration at the temperature between 200 and 300 °C. This observation may also help to explain why we

observe a much slower dehydration rate for 2-phenylethanol than for 1-phenylethanol and 2-phenyl-2-propanol at 200 °C.

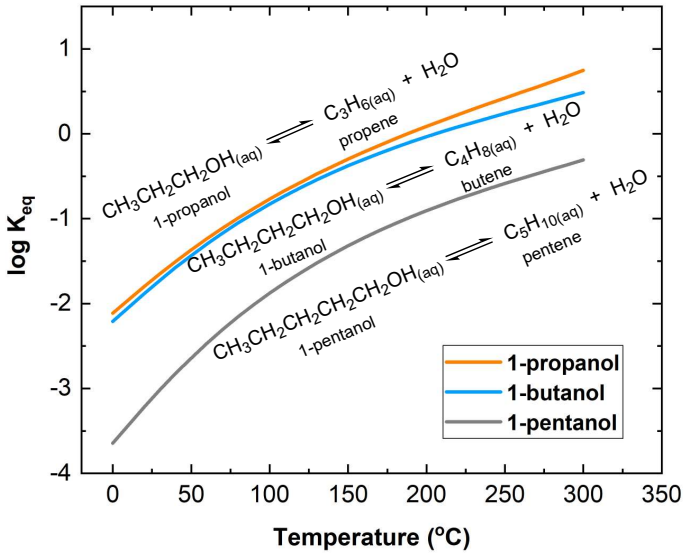


Figure 9. Calculated equilibrium constant (log K_{eq}) for dehydration of 1-propanol (orange curve), 1-butanol (blue curve), and 1-pentanol (gray curve) as a function of temperature at P_{sat} (water saturation vapor pressure). When log K_{eq} is above zero, the equilibrium favors the alcohol dehydration direction to form alkene and water. The log K_{eq} values were calculated by SUPCRT92, assuming $aH_2O = 1$.

Compared to the thermodynamically favored dehydration pathway, the oxidation of alcohols is much less favored according to geochemical calculations. Oxidation reaction of alcohols to form aldehydes can be written as follows (eq 3).

$$\underset{alcohol}{CH_3(CH_2)_nOH_{(aq)}} \rightleftarrows \underset{aldehyde}{C_{n+1}H_{2n+2}O_{(aq)}} + H_{2(aq)} \quad (3)$$

$$k_{eq} = \frac{a(aldehyde_{(aq)})aH_{2(aq)}}{a(alcohol_{(aq)})} \quad (4)$$

where n ($\geqslant 0$) represents the number of $-CH_2$ groups in the alcohol structure. Similarly, the equilibrium constant for this reaction can be given by eq 4. Using ethanol

and butanol as an example, the calculated log K_{eq} values for their oxidation reactions also increase with temperature but are all negative below 300 °C (Figure 10), which are more than 4 orders of magnitudes lower than the log K_{eq} for alcohol dehydration reactions at the same temperature range (Figure 9). These modeling results suggest that alcohol oxidation is not favored in pure hydrothermal water, which is consistent with our experimental results (Figures 6,7,8). The equilibrium of this reaction, however, can be greatly shifted by the presence of oxidizing metal ions such as Cu^{2+}. For example, oxidation of ethanol with Cu^{2+} to form acetaldehyde can be written as eq 5. and the equilibrium constant can be given by eq 6. In this case, the equilibrium considerably shifts to the aldehyde as the log K_{eq} becomes positive at temperature as low as 70 °C (Figure 10). Similarly, the log K_{eq} curve for butanol oxidation with Cu^{2+} also shifts upward by orders of magnitude (Figure 10), which favors the aldehyde formation between 100 and 300 °C. Note that these calculations are simplified without considering the aqueous speciation of Cu(II) and Cu(I) at elevated temperatures and pressures (mainly due to the lack of actual Cu^{2+} and Cu^{+} activity measurements in the hydrothermal experiments), although it is known that copper tends to form complexes (e.g., with chloride) under hydrothermal conditions.[71,19] From these simplified and nonideal calcuations, however, the shifts in log K_{eq} do suggest a strong thermodynamic drive for alcohol oxidation by the metal ions (e.g., $Cu^{2+)}$. The consistency between the hydrothermal experiments and the geochemical modeling reveals that hydrothermal transformations of alcohols can be controlled by surrounding dissolved metals at the seafloor and deep sedimentary basins. Along with other key parameters such as pH, temperature, and the oxidation state of hydrothermal fluids,[53,115-117] the type, speciation,

and concentration of redox- sensitive metal salts may also serve as important geochemical indicators for organic functional group interconversions in hydrothermal systems.

$$\underset{ethanol}{CH_3CH_2OH_{(aq)}} + 2Cu^{2+} \rightleftarrows \underset{acetaldehyde}{CH_3CHO_{(aq)}} + 2Cu^{2+} + 2H^{+} \quad (5)$$

$$k_{eq} = \frac{a(acetaldehyde_{(aq)})a(Cu^{+})^2 a(H^{+})^2}{a(ethanol_{(aq)})a(Cu^{2+})^2} \quad (6)$$

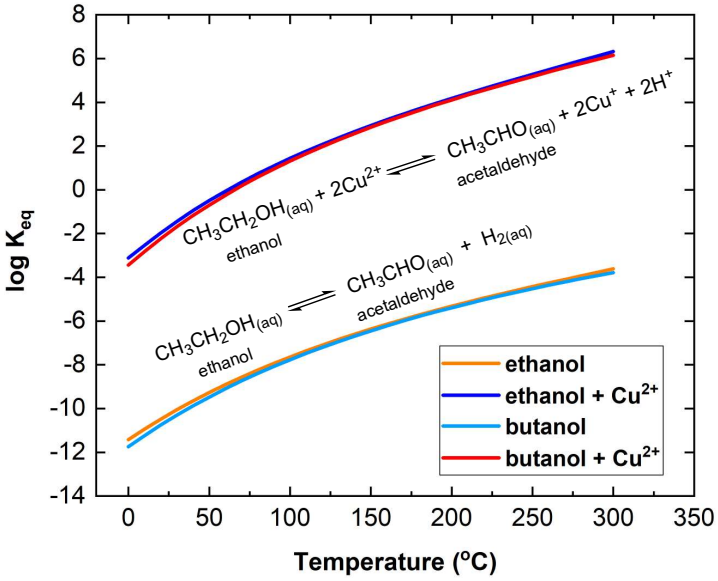


Figure 10. Calculated equilibrium constant (log Keq) for oxidation of ethanol (orange) and butanol (light blue) without Cu^{2+} and oxidation of ethanol (blue) and butanol (red) with Cu^{2+} as a function of temperature at P_{sat} (water saturation vapor pressure). Note that the calculation was simplified without considering the speciation of copper at elevated temperatures and pressures (see the text). When log K_{eq} is above zero, the equilibrium favors the alcohol oxidation to form aldehyde. The log K_{eq} values were calculated by SUPCRT92, assuming $aH_2O = 1$.

2.4 Conclusion

In this work, hydrothermal experiments of model primary, secondary, and tertiary alcohol compounds are performed to examine the alcohol reaction pathways and the influence of dissolved metal salts. Dehydration is a favorable and dominating pathway for alcohols under hydrothermal conditions, while the reactivity of alcohols follows the trend of tertiary>secondary>primary. The oxidation pathway is also observed for alcohols that can form oxidized products such as aldehydes and carboxylic acids, and the pathway can be expedited by the presence of copper(II) and iron(III) salts. The oxidative effects are similar between the copper and iron salts with the same counterions, whereas the extent of oxidation is strongly dependent on the type of the anions, with the nitrate exhibiting the highest oxidizing capacity. These uncovered dissolved metal-promoted alcohol reactions provide an alternative and effective path for interconverting and diversifying organic functional groups in hydrothermal geological environments. In addition, these remarkable reactions also demonstrate the important but often overlooked roles of surrounding inorganic materials in organic matter transformations at elevated temperatures and pressures. Further work on other Earth-abundant materials such as dissolved zinc and manganese would also be worth investigating to identify the complex organic−inorganic interactions in oceanic hydrothermal systems.

CHAPTER THREE

ANAEROBIC OXIDATION OF ALDEHYDES TO CARBOXYLIC ACIDS UNDER HYDROTHERMAL CONDITIONS

3.1 Introduction

The oxidation of aldehydes holds a pivotal role in the realm of organic transformations. It's a core reaction with considerable significance, not only for biological metabolism but also for the production of chemicals in industrial processes.[118-119] For instance, within biological systems, aldehydes can be oxidized to carboxylic acids through the action of enzymes known as aldehyde dehydrogenases, which serve to detoxify and inactivate aldehydes, facilitating their removal from the body.[120-121] In an industrial context, the oxidation of aldehydes finds applications in the manufacturing of a variety of goods, including cosmetics, plasticizers, fibers, and chemicals derived from biomass.[122-123] Given the extensive processes and applications associated with it, there is an urgent requirement for efficient and environmentally friendly methods to oxidize aldehydes to carboxylic acids. Aldehyde conversions in water encompass a broad spectrum of chemical reactions where aldehydes are morphed into different compounds. This includes hydration, where aldehydes can be transformed into geminal diols, such as when formaldehyde changes to methanediol in the presence of acid or base catalysts.[124] Aldehydes can also be oxidized into carboxylic acids using oxidizing agents such as Tollens' reagent or Fehling's solution, a process exemplified when ethanol is converted first to acetaldehyde, and then to acetic acid.[125] Another transformation is the Cannizzaro reaction, where, in a strongly alkaline aqueous solution, an aldehyde without an alpha-

hydrogen atom can be converted to a carboxylic acid and an alcohol, as seen with benzaldehyde's conversion to benzoic acid and benzyl alcohol.[126] Lastly, aldehydes can undergo an aldol reaction in the presence of a base and water, leading to the creation of a beta-hydroxy aldehyde, like the transformation of acetaldehyde into 3-hydroxybutanal.[127] Each reaction is contingent upon specific conditions such as pH, temperature, and the presence of catalysts. In these traditional methods, aldehydes are oxidized stoichiometrically, often using hazardous oxidants such as the Cr(VI)-based Jones reagent, the Ag(I)-based Tollen's reagent, the Cu(II)-based Fehling's reagent, or permanganate-based catalysts.[128-131] These conventional methods also generate stoichiometric amounts of waste by-products, which are often toxic and expensive to recycle.[122] To alleviate these problems, chemists have focused on developing "greener" processes for catalytic oxidation of aldehydes. For example, previous studies have used water as an environmentally friendly solvent for oxidation of aldehydes,[118,119,122,132,133] which prevents the involvement of harmful organic solvents. However, this method could suffer from the necessity for large amounts of additives and expensive or toxic catalysts. Recently, studies have focused on finding alternative catalysts that are more naturally abundant and low-cost. For example, metal salts such as iron and copper have been applied to the oxidation of aldehydes as catalysts in aqueous solutions.[130]

Currently, most investigations on aldehyde oxidations focus on aerobic oxidation, i.e., using molecular oxygen (O_2) to oxidize aldehydes into the corresponding carboxylic acids.[122,129,134] Autoxidation of aldehydes with O_2 also takes place at ambient conditions, which usually involves a free radical chain reaction to form peracid, followed by the Baeyer–Villiger oxidation.[135-136] In comparison, fewer studies have explored the

anaerobic oxidation pathway for aldehydes, especially in catalyst-free aqueous environments. Hydrothermal systems, however, may provide a unique environment for anaerobic organic redox reactions. Our recent research on alcohols, carboxylic acids, and amides have shown that organic oxidations can readily occur in the presence of metal salts such as Cu(II) under O_2-absent hydrothermal conditions.[41,71,74] In those reactions, water serves as a green solvent, while Cu(II) acts as an efficient oxidant. The metal-promoted hydrothermal reactions also mimic natural geochemical processes on Earth, which provides the new "geomimicry" concept of using Earth-abundant metals as the oxidant/reductant for green organic reactions.[19,41,70] In this study, we investigated the oxidation of aldehydes to carboxylic acids in an anaerobic and mild hydrothermal environment, using simple Cu(II) and non-toxic Fe(III) salts as the oxidizing agent. The optimal reaction condition and the substrate scope were both studied.

3.2 Experimental Methods

3.2.1 Materials

Aldehydes including benzaldehyde (99%), 2-(trifluoromethyl)benzaldehyde (98%), 2- bromobenzaldehyde (98%), 4-bromobenzaldehyde (99%), hydrocinnamaldehyde (90%), p- tolualdehyde (97%), 4-methoxybenzaldehyde (98%), cyclohexanecarboxaldehyde (97%), cinnamaldehyde (95%) and 2-naphthaldehyde (98%) were purchased from Sigma-Aldrich and used without purification. Carboxylic acids including benzoic acid (99%), 2- (trifluoromethyl)benzoic acid (98%), 2-bromobenzoic acid (97%), 4-bromobenzoic acid (98%), hydrocinnamic acid (99%), p-toluic acid (98%), 4-methoxybenzoic acid (99%), cyclohexanecarboxylic acid (98%), trans-cinnamic acid (97%), and 2-naphthoic acid (98%) were also obtained from Sigma-Aldrich and used as

standards for product identification and quantification. Metal salts including cupric nitrate (99%), ferric nitrate (99%), sodium nitrate (99%), cupric chloride (99%), ferric chloride (99%), cupric sulfate (99%), and ferric sulfate (99%) were all obtained from Sigma-Aldrich. Styrene (99%), α−methylstyrene (99%), acetophenone (99%), diphenylmethanol (99%), benzophenone (99%), benzaldehyde (99%), and benzoic acid (99%) were also obtained from Sigma-Aldrich and used as received. Dichloromethane (DCM, 99.9%) was obtained from VWR and used as the organic extraction solvent. Decane (≥99%) was purchased from Sigma-Aldrich and used as the gas chromatography (GC) internal standard. Deionized water (18.2 MΩ·cm) used for the hydrothermal experiments was obtained from a Barnstead Nanopure system.

3.2.2 Methods

General experimental procedure for the hydrothermal oxidation of aldehydes is as follows: the aldehyde (0.03 mol) was first loaded to a fused silica glass tube (2 mm ID and 6 mm OD), followed by the addition of 0.3 mL of N_2-purged deionized water or metal salt solution (0.03 – 0.06 mol). Then the tube was placed in liquid nitrogen, evacuated through three freeze-pump-thaw cycles to remove air/oxygen, and sealed with an oxyhydrogen flame. The reaction mixture in the tube was then heated in a GC oven at 200 °C and 15 bar (P_{sat}, calculated using SUPCRT92)[101] for up to 24 h, and the reaction was quenched by submerging the silica tubes in a cold water bath. The products were extracted with 3.0 mL DCM containing 8.8 mM decane, and the pH of the aqueous layer was adjusted to ~2 with HCl solution before the extraction. An Agilent 7820A GC system equipped with an autosampler and a flame-ionization detector was used to analyze and quantify the carboxylic acid products and the remaining of the starting aldehydes.

The concentration of each aldehyde and carboxylic acid was quantified by GC using calibration curves established with authentic samples. The product identification was further confirmed by a gas chromatograph-mass spectrometer (Agilent 7890A/5975C) based on fragmentation patterns in the mass spectra. Small amounts of by-product include nitro compounds (from nitrate experiments), C–C cleavage products, and possible isomer structures were also detected.

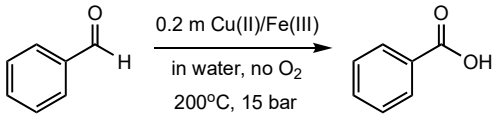
3.3 Results and Discussion

3.3.1 Investigation of oxidation of benzaldehyde with varied hydrothermal conditions

Hydrothermal experiments were conducted in sealed fused silica tubes under an aqueous condition of 200 °C and 15 bar (P_{sat}, calculated using SUPCRT92)[101] in the absence of O_2, following a previously developed method.[71,100] We started our investigation by examining the oxidation of benzaldehyde (compound 1) under hydrothermal conditions using various Cu(II) and Fe(III) salts, including $CuCl_2$, $CuSO_4$, $Cu(OAc)_2$, $Cu(NO_3)_2$, $FeCl_3$, $Fe_2(SO_4)_3$, and $Fe(NO_3)_3$ (Table 4). In pure water without additives, only 4% of benzaldehyde reacted at 200 °C after 24 h, forming benzoic acid with a yield of ~3% (entry 1). This slow reaction indicates that benzaldehyde is relatively inert under the anaerobic hydrothermal conditions, which is consistent with a previous study reporting <1% conversion for benzaldehyde at 250°C after 36 h.[93] In the presence of $CuCl_2$, $CuSO_4$, and $Cu(OAc)_2$, both the benzaldehyde conversion (6–9%) and the acid yield (5–8%) at 200°C were slightly increased after 24 h (entries 2–4). However, their effects were not as prominent as $Cu(NO_3)_2$, which increased the yield to 10% and 26% after 0.5 and 2 h, respectively (entries 5 and 7). $NaNO_3$ was also tested and gave a yield

of 10% after 2 h (entry 9), suggesting that the aldehyde oxidation could be driven by the nitrate ions, but not as strong as the copper–nitrate complex. In the presence of $FeCl_3$ and $Fe_2(SO_4)_3$, the acid yields were 10– 13% at 200℃ after 24 h (entries 10 and 11), which were similar to those with $CuCl_2$ and $CuSO_4$. The most dramatic effect comes from $Fe(NO_3)_3$, which converted 64% of benzaldehyde with a boosted yield of 60% at 200℃ only undergoing 0.5 h heating(entry 15). Increasing the reaction time to 2 h allowed $Fe(NO_3)_3$ to fully oxidize benzaldehyde, reaching the highest acid yield (98%, entry 17) among all the conditions studied. Halving the starting concentration of $Fe(NO_3)_3$ lowered the yield to 90% (entry 18), while decreasing the reaction temperature also reduced the yield significantly (entries 12–14). Interestingly, combining $FeCl_3$ with $NaNO_3$ exhibited a very high yield as that with $Fe(NO_3)_3$ (entries 19 and 20), which suggests the key of this aldehyde oxidation is having both Fe(III) and nitrate ions present. Additionally, nitrates of redox-neutral metals such as $Mg(NO_3)_2$ and $Ca(NO_3)_2$ were also investigated (entries 21 and 22), which showed a significantly lower yield than that of $Fe(NO_3)_3$ or $Cu(NO_3)_2$. These results further indicate that both the redox metals and nitrate ions play an oxidizing role in this reaction.

Table 4. Investigation of oxidation of benzaldehyde using copper(II) and iron(III) salts at different reaction conditions (*yield determined by gas chromatography).

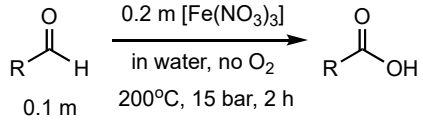


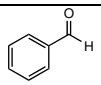
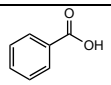
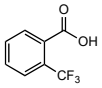
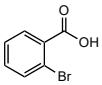
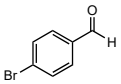
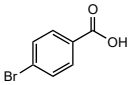
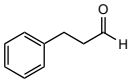
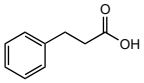
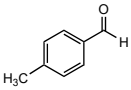
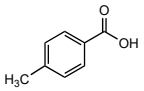
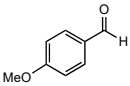
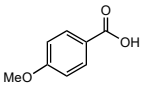
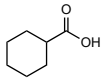
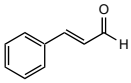
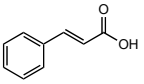
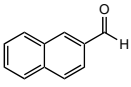
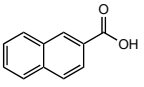
Entry	Condition	Additive	Conversion	Benzoic acid yield*
1	200 ºC, 24 h	None	4%	3%

Table 4. Investigation of oxidation of benzaldehyde using copper(II) and iron(III) salts at different reaction conditions (*yield determined by gas chromatography). (Continued)

Entry	Condition	Additive	Conversion	Benzoic acid yield*
2	200 ºC, 24 h	0.2 m $CuCl_2$	8%	7%
3	200 ºC, 24 h	0.2 m $CuSO_4$	9%	8%
4	200 ºC, 24 h	0.2 m $Cu(OAc)_2$	6%	5%
5	200 ºC, 0.5 h	0.2 m $Cu(NO_3)_2$	12%	10%
6	200 ºC, 1 h	0.2 m $Cu(NO_3)_2$	25%	24%
7	200 ºC, 2 h	0.2 m $Cu(NO_3)_2$	30%	26%
8	200 ºC, 2 h	0.1 m $Cu(NO_3)_2$ + 0.1 m $NaNO_3$	15%	13%
9	200 ºC, 2 h	0.2 m $NaNO_3$	11%	10%
10	200 ºC, 24 h	0.2 m $FeCl_3$	14%	13%
11	200 ºC, 24 h	0.2 m $Fe_2(SO_4)_3$	11%	10%
12	100 ºC, 2 h	0.2 m $Fe(NO_3)_3$	39%	38%
13	140 ºC, 2 h	0.2 m $Fe(NO_3)_3$	59%	57%
14	170 ºC, 1 h	0.2 m $Fe(NO_3)_3$	62%	59%
15	200 ºC, 0.5 h	0.2 m $Fe(NO_3)_3$	64%	60%
16	200 ºC, 1 h	0.2 m $Fe(NO_3)_3$	>99%	94%
17	200 ºC, 2 h	0.2 m $Fe(NO_3)_3$	>99%	98%
18	200 ºC, 2 h	0.1 m $Fe(NO_3)_3$	>99%	90%
19	200 ºC, 2 h	0.2 m $FeCl_3$ + 0.2 m $NaNO_3$	>99%	97%
20	200 ºC, 2 h	0.2 m $FeCl_3$ + 0.6 m $NaNO_3$	>99%	98%
21	200 ºC, 2 h	0.2 m $Mg(NO_3)_2$	23%	21%
22	200 ºC, 2 h	0.2 m $Ca(NO_3)_2$	9%	8%

Table 5. Investigation of substrate scope under a hydrothermal condition of 200 °C, 15 bar after 2 h (*yield determined by gas chromatography).

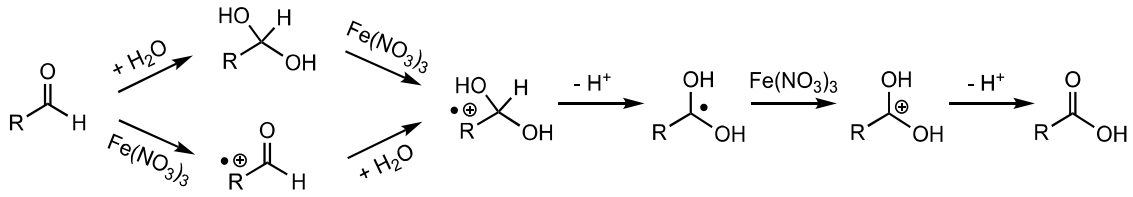


Comp#			Conversion	Acid yield*
1			>99%	98%
2			83%	82%
3			56%	47%
4			68%	66%
5			66%	45%
6			55%	54%
7			63%	46%
8			66%	58%
9			48%	30%
10			42%	41%

3.3.2 Investigation of substrate scope under optimal anaerobic hydrothermal oxidation method

After identifying the optimal reaction conditions, we then tested with a group of 9 different functionalized aldehydes to examine the scope of this method (Table 5). All of these experiments were conducted using 2 equiv. $Fe(NO_3)_3$ at 200℃ and 15 bar for 2 h. Compared to the 98% yield from benzaldehyde, the aromatic aldehyde with an electron-withdrawing group (compound 2) gave a yield of 82%, whereas the ones with electron-donating groups such as p-tolualdehyde (compound 6) and 4-methoxybenzaldehyde (compound 7) gave a much lower yield of 54% and 46%, respectively. However, the relatively low yields from the electron-rich aldehydes are mainly due to the less-complete conversion of the starting material, which is expected to increase at longer reaction times. Halogen- substituted aldehydes such as 2-bromobenzaldehyde (compound 3) and 4-bromobenzaldehyde (compound 4) gave an acid yield of 47% and 66%, respectively, indicating the tolerance of this method for halogens and also a potential steric effect. Non-aromatic aldehydes such as hydrocinnamaldehyde (compound 5) and cyclohexanecarboxaldehyde (compound 8) also gave a moderate yield of 45% and 58%, respectively. Unsaturated aldehyde cinnamaldehyde (compound 9) also worked with this method, but the yield (30%) was lower than that of hydrocinnamaldehyde. The result suggests that the C-C double bond potentially interferes with the oxidation, which seems consistent with the results from another study on silver-catalyzed aldehyde oxidation.[119] In addition, other aldehydes such as 2-naphthaldehyde (compound 10) resulted in a 41% yield under the same experimental conditions, demonstrating this method is also applicable to fused-ring aldehyde structures.

We also proposed a tentative mechanism for this Fe(III)-involved aldehyde oxidation. As shown in Scheme 5, aldehydes are expected to undergo either the hydration followed by oxidation pathway or the oxidation followed by hydration pathway to form a radical cation intermediate. Resulting from losing a proton, the radical cation could be subsequently oxidized by $Fe(NO_3)_3$ to form a carbocation before the corresponding acid is produced. This reaction mechanism is also based on proposed mechanisms in previous studies, where Cu(II) has been found as an oxidant for the oxidation of benzyl alcohol and benzaldehyde under similar hydrothermal conditions.[71,74] In the present study, however, the electron-donating $–CH_3$ and $–CH_3O$ substituted benzaldehyde resulted in a lower conversion than that of the $–CF_3$ substituted benzaldehyde (Table 5), which does not seem to support the formation of a positively charged intermediate. It is thus more likely that the hydrate formation is the rate-determining step, since the substituent effect on hydrate formation could be opposite to that on oxidation.[19,137] More ring-substituted structures and detailed kinetics studies are needed to further pinpoint the reaction mechanisms.



Scheme 4. Proposed mechanism for anaerobic oxidation of aldehydes to carboxylic acids with $Fe(NO_3)_3$ as the oxidant.

3.3.3 Thermodynamic Calculations

In addition, we performed thermodynamic calculations for the anaerobic oxidation of aldehyde under a range of hydrothermal conditions. Thermodynamic calculations on aqueous oxidation of aldehyde were conducted using the software SUPCRT92,[101] with the revised Helgeson-Kirkham-Flowers equation of state.[10,138] Acetaldehyde was chosen as a representative aldehyde structure based on its availability in the geochemical database.

Equilibrium constants (log K_{eq}) were calculated for the oxidation of acetaldehyde to acetic acid in pure water (Eqn 6) and in the presence of $Fe(NO_3)_3$ (Eqn 7), respectively, at temperatures from 0 to 300 °C at P_{sat}. Using acetaldehyde as a model aldehyde, results show that the logarithm of equilibrium constant (log K_{eq}) of oxidation of acetaldehyde to acetic acid in pure water was between 0 and 1 under the hydrothermal condition and slowly increased with temperature (Figure 11). In contrast, the log K_{eq} for $Fe(NO_3)_3$-promoted acetaldehyde oxidation was orders of magnitude higher, which suggests the reaction is highly favorable when $Fe(NO_3)_3$ is present (Figure 11). Although the actual log K_{eq} values for the aromatic aldehydes could be quite different from that of acetaldehyde, the increasing trend of log K_{eq} by the addition of $Fe(NO_3)_3$ may hold true for other aldehyde structures. The results of geochemical modeling are consistent with our experimental observations.

$$\underset{acetaldehyde}{CH_3CHO_{(aq)} + H_2O} \rightleftarrows \underset{acetic\ acid}{CH_3COOH_{(aq)} + H_2} \tag{7}$$

$$k_{eq} = \frac{a\left(acetic\ acid_{(aq)}\right) aH_{2(aq)}}{a\left(acetaldehyde_{(aq)}\right)} \tag{8}$$

$$\underset{\textit{acetaldehyde}}{CH_3CHO_{(aq)}} + 2Fe^{3+} + 6NO_3^- + H_2O \rightleftarrows \underset{\textit{acetic acid}}{CH_3COOH_{(aq)}} + 2Fe^{2+} + 4NO_3^- + 2HNO_{3(aq)} \quad (9)$$

$$k_{eq} = \frac{a(acetic\ acid_{(aq)})\,a(Fe^{2+})^2\,a(HNO_{3(aq)})^2}{a(acetaldehyde_{(aq)})\,a(Fe^{3+})^2\,a(NO_3^-)^2} \quad (10)$$

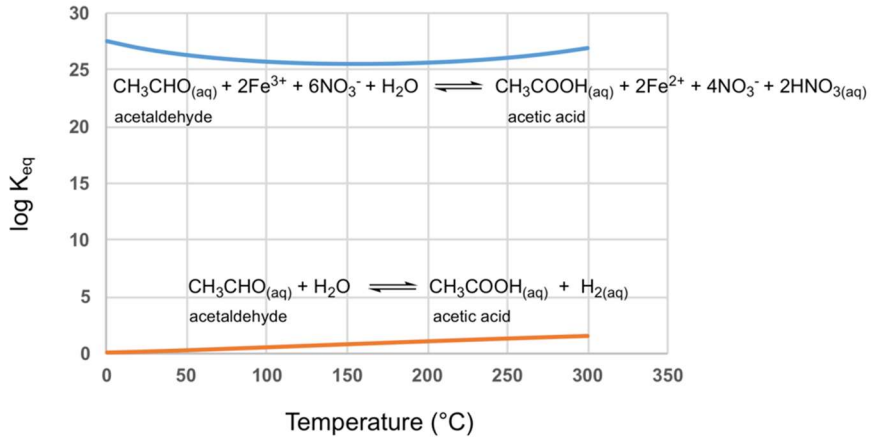


Figure 11. Calculated equilibrium constant (log K_{eq}) for oxidation of acetaldehyde to acetic acid in water with (blue) and without (orange) $Fe(NO_3)_3$, as a function of temperature at water saturation vapor pressure, using SUPCRT92. [93]

3.4 Conclusion

In conclusion, we reported the first examples of oxidation of aldehydes with $Fe(NO_3)_3$ in water under anaerobic hydrothermal conditions. The oxidation is green and relatively clean, with relatively high yields of carboxylic acids achieved within hours. Different aldehyde structures were tested to show a good versatility of the reaction. This method also represents one of the "geomimicry" approaches that use Earth-abundant geological materials for organic synthesis and green chemistry applications. Future investigation on the reaction mechanism and the potential effects of other metal salts is anticipated.

Similar to the hydrothermal oxidation method, supercritical water oxidation (SCWO) processes also occur in water but above its critical point (374°C and 218 atmospheres).[139] Above this threshold, water enters a 'supercritical' state where it exhibits properties of both a liquid and a gas, including increased reactivity and the ability to mix with both organic and inorganic compounds. This makes SCWO a more efficient process, allowing for faster and more complete oxidation of organic compounds. However, the SCWO of aldehydes are drastic and always convert completely compounds to carbon dioxide and water, which may not derive the formation of goal acids even though the method exhibits high efficiency.[140] While the specific conditions and efficiencies of the SCWO can greatly impact the course of the reactions and the products formed, hydrothermal oxidation is typically associated with natural geological processes and more benign conditions so we can utilize Earth-abundant oxidants and solvents where the processes could be well controlled and avoid secondary by-products .

CHAPTER FOUR

KINETICS STUDY ON THE DEAMINATION OF AMINES UNDER HYDROTHERMAL CONDITIONS

4.1 Introduction

The cycle of organic nitrogen (N) in geological settings has recently garnered significant attention due to the vital roles of organic N compounds in Earth's life processes.[141-142] In some extents, understanding the behavior of organic nitrogen compounds under a variety of geochemical circumstances will enhance our quantitative models of both current and prehistoric global nitrogen cycles on Earth.[143-144] The transformation of nitrogen compounds under ambient conditions has been thoroughly explored through traditional experiments in gas-phase and aqueous-phase organic chemistry.[145-146] Given the significance of nitrogen-rich structures in biochemistry, the nitrogen cycle at the Earth's surface has been given particular emphasis.[147-149] However, the more extensive subject of geological nitrogen cycling, which involves considerable variations in temperature, pressure, and composition, has received considerably less focus, especially from an organic mechanistic standpoint.

It’s estimated that the amount of organic nitrogen present in sediment and crustal rocks considerably surpasses that in the biosphere, and this disparity is primarily attributed to the burial of biomass.[150-151] Proteins and nucleic acids are the primary storage of organic nitrogen found in all living organisms, with proteins significantly exceeding nucleic acids in terms of their portion of cellular mass.[152] One of the predominant decomposition reactions for proteins in water is their hydrolysis into amino

acids, particularly under high-temperature conditions.[153] This suggests that ensuing reactions of amino acids, such as deamination, might significantly influence geological nitrogen cycling. Correspondingly, high concentrations of ammonium have been detected in both marine and continental hydrothermal fields, and even the analyzing results from collected carbonaceous meteoritic samples.[154] Due to abundant amines and amino acids in these areas, deamination reactions were implied as the critical processes in N cycle in abiotic environment either on Earth or beyond the solar system.[155]

The reaction pathways and mechanisms of organic nitrogen components, including amines, amino acids, and amides, have been the subject of exploration under deep subsurface conditions.[156,157] Importantly, amino acids and peptides are essential for microorganisms, in both ordinary and extreme environments, such as land-based hot springs and deep-sea hydrothermal vents.[158] Hydrothermal settings, defined by high-pressure, high-temperature aqueous conditions, are not just widespread on Earth, but are also believed to exist beyond our planet, for instance, within Saturn's ice-encrusted moon, Enceladus.[159-160] Hydrothermal organic reactions could influence the maturation process of petroleum and generate key biomolecules that feed the deep biosphere.[161] Furthermore, it is speculated that the abiotic creation of organic nitrogen might have a significant impact on the initiation and evolution of life within hydrothermal systems.[162] Despite this, our understanding of hydrothermal transformations of organic nitrogen remains incomplete, limiting our grasp of the deep nitrogen cycle and our capacity to assess the habitability of other planets.

Organic compounds hold potential to act as geochemical markers in a variety of extraterrestrial aqueous environments throughout the solar system's history. These

environments range from primordial entities such as carbonaceous meteorites to active icy ocean worlds that may harbor current life-sustaining conditions.[163-166] However, many of these systems contain or have contained aqueous solutions that are chillier than the Earthly systems where the balancing of organic carbon redox reactions has been noted.[167-168] Hydrothermal experiments cited earlier suggest that to achieve balance in such reactions, temperatures may need to exceed 200 °C.[169-170] This implies that redox reactions may be too sluggish to serve as geochemical indicators in low-temperature environments. Fortunately, a distinct set of reactions known as substitution reactions are common to naturally occurring organic compounds and tend to proceed at a faster pace than redox reactions. This indicates that substitution reactions may reach equilibrium at lower temperatures than redox reactions, thereby providing the potential to document reaction conditions in colder settings.

Deamination of amines through substitution has been demonstrated to reach equilibrium more swiftly than corresponding organic redox reactions under hydrothermal conditions.[171] For instance, the deamination of benzylaminium via water substitution, yielding benzyl alcohol, was seen to near metastable equilibrium in less than or equal to 72 hours at 250 ℃.[117] This was observed in experiments initiated with either the reactants or the products. Conversely, numerous redox reactions tested under similar conditions at temperatures of 250 ℃ or above showed no noticeable signs of reaching metastable equilibrium even after hundreds of hours.[68-69] This comparison implies that, even in systems with lower temperatures, deamination substitution reactions are likely to equilibrate more quickly than redox reactions. The aim of this study is to measure the

rates of deamination across a spectrum of temperatures that could be pertinent to a variety of environmental deamination reactions.

Numerous hydrothermal reactions of amines and amino acids were studied, demonstrating the presence of abundant hydrothermal reaction pathways.[172] To investigate the uncertainties in synthetic pathways and mechanisms of amide formation in hydrothermal systems, we previously examined the hydrothermal synthesis scope on 4 carboxylic acids including formic acid, acetic acid, benzoic acid, and phenylacetic acid with 3 amines including benzylamine, cyclohexylamine, and cyclohexanemethylamine, finding the targeted amides can be readily synthesized through a direct condensation between amines and carboxylic acids, with an amide yield of up to 90% over a timescale of hours. Robinson et al. also reported the deamination of protonated benzylaminium and various ring-substituted benzylaminium and methylbenzylaminium derivatives to obtain the S_N1 and S_N2 mechanism and the impact on kinetics from the substituents with pH buffer at 2.2.[46] This diversity in reactivity results partially because of the sensitivity of amine reactions to pH. To illustrate, the pH-dependence (0.15–9.50) of solvolysis of cytosine and cytidine was explored at the elevated temperature from 70 to 90°C,[173] suggesting both acid and base catalyzed deamination reactions and provided comprehensive mechanistic interpretations. By using aqueous buffers to control pH, and maintaining the amines in their protonated forms, it is possible to avoid minerals that can add the complexities of surface catalytic or reactive effects and complicate mechanistic analysis.[174]

With a goal of understanding deamination mechanisms under hydrothermal conditions, we decided to experimentally study their kinetic rate and pathway in different

hydrothermal temperature and pH. Since the deamination mechanisms were studied with aromatic amines, the scope of mechanistic study still requires extending in other non-aromatic N compounds. Inspired by the exciting results from our amide synthesis research, benzylamine, cyclohexylamine, and cyclohexanemethylamine were selected as the model compounds to probe the rate of temperature and pH-dependence in hydrothermal conditions. Aromatic ring structures are not only applicable for mechanistic probes since they can be used to probe charge generation in the rate determining steps,[175-176] but their reaction products are also easily extracted and quantified by analysis on gas chromatography-flame ionization detection. Similar to amines with aromatic rings, cyclohexane amines, which are amines contain cyclohexane ring, are important components in a variety of biological and environmental processes. For instance, histamine and serotonin, as well as numerous alkaloids such as nicotine and morphine, serve as critical neurotransmitters or metabolic pathway components. Environmentally, the breakdown of proteins and other nitrogenous organic matter can yield cyclohexane amines. These compounds can then engage in different environmental reactions, such as acting as aerosol nucleation sites, which influences cloud formation and potentially climate dynamics. Some cyclohexane amines, like pyrrolidine, piperidine, and quinuclidine, can be produced by specific microbial populations and might signal microbial activity in environmental samples such as soils. Moreover, within the realm of prebiotic chemistry, alicyclic amines are postulated to be starting materials in the synthesis of complex organic molecules, such as nucleotides, under conditions that might have been present on the early Earth.[177-180] Here, we perform a study to investigate the

amine deamination pathway and mechanisms using both aromatic and non-aromatic amines in different buffered water (i.e., 2.2 and 7.9) at different temperature.

4.2 Experimental

4.2.1 Materials.

Organic reagents, inorganic buffers, and gases used in this study were purchased from Sigma-Aldrich. Organic reagents purchased fit the following specifications: ≥ 99.5% benzylamine, ≥99.9% cyclohexylamine, ≥98% cyclohexanemathylamine, ≥ 99% N-benzylidenebenzylamine(dibenzylamine), ≥98% cyclohexanol, ≥99.5% benzyl alcohol, ≥99.9% cyclohexane, ≥98% cyclohexanemethanol, ≥99% bis(cyclohexanemethyl)amine, ≥98% cyclohexenol, ≥98% dicyclohexylamine and >98% cyclohexene. As an internal standard for organic analysis, ≥99.0% decane was used. Dichloromethane (99.9%) was used as the solvent for organic extraction and analysis. Reagents used for generating inorganic buffers included 85.0% of aqueous phosphoric acid, ≥99.9% of monosodium (dihydrogen) phosphate, and ≥99.5% of sodium carbonate. Gases used for experimental preparation and analyses included ultrahigh purity (≥99.999%) helium, ultrahigh purity (≥99.999%) argon, ≥99.95% hydrogen , and ≥99.5% oxygen . A high-purity silica "fused quartz" 2 × 6 mm^2 (inner diameter × outer diameter) tubing for constructing reaction vessels was purchased from GM Quartz.

4.2.2 Method

Deamination rates of selected amines were measured in hydrothermal solutions. Reactant solutions were prepared with target concentrations of 0.1 molal benzylamine,

cyclohexylamine, and cyclohexanemethylamine in deionized water that was buffered using phosphoric acid and sodium phosphate salts at a targeted total phosphorus concentration of 50 mmolal. pH buffer at 2.2 and 7.9 was selected to access the rate in acidic and neutral environments. Acid-buffered hydrothermal solution would lead to formation of protonated amines like benzylaminiums.[46] Titration of phosphoric acid and sodium hydroxide to achieve the desired pH sometimes resulted in starting concentrations that varied slightly among protonation, but these differences were not expected to affect the pseudo-first-order kinetics of deamination.[46] Buffered solutions were sparged with argon to remove atmospheric oxygen. Buffer catalysis was previously determined to be negligible by comparing reaction kinetics after doubling buffer concentrations.[46] Buffers were prepared according to calculations performed using the revised Helgeson−Kirkham−Flowers (HKF) equations of state[181-182] and associated thermodynamic data[12,138] within the software programs EQ3/6 and SUPCRT92.[101] These calculations determined the target pH at 25 °C and 1 bar that would yield the desired pH at the experimental conditions of 200 and 275 °C at the liquid−vapor saturation pressure of water (P_{sat} of 16 bar and 71 bar, respectively), following the same methods in the previous study conducted at 250 °C and 40 bar.[117] Experimental solutions were loaded into high-purity silica glass reaction vessels, frozen in liquid nitrogen, and sealed under vacuum to preserve anoxic reaction conditions.

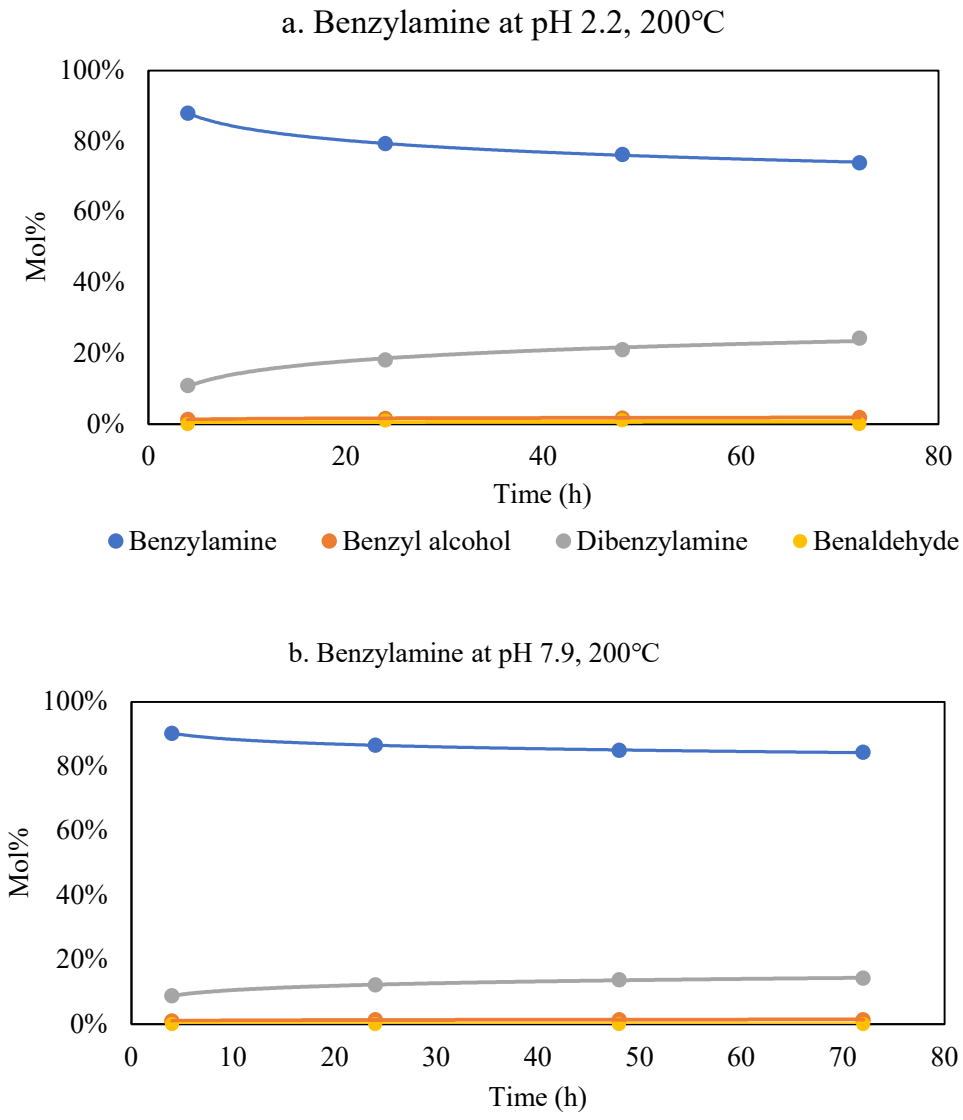


Figure 12. Reactant and product concentrations (as mole%) vs. time in phosphate-buffered hydrothermal experiments with 0.1 molal benzylamine. Reaction condition of Figure 12a. is pH 2.2, 200°C and 16 bar (P_{sat}); Reaction condition of Figure 12b. is pH 7.9, 200°C and 16 bar (P_{sat})

Experiments were performed by placing reaction vessels into preheated steel pipes within gas chromatography ovens.[41,71,74] The experimental temperatures were set to 200, 250, and 275 °C (P_{sat} of 16, 40, and 71 bar, respectively) to measure deamination rates

(and ultimately quantify individual mechanistic contributions) as functions of temperature. Experimental durations (i.e., heating times) ranged from 0.5 hours for the earliest time points of the faster reactions to 120 hours for the longest time points of the slowest reactions. Differences in pressure between sets of experiments were expected to have a negligible effect on the kinetics of the reactions.[90,92] The use of fused silica reaction vessels necessitates that a gas phase (i.e., headspace) exists at experimental conditions, but this was not expected to have an impact on the kinetics of the reactions due to the ionic nature of the reaction mechanisms that must take place in water and low partitioning of reaction species into the gas phase, especially given the low pH of experimental solutions.[46,174]

Upon completion of the experiments, the reaction vessels were submerged in room-temperature water to quench the reactions. Post-reaction solutions were titrated with aqueous sodium hydroxide to neutralize any protonated organic compounds (e.g., benzylamine, dibenzylamine, tribenzylamine, dibenzylimine) [117] for liquid/liquid organic extraction. A subset of experiments (not used in the kinetic analysis) conducted at 250 °C with the parent (i.e., unsubstituted) benzylaminium and otherwise similar experimental conditions were left acidic during extraction to analyze for benzoic acid, which was not detected. Dichloromethane, with decane as an internal standard, was used to extract the organic products from the completed experiments. The organic extract was analyzed using gas chromatography with flame ionization detection. An Agilent 7820 GC system equipped with an autosampler and a flame-ionization detector was used to analyze and quantify the organic products and the remaining starting materials. The GC oven was programmed to start at 50 °C (hold 8 min), ramp at 10 °C min^{-1} to 220 °C (hold 10 min),

and ramp at 20 °C min^{-1} to 300 °C (hold 5 min). The injector temperature was set at 300 °C. A gas chromatograph-mass spectrometer (Agilent 7890A/ 5975C) was also used to confirm the product identification based on ion fragmentation patterns in the mass spectra. Retention time matching with authentic standards was used for product identification; in some cases, standard compound addition to experimental extracts was also used. Product quantification was achieved via five-point linear calibration curves (R^2 ⩾ 0.995) that produced response factors relative to the fixed internal standard, decane.

4.3 Results and Discussion

4.3.1 Reaction pathway and kinetics of benzylamine

Reaction of benzylamine at 200 ℃ (Psat,16 bar) and pH 2.2 produces benzyl alcohol and dibenzylamine, which was shown in figure 12. Benzylamine converted by 26% after 72 hours reaction. Meanwhile, the yield of dibenzylamine formed via electrophilic aromatic substitution reaction was 24% and benzyl alcohol only formed up to 2%, suggesting that condensation of benzylamine is the primary reaction path of benzylamine, whereas the substitution reaction with water is much slower. Although dibenzylamine and benzyl alcohol are by far the predominant products at early timepoints, another minor product, benzaldehyde, was also detected. The yield of benzaldehyde is not consistent, which suggests the formation of benzaldehyde from benzylamine was due to unremoved air. Robinson et al. also observed more minor products like toluene, dibenzylimine, benzyl ether, and tribenzylamine, but these compounds were not observed in this study due to the shorter reaction duration. In neutralized pH 7.9, even though the in-situ pH would be lower during the reaction at the higher temperatures, the conversion of benzylamine decreased to 16% after 72 hours

reaction, which is consistent with findings from Robinson(2019); the reactivity is enhanced because there are more benzylaminiums at lower pH values for because there are more protons in solution, which increases the benzylaminium formation.[174] Benzyl alcohol yielded only 1% and dibenzylamine was still observed as the main product at 14% yield. Since multi ring compounds were likely produced from unprotonated benzylamine, the increasing pH would reduce the reactivity of both benzylaminium and benzylamine in 200℃ reactions, whereas deamination inherently become more unlikely because lower acidity leads to decreases in protonated amines.[174] However, benzaldehyde was not detected, probably due to the improvement in oxidation from acid catalysis.[183]

Reaction of benzylamine at 250℃ generated the same products as the 200℃ experiments(Figure 13.). After 72 h reaction duration, the conversion of pH 2.2 experiments reached 62% . While the yield of the deamination product, benzyl alcohol, was enhanced by elevated temperatures to 23%, the formation of dibenzylamine was still the primary reaction path with a yield of 38%. Generation of benzaldehyde was still not consistent, but it was higher compared to low temperature reactions. According to the results from samples in pH 7.9, conversion of benzylamine was only 27% with the yield of benzyl alcohol and dibenzylamine at 5% and 21% respectively. The decreased reaction rate in both deamination and condensation pathways could be accounted for the lack of catalysis from the acidic protons. Compared with the 200℃ experiments, the results indicated that the increasing reaction temperature would protonate more benzylamine to benzylaminiums. However, the incomplete deamination may be attributed to the lack of positive charge or enough heat. In this case, a staggering proportion of benzylamine is

preserved instead of the aminium form, resulting in the unprotonated amines to react faster at the higher temperatures.

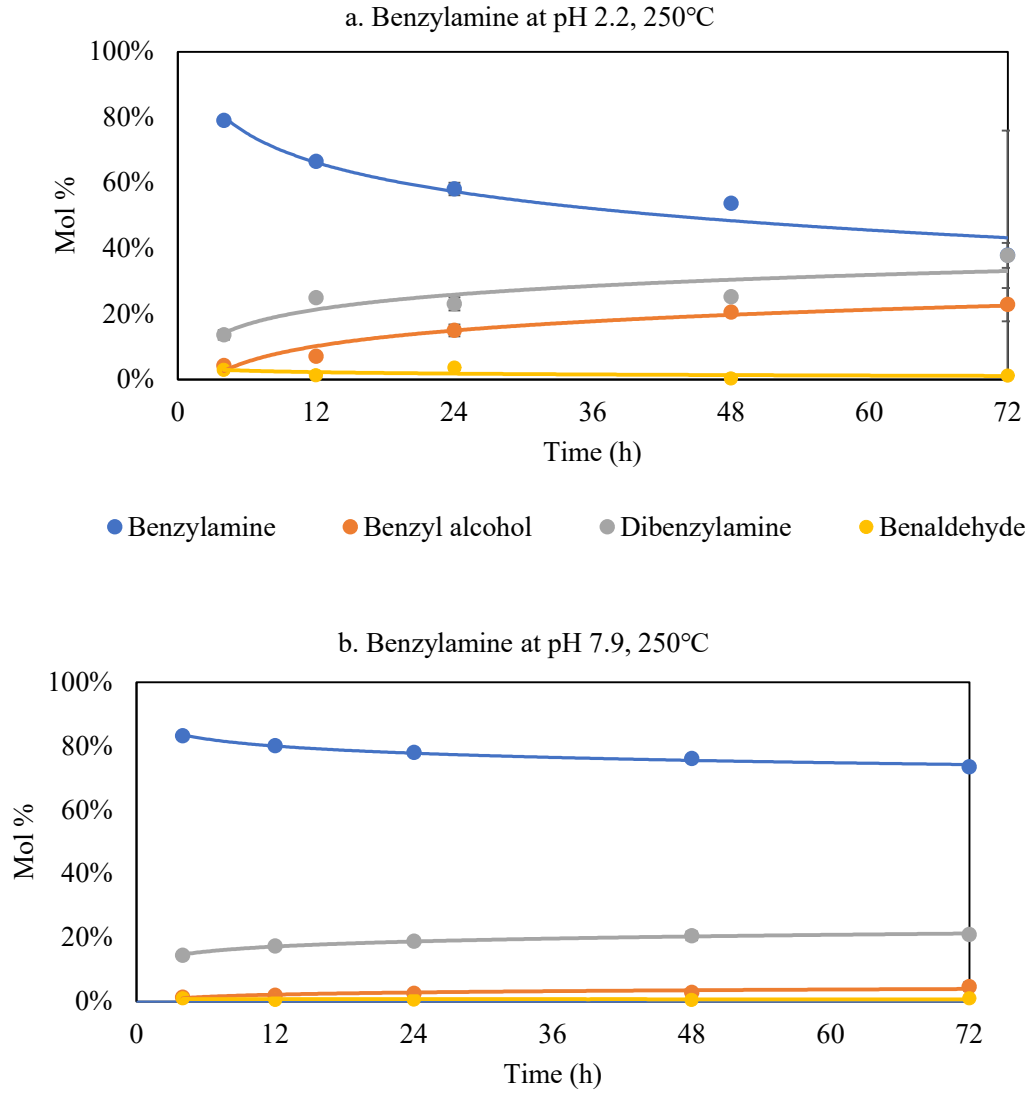


Figure 13. Reactant and product concentrations (as mole%) vs. time in phosphate-buffered hydrothermal experiments with 0.1 molal benzylamine. Reaction condition of Figure 13a. is pH 2.2, 250°C and 40 bar (P_{sat}); Reaction condition of Figure 13b. is pH 7.9, 250°C and 40 bar (P_{sat})

When the reaction temperature was changed to 275℃, conversion of benzylamine in pH 2.2 experiments increased to 41% after just 10 hours heating, as shown in Figure 13. Benzyl alcohol became the predominant product at the yield of 25% with a continuously elevated trend. Dibenzylamine increased in yield from 13% to 18% from 0.5 hours reaction to 4 hours but its formation reduced from 18% to 14% from 4 h to 10 h reactions. This suggests the main formation of dibenzylamine occurred early in reactions, but it could decompose in longer reactions at 275 ℃. The detection of yielded benzaldehyde is higher than that of experiments at lower temperature, but its content is relatively stable, further suggesting that it is still due to exposure to oxygen. Not surprisingly, the benzylamine reaction were slowed in pH 7.9 experiments with a lower conversion of 28%. Similar to the lower temperature reactions, the yield of dibenzylamine was the dominant product with 20% yield, rather than benzyl alcohol at very low yield of 7%. Therefore, the presence of benzylaminium is likely the key factor in determining the proportion of deamination in the reaction path at higher hydrothermal temperature. Generation of benzaldehyde was still restrained by the relatively basic conditions, and its yield was constant at 1% after 2 h reactions.

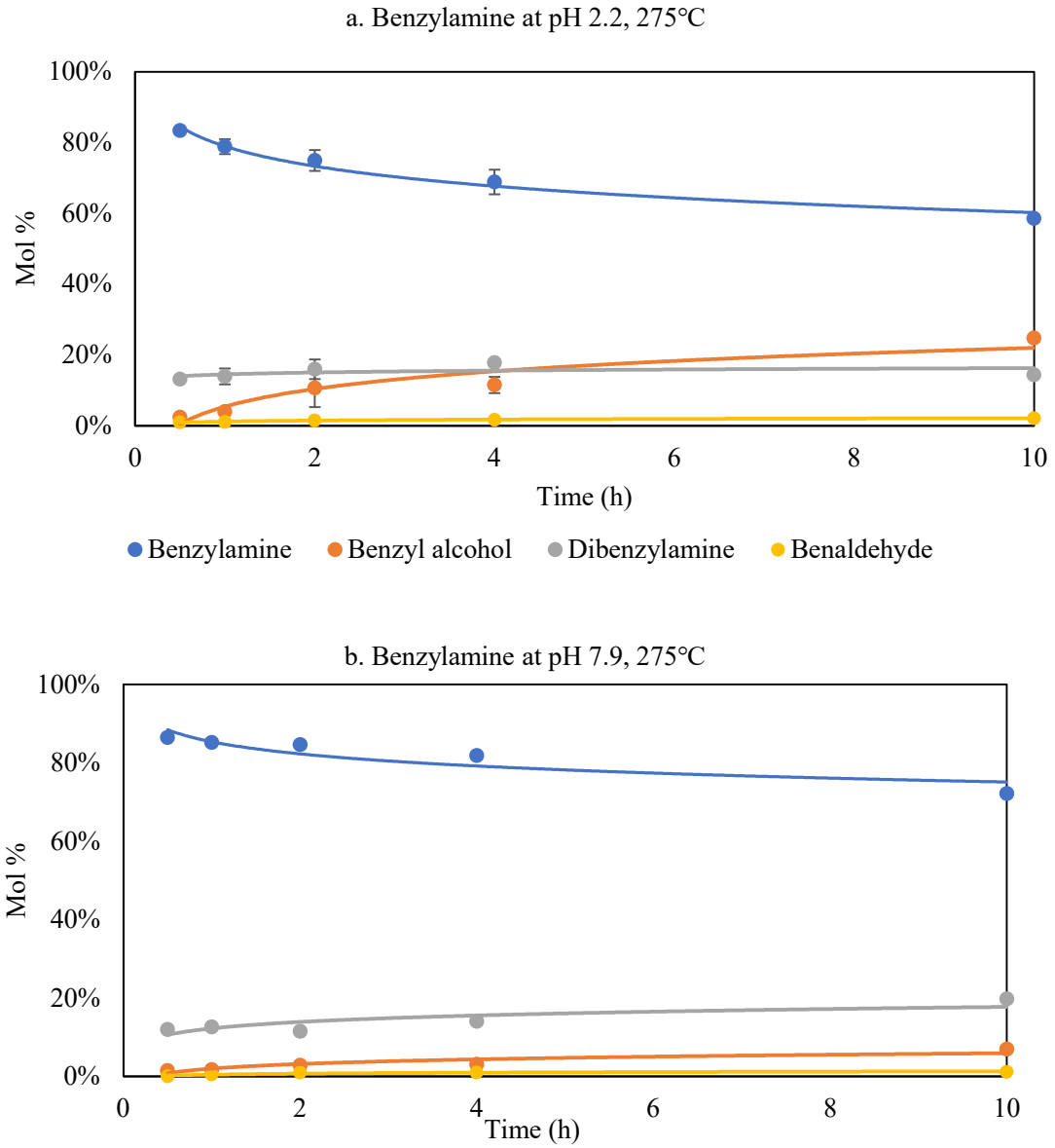


Figure 14. Reactant and product concentrations (as mole%) vs. time in phosphate-buffered hydrothermal experiments with 0.1 molal benzylamine. Reaction conditions of Figure 14a. is pH 2.2, 275°C and 71 bar (P_{sat}); Reaction conditions of Figure 14b. is pH 7.9, 275°C and 71 bar (P_{sat})

Based on the products distribution from hydrothermal experiments at elevated temperatures, we proposed the pathway for the hydrothermal conversion of benzylamine

without the effects from minerals or metal salts. Under different pH conditions, benzylamine becomes benzylaminium by the addition of H^+ from hydrothermal water, and then undergoes addition of water and loss of hydrogen to form benzyl alcohol. On the other hand, the benzylaminium or benzyl alcohol would undergo the electrophilic aromatic substitution to yield dibenzylamine. This finding is consistent with the pathway examined by Robinson(2019), but we propose the formation of dibenzylamine is reversible due to the reduced production in 10h reactions at 275℃.[174]

The kinetics of amine group transfer in the presence of pH buffer were also studied over selected durations (<72 h). As shown in Figure 12-14, conversion of benzylamine was near-stoichiometrically equal to the yield of benzyl alcohol and dibenzylamine. Thus, data of amine concentration decay (in mol %) were best fitted with pseudo-first-order kinetics under the condition. Rate constants derived from the time-dependent data according to the equation

$$[benzylamine] = [benzylamine]_0 \cdot exp(-k_{obs} \cdot t) \quad (11)$$

where [benzylamine] refers to the concentration of benzylamine at a given time t and k_{obs} is the apparent rate constant under experimental conditions. The calculated k_{obs} decreased in the order of benzylamine at pH 2.2, 275 ℃, 71 bar ($0.0127\ h^{-1}$) > benzylamine at pH 2.2, 250 ℃, 40 bar ($9.5\times10^{-3}h^{-1}$) > benzylamine at pH 7.9, 275 ℃, 71 bar ($7.3\times10^{-3}h^{-1}$) > benzylamine at pH 2.2, 200 ℃, 16 bar ($2.4\times10^{-3}h^{-1}$) > benzylamine at pH 7.9, 250 ℃, 40 bar ($1.7\times10^{-3}h^{-1}$) > benzylamine at pH 7.9, 200 ℃, 16 bar ($1.0\times10^{-3}h^{-1}$), which implies that the hydrothermal reactivities of amines were different in amide formation. It is clear that the reactivity of amines in the same pH solution

increases with increasing temperatures (both at pH 2.2 and 7.9) and that the reactivity of amines at the same temperature are higher at lower pH values.

4.3.2 Reaction pathway and kinetics of cyclohexylamine and cyclohexanemethylamine

Reactions of cyclohexylamine and cyclohexanemethylamine were also performed in different hydrothermal temperatures at pH 2.2 or pH 7.9 in up to 120h duration. The cyclohexylamine was relatively inert, only converting about ~14% after 120hr reactions at pH 2.2, 250℃ (P_{sat}). The products were identified as cyclohexanol, cyclohexene, and dicyclohexylamine. Cyclohexanol was proposed to be the primary product due to the deamination reaction, which subsequently undergoes the elimination of water to form cyclohexene. The dicyclohexylamine was produced through the condensation of 2 cyclohexanol molecules, which is similar to the formation of dibenzylamine. Cyclohexanemethylamine reacted quicker than cyclohexylamine, resulting in ~30% conversion after 120h reaction at pH 2.2, 250℃ (P_{sat}). The detected products are cyclohexanemethanol and 1-cyclohexyl-N-(cyclohexylmethyl)methanimine. The relatively inert reactivity of these two cyclic amines cannot generate gas products, which also was observed during the analysis of the products (no popping sound appeared after cutting quartz tubes for extractions). However, yields of both cyclohexylamine and cyclohexanemethylamine were stoichiometrically different with the total products. This error limited our calculations of percentage of total moles for each compound. We hypothesize some small ring molecules could also form in these alicyclic amine hydrothermal reactions and the technical limitation on the GC detector caused neglection of their appearance in spectrum. The GC method may be optimized in future experiments

and the hydrothermal conversion on the detected products here could be conducted at the same hydrothermal conditions to examine the complete products distribution and reaction pathways of these two alicyclic amines.

4.4 Conclusion

Here we expect to track the pathway of both aromatic amines and non-aromatic cyclic benzylamine, cyclohexylamine, and cyclohexanemethylamine to extend the scope of kinetic understanding of hydrothermal deamination. Even though the kinetics calculation previously elucidated aminiums undergo hydrothermal deamination via competing between S_N1 and S_N2, we still need to study if the mechanism is still applicable on non-aromatic amines. This study delivers important mechanistic understandings by kinetic and thermodynamic calculations to build modeling to probe the hydrothermal reactivity of amines. On a broader note, this research sets a precedent by offering an experimental structure that focuses on distinct reactions using model compounds. This approach can be instrumental in comprehending organic chemistry under conditions that are geochemically relevant.

CHAPTER FIVE

ROLE OF MINERALS AND METAL IONS ON THE HYDROTHERMAL CONVERSION OF AMINES

5.1 Introduction

Hydrothermal environments, which harbor life deep within Earth's crust, are intriguing due to their extreme conditions of high temperature and high pressure.[184] (185)Life forms dwelling in these zones rely on sustenance and energy derived from hydrothermal fluids, including those circulating in the deep ocean.[186-187] It's also speculated that such hydrothermal systems extend beyond Earth, possibly existing within Saturn's icy moon, Enceladus.[167,188,189] Various theories have been posited suggesting that hydrothermal processes could be linked with prebiotic organic synthesis and pathways leading to the origin of life on early Earth.[190-192] To validate these hypotheses, numerous hydrothermal experiments have been undertaken. Over the past few decades, the hydrothermal chemistry of organic compounds has increasingly caught the attention of geochemistry and environmental research fields, with significant reaction pathways and mechanisms being identified.[4,13,115,170] Take, for instance, the hydrothermal interconversions of organic functional groups such as alkanes, alcohols, ketones, and carboxylic acids that have been noted in studies.[47,68,69,94] Specific reaction mechanistic pathways, like the dehydration of alcohols and decarboxylation of organic acids, have been discovered to be prevalent under hydrothermal conditions.[47,94] However, these organic transformations in a hydrothermal setting can be significantly influenced by minerals and metals that are abundant on Earth. For instance, in the presence of iron

sulfide minerals, ketones were readily reduced.[57] Similarly, selective reduction of alkanes to alkenes occurred with iron and nickel,[70] and the oxidative decarboxylation of organic acids was facilitated by dissolved copper salts.[71] Our recent research also revealed the oxidative role of copper(II) and iron(III) on hydrothermal reactions of alcohols and aldehydes.[74-75] Hydrothermal organic-mineral/metal interactions thus not only represent the geochemical processes in natural hydrothermal environments but also provide new avenues for using "geomimicry" in sustainability and green chemistry.[19,70,71]

Although conventional hydrothermal studies have predominantly concentrated on organic carbon (C) compounds, there's been comparatively less focus on organic nitrogen (N) entities, which include amines, amino acids, and amides.[90,117,174] Organic N plays important roles in metabolic cycles in the subsurface biosphere, and their transformations are critical for synthesis of biomolecules in hydrothermal systems on Earth and possibly on other planets.[89,190,193] Organic nitrogen compounds, such as amines, are not only the key components of amino acids and proteins forming the backbone of organisms, but they are also precursors to amino acids and peptides in prebiotic context. In hydrothermal systems, amines can undergo various transformations, including deamination reactions resulting in the formation of alcohols or other organic compounds.[190,191,194,195] Additionally, amines can act as ligands, binding to metal ions present in the hydrothermal environment, potentially influencing the mobility and reactivity of these metals, affecting the overall geochemistry of the system.[196-197] Therefore, understanding the reactivity and stability of amines under these different conditions can help us to better understand biogeochemical cycling, energy flow, and the potential for life in these extreme environments.

The roles of amines can vary significantly depending on the specific conditions (temperature, pressure, pH, mineralogy) of the hydrothermal system. However, attention is primarily focused on physical parameters such as temperature, pressure, or acid-base catalysis, and studies on the influence of surrounding minerals or ions are rare.[46,174] Our recent work uncovered an environmentally friendly pathway for amide bond formation through direct condensation reaction between amines and carboxylic acids under hydrothermal conditions, and we also found the formation of amides would be hindered by the presence copper(II) salts due its oxidative role on both acids and amines.[41,198] Since natural organic hydrothermal transformations are inevitably influenced by surrounding minerals and dissolved ions, how these inorganic species influence amine hydrothermal reactions needs to be investigated in greater detail. Robinson et al. found the deamination substitution of protonated benzylamine and its methyl derivatives were readily occurring in hydrothermal conditions.[174] The study of hydrothermal deamination impacted by minerals and metal salts is significant for our understanding of the potential prebiotic chemistry that could occur in similar geological environments, with such conditions thought to be like those present during the early Earth when life first emerged. In this study, the effects of minerals and their corresponding metal ions on amine deamination will be studied in laboratory-simulated hydrothermal environments. The minerals we study here include gibbsite, brucite, corundum, hematite, magnetite and pyrrhotite because these isolated minerals were found located near hydrothermal vents and most of them were reported to play a role in surface catalysis or adsorption in other organic transformations.[57-58] Chloride salts were selected due to the highest abundance of chloride in oceanic environments, including those containing the same metal ions with

minerals like iron(III) chloride, aluminum(III) chloride, magnesium(II) chloride and zinc(II) chloride. Copper(II) chloride was also included because they are widely distributed at the seafloor from hydrothermal dissolution of copper-bearing minerals,[97,199] such as chalcopyrite, but also due to their highly selective effects on organic hydrothermal transformations observed in recent studies.[74,75,198] The selection of sodium chloride is due to its abundance in seawater and the discovery of its influence on hydrothermal stability of collagen and amino acids.[200-201] Therefore, the goal of this study was to examine the influence of different types of minerals and salts on the reactivity and pathway of amines under hydrothermal conditions

5.2 Experimental Section

5.2.1 Materials

Organic reagents purchased fit the following specifications: ⩾99.5% benzylamine, ⩾99.5% benzaldehyde, ⩾99.9% cyclohexylamine, ⩾98% cyclohexanemathylamine, ⩾99% N- benzylidenebenzylamine(dibenzylamine), ⩾98% cyclohexanol, ⩾99.5% benzyl alcohol, ⩾99.9% cyclohexane, ⩾98% cyclohexanemethanol, ⩾99% bis(cyclohexanemethyl)amine, ⩾98% cyclohexenol, ⩾ 98% dicyclohexylamine and >98% cyclohexene. Minerals including Al_2O_3 (98%), $Al(OH)_3$ (97%), Fe_2O_3 (98%), Fe_3O_4 (98%), FeS (98%), $Mg(OH)_2$ (98%) and ZnS (97%) were purchased from Sigma-Aldrich and rinsed with deionized water and dried to powder before use. Chloride salts including cupric chloride (99%), sodium chloride (99%), ferric chloride(98%), aluminum chloride(98%), magnesium chloride(99%), zinc chloride(99%) and cuprous chloride(98%) were also obtained from Sigma-Aldrich and used as received.

Dichloromethane (DCM, 99.9%) was obtained from VWR and used as the solvent for organic extraction. Decane (≥99%) was purchased from Sigma-Aldrich and used as the internal standard for the GC analysis. Deionized water (18.2 MΩ • cm) was obtained from a Barnstead Nanopure system. Reagents used for generating inorganic buffers included 85.0% of aqueous phosphoric acid, ≥99.9% of monosodium (dihydrogen) phosphate, and ≥99.5% of sodium carbonate were purchased from Sigma-Aldrich as well. Gases used for experimental preparation and analyses included ultrahigh purity (≥ 99.999%) helium, ultrahigh purity (≥99.999%) argon, ≥99.95% hydrogen , and ≥ 99.5% oxygen . A high-purity silica "fused quartz" 2 × 6 mm2 (inner diameter × outer diameter) tubing for constructing reaction vessels was purchased from GM Quartz.

5.2.2 Method

For samples containing minerals, 2 equivalents of mineral powder (0.2 molal in 0.3 mL water) were dropped into the quartz tubes. To achieve the target concentrations of 0.1 molal benzylamine, cyclohexylamine, and cyclohexanemethylamine, the corresponding volume of amines was injected into tubes by syringe, followed by the addition of 0.3 mL deionized water that was buffered to pH 2.2 using phosphoric acid and sodium phosphate salts at a targeted total phosphorus concentration of 50 mM. In the samples that were testing the effects of dissolved ions, after injection of 0.1molal selected amine, 1 equivalent of salt (0.1 molal in 0.3 mL water) would be dissolved in pH 2.2 phosphoric buffer to make solutions that then was injected into tubes. pH buffer at 2.2 was selected to stabilize the solution's pH and ensure the amines were protonated to promote the deamination.[174] The pH of each starting solution with dissolved salts was measured at

room temperature, and was in the range of 3-4. Buffered solutions with and without salts were sparged with argon to remove atmospheric oxygen. Buffer catalysis was previously determined to be negligible by comparing reaction kinetics after doubling buffer concentrations. [46] Buffers were prepared according to calculations performed using the revised Helgeson−Kirkham−Flowers (HKF) equations of state[132-133] and associated thermodynamic data[12,134] within the software programs EQ3/6 and SUPCRT92. [90] The tubes went through three pump-freeze-thaw cycles to remove air prior to sealing under vacuum. The tubes were put into metal vessels and heated inside a GC oven at 250 °C for the goal reaction duration (Table 6.).

Table 6. Reaction duration designed for different amines(benzylamine, cyclohexylamine, cyclohexanemethylamine) with different additives

Amine / Additives	Benzylamine(BA)	Cyclohexylamine(CA)	Cyclohexanmethylamine(CM)
Mineral	24 hours	72 hours	72 hours
Salts	4 hours	24 hours	24 hours

The oven was preheated, and the heating time for the tubes to reach 250 °C was <2 min. The reaction time was designed based on previous research to avoid formation of secondary or side products.[174,198] The temperature during the reaction was monitored by a thermocouple inside the GC oven.

The hydrothermal reactions were quenched by submerging the silica tubes in a cold-water bath, and cooling time was <1 min to prevent retrograde reactions. The extraction procedures for the products were similar to those described previously.[198] In brief, two

separate extraction methods were used: amines and amides were extracted by a mixture of 3.0 mL DCM solution (containing 8.8 mM dodecane) with 60 μL of sodium hydroxide (NaOH, 5 M). The purpose of using NaOH and HCl was to ensure that amines were fully extracted from the aqueous phase and transferred to the DCM solution, considering the acidic reaction environment protonated compounds, reducing their solubility in organic solvents. The organic products were analyzed and quantified on an Agilent 7820A GC equipped with a poly-capillary column and flame-ionization detector. The GC oven was programmed to start at 50 °C (hold 8 min), ramp at 10 °C min^{-1} to 220 °C (hold 10 min), and ramp at 20 °C min^{-1} to 300 °C (hold 5 min). The injector temperature was set at 300 °C. A gas chromatograph-mass spectrometer (Agilent 7890A/ 5975C) was also used to confirm the product identification based on ion fragmentation patterns in the mass spectra. Retention time matching with authentic standards was used for product identification; in some cases, standard compound addition to experimental extracts was also used. Product quantification was achieved via five-point linear calibration curves (R^2 $\geqslant$ 0.995) that produced response factors relative to the fixed internal standard, decane.

5.3 Results and Discussion

5.3.1 Hydrothermal reactions of amines in the presence of minerals

As shown in Figure 14, the conversion rates of benzylamine, cyclohexylamine, and cyclohexanemethylamine were obtained by the characterization of their hydrothermal reaction at pH 2.2, 250℃ (P_{sat}). Compared to experiments conducted without minerals, benzylamine showed insignificant differences in the presence of most of the minerals studied here. However, magnetite (Fe_3O_4) accelerated the conversion of benzylamine by 23%, primarily by enhancing the formation of benzaldehyde via the oxidation pathway

(Figure 15). This result may be due to the dissolved iron ions from the reaction between magnetite and the acidic buffer, which is supported by the enhanced oxidation pathway observed in the presence of hematite (Fe_2O_3) that contains the same metal ions as magnetite. These iron ions have been shown in previous studies to enhance oxidation pathways, which supports the observations in this study. Another reason for the enhanced conversion of benzylamine in the presence of minerals may be related to oxidation by air bubbles that were buried in the mineral powders, which can help explain the observation of more benzaldehyde in magnesium hydroxide reactions. In terms of products distribution, aluminum hydroxide, iron sulfide, and zinc sulfide slightly improve the formation of dibenzylamine but reduce the content of benzyl alcohol, which suggests they may play a role in electrophilic aromatic substitution and deamination. These minerals also mildly increased the conversion of the other 2 alicyclic amines, but whether the mechanism of the enhancement is owing to the surface catalysis of the minerals requires further investigation. Additionally, cyclohexylamine and cyclohexanemethylamine still require accurate characterizations of all products, the effects of minerals on product distributions still needs to be distinguished.

5.3.2 Roles of metal salts on conversion of benzylamine deamination

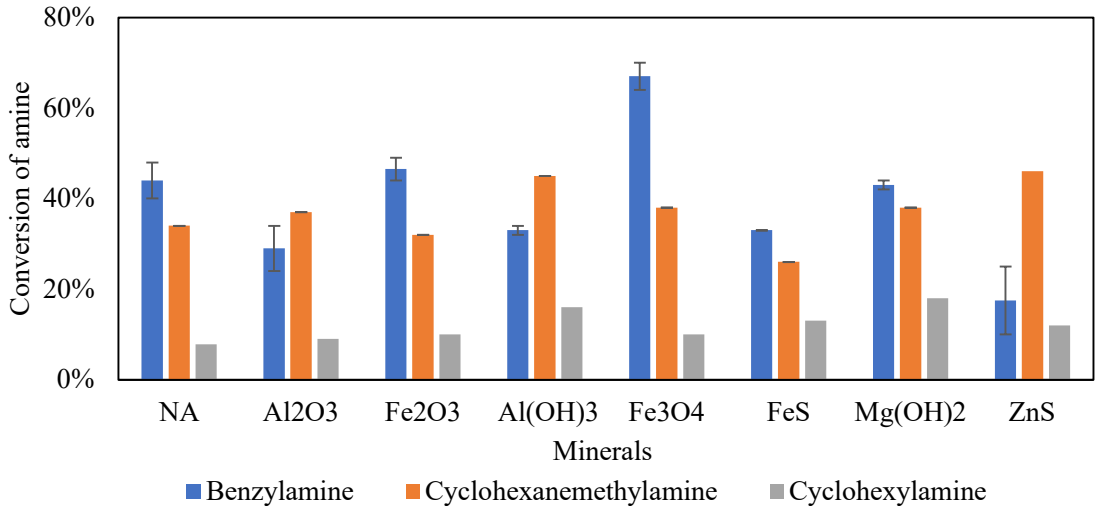


Figure 15. Percentage of amine conversion from the hydrothermal reactions of 0.1 molal amine with or without minerals (2 equiv.) at pH 2.2, 250°C (P_{sat}) for 24 hours (benzylamine) and 72 hours (cyclohexanemethylamine and cyclohexylamine).

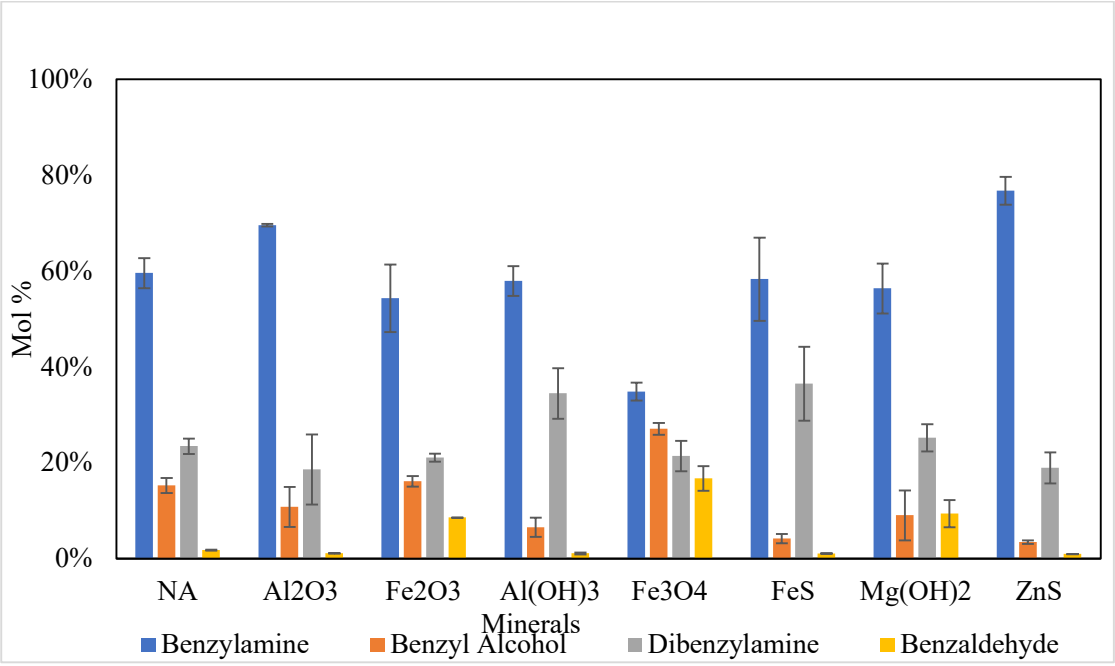


Figure 16. Products distribution of benzylamine hydrothermal conversion from in the reactions with or without minerals (2 equiv.) at pH 2.2, 250°C (P_{sat}) for 24h.

Benzylamine was used to examine the effect of metal ions on the deamination reaction. The hydrothermal reaction was conducted at pH 2.2, 250℃ (P_{sat}) for 4h. With little change in benzylamine conversion with the addition of NaCl, almost all metal chloride salts facilitated the conversion of benzylamine. Copper(II) exhibited the greatest effect by accelerating the oxidation of benzylamine to form 33% benzaldehyde, which is followed by aluminum chloride and magnesium chloride which yielded 13% and 11% benzaldehyde, respectively. Unlike what was observed in benzaldehyde experiments in our previous research, iron(III) did not exhibit as strong of an oxidative effect as it did on aldehyde conversion,[75] indicating that the oxidative effect from metal ions could vary depending on different functional groups and compound structures they interact with. Additionally, the addition of all chloride salts (aside from NaCl) resulted in the increased generation of benzyl alcohols, which is plausibly accounted for the increasing acidity from Lewis acids in the salt solutions. Nevertheless, the change in pH is less likely to influence the oxidation based on our previous observations on amine reactions with different pH buffers without the participation of metal ions. To extend the scope of oxidative role of the dissolvable metal salts, alicyclic amines could also become the objective substrates in hydrothermal reactions in the presence of metal ions when the proposed products spectrum can be fully detected.

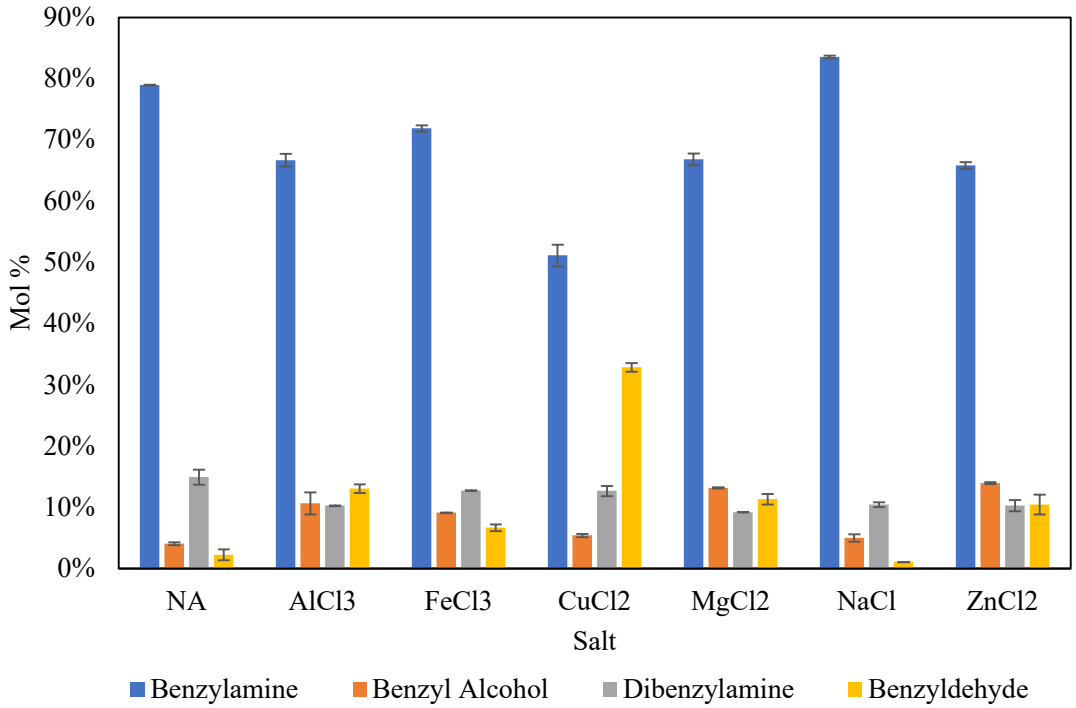


Figure 17. Products distribution of benzylamine hydrothermal conversion from in the reactions with or without metal salts (0.1 molal) at pH 2.2, 250°C (P_{sat}) for 4h.

5.4 Conclusion

This research revealed the effects on deamination of an aromatic amine and non-aromatic amines from minerals and metal salts dissolved from minerals in hydrothermal systems, using benzylamine, cyclohexylamine, and cyclohexanemethylamine as the organic probe. Regardless of the adsorption property of minerals to organic compounds, the minerals showed minor influences on hydrothermal transformation of selected amines. Even though copper(II) exhibited the strongest role on stimulating benzylamine oxidation which is consistent with previous research on oxidative decarboxylation of carboxylic acids, other non-oxidizing ions also accelerated the oxidation pathway,

highlighting the oxidative roles of inorganic ions on the compound structure. These exciting findings help us understand how inorganic matters surrounding the hydrothermal fields can influence the decomposition of amino acids and peptides. This implies that the corresponding organic N-inorganic interactions should be considered for better predictions of biomolecule synthesis in hydrothermal systems on Earth and other planets. In this case, the mechanism of the oxidative effect from metal ions still requires the subsequent investigation. Moreover, these oxidation approaches included natural-abundant salts and water as the solvents, which may introduce new avenues for industry on oxidative decomposition of pollutant amines or biomass transformations to valuable fuels and other chemical products, but the methods must still be optimized to improve the selectivity and efficiency.

CHAPTER SIX

CONCLUSIONS AND PROSPECTS

The investigations detailed in this dissertation have shed light on the hydrothermal transformation of organic functional groups in natural environments, potential sustainable chemistry techniques, and prospective strategies for industrial processing. The reactivity and behavior of a variety of functional groups were examined, under both oxidizing and non-oxidizing conditions. These observations can assist in forecasting the destiny of organic carbon and organic nitrogen under hydrothermal circumstances in natural settings. The reaction pathways in the scheme proposed by Seewald, showing the pathway between alcohols, aldehydes, and carbocyclic acids, have been re-validated by this work. [4] We have been able to expand on this scheme, as well as enhance certain steps and open up new pathways with the participation of minerals and dissolved salts, with the focus on N cycle. The mechanisms behind most reactions investigated in this study have been explored. Gaining insights into the mechanistic aspects of hydrothermal reactions, which have been largely overlooked in geological literature, is crucial. Not only do these insights enhance our understanding of the practical usefulness of such reactions, but they also assist in the analysis of organics detected in the environment. For example, it has been proposed in hydrothermal organic interconversions that ketones are the central compound connected to alcohols and carboxylic acids where both reactions are reversible, but previous hydrothermal ketone reactions only revealed the reduction to alkene as the primary reaction and no carboxylic acid formation.[69] However, our alcohol experiments found that ketones can be formed from alcohols and then produce carboxylic

acid in the presence of Fe(III). There may also be an alternative pathway to form carboxylic acids in natural hydrothermal process.

Alcohols play a crucial role as redox intermediates in organic functional group interconversions that link hydrocarbons and carboxylic acids in deep sedimentary basins. While the dehydration of alcohols to create hydrocarbons such as alkenes is thermodynamically favorable under hydrothermal conditions (e.g., above 200 °C), the oxidation of alcohols to aldehydes and carboxylic acids is often less likely due to a lack of oxidative power. In this dissertation, we examined the impacts of six different copper(II) and iron(III) salts on hydrothermal reactions of model alcohol compounds, including primary, secondary, and tertiary alcohols. We found that, in the absence of dissolved metals, dehydration is the dominant pathway for alcohols in hydrothermal fluids. However, in the presence of copper(II) or iron(III) salts, the oxidation of alcohols is significantly promoted, becoming a competitive pathway to form aldehydes and carboxylic acids as the primary products. Geochemical calculations on the aqueous properties of reactions further support the notion that alcohol oxidations could be thermodynamically favorable with the presence of metal ions under hydrothermal conditions. Our results suggest a crucial role for dissolved metal ions in hydrothermal transformations of alcohols. This may provide new understanding of how inorganic materials regulate organic transformations in natural hydrothermal environments, which could have significant implications for our understanding of these processes on both a geological and a biochemical level.

Aldehydes represent another crucial intermediate in organic interconversions in hydrothermal systems. They play a vital role not just in the context of geochemistry but

also in biological metabolism and industrial medical production. In this study, we report the first instances of oxidation of aldehydes with ferric nitrate [$Fe(NO_3)_3$] in water under anaerobic hydrothermal conditions. This process represents a greener and cleaner approach to oxidation, yielding relatively high amounts of carboxylic acids within hours. The versatility of the reaction was confirmed by testing different aldehyde structures. This methodology also represents a geomimic approach that employs Earth-abundant geological materials for organic synthesis and green chemistry applications. This kind of approach is potentially transformative, as it combines principles from geochemistry and green chemistry to find new and more sustainable ways of conducting chemical transformations. In the future, further investigations into the reaction mechanism and potential effects of other metal salts are expected. These studies could further enhance our understanding of how geological materials can drive chemical reactions and open new avenues for developing sustainable and environmentally friendly chemical processes.

Amines work as the important precursor of amino acids and peptides, and their reactivity in hydrothermal conditions are relevant to the origin of life and exploration in other solar planets. Here we studied the pathway of amines in different structures(benzylamine, cyclohexylamine and cyclohexanemethylamine) to extend the scope of kinetic study on hydrothermal deamination. Even though the kinetics calculation previously elucidated aminiums undergo hydrothermal deamination via competing between S_N1 and S_N2, it is still unknown if the mechanism is applicable on non-aromatic amines. This study delivers important mechanistic understandings by kinetic and thermodynamic calculations to build modeling to probe the hydrothermal reactivity of

amines. Even though the kinetic study of aromatic amines was well done, our findings on the kinetics and mechanisms of both benzylamine and alicyclic amine will fill up the blank of hydrothermal deamination on non-aromatic amines with the sense of the crucial role of alicyclic amines in antient biological metabolism. The results are of great potential to extend our understanding on not only the nitrogen cycle in deep atmosphere of Earth but also the abiotic peptides and protein synthesis in another planetary environment similar to hydrothermal.

Benzylamine was used to examine the effect of metal ions on deamination reactions. With little change inflicted on reaction pathways in the presence of NaCl, almost all chloride salts facilitated the conversion of benzylamine. Copper(II) exhibited the greatest effect on the reaction pathways by accelerating the oxidation of benzylamine to form 33% benzaldehyde, followed by aluminum chloride and magnesium chloride, which yielded 13% and 11% benzaldehyde respectively. Unlike the benzaldehyde experiments in our previous research, iron(III) exhibited less of an oxidizing effect on benzylamine,[75] indicating the oxidative effect from metal ions could vary depending on different functional groups and compound structures. Also, the addition of all chloride salts (aside from NaCl) resulted in the increased generation of benzyl alcohols, which is plausibly accounted for by the increased acidity from Lewis acids formed in salt solutions. Nevertheless, this change on pH is less likely to influence the oxidation based on our previous observations on amine reactions with different pH buffers without the participation of metal ions. To extend the scope of the oxidative role from the dissolvable salts, alicyclic amines could also become the studied substrates in hydrothermal reactions in the presence of metal ions. In natural hydrothermal systems, the presence of amines

may imply potential prebiotic synthesis and metabolic pathways in the deep subsurface, and their reactivity could be sensitive and vulnerable to the surrounding geochemical environments. Future mechanistic study on reactivity of amines on surface of minerals and in the presence of different metal salts with functionalized amines as the probe on mineral surfaces should also be considered for better predictions of biomolecule synthesis in hydrothermal systems on Earth and other planets.

Overall, investigation on laboratory-simulated hydrothermal reactions would offer our insights into the organic transformation of C and N cycle in the deep sediments of Earth or another planetary atmosphere beyond Earth. Interconversion of organic matters in hydrothermal condition made that possible to supply nutrients and energy to biosphere in deep ocean even in the prebiotic ecosystems that related to origin of life. Due to discovery of hydrothermal traces in solar planets, outcomes from mechanisms in hydrothermal reactions would optimize our knowledge on explorations of interstellar habitability and extraterrestrial life.

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