

Oxidation of Cyclohexanol

Oxidation-reduction reactions play an important role in organic chemistry. Oxidation of alcohols to form aldehydes, ketones or carboxylic acids is a fundamental and widely used reaction. Primary alcohols can be oxidized to aldehydes or carboxylic acids while secondary alcohols oxidize to ketones. Tertiary alcohols are resistant to oxidation.

In this experiment common household bleach will be used as a source of sodium hypochlorite, NaOCl (aq), an oxidizing agent to oxidize cyclohexanol into cyclohexanone. Bleach solution will be added to a mixture of cyclohexanol and acetic acid. No additional solvent will be used, so the only solvent will be water from bleach solution.

This oxidation reaction is exothermic, which means it releases heat to the environment as the reaction progresses. The reaction can be considered complete when the reaction mixture cools back to room temperature. However, it is necessary to check to see if enough oxidizing agent was added, since commercial bleach is not a chemical reagent of a constant composition. It is usually 5.25 % (0.74 M) sodium hypochlorite. Potassium iodide-starch paper is used to check for an excess of an oxidizing agent. The test is positive (that is, the solution contains an oxidizing agent), if wet iodide-starch paper turns blue-black when a drop of this solution is placed on it. If a piece of iodide-starch paper remains colorless after a drop of a solution is placed on it, the test is negative (no oxidizing agent is present in the solution).

Cyclohexanol has a significantly higher solubility in water than cyclohexanone. Remember your solubility rules from lecture. The product (cyclohexanone) will form as a separate layer during the reaction. The density determines if the new layer will form on the top (floats) or on the bottom (sinks). You will add NaCl to decrease its solubility in water. Infrared spectroscopy will be used to derive information about the structure and purity of the isolated product. A 2,4-dinitrophenyl hydrazine test may be used to determine the presence of a carbonyl group.

PRE-EXPERIMENT ASSIGNMENT

Read sections 12.2 and 12.4 of Chapter 12 in your lecture textbook (Solomons and Fryhle). Study this chapter and the information on the Chemistry Department web site. Do the first part of your notebook writeup.

A student who has prepared for the Oxidation of Cyclohexanol experiment should be able to:

1. Identify the process occurring. It is an oxidation reaction. During the process, NaOCl reacts with acetic acid to give HOCl . The HOCl oxidizes cyclohexanol, a secondary alcohol, to cyclohexanone, a ketone. The process

involves chlorine in the +1 oxidation state; it accepts two electrons from cyclohexanol to be reduced to chloride ion (Cl^-). Cyclohexanol loses two electrons to be oxidized to cyclohexanone.

2. Give the equation for the overall reaction occurring.
3. Give the equation for the reaction between NaOH and molecular chlorine, and reaction between glacial acetic acid and NaOCl.
4. Give the equation and the mechanism for the oxidation of cyclohexanol to cyclohexanone by hypochlorous acid (HOCl). Write equations for the oxidation of other primary and secondary alcohols (this is a review from CHEM 2220 lecture).
5. Explain the necessity of the iodide-starch test; and tell how to perform it and how to distinguish a positive from a negative result. Explain the function of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium chloride, and CaSO_4 (Drierite) in this experiment.
6. Calculate the theoretical yield and the percent yield for this and similar experiments given the necessary data, and perform any of the intermediate calculations required by this process.
7. Draw the structure given the name, or give the name from the structure, of the compounds used in the day's experiment, and give the role of each (reactant, solvent, catalyst, drying agent, etc.)
8. Identify and explain safety considerations for this experiment.
9. Perform the day's experiments safely and successfully.

Quizzes given after the experiment has been performed may also include:

10. Recognize an oxidation-reduction reaction. Be able to identify an oxidizing agent and a reducing agent.
11. Identify the functional groups present in the IR spectra of cyclohexanol and cyclohexanone. You may need to review a table of important IR frequencies.
12. Be able to predict the product from other alcohol oxidation reactions.

Safety Information

Cyclohexanol is an irritant. Avoid contact with skin, eyes, and clothing. **Glacial acetic acid** is a dehydrating agent, an irritant, and causes burns. Dispense it in a fume hood and avoid contact with skin, eyes, and clothing. **Sodium hypochlorite** solution emits chlorine gas, which is a respiratory and eye irritant. Dispense it in a fume hood. Keep reaction in fume hood until the excess oxidizing agent has been quenched with sodium thiosulfate.

The Reaction

Pour approximately 2 mL of cyclohexanol and 1 mL of glacial acetic acid into a 250 mL Erlenmeyer flask. (Do not waste time measuring out exactly 2.00 mL but record exactly how much material is obtained) Under a fume hood,

pour 30 mL of household bleach (0.74 M sodium hypochlorite) into the flask, portion by portion, over about 2 minutes while stirring frequently. Again, do not waste time obtaining exactly 30.0mL of bleach, but do record exactly how much material used. The flask will become significantly warm because of the exothermic reaction. Swirl the flask containing the reaction mixture frequently for a full 20 minutes, also in the fume hood. During this time the reaction mixture should cool back to room temperature.

Wet a piece of a potassium iodide-starch test paper and put a drop of the reaction mixture on it. Be sure to test the bleach solution, not the product cyclohexanone that has risen to the top. If the paper does not change its color the test for an oxidizing agent is negative. If this occurs add another 3 mL of bleach to the reaction mixture, swirl the flask for another 5 minutes, and repeat the test. At this time the test should be positive (the iodide-starch paper turns blue-black), signifying the presence of excess hypochlorite.

Add 0.5-1.0 g of solid sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to the reaction mixture, swirl the mixture for about 2 minutes, and repeat the iodide-starch test. The test should be negative at this point (*explain why*). Once the test is negative you can work outside the fume hood.

Check the pH of the reaction mixture with a strip of pH paper on a watch glass. To do this, stir the solution in the flask with a clean stirring rod, then touch the wet rod to the pH paper. If the reaction mixture is acidic, add about 1.8 g of solid sodium bicarbonate. Check the pH again and add another 0.5-1 g portion of sodium bicarbonate, if necessary to bring the pH to neutral.

The Workup and Product Recovery

Add about 5 g of solid sodium chloride to the reaction mixture to decrease the solubility of cyclohexanone in the aqueous phase. Stir the mixture until most of NaCl dissolves. If all of it dissolves, add a little bit more until some of the NaCl remains undissolved. Decant the liquid from the undissolved NaCl in the Erlenmeyer flask into a separatory funnel. You will see a narrow clear organic layer on top of a cloudy aqueous solution.

Let the solution sit and separate for a few minutes. Drain all of the bottom aqueous layer, and none of the top organic layer into the Erlenmeyer flask. Drain the top organic layer into a small shell vial. Having a small amount of aqueous layer in the shell vial is acceptable. The aqueous layer will appear as a small bubble or layer on the bottom of the vial.

If a small bubble or aqueous layer is present in the shell vial, carefully pipette out the entire aqueous bubble or layer from the shell vial. When you collect the solution in your pipette, if any organic has been obtained, the layers will separate within the pipette. The aqueous layer is on the bottom. Using the pipette as a mini separatory funnel, drain the bottom layer of the pipette back into the Erlenmeyer flask being careful not add the top layer back. Place the top layer back in the shell vial.

The less water layer you put in the cylinder, the easier the drying step will be and the better your IR will look.

Add a small amount of drying agent (Sodium Sulfate, Na_2SO_4 or Magnesium Sulfate MgSO_4) to the shell vial. If too much drying agent is added, product will be lost. If too little drying agent is added the IR will show the contamination. Remember from first semester, to add just enough to still have some free moving particulate. Let the liquid remain on the drying agent for 5 minutes. The dry liquid should be clear and not cloudy.

Finally, transfer the product from the drying agent with a clean Pasteur pipette into a clean pre-weighed vial. Reweigh the vial and determine the yield.

Product Analysis: Infrared Spectroscopy

Place 2-3 drops of a neat sample of your product between two salt plates, take an IR spectrum of your product. You will be given an IR spectrum of cyclohexanol, your starting material.

Product Analysis: 2,4-Dinitrophenyl Hydrazine (optional, check with instructor)

Obtain and label two clean test tubes. Ensure no residual acetone is present. Add ten drops of ethanol into each test tube. Add 2 drops of starting material to one test tube, add 2 drops of product to other test tube. Add 15 drops of 2,4-dinitrophenyl hydrazine (2,4-DNP) reagent to both. Note the color of test reagent. Let sit 15 minutes. The presence of a thick orange or red precipitate confirms the presence of a carbonyl in a ketone or aldehyde group (not as part of an acid or ester.)

CLEANUP

The aqueous layer contains salt, sodium bicarbonate, neutralized acid, and quenched bleach. This solution should be poured down the sink.

The cyclohexanone product and excess cyclohexanol should be placed in the nonhalogenated liquid waste container under the hood. Used drying agent should also be placed in a waste container in the hood. Used Pasteur pipettes and shell vials should be placed in the broken glass box.

POST-EXPERIMENT ASSIGNMENT

Write the lab report and have it ready to turn in by the beginning of the next lab. Determine the limiting reagent. Remember the bleach is a dilute solution of sodium hypochlorite and not a neat liquid. The molarity must be used to determine the moles of NaOCl present. Consult the percent yield information sheet for an example. Determine the percent yield. Include your IR spectra in the Data section. In your Conclusions section, interpret the spectrum of your product and compare it to the spectrum of your starting cyclohexanol given to you by your instructor. Explain the significant changes

which occurred over the course of the reaction. Which peaks in the spectrum are most useful for you to make a conclusion about your experiment? Specify which peak(s) were present in the starting material and not present or greatly diminished in intensity in your product. Specify which peak(s) are present in your product that were not present or were only minor in your starting material. Prepare for the oxidation portion of the next quiz.