Dehydration of Alcohols-Gas Chromatography

OBJECTIVE

In this lab, we will examine the phosphoric acid catalyzed dehydration of 2-methylcyclohexanol. Gas chromatography will be used to monitor the outcome of the reaction. From the chromatogram, we will calculate the retention times of the product(s) as well as the relative ratio of product(s).

INTRODUCTION

Under acid-catalysis an alcohol may be dehydrated to form an alkene. The most common acids employed for the reaction are sulfuric or phosphoric acids. Mechanistically, the reaction proceeds via initial protonation of the hydroxyl group (a typical acid-base reaction). This converts the hydroxyl unit from a poor leaving group (–OH) into a much better one (H_2O). Loss of water generates a carbocation, which can stabilize itself by elimination of a proton from an adjacent carbon to produce the alkene. The elimination of the proton will predominately occur in the direction that results in the production of the more highly substituted carbon-carbon double bond.

The carbocation has other fates depending upon substrate, reaction conditions, and acid employed. The carbocation can undergo rearrangement to a more stable species (i.e., 1° to a 2°, or 3°) via a shift of a hydride (or CH_3^-) from an adjacent carbon, followed by elimination.

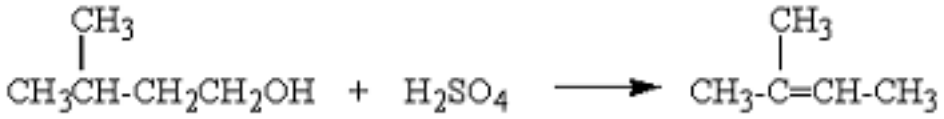

Figure 1

If we use a hydrogen halide as the acid, we produce the substitution product rather than the elimination product. The reason is that the conjugate bases of these acids are more nucleophilic than the HSO_4^- or $H_2PO_4^-$ produced from sulfuric or phosphoric acids. This nucleophilic conjugate base then adds to the carbocation rather than abstracting a proton from the adjacent carbon, thus substitution occurs.

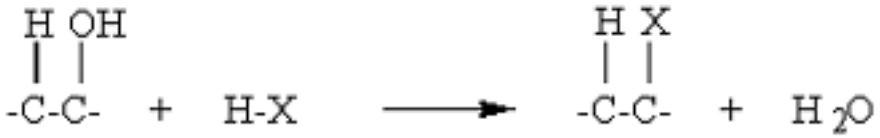

Figure 2: Dehydration of 2-methylcyclohexanol: Gas Chromatographic Analysis of the resulting product mixture.

In Gas Chromatography ("GC," or sometimes "VPC" for Vapor Phase Chromatography), we inject a liquid solution which is rapidly vaporized and then passed as a vapor over a solid mate-

rial which usually has a very high boiling liquid (such as Carbowax) adsorbed on it to act as the "adsorbent." The separation takes place as the vaporized mixture is adsorbed, vaporized, readsorbed, vaporized, etc. as it passes along the column. Since different materials will be adsorbed and vaporized at different rates, separation will take place if the column is long enough. The various components will come off the column at different times ("retention times," or 'Rt'). As each component exits the column, it will be detected and registered as a "peak" on the recorder.

Helium is commonly used as a carrier gas. The gas must be supplied at a controlled flow rate. Liquid samples are vaporized in a heated chamber. A thermal conductivity cell is commonly used as the detector. A record of the elution of components of the mixture is made by a chart recorder.

The column is the critical component of a vapor phase chromatograph. For a separation to occur, conditions must be achieved that result in components of the mixture having different retention times on the column.

Four experimental factors affect the retention time of a given compound:

- the length of the column
- the temperature at which the column is maintained
- the rate of flow of the carrier gas
- the nature of the stationary liquid phase

$$\text{Apiezon grease (SE-30) (nonpolar)} < \text{Silicone oil} < \text{Carbowax (polar)} \qquad (1)$$

A vapor phase chromatogram may be used in the qualitative and quantitative analysis of a sample of volatile components.

$$\text{Retention Time, RT} = \frac{\text{Length}}{\text{Paper Rate}} \qquad \text{pay attention to units} \qquad (2)$$

For a given set of conditions, retention time is a reproducible property of a compound. It is useful in the identification of a compound. The area under the peak is related to the amount of compound that is characterized by the peak. The relative area of the two peaks of a chromatogram of a binary mixture essentially describes the weight percentage ratio in the mixture.

Figure 3: Gas Chromatography Instrument

PRE-LAB

Answer all assigned WebAssign questions.

PROCEDURE

1 Before you start to set up for the microscale distillation, watch the short video[1] to familiarize yourself with the process.

2 To a clean, dry 5 mL reaction vial containing 2 or 3 boiling chips, add 1.0 mL of 2-methylcyclohexanol followed by 2 mL of 85% phosphoric acid.

3 Attach a Hickman still head with thermometer and heat the reaction mixture to boiling (**using the hot plate and the aluminum heating blocks**). The setup is shown below.

[1] https://www.youtube.com/watch?v=46gqI90ELuU

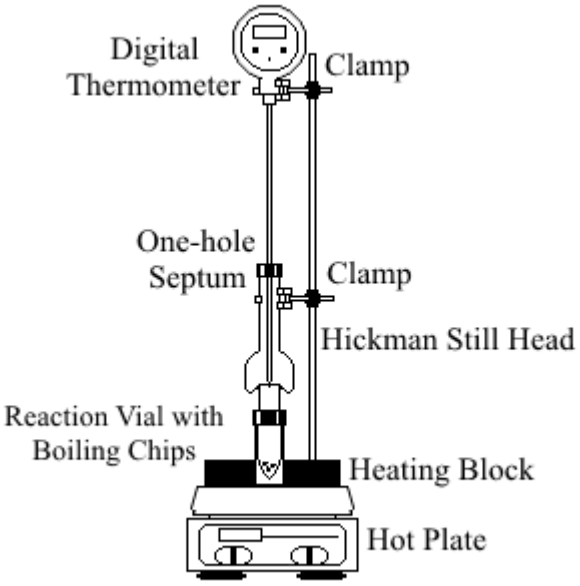

Figure 4: Hickman Distillation Apparatus

4 Note the temperature of the still head (measured by positioning the tip of the thermometer about 1 cm above the liquid level) as you are collecting distillate, and try to keep the temperature of the **vapor** below 95°C. Distill until 0.5-0.7 mL of distillate is collected (you will see that the lip on the Hickman condenser fills up).

5 Transfer the distillate from the still head to a small test tube using a Pasteur pipet.

6 Dry the product for about five minutes over anhydrous Na_2SO_4 using just enough drying agent to make a thin layer at the bottom of the small test tube.

7 You can watch a video[2] that demonstrates how to dry an organic liquid using anhydrous sodium sulfate.

8 Using a Pasteur pipet, transfer the dried liquid to a clean test tube for gas chromatographic analysis.

9 You can watch a video[3] that describes how to inject your sample in the GC. Watch it before you proceed.

10 Your TA can also show you how to inject your sample in the GC.

11 After you get your chromatogram, calculate the percentage of each product in the mixture by calculating the area of each peak. Which one do you think is the major product?

12 Calculate the percent composition of the mixture using the equations shown below. You can watch a video[4] that will walk you through the process.

[2] https://www.youtube.com/watch?v=XcLSetPie_M
[3] https://www.youtube.com/watch?v=X8hQUQHOYlA
[4] https://www.youtube.com/watch?v=03uDmX9ycIg

IN-LAB QUESTIONS

Please print the worksheet for this lab. You will need this sheet to record your data.

Questions

1 Reaction Equation:

2 Chart Speed _____

3 Retention Time for 1-methylcyclohexene _____

Retention Time for 3-methylcyclohexene _____

4 Area of 1-methylcyclohexene _____

Area of 3-methylcyclohexene _____

5 Percent 1-methylcyclohexene _____

Percent 3-methylcyclohexene _____

How to Calculate the % Composition of a Mixture from a GC Printout

The area under a gas chromatograph peak is proportional to the amount (moles) of the compound eluted. Therefore, the molar percentage composition of a mixture can be approximated by comparing relative peak areas. This method of analysis does assume that the detector is equally sensitive to all compounds eluted and that it gives a linear response with regard to amounts. It is a useful method because it gives reasonably accurate results.

The simplest method of measuring the area of a peak is by triangulation. In this method, one multiplies the height (h) of the peak above the base line of the chromatogram by the width of the peak at half of its height ($\frac{1}{2}w$). This is illustrated in the figure below. The base line is approximated by drawing a line between the two "sidearms" of the peak. Approximate area $= h \times \frac{1}{2}w$.

To obtain a percent composition for the mixture, we first add all the peak areas. Then, to calculate the percentage of any compound in the mixture, we divide its individual area by the total area and multiply the result by 100. A sample calculation is included in the figure.

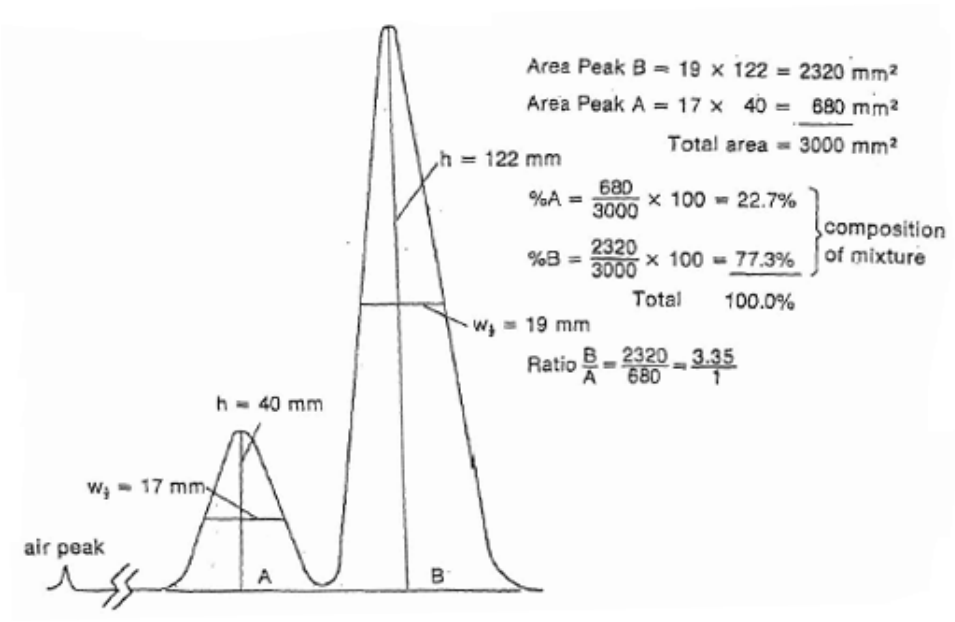

Figure 5: Sample GC Printout with Calculations

