Experiment 11: Dehydration of Cyclohexanol

INTRODUCTION

In this experiment, cyclohexanol is dehydrated by aqueous sulfuric acid to produce cyclohexene as the sole product [equation (1)], and no rearrangement is possible in this reaction.

\[
\text{cyclohexanol} \xrightarrow{\text{H}_2\text{SO}_4, \text{heat}} \text{cyclohexene} + \text{H}_2\text{O} \quad (1)
\]

The mechanism of this reaction is shown in equation 2. The hydroxyl group of an alcohol is a poor leaving group but is converted to a much better one by protonation of oxygen to give an oxonium ion. These types of proton transfers are typically very fast reactions and can be reversible. Next, in the rate-determining step, loss of a molecule of water gives the carbocation intermediate. Finally, deprotonation gives the desired alkene product and regenerates the acid catalyst. Note that even weakly basic compounds, such as water, can deprotonate a carbocation to form an alkene. Overall, this mechanism is referred to as an E1 elimination reaction

\[
\begin{align*}
\text{H} &-\text{C} \equiv \text{C} & + \text{H}^+ & \quad \text{fast} & \quad \text{H} &-\text{C} \equiv \text{C} \quad \text{slow} & \quad \text{H} &-\text{C} \equiv \text{C}^+ & + \text{H}_2\text{O} \\
\text{H} &-\text{C} \equiv \text{C}^+ & \quad \text{fast} & \quad \text{C} \equiv \text{C} & + \text{H}^+
\end{align*}
\]

The mechanism for this reaction depends on the class of alcohol being dehydrated, and the one shown in equation (2) is for 2º and 3º alcohols. The -OH group in an alcohol is a poor leaving group but is converted to a better one by protonation of oxygen to give an oxonium ion. The oxonium ion undergoes decomposition by loss of a molecule of water to give a carbocation intermediate whose formation is the rate-determining step. This mechanism is referred to as an E1 mechanism. Careful examination of the mechanism reveals that hydrogen ion (the proton) is a catalyst in the reaction; it is consumed at the beginning and regenerated at the end.

For this alcohol, cyclohexanol, carbocation rearrangements to form a more stable carbocation are not possible and so cyclohexene is observed as the only product.
Compelling evidence for carbocation intermediates comes from the observation that 2° carbocations derived from certain 2° alcohols may undergo rearrangement to form more stable carbocations. This can result in the formation of rearranged isomeric alkenes.

Both 2° and 3° alcohols primarily undergo the E1 reaction under these conditions, whereas for 1° alcohols and methyl alcohol, symmetrical ethers are the major products; these are formed by nucleophilic attack of an alcohol molecule on the oxonium ion formed from protonation of another alcohol molecule. Some dehydration of 1° alcohols may also occur to give alkenes but in this case, the mechanism is a concerted E2 elimination process in which loss of water (from the protonated hydroxyl group) occurs simultaneously with loss of the proton. In this way, the formation of a very high-energy primary carbocation intermediate is avoided.

Finally, it should be noted that this type of dehydration reaction is entirely reversible. In fact, if you read the mechanism shown in Equation 2 from right to left, you may recognize it as the acid-catalyzed hydration of an alkene! The position of this equilibrium is strongly dependent upon the reaction conditions.

Compelling evidence for the intervention of a carbocation intermediate comes from the observation that secondary carbocations derived from certain 2° alcohols may undergo molecular rearrangement to a more stable carbocation. This results in the formation of rearranged, isomeric alkenes. Carbocation rearrangements are discussed in your textbook and in lecture.

**DISCUSSION OF THE EXPERIMENT**

Since this dehydration reaction is reversible, LeChatelier's principle provides several ways in which we might shift the position of the equilibrium towards the products. One possibility would be to remove water as it is formed. However, in this reaction, the position of equilibrium will be shifted to the right by continuously removing cyclohexene as it is formed using fractional distillation with a packed fractional distillation column. Fractional distillation also ensures that the cyclohexene product (boiling point = 83°C) is not contaminated with the cyclohexanol starting material (boiling point = 161°C). In practice, the distillate does not even boil at 83°C because cyclohexene and water form an azeotrope whose boiling point is 70°C; it is this cyclohexene-water mixture that is collected as the distillate.

The distillate is transferred to a separatory funnel and aqueous NaOH solution is added to the funnel. (This process is called “washing”.) The NaOH removes any trace of acid that may have co-distilled with the product. The aqueous layer is carefully removed, leaving the product in the funnel. The “wet” product is then transferred to a sample vial and treated with calcium chloride, CaCl₂, to remove traces of moisture that are
contained in the cyclohexene. The preparation concludes by filtering the dry product from the solid drying agent, CaCl₂.

If enough product was formed, it could be purified further by simple distillation, but with the apparatus available, this will not be done. The cyclohexene you obtain will be pure enough for comparing its infrared spectrum with that of the starting material, cyclohexanol.

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**REAGENT/PRODUCT TABLE:**

<table>
<thead>
<tr>
<th>Reagents</th>
<th>MW (g/mol)</th>
<th>MP (ºC)</th>
<th>BP (ºC)</th>
<th>Density (g/mL)</th>
<th>Molarity (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexanol</td>
<td>100.16</td>
<td>23-25</td>
<td>161</td>
<td>0.965</td>
<td>N/A</td>
</tr>
<tr>
<td>sulfuric acid</td>
<td>98.07</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>9 M</td>
</tr>
<tr>
<td>water</td>
<td>18</td>
<td>0</td>
<td>100</td>
<td>1.00</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Products</th>
<th>MW (g/mol)</th>
<th>MP (ºC)</th>
<th>BP (ºC)</th>
<th>Density (g/mL)</th>
<th>Molarity (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexene</td>
<td>82.15</td>
<td>-104</td>
<td>83</td>
<td>0.811</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**FOR YOUR SAFETY**
1. Wear gloves at all times when handling the aqueous sulfuric acid at the beginning of the reaction and when disposing of the acid remaining in the reaction flask after the distillation of the crude cyclohexene is complete.
2. Make certain the reaction flask is COOL before disassembling the distillation apparatus and cleaning the flask.

**EXPERIMENTAL PROCEDURE**

1. Into a clean 100-mL round-bottom flask (it does not have to be dry - why?) place 10 mL of cyclohexanol (density = 0.963 g/mL) and then add 5 mL of 9 M sulfuric acid (wear gloves when handling the acid). Mix the contents of the flask by swirling it carefully. Clamp the flask and place a heating mantle under it.
2. Place 2-3 boiling chips in the reaction flask, and assemble a fractional distillation apparatus using a packed column. Have your instructor check your apparatus to be sure it is correct before going further.

3. Turn on the power to the VARIAC, set it to 90-95 and heat the reaction mixture. Collect all the distillate in a clean (why not dry?) 25-mL round-bottom flask that is clamped just below the condenser outlet. Discontinue heating when no distillate comes off, at which time the 25 mL round-bottom flask should be 1/3 to 1/2 full, or when the head temperature either drops below 60ºC or rises above 70ºC and no oily layer is visible in the reaction flask. You may also see “smoke” in the round-bottom flask, indicating the reaction/distillation is complete.

4. Transfer the distillate to a clean separatory funnel (why not dry?), making sure the stopcock is closed. Add about 10 mL of aqueous 3 M NaOH solution to the funnel and shake well with periodic venting. Drain the lower aqueous layer from the funnel (remove the stopper from the funnel before trying this) into a clean small beaker and leave the upper organic layer in the funnel. Do NOT discard the aqueous layer until the end of the experiment.

5. Pour the organic layer in a clean, dry large sample vial. Add enough anhydrous CaCl₂ so that the bottom of the vial is covered. Cap the vial (make sure the cap has an insert in it or it may leak), and swirl it for about 5 minutes. If the organic product is not clear or if the CaCl₂ clumps and sticks to the bottom, the drying agent is completely hydrated. Continue to add CaCl₂ in small amounts (each time with swirling) until the solution is clear and the CaCl₂ is freely moving.

6. Take a clean, dry short-stemmed glass funnel, place a piece of fluted filter paper and clamp the funnel by the stem. Place a dry, tared (pre-weighed) large sample vial under the stem of the funnel; move the funnel so the stem extends into the vial, and pour the dried cyclohexene into the funnel. This procedure is useful for removing solids, such as drying agents, from an organic liquid.

7. When the filtration is complete, reweigh the vial to determine the weight of product obtained. This is accomplished by subtracting the weight of the empty vial from the weight of the vial containing the product.

8. Run an IR spectrum of your product and hand-in the properly labeled product.
WASTE DISPOSAL AND CLEAN-UP

1. Place the basic aqueous layers from the washing (Step 4) in the appropriate labeled container in the waste hood.
2. Place the acid solution remaining in the reaction flask (Step 3) in the appropriate labeled container. Be sure the flask is cool before handling it.
3. Wash the round bottom reaction flask (Step 3) with water and clean the flask with a brush as well as possible. Then wash the flask with acetone. Acetone rinses should be disposed of in the appropriate labeled container.
4. Place the packing from the fractional distillation column in the “used packing” container.
5. Clean all glassware that was used in this experiment and place it in the appropriate locker - your personal drawer or the common locker. If you wash any glassware with acetone, wash it again with water before putting it away. Do not put any glassware containing acetone in the glassware kit in the common locker.

REQUIRED CALCULATIONS

Do the following calculations in your laboratory notebook:
1. Calculate the number of moles of cyclohexanol used in your experiment.
2. Calculate the theoretical yield of cyclohexene, based on the amount used in your experiment.
3. Calculate the percent yield for your experiment.