OXIDATION OF CYCLOHEXANOL TO CYCLOHEXANONE

INTRODUCTION
Alcohols can be oxidized to aldehydes and ketones using common oxidizing agents. Primary alcohols may be oxidized to aldehydes, and then to carboxylic acids. Secondary alcohols may be oxidized to ketones, while tertiary alcohols will not oxidize. This exercise will oxidize cyclohexanol to cyclohexanone using an acidic solution of sodium hypochlorite.

\[
\begin{align*}
\text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} & \rightarrow \quad \text{Catalyst} \\
& \quad \rightarrow \text{CH}_3\text{CH(O)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} + \text{H}_2
\end{align*}
\]

Sodium hypochlorite, NaOCl, is the component of common bleach, at about 5%, and the "chlorine" added to swimming pools. This concentration is almost 13%. The hypochlorite solution used in this experiment is the same as is added continually to the swimming pool at KVCC.

Today, you will be conducting a rearrangement reaction in which you will convert cyclohexanol into cyclohexanone. Our oxidation of cyclohexanol begins by generating the hypochlorous acid which will be the oxidizing agent. The balanced chemical equation is as follows:

\[
\begin{align*}
\text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} & + \text{NaOCl} \\
& \rightarrow \quad \text{H}_2\text{C} \text--\text{C} \text--\text{OH} \\
& \quad \rightarrow \text{CH}_3\text{CH(O)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} + \text{NaCl} + \text{H}_2\text{O}
\end{align*}
\]

As you can see from its formula, the chlorine in hypochlorous acid has an oxidation state of +1. Recall that chlorine normally has an oxidation number of -1. This deficiency of electrons makes this particular species very reactive. Since this is a very strong oxidizing agent, we will be generating it in situ through the reaction of acetic acid and sodium hypochlorite (regular household bleach). In the next step, the hydrogen on the hypochlorous acid undergoes nucleophilic attack by the oxygen of the cyclohexanol to form protonated cyclohexanol and a hypochlorite ion. This is followed by nucleophilic attack by the hypochlorite ion and displacement of water. The water then abstracts a hydrogen which initiates a cascade that results in the chlorine leaving as chloride ion and the generation of cyclohexanone.
**Procedure:**

1. Add 5.0 ml of cyclohexanol to a 100 ml round bottom flask and add 15 ml of glacial acetic acid. Cool the mixture in an ice bath to as close to 0 °C as possible.

2. Add 35 ml of sodium hypochlorite solution to a glass fitted separatory funnel and attach it to the round bottom flask. (note, your flask may only have two openings). Position the thermometer so it is immersed but is not hit by the magnetic stirring bar. Support your apparatus on a magnetic stir motor and adjust the speed of the motor so that the contents of the flask are stirred vigorously.

3. Monitor the temperature as the reaction proceeds. Add the hypochlorite solution slowly to the alcohol solution. Maintain the temperature of the reaction mixture at 30 - 40°C by controlling the rate of addition of NaOCl and the use of your ice - water bath, whenever necessary. **Do not over-cool your reaction mixture.** Maintain the reaction between these temperatures until all the hypochlorite is added. The addition should take a minimum of 10-15 minutes.

4. Remove the cooling bath and stir for fifteen minutes at room temperature.

5. Add saturated sodium bisulfite (NaHSO₃) to remove any yellow color remaining, which will remove any excess chlorine that is in the solution. The reaction mixture should turn colorless.

6. Rearrange your apparatus for steam distillation. Attach a Claisen adapter and a condenser to the round bottom flask.
Add 20 - 30 ml of water to the round bottom and distill about 30 ml of distillate into a graduated cylinder. The distillate should be a mixture of cyclohexanone and water that contains excess acetic acid. Transfer the distillate to a separatory funnel or beaker.

6. Add 3.5 grams of sodium carbonate to neutralize any excess acetic acid, and then add a small amount, about 3 grams of sodium chloride to "salt" out any cyclohexanone from the aqueous phase. Caution! All solids must completely dissolve! You might want to do this in a beaker to ensure that all of the solids dissolve and then transfer the solution to a separatory funnel.

7. Separate the layers. Collect the upper cyclohexanone layer in a small beaker and add a small amount of drying agent (calcium II chloride 4-20 mesh solid or anhydrous magnesium sulfate). Allow it to set and then decant into a clean, dry, tarred weighing bottle.

REPORT AND ANALYSIS

1. Calculate the theoretical, actual, and percent yields for cyclohexanone. (Make sure you show your work in your lab report).
2. Compare your boiling point with the literature value, what does this say about the purity of your product?
3. Determine the refractive index of the starting material, cyclohexanol, and your product, cyclohexanone.
4. Compare and contrast your FTIR versus the literature IR for the starting material and the product (see below). Make sure to discuss and label
   - The O-H stretch and the C-O stretch on the cyclohexanol spectrum.
   - The C=O stretch on the cyclohexanone spectrum and show the absence of the alcohol stretches.
5. Make sure to include in your lab report the complete reaction and mechanism for this reaction.
Reference Spectrum

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