# *Lab 5* Copper-Catalyzed Oxidation

## *Objectives*

- Identify organic redox reaction components
- Understand the regeneration process of the catalyst
- Prepare benzil from benzoin using a copper catalyst

## *Background*

### Oxidation-Reduction Reactions of Organic Molecules

An oxidation-reduction reaction, also known as a redox reaction, is a category of chemical reactions that involves the transfer of electrons from one species to another. Redox reactions control the flow of energy in a variety of systems, including biological systems.

In a redox reaction, one species is oxidized, meaning that it loses electrons. For inorganic species, like metal ions, oxidation is easily recognized as an increased oxidation number or positive charge, as seen in Figure 1. The redox reaction also needs to include a species that is reduced, which corresponds to gaining electrons. For ions, reduction appears as a decrease in positive charge or increase in negative charge.

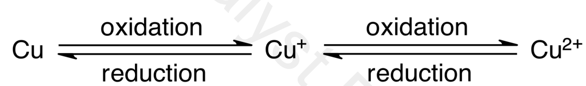


Figure 1 Oxidation-reduction relationships between copper and copper ions

When organic molecules appear in redox reactions, recognizing whether a molecule is oxidized or reduced becomes more difficult and relies on knowing each molecule's structure. Organic reduction appears as an increase in the number of carbon-hydrogen bonds. Organic oxidation appears as the loss of a carbon-hydrogen bond in favor of a bond with a more electronegative atom, which is often an oxygen, as seen in Figure 2.

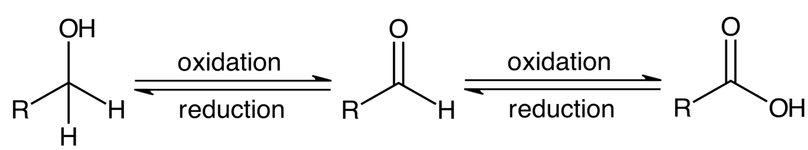


Figure 2 Oxidation-reduction relationships between an alcohol, aldehyde, and carboxylic acid

### Catalytic Mechanism of Oxidation

To cause an oxidation reaction of a specific molecule, some oxidant species must be included. The added oxidant will be reduced throughout the reaction as it oxidizes the desired molecule. The added oxidant is catalytic if it can be oxidized back to its original state, allowing it to repeatedly act as an oxidant with new molecules.

In this lab, benzoin is oxidized to benzil. The added oxidant is a copper(II) ion that is reduced to copper(I). The copper(II) ion acts as a catalyst as it is continuously regenerated by the inclusion of ammonium nitrate in the reaction. When ammonium nitrate is reduced in the process of oxidizing the copper(I) ion, ammonium nitrite is formed, which reacts further to release nitrogen gas and water, effectively removing it from the reaction. The reaction is summarized in Figure 3, highlighting the cyclic nature of the copper ion catalyst.

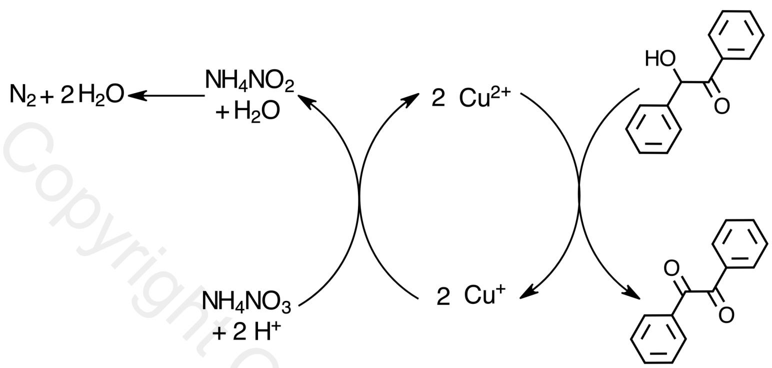


Figure 3 Catalytic cycle of the copper(II) ion being reduced by oxidizing benzoin and being regeneratively oxidized by ammonium nitrate

## Materials

- Glacial acetic acid
- Ammonium nitrate ($NH_4NO_3$)
- Benzoin
- Copper acetate solution
- Microscale glassware kit
- Filter paper
- Melting point apparatus
- FTIR

***Safety goggles are required!***

***All work should be performed in the fume hood.***

*Benzil is an irritant. Glacial acetic acid is corrosive. Ammonium nitrate is oxidizing and an irritant. Copper acetate is corrosive and an irritant.*

## Procedure



### Copper-Catalyzed Oxidation of Benzoin

1. Add a stir bar and 1.5 mL of glacial acetic acid, 0.250 g of $NH_4NO_3$ and 0.500 g of benzoin to a round bottom flask for refluxing.
2. Add 0.50 mL of the copper acetate solution to the flask. The mixture will not all dissolve in the solution at first and must be heated.
3. Assemble the reflux apparatus.
4. Heat the reaction mixture to a boil, and reflux for 60 minutes.
5. Cool the flask down to about room temperature.
6. Place 10 mL of ice-cold water in a 50 mL beaker in an ice bath.
7. Pour the contents of the flask into the ice-cold water and stir to break up any clumps that may form. Scratching the bottom of the flask with a stirring rod may be necessary to produce crystals.
8. Assemble a vacuum filtration system using the Hirsch funnel.
9. Vacuum filter the solid and wash with 5 mL of distilled water.
10. Allow the crystals to dry in the Hirsch funnel on the vacuum filtration apparatus for 10 minutes with the vacuum on.
11. Weigh the mass of your product and record on your data sheet.
12. Measure the melting point of your dry product and record on the data sheet.
13. Take a small sample of your solid product to run an FTIR and print your spectrum.
14. Place the remaining product in the container labeled “Benzil”. All solutions should go in the non-halogenated waste. Wash all glassware and clean up.

## Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. What safety precautions should be used when working with glacial acetic acid?

2. Calculate the theoretical yield for the oxidation of 0.500 g of bezoin using an excess of ammonium nitrate and copper (II) acetate. Show all calculations.

# Lab 5: Copper-Catalyzed Oxidation Report Sheet

Name ______________________ Section ______________________

Date ______________________ Instructor ______________________

## Copper-Catalyzed Oxidation of Benzoin

Amount of reactant used (grams) ____________________________

Amount of reactant used (moles) ____________________________

*Space for calculations:*

Product obtained (grams) ____________________________

Product obtained (moles) ____________________________

*Space for calculations:*

Product theoretical yield ____________________________

*Space for calculations:*

Product percent yield ____________________________

*Space for calculations:*

Product melting point ____________________________

Write the equation for the reaction.

## Post-lab Questions

1. Is your percent yield within reason of what you would expect? Explain your answer.

2. How can the IR spectrum be used to show that there is not starting material left and the products are ketones?

3. Describe the major differences and similarities between the IR spectra of benzoin and benzil. Compare your IR spectrum with those of benzoin and benzil.