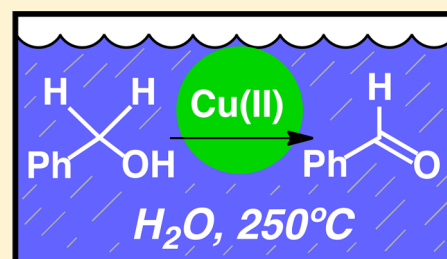


Organic Oxidations Using Geomimicry

Ziming Yang,[†] Hilairy E. Hartnett,^{*,†,‡} Everett L. Shock,^{*,†,‡} and Ian R. Gould^{*,†}[†]The School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, United States[‡]School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, United States

Supporting Information

ABSTRACT: Oxidations of phenylacetic acid to benzaldehyde, benzyl alcohol to benzaldehyde, and benzaldehyde to benzoic acid have been observed, in water as the solvent and using only copper(II) chloride as the oxidant. The reactions are performed at 250 °C and 40 bar, conditions that mimic hydrothermal reactions that are geochemically relevant. Speciation calculations show that the oxidizing agent is not freely solvated copper(II) ions, but complexes of copper(II) with chloride and carboxylate anions. Measurements of the reaction stoichiometries and also of substituent effects on reactivity allow plausible mechanisms to be proposed. These oxidation reactions are relevant to green chemistry in that they proceed in high chemical yield in water as the solvent and avoid the use of toxic heavy metal oxidizing reagents.



INTRODUCTION

Hydrothermal organic reactions under geochemically relevant conditions have attracted attention for possible green chemistry applications.¹ The primary reasons are that water is the solvent^{1–4} and that many functional group transformations can be accomplished without the need for additional reagents.^{1–5} Most hydrothermal organic reactions in geochemically relevant systems, however, take place in the presence of minerals and other inorganic species.^{6–12} Organic/inorganic hydrothermal reactions have been less well explored for green chemistry applications. As part of our investigations of mineral effects on hydrothermal organic reactivity,¹³ we have discovered some simple organic oxidation reactions that use copper in oxidation state (II). In the context of classical organic chemistry, oxidations generally use heavy, often toxic, or expensive metals,^{14–17} whereas enzymatic and also geologic redox reactions use more Earth-abundant metals such as iron, nickel, zinc, and copper.^{18–21} Copper(I) and copper(II) are mild oxidizing agents for organic chemistry; nevertheless, copper salts have previously found use in several organic oxidations.²² In particular, copper salts are useful catalysts for organic oxidations where oxygen (O₂) is the oxidant,^{16,22–24} including some hydrothermal reactions.²⁵ Cu(II) has been used as an oxidant in the formation of copper(I) coordination polymers under hydrothermal conditions,²⁶ but there are very few reports of Cu(II) ions as a simple oxidizing reagent for organic reactions, especially in the absence of molecular oxygen.^{27,28}

Here we report a series of simple organic oxidation reactions that use copper(II) chloride as the oxidizing agent in water as the solvent, in the absence of oxygen and at a temperature that mimics geochemically relevant conditions. Compared to ambient, water at temperatures above 100 °C has a lower dielectric constant and a higher dissociation constant K_w .^{29,30} Consequently, organic compounds are much more soluble as compared to ambient conditions, but ions tend to be less

solvated, and formation of complexes between simple cations and anions is common under hydrothermal conditions.³¹ Speciation calculations relevant to geochemical conditions show that the oxidizing species in these oxidation reactions is not freely solvated copper(II) ions, but that the reactions involve copper(II) complexes.

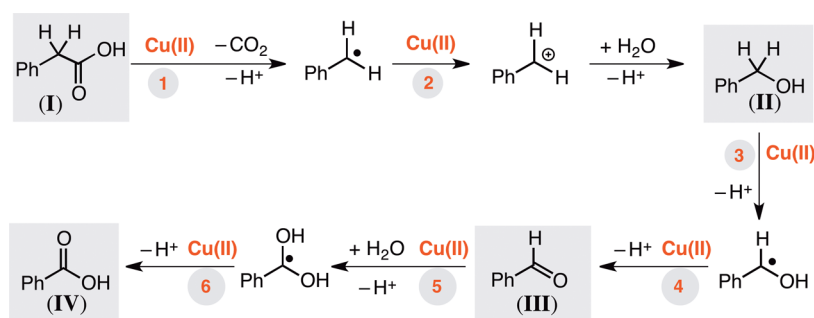
RESULTS AND DISCUSSION

Oxidation Reactions. The oxidation reaction sequence is summarized in Scheme 1. Conversion of phenylacetic acid (I) and benzyl alcohol (II) to benzaldehyde (III), and also benzaldehyde (III) to benzoic acid (IV), can be readily accomplished under the present conditions with high chemical yield. The reactions are performed in sealed glass tubes in pure water at 250 °C in the absence of oxygen, and with cupric chloride (CuCl₂) as the only additive. The reaction pressure, ca. 40 bar, is determined by the water saturation vapor pressure at 250 °C.²⁹ At the end of the reaction, the products are simply extracted into an organic solvent with no additional workup. The oxidizing reagent is indicated as Cu(II) in Scheme 1, but this does not mean that freely solvated Cu(II) ions are involved in the reactions.

Reactant Speciation Under Hydrothermal Conditions. As mentioned above, water at the higher temperatures and pressures that characterize geochemically relevant conditions has a much lower dielectric constant than at ambient. The experimental temperature and pressure are 250 °C and ca. 40 bar, respectively, and under these conditions the dielectric constant is ca. 27.1,³⁰ causing ionic solutes to speciate compared to ambient.³¹ An accurate description of speciation of inorganic and organic species in high temperature and high

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Scheme 1. Oxidation Reaction Sequence Linking Phenylacetic Acid (I) via Benzyl Alcohol (II) and Benzaldehyde (III) to Benzoic Acid (IV)^a


^aSix equivalents of Cu(II) are consumed going from (I) to (IV); the six proposed oxidation steps are shown in red. The oxidizing species at each step is not freely solvated Cu(II) ions; see text.

pressure water is critical to the understanding of many geochemical processes, and geochemists have developed thermodynamic tools that can predict the speciation of many inorganic and organic solutes under hydrothermal conditions.³² The results of such thermodynamic calculations for water at 250 °C and 40 bar, with 0.2 molal CuCl₂ and 0.1 molal acetic acid as solutes, are shown in Figures 1 and 2. Acetic acid is used

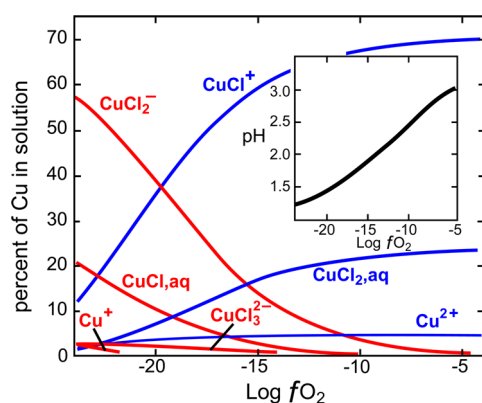


Figure 1. Distribution of the major aqueous copper species (expressed as a percent of the total copper in solution) as a function of solution oxidation state, defined in terms of oxygen fugacity, for 0.2 molal CuCl₂ in the presence of 0.1 molal acetic acid in water at 250 °C and 40 bar at equilibrium. The blue curves correspond to aqueous forms of Cu(II) and the red curves to aqueous forms of Cu(I). At relatively oxidizing conditions the monocation Cu(II)Cl⁺ dominates, and at relatively reducing conditions (more negative values of log *f*O₂) the monoanion Cu(I)Cl₂⁻ dominates. Copper-acetate complexes also form but at concentrations too low to be observed in this figure (see Figure 2). The inset shows the calculated variation in solution pH with oxidation state, showing lower pH in the more reduced solutions.

in place of phenylacetic acid because the relevant thermodynamic data are not available for the aromatic acid, and acetic acid should be a good model for the carboxylic acid and carboxylate functional groups under these conditions. The calculations were performed by combining mass action, mass balance, and charge balance reactions for Cu(I) and Cu(II) hydroxide, chloride, and acetate complexes, together with activity coefficients calculated with an extended Debye–Hückel equation, in a geochemical speciation code³³ using equilibrium constants evaluated with the revised Helgeson–Kirkham–Flowers equations of state.^{31,34}

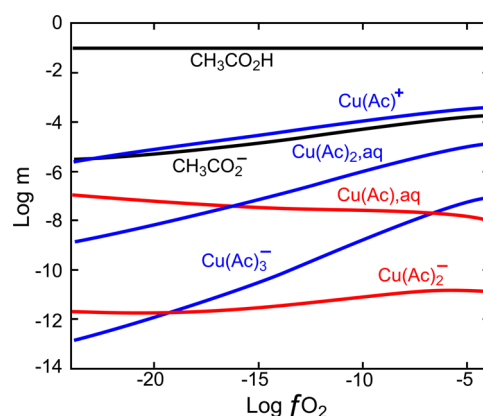
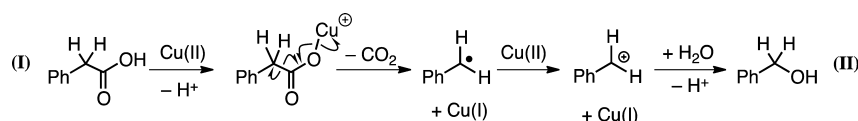


Figure 2. Log molal concentrations of acetic acid, acetate and copper-acetate complexes at equilibrium for an aqueous solution of 0.2 molal CuCl₂ and 0.1 molal acetic acid, at 250 °C and 40 bar at equilibrium, as a function of solution oxidation state, defined in terms of oxygen fugacity. The black curves correspond to acetic acid and acetate, the abbreviation Ac stands for acetate, the blue curves correspond to aqueous Cu(II)-acetate complexes and the red curves to aqueous Cu(I)-acetate complexes.

The dominant aqueous forms of Cu(II) and Cu(I) as functions of solution oxidation state at equilibrium are summarized in Figure 1. Chloride complexes dominate the copper speciation under all oxidation conditions; the predominant form of Cu(II) in solution is the CuCl⁺ cation while the predominant form of Cu(I) is the CuCl₂⁻ anion. Neutral complexes rarely account for more than 20% of the copper in solution, and the uncomplexed ions are minor components in the copper speciation. Both oxidation states of copper are present at percent levels over the entire *f*O₂ range considered, and the transition from dominantly oxidized to dominantly reduced occurs around log *f*O₂ = -20. The strong chloride complexation of copper suggests that uncomplexed Cu(II) ions are unlikely to be the oxidizing species that take part in the reactions. Together with the known temperature dependence of *K*_w, these complexes partially account for the pH of the solution being considerably lower than at ambient, Figure 1. The pH decreases further as the solution becomes more reducing, as shown in the inset of Figure 1.

The calculated speciation of acetic acid and copper–acetate complexes is shown in Figure 2, which plots the log molality of aqueous species vs log *f*O₂. Note that copper–acetate complexes form at much lower concentrations (generally

Scheme 2. Proposed Mechanism for Oxidative Decarboxylation of Phenylacetic Acid to Benzyl Alcohol in Water at 250 °C and in the Presence of CuCl₂^a



^aThe Cu(II) and Cu(I) species are almost certainly not present as the uncomplexed cations, see text.

$<10^{-6}$ molal) relative to copper–chloride complexes which are present at the percent level ($>10^{-2}$ molal) (see Figure 1). The associated form of acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) predominates under all conditions, but acetate (CH_3CO_2^-) becomes somewhat more abundant at high values of $f\text{O}_2$ (see further below). The $\text{Cu}(\text{Ac})^+$ complex is calculated to be as abundant or slightly more abundant than the free acetate ion, which suggests the aqueous species involved in the first step of the reaction mechanism could be the metal–organic complex rather than the anionic form of the acid. Hydroxide complexes of copper are also formed according to the calculations, at concentrations similar to those of the acetate complexes.

Phenylacetic Acid Oxidation Mechanism. At 250 °C in water in the absence of CuCl_2 , phenylacetic acid (I) undergoes very slow decarboxylation ($<5\%$ conversion in 6 h) to yield toluene.³⁵ In the presence of 0.20 molal CuCl_2 , however, reaction is much faster so that conversion is essentially complete after 2 h. The product is now benzaldehyde, formed in $>90\%$ chemical yield. Experiments were performed in the presence of 0.20 molal CuCl_2 to determine the number of moles of Cu(II) consumed. The decrease in Cu(II) ion concentration was measured spectrophotometrically at 700 nm and was compared to the number of moles of acid reacted, determined gas chromatographically (see Experimental Section). The measured consumed mole ratio (Cu(II)/acid) ranged from 3.6 to 3.9 depending upon reaction time and approached 4.0 at high conversion, suggesting that 4 equivalents of Cu(II) are required to convert phenylacetic acid (I) into benzaldehyde (III). A white insoluble solid is observed to form at high conversions, consistent with formation of an inorganic copper product.

Increased conversion of phenylacetic acid was observed with increasing Cu(II) concentration, suggesting that Cu(II) reduction is involved in the rate-determining step. Benzyl alcohol (II) also reacts with Cu(II) to give benzaldehyde (see below), suggesting that II is on the pathway from I to III. Reaction of sodium phenylacetate with 0.20 molal CuCl_2 resulted in higher conversion (85% conversion after 0.17 h) compared to the acid (68% after 0.17 h), which further suggests participation of a deprotonated form of the acid in the reaction, but not necessarily the freely solvated phenylacetate ion. The reaction is reminiscent of the known decarboxylations of benzoic and other carboxylic acids that are catalyzed by copper(I)³⁶ and copper(II) salts,^{37,38} and, in particular, oxidative decarboxylations of carboxylic acids where copper(II) is the oxidizing reagent.^{39–41} Based on the previously proposed mechanisms of copper(II) decarboxylations and also the speciation calculations described above, a plausible mechanism for the phenylacetic acid reaction can be proposed, Scheme 2.

Consistent with both the mechanisms suggested for copper(II) catalyzed decarboxylation of benzoic acids^{36,37} and the results of the speciation studies described above, formation of a complex between a copper(II) cation and the carboxylate is proposed as the primary intermediate. Decarboxylation of this

phenylacetate/copper(II) complex forms a reduced copper ion, which will presumably exist primarily as the CuCl_2^- anion under the reaction conditions (Figure 1), and the benzyl radical. Whether these products are formed in a concerted process as indicated by the curved arrows in Scheme 2 cannot be determined from the experimental results, but the curved arrows clarify the origin of the copper(II) to copper(I) reduction process and the formation of the benzyl radical. The next step, single electron transfer oxidation of the benzyl radical by copper(II), is already known to occur rapidly at ambient in water and has been described in the literature.⁴² In addition, independent photochemical generation of benzyl radicals under hydrothermal reaction conditions in the presence of Cu(II) has also previously been shown to result in oxidation of benzyl radicals, with benzyl alcohol and benzaldehyde as the products of this reaction.⁴³ Thus, both uncomplexed copper(II) ions at ambient conditions and copper(II) chloride complexes formed under hydrothermal conditions are capable of oxidizing benzyl radicals. The product of one-electron oxidation of the benzyl radical is a benzyl cation, which is known to rapidly add a water molecule⁴⁴ and form benzyl alcohol (II) upon deprotonation.

The mechanism is consistent with ring substituent effects. Reaction for 0.17 h of 0.20 molal Cu(II) with 0.05 molal phenylacetic acids that are substituted in the *para*-position with $-\text{CH}_3$, $-t\text{-Bu}$, and $-\text{F}$ substituents gave conversions of 67%, 68%, and 66%, respectively. These can be compared to 68% conversion for the unsubstituted acid under the same conditions. Thus, there is no significant influence on the reaction rate from an electron-donating or -withdrawing substituent on the benzene ring. This is consistent with a rate-determining step that involves formation and fragmentation of a phenylacetate/copper complex via a radical process, Scheme 2, i.e. one that does not develop a charge on the ring. The phenylacetic acid oxidation could not be stopped at benzyl alcohol even with 2 equivalents of copper(II) because the alcohol oxidation was sufficiently fast that benzaldehyde was the major product at all reaction times.

Benzyl Alcohol Oxidation Mechanism. According to Scheme 1, benzyl alcohol (II) is on the reaction pathway from phenylacetic acid to benzaldehyde; therefore, II should also be oxidized to benzaldehyde with 2 equivalents of Cu(II). This was confirmed by experiment. Reaction of 0.05 molal benzyl alcohol with 0.10 molal Cu(II) for 1 h resulted in 65% conversion to benzaldehyde with a chemical yield of 92%. Under these conditions, $>90\%$ of the product is benzaldehyde; benzoic acid dominated the other products. Experiments were performed to determine the stoichiometry of the alcohol oxidation reaction. Reaction of 0.05 molal benzyl alcohol with 0.20 molal CuCl_2 resulted in 43% conversion of the alcohol in 0.5 h. As before, the quantity of Cu(II) consumed was measured spectrophotometrically and compared to the quantity of alcohol consumed measured by gas chromatography. The molar ratio of consumed Cu(II)/alcohol was 1.8–2.4 depend-

these two pathways with certainty using the current experimental data.

Hydrothermal Reaction Conditions. Previous work on green organic oxidations has emphasized the importance of eliminating halogenated solvents and toxic reagents such as Cr(VI).⁵² Here, the reactions are performed in water as the solvent using the relatively benign Cu(II). Interestingly, conditions can be found such that the major product of the benzyl alcohol oxidation reaction is benzaldehyde. This is interesting because most oxidations of aldehydes in aqueous media form the corresponding carboxylic acid (the aldehyde cannot be isolated) due to oxidation of the hydrate that forms from the aldehyde primary product.⁴⁸ Even alcohols with lower propensities for hydrate formation, such as benzyl alcohol, are normally oxidized in nonaqueous solvents for this reason.⁵³ At high temperatures, the enthalpic drive to form the hydrate due to covalent bond formation is offset by the entropic drive for dehydration. This diminished propensity for hydrate formation under hydrothermal conditions favors formation of the aldehyde as the major product even though water is the solvent. Of course, with additional copper(II) reagent and longer reaction times the reaction can be pushed to the acid as the major product, and it has been shown elsewhere that copper salts can catalyze decarboxylation of benzoic acid with extended reaction times.¹⁶ Nevertheless, the fact that benzyl alcohol oxidation can be stopped at the aldehyde stage highlights the fact that the hydrothermal reaction conditions are important not just to provide thermal energy. As mentioned above, at elevated temperatures the dielectric constant for water is decreased making it an excellent solvent for organics and the K_w is increased, which results in higher concentrations of hydronium and hydroxide ions to catalyze the proton transfer reactions of Scheme 1. The water properties at high temperatures also significantly influence the speciation of the ionic reactants, which may also be important in controlling the selectivity of the reactions. Further characterization of the Cu(II) complexes that are involved in the reactions studied here will require real-time spectroscopic analysis under hydrothermal conditions.

The vast majority of the organic material on Earth does not participate in the more familiar, conventional surface carbon cycle because it is located deep within the crust and therefore undergoes chemical reactions under hydrothermal conditions, such as those used in the oxidation reactions described here.⁵⁴ In contrast to the majority of organic reactions close to ambient, which tend to be controlled by enthalpic and kinetic factors, reactions of this huge quantity of organic material under hydrothermal geochemically relevant conditions tend to be controlled by entropic and thermodynamic factors. Together with the unique properties of water as a solvent under these conditions mentioned above, this suggests that much new useful organic chemistry may be uncovered via the development of reactions that are inspired by reaction conditions relevant to geology. To this end, the term “geomimicry” was adopted,^{1–5} in analogy to the more established biomimicry.⁵⁵

EXPERIMENTAL SECTION

Materials. The following materials were obtained from commercial sources: phenylacetic acid (99%), *p*-fluorophenylacetic acid (98%), *p*-methylphenylacetic acid (99%), *p*-*tert*-butylphenylacetic acid (98%), *p*-trifluoromethyl-phenylacetic acid (97%), *p*-methoxyphenylacetic acid (99%), benzaldehyde (99%), *p*-trifluoromethylbenzaldehyde (98%), *p*-methylbenzaldehyde (97%), benzylalcohol (99.8%), *p*-trifluoromethyl-

benzylalcohol (98%), *p*-methylbenzylalcohol (98%), *p*-methoxybenzylalcohol (98%), hydrochloric acid, sodium hydroxide (98%), cupric chloride (97%), dichloromethane (99.9%), and *n*-decane (99%). Fresh solutions of cupric chloride with concentrations ranging from 0.05 to 0.2 molal were prepared using high-purity water (18.2 M Ω -cm resistivity) obtained from a commercial water purification system. Sodium phenylacetate was prepared by neutralizing phenylacetic acid with sodium hydroxide. The purities of all organic materials (except phenyl acetate) were verified by gas chromatography.

Methods. Hydrothermal experiments were performed in fused silica glass tubes with a 6 mm inner diameter (ID) and a 12 mm outer diameter (OD). The relatively large diameter tubes allow easy loading of the solid starting materials and also guarantee an adequate quantity of organic material for analysis after the experiments. The organic starting material (0.10 mmol) and 2.0 mL of argon-purged cupric chloride solution were loaded into each tube to obtain a molality of 0.05 molal for the organic species. The samples were frozen in liquid nitrogen, degassed using three pump–freeze–thaw cycles on a small vacuum line, and then sealed with a hydrogen flame under vacuum. Each fused silica glass tube (~15 cm long) was placed into a small steel pipe (~21 cm long, ID \approx 2 cm) to contain the glass in the event of tube failure. The pipe was closed with loose screw caps, and the screw caps had a hole drilled through the end to prevent pressure from building up inside the steep pipe. The glass-within-steel tube setup was heated in a gas chromatography (GC) oven at 250 °C. At 250 °C the pressure inside the silica glass tube is calculated to be ca. 40 bar based on equilibrium thermodynamics calculations using SUPCRT92.^{32b} A thermocouple inside the GC oven next to the sample tubes was used to verify the reaction temperature. The estimated uncertainty in the temperature of the sample was ± 2 °C over the duration of the experiment. Approximately 10 min of preheating time were necessary for the samples to reach the experimental temperature of 250 °C.

The experimental reaction times ranged from 10 min to 8 h at 250 °C and 40 bar, depending on the particular reaction. When the desired reaction time was reached, the experiment was quenched by placing the steel pipe into a room temperature water bath. The extraction procedure was similar to that described in previous work.^{5a,43} After the fused silica tube was opened using a tubing cutter, the sample was transferred into a 20 mL glass vial, and the reaction tube was rinsed twice with 10.0 mL of dichloromethane solution containing the internal gas chromatography standard, *n*-decane (0.067% by volume). The water and dichloromethane phases were combined in the 20 mL vial. For the phenylacetic acid and the sodium phenylacetate samples, two drops of 1 M aqueous HCl was added to the reaction tube after opening to ensure protonation of any organic acid species and extraction into the organic layer. The 20 mL vials were capped and shaken vigorously to facilitate extraction of the organics into the dichloromethane phase. The aqueous layer was separated into a small centrifuge tube, and any suspended solid particles were separated by centrifugation before the analysis of cupric ions in clear aqueous solutions.

Quantitative analysis was performed for both the organic species in the dichloromethane phase and the aqueous species that remained in the water phase. The organic species were analyzed using gas chromatography with a flame ionization detector. Reproducibility was ensured by triplicate injections using an autosampler. The identities of the organic products were verified by using authentic standards, and their quantities were determined based on the calibration curves that were referenced to the internal standard. Mass balance was calculated by comparing the number of benzene rings in the products and the reactants. The aqueous samples were analyzed quickly after centrifugation, in order to minimize any air oxidation of Cu(I) to Cu(II). The absorbance of Cu(II) ions in solution were determined at 700 nm (at room temperature) using a UV–visible spectrophotometer. The copper(II) concentrations were quantified using a calibration curve built with authentic copper(II) standards ranging from 0.01 to 0.20 molal. The 700 nm wavelength was selected to ensure a measurable absorbance (i.e., greater than 0.1 and less than 1.0 absorbance units) over the range of copper(II) concentrations that were studied. Measurement of copper(I) concentration in the aqueous

sample was not attempted since the solubility of copper(I) chloride is low at room temperature.⁵⁶ Triplicate measurements were taken to ensure reproducibility of the copper(II) measurements using the spectrophotometer. Based on repeated measurements, the uncertainties in the reactant conversions are estimated to be $\pm 10\%$ in all experiments, the uncertainties in the chemical yields are estimated to be $\pm 3\%$, and the estimated uncertainties in the molar ratios for consumed reactants are $\pm 20\%$.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02109.

Tables with experimental reaction times and conditions, conversions, measurements of consumed organic reactants and Cu(II)Cl₂, mole ratios of consumed organics to Cu(II)Cl₂, chemical yields and mass balances for all hydrothermal oxidation experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: h.hartnett@asu.edu.

*E-mail: Everett.Shock@asu.edu.

*E-mail: igould@asu.edu.

Notes

The authors declare no competing financial interest.

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