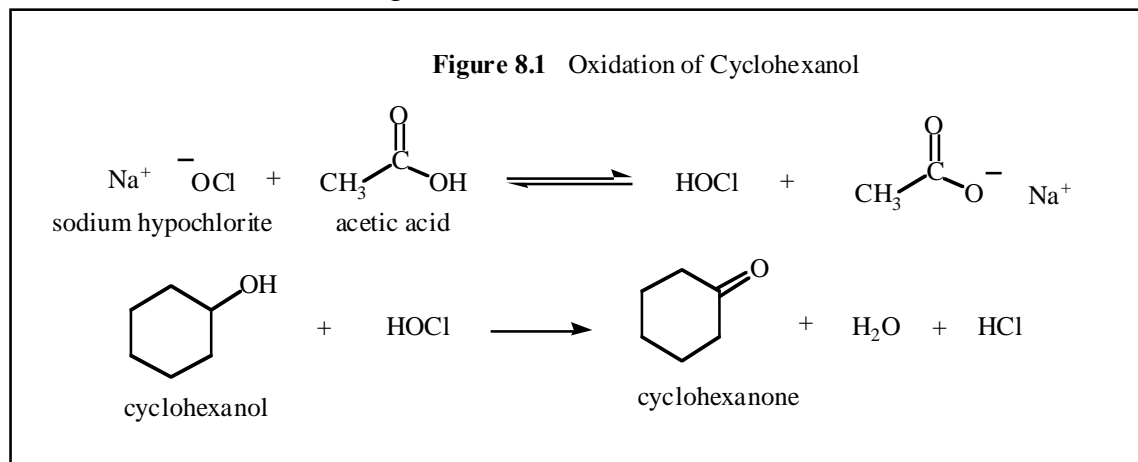


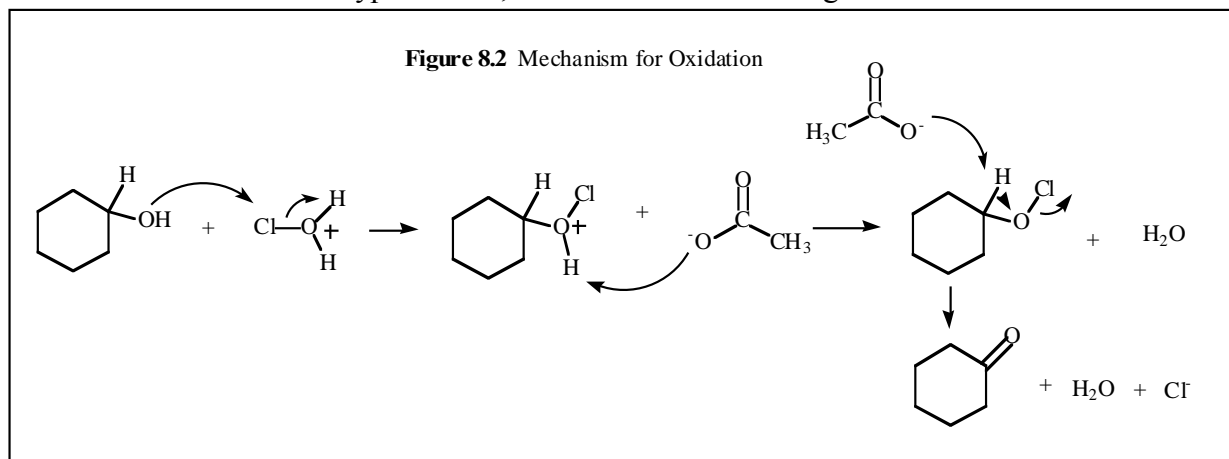
Experiment 8

Preparation of Cyclohexanone by Hypochlorite Oxidation

In this experiment we will prepare cyclohexanone from cyclohexanol using hypochlorite oxidation. We will use common household bleach that is a 5.25% (0.75 M) aqueous solution of sodium hypochlorite. The overall reaction is shown in Figure 8.1.



The exact reaction mechanism is not known but a plausible mechanism is given below. It is known that the mechanism does not involve free radicals and that yields are better in acidic rather than basic conditions. This is why we use acetic acid. It reacts with the sodium hypochlorite to give hypochlorous acid, which then reacts with the oxygen of the alcohol. Note the oxygen is more electronegative than chlorine so the oxygen attacks the chlorine of the hypochlorite, which has a formal charge of +1.



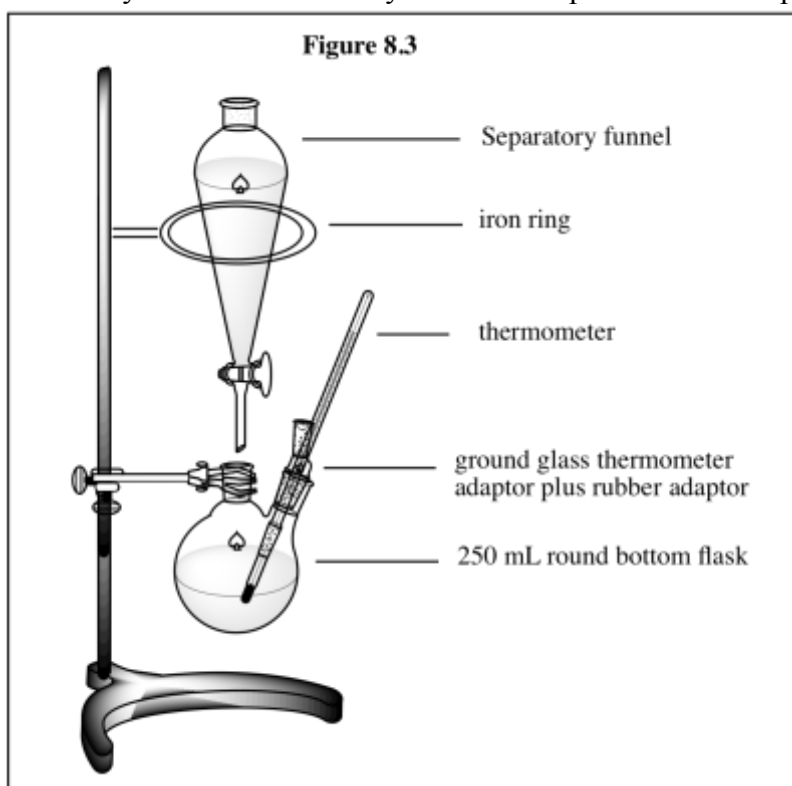
Physical Constants

| Compound | Mol. Wt (g/mol) | Density (g/mL) | b.p. (°C) | m.p. (°C) |
|-----------------|-----------------|----------------|-----------|-----------|
| Cyclohexanol | 100.16 | 0.96 | 161.5 | 25.5 |
| Cyclohexanone | 98.15 | 0.947 | 155 | -47 |
| Dichloromethane | 84.93 | 1.325 | 39-40 | -97 |

Procedure:

Set-up your 250 mL 2-necked round bottom flask as shown in Figure 8.3. Attach the thermometer using the red neoprene adapter. Add 6.0 mL cyclohexanol to the round bottom flask. In the 400 mL beaker, get 85 mL of bleach and add 4.0 mL glacial acetic acid in the hood.

Pour the bleach and acetic acid mixture into your separatory funnel and suspend it by an iron ring as shown in Figure 8.3. If you have a separatory funnel that is furnished with a ground glass joint at the bottom, DO NOT connect the joints since you want to have a system that is open to the atmosphere.



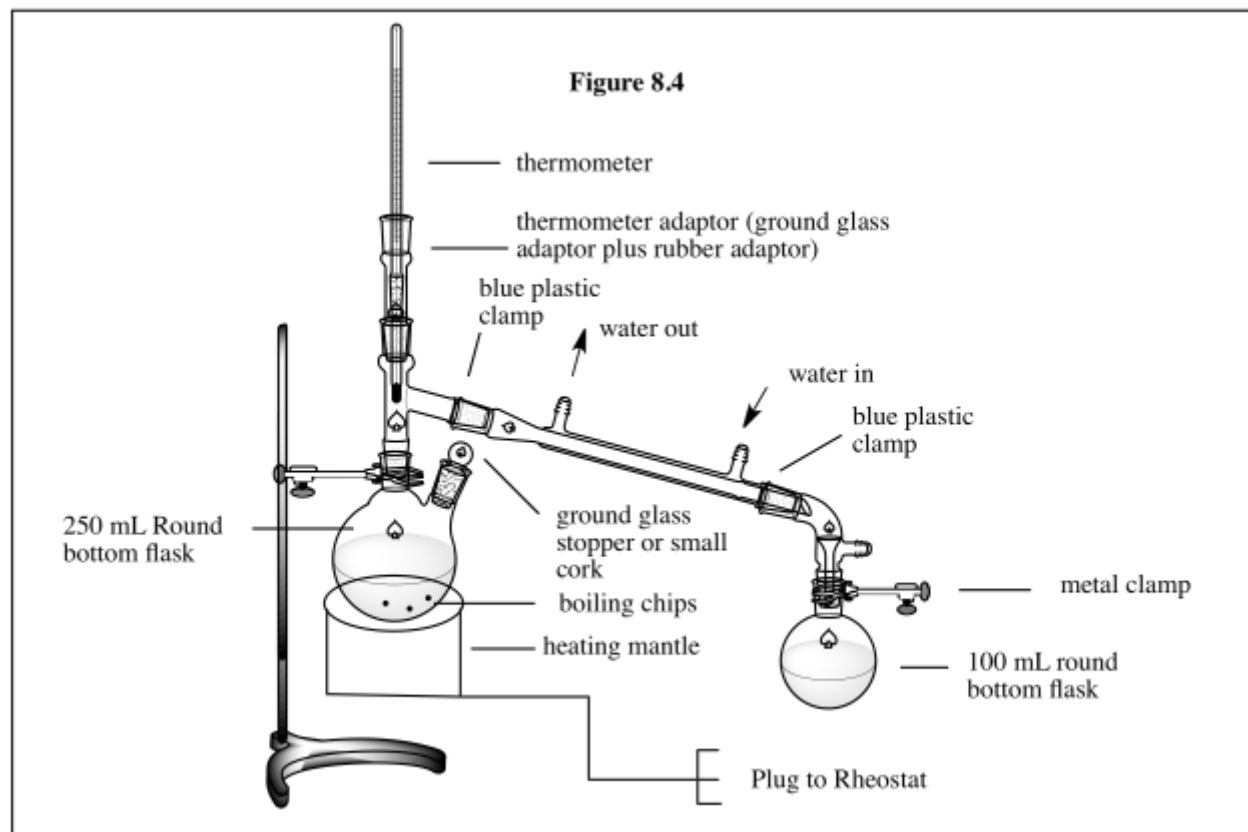
Begin adding the bleach solution slowly a few drops at a time. Monitor the temperature. You want to maintain the temperature between 40 – 50 °C. Do not allow the temperature to rise above 50 °C. Use the cooling bath if necessary. And, do NOT allow the temperature to fall below 40 °C. Otherwise the oxidation will not go to completion. The addition should take about 15 – 20 minutes to complete. Be patient. Add a few mL of the bleach, swirl the flask to mix and monitor the temperature.

When all of the bleach has been added, there should be a slight yellow color. If not, add more bleach until a faint yellow color persists. Sometimes it can be difficult to determine if there is actually a yellowish tint persists. Do not add more than 5-10 ml additional bleach. Holding a white piece of paper behind the flask can be helpful.

After all the bleach has been added, allow the reaction mixture to stand for 15 minutes with occasional swirling.

After 15 minutes, check the color of your reaction. If there is a slight yellow color, this indicates that there is an excess of hypochlorous acid. Add sodium bisulfite (NaHSO_3) solution until the yellow color disappears. Sodium bisulfite is a mild reducing agent and it will react with the hypochlorous acid. A few mL is usually sufficient.

Remove the separatory funnel and set-up your apparatus for a simple distillation as shown in Figure 8.4. Use the same 250-mL round bottom flask and use a 100 mL receiving flask. Transfer your thermometer to the



three-way adapter as shown in Figure 8.4. Place a secure cork in the small opening. Add a few boiling chips and distill your product, setting the rheostat on the heating mantle to about 70-80 V.

This will be a steam distillation. You will distill a mixture of water and cyclohexanone. Continue the distillation until you have collected about 40 mL. You should see a layer of cyclohexanone on the top and an aqueous layer of water and acetic acid on the bottom.

Work-up

When you have collected 40 mL stop the distillation. Remove the receiving flask and **CAREFULLY** add solid sodium carbonate (Na_2CO_3) using your spatula until you have neutralized all of the acetic acid that distilled over with your product. Add a small spatula tip of the solid sodium carbonate and stir with your spatula. You should see evolution of CO_2 gas. **DO NOT ADD THE SODIUM CARBONATE TOO QUICKLY TO THE SOLUTION BECAUSE IT CAN BUBBLE OVER.** Keep adding the solid until there is no more bubbling. Remove some of the aqueous layer on the bottom with a medicine dropper and test with litmus to see that it is neutral.

Cyclohexanone has some solubility in water. Add solid sodium chloride (add about 0.2 g of NaCl per milliliter of water present) to salt out the cyclohexanone from the water layer. Just as we did in the cyclohexene experiment, the idea is to saturate the aqueous layer with the very polar sodium chloride to drive the cyclohexanone from the water layer. Do not add too much of the sodium chloride. Add a spatula tip full, stir to dissolve and then add a bit more. Continue adding the NaCl until you see some solid material remaining.

Decant the solution from the round bottom flask into the separatory funnel. As before, be careful not to transfer any of the excess NaCl. It can clog the separatory funnel. The aqueous layer is on the bottom and the cyclohexanone organic layer is on the top. Drain off the bottom layer into a small beaker and save this. Pour the cyclohexanone into clean, dry 50 mL Erlenmeyer flask and set this to the side.

Pour the aqueous layer back into the separatory funnel and add 10 mL of dichloromethane (methylene chloride) to the separatory funnel. We are going to do a liquid-liquid **EXTRACTION** using the dichloromethane as the extracting solvent.

The theory behind this technique is simple: cyclohexanone is somewhat soluble in water so that some of it has remained in the water but it is much more soluble in an organic solvent such as dichloromethane. We therefore add dichloromethane to the water layer and shake the two layers vigorously so that small droplets of each solvent are formed and there is intimate mixing of the layers. It is very important that the layers are mixed thoroughly since we want any cyclohexanone that is remaining in the water layer to travel into the dichloromethane layer where it is more soluble. Shake the separatory vigorously for several minutes. Be sure to **VENT** the separatory funnel several times. Allow the layers to separate fully. This can take several minutes, particularly if you have an emulsion. If this occurs, gentle swirling of the separatory funnel may help to break up the emulsion.

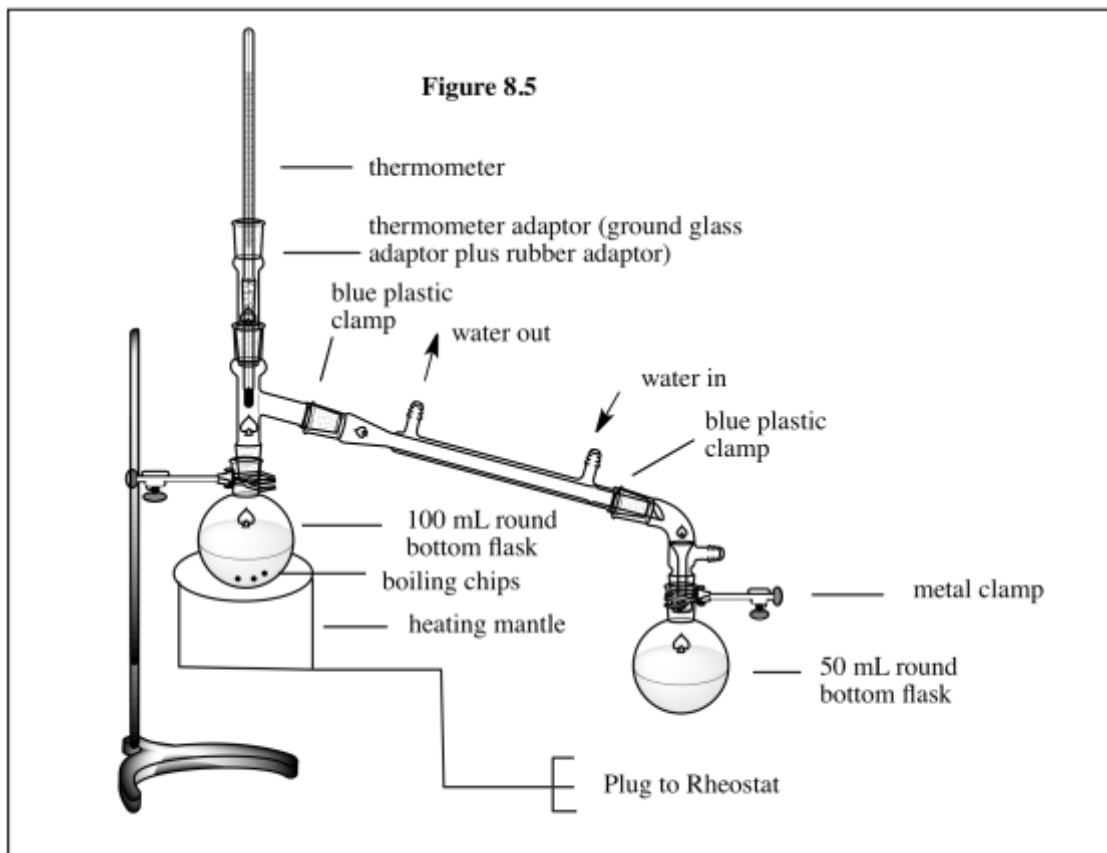
The organic layer may be on the bottom depending on how much NaCl you have added. Dichloromethane is **MORE DENSE** than the water but the addition of the NaCl will increase the density of the water layer until it may be more dense than the CH_2Cl_2 . Usually, however, the organic CH_2Cl_2 layer is on the bottom. Drain this layer into an Erlenmeyer flask and then check to ensure that the water layer is the one remaining in the separatory funnel. To do this, pour 2-3 mL water into the separatory funnel and check that there is still only one layer. If there is, then you have isolated the CH_2Cl_2 organic layer. Pour this into the flask containing the cyclohexanone.

Cover the bottom of the Erlenmeyer with anhydrous magnesium sulfate, stopper with a cork and allow to stand for 10 – 15 minutes with occasional swirling. Note that since water is lighter than the dichloromethane it tends to float on top of the dichloromethane and does not easily come into contact with the drying agent, which is on the bottom of the flask. If you see drops of immiscible liquid on top of the CH_2Cl_2 , then you will need to stir the solution vigorously with your spatula so that the water comes into contact with the drying agent.

Set up the apparatus for a simple distillation using the same set-up shown in Figure 8.4. This is pictured again in Figure 8.5. Use the 100 mL round bottom as the distilling flask and your 50 mL round bottom for collecting the initial fraction. Be sure that all of the glassware is dry. Filter the organic layer from the drying agent into the 100 mL round-bottom flask through a small plug of cotton using your stem-less funnel.

We will do a simple distillation. Our organic layer contains two compounds: dichloromethane and the desired product, cyclohexanone. Since there is a very large difference in boiling point between the dichloromethane (b.p. 39-40 °C) and the cyclohexanone (b.p. 161.5 °C), we do not need to use the copper wool as we did in Experiment 4.

First set the rheostat on your heating mantle in the 35-45 range for the distillation of the dichloromethane. **Be sure to add boiling stones.** Collect the dichloromethane in your 50 mL round bottom flask. This will be the material that boils around 40 °C. This is **NOT** your product but is essentially waste solvent. Discard this in the waste container for halogenated solvents under the hood.



When all of the dichloromethane has distilled over, increase the setting on the rheostat to the 90-100 range. Do not change your collecting flask until the temperature of the distillate approaches the boiling point of cyclohexanone. Then quickly switch to your 25 mL flask and collect material that boils between 150-155 °C. This is your product. When the temperature of your distillate rises above 150 °C (or falls below 155 °C) or no more material is distilling over, stop your distillation. **Be careful. The glassware is very hot.** Allow everything to cool before disassembling.

Obtain the weight of cyclohexanone, record the weight in your notebook and on the Yield report Sheet. Calculate your percent yield. Turn in your Yield Report Sheet.