22. 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, the only solvent will be the water from the 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. Recently a higher concentration bleach has become available. Its nominal molarity is 1.11M. 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. 1H NMR may also be utilized to verify product identity.

PRE-EXPERIMENT ASSIGNMENT


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\textsuperscript{−}). 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 (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}), sodium chloride, and CaSO\textsubscript{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.
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 Considerations
Cyclohexanol is an irritant. Avoid contact with skin, eyes, and clothing. Glacial acetic acid is a dehydrating agent, an irritant, and it is corrosive. Dispense the acetic acid 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.

EXPERIMENT
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 standard household bleach (0.74 M sodium hypochlorite) into the flask, portion by portion, over about 2 minutes while stirring frequently. If “concentrated” bleach is available, only ~20 mL of bleach is required. Add
portionwise over about 2 minutes. Again, do not waste time obtaining the exact target volumes of bleach, but do record exactly how much material was 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 in the fume hood. During this time the reaction mixture should cool back to room temperature. Examine the flask during this process and record all observations in notebook.

To improve efficiency, one person can swirl two flasks, and the other person can weigh out the sodium bicarbonate, sodium chloride, and sodium thiosulfate for both people. (Remember to label these similar appearing white crystalline solids and to write the mass measurements directly in lab notebook.)

Place a piece of potassium iodide-starch test paper on a watch glass. Place a drop of the reaction mixture on the paper. Be sure to test the aqueous bleach layer and not the organic product layer that has risen to the top. Observe any color changes of the paper. If the paper turns a gray or black, excess oxidizing agent is present and you may proceed to the quench step. If the paper does not change its color the test for an oxidizing agent is negative. If this occurs add another 5 mL of bleach to the reaction mixture, swirl the flask for another 5 minutes, and repeat the test. If the paper turns black proceed to quench. If the paper still does not turn color add one more 5 mL aliquot of bleach, swirl for another 5 minutes then proceed.

Add 0.5-1.0 g of solid sodium thiosulfate (Na$_2$S$_2$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 blue litmus 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 2 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. Try to leave the undissolved sodium chloride solid behind in the Erlenmeyer flask. A narrow clear organic layer can be observed floating on top of a cloudy aqueous solution in the separatory funnel.

Let the solution sit undisturbed and separate for about five minutes. Slowly drain the entire 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 tiny 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 organic layer back in the shell vial.

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

Add a small amount of drying agent (sodium sulfate, Na$_2$SO$_4$) 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 water 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 at least 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.

**CLEANUP**

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

Your instructor may collect your product so that it can be used next week as the starting material for the next synthesis experiment. Before turning it in, make sure your name is clearly written on the shell vial with an indelible ink Sharpie pen.

If the product is not going to be collected, the cyclohexanone product and excess cyclohexanol should be placed in the non-halogenated liquid organic 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. Wipe work area down with sponge.

**POST-EXPERIMENT ASSIGNMENT**

Complete datasheet for this experiment.

Revised: March 13, 2014 S. L. Weaver
1 Personal Communication between S. L. Weaver and Steven Schultz, Chlorox PPD Technical Service on October 17, 2013