EXPERIMENT 1
DEHYDRATION OF 2-BUTANOL
&
DEHYDROBROMINATION OF 2-BROMOBUTANE: ANALYSIS OF GASEOUS PRODUCTS BY GAS CHROMATOGRAPHY

A part of this procedure is adopted from an article published by H.M. Gilow in the *Journal of Chemical Education,* **1992**, *69*, A265

Reading Assignment for Experiment 1:

Review ***Pavia*** Sections 22.1-22.12.
Supplementary information can be found in ***Smith***, sections 8.4-8.6, 8.8-8.9, 9.8.

Pre-lab Questions:

1) Pavia chapter 22 Questions #1, #2.
2) Predict the major product expected in the dehydration reaction, and in the dehydrobromination reaction.

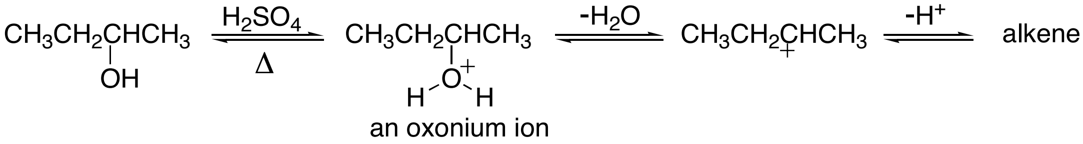
In this experiment, we will compare and contrast the acid-catalyzed dehydration of a secondary alcohol and the dehydrobromination of an isomeric halide with strong base. These reactions are used extensively for the preparation of alkenes. The stereo- and regio-chemistry of the two reactions will be investigated using gas chromatography to analyze the product mixture.

Background Discussion

The acid-catalyzed dehydration of a 2-butanol and the base-induced dehydrobromination of 2-butanol with strong base both lead to the formation of a mixture of butene isomers. The composition of this mixture varies, however, as a result of mechanistic differences in these two pathways.

Acid-catalyzed dehydration reaction: An E1 reaction

Dehydration of a secondary alcohol proceeds readily with the presence of strong acid such as sulfuric or phosphoric acid, and proceeds via an E1 mechanism. In step 1, protonation of the hydroxyl group of the alcohol with the acid catalyst converts the poor leaving group -OH to a much better leaving group, H_2O. The loss of a water molecule from the oxonium ion intermediate results in a carbocation intermediate, which undergoes E1 elimination to form an alkene.

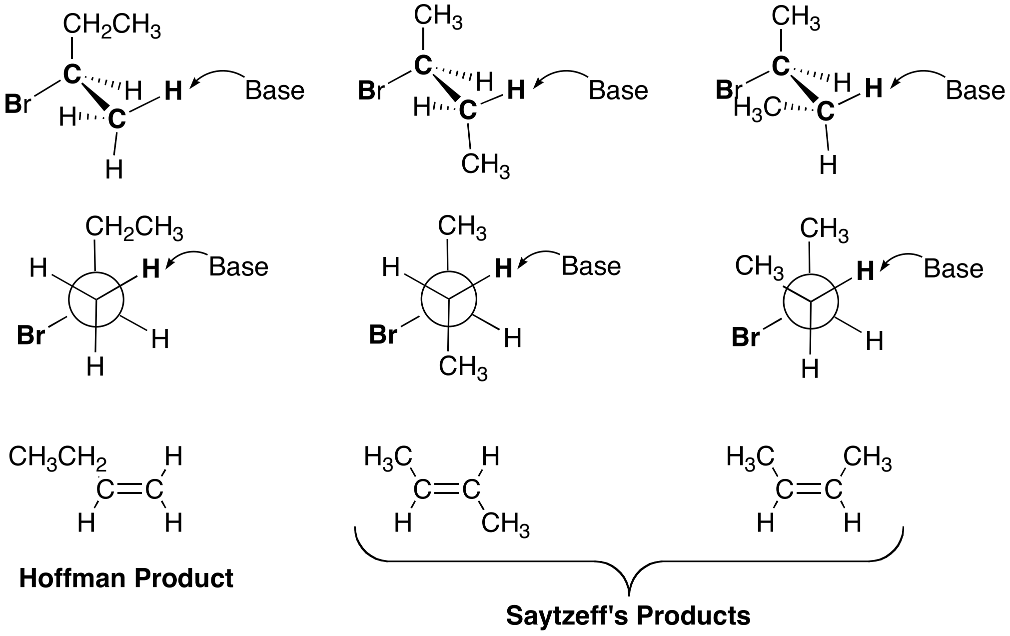


$$CH_3CH_2\underset{OH}{CH}CH_3 \xrightleftharpoons[\Delta]{H_2SO_4} CH_3CH_2\underset{\underset{H\quad H}{O^+}}{CH}CH_3 \xrightleftharpoons{-H_2O} CH_3CH_2\underset{+}{C}HCH_3 \xrightleftharpoons{-H^+} \text{alkene}$$

This is a reversible reaction that must be driven to completion. According to LeChatelier's principle, removing a product from a chemical system at equilibrium shifts the equilibrium in the direction favoring the formation of the products. You will carry out the dehydration reaction in a reaction tube connected to a gas collector so that the product will continuously escape out of the reaction mixture as it is formed. Removal of the product will shift the equilibrium to the right and thus complete the reaction. The collected gaseous product will be analyzed by gas chromatography, which will show peaks with fair resolution. From the relative area of peaks, you can calculate the percentage composition of the product mixture.

Dehydrobromination Reaction: An E2 reaction

Base-induced dehydrohalogenation of an alkyl halide is another alternative for synthesizing alkenes, and proceeds *via* an E2 mechanism. The use of strong and bulky base promotes the elimination reaction and disfavors the competing S_N2 reaction, which is disfavored when bulky reagents are used. The E2 reaction requires an *anti*-periplanar arrangement of the β-H and leaving group (the β-H and leaving group must be in the same plane and *anti* to each other). Because 2-bromobutane has two different types of β-H's, elimination on either side can lead to both internal and terminal alkenes. Newman projections of the three possible antiperiplanar elimination pathways are shown below. The most thermodynamically stable arrangement is expected to form the major product.



The **Hoffman** product is the least substituted alkene product, and the **Saytzeff** products are the most-substituted, and therefore most stable alkenes. Of the two possible Saytzeff products, the *trans*-alkene is the most stable. When the base and the alkyl halide are both sterically hindered, it can be difficult for the hindered base to remove a β-hydrogen on a more substituted carbon, and the less substituted alkene product predominates. An elimination that gives the least substituted alkene as a major product is called a **Hoffman Elimination**. When the β-hydrogen is removed preferentially from a carbon atom that has fewer hydrogens, more substituted, and therefore more stable, alkenes are formed and this pathway follows **Saytzeff's rule.**

In this experiment, you will carry out the dehydration of 2-butanol and the dehydrobromination of 2-bromobutane. An analysis of the product distribution for each reaction will give information about the mechanism of the reaction, and give an indication of steric constraints in the two alternate mechanisms.

CAUTION

All **alkyl halides** are harmful if inhaled, ingested, or absorbed through the skin. Wear gloves, an keep all chemicals/reactions in the hood at all times.

Potassium tert-butoxide is corrosive and moisture-sensitive. Avoid contact with skin, eyes, and clothing.

Sulfuric acid is corrosive and causes burns. Notify the instructor if any acid is spilled.

2-butanol is flammable and toxic. Avoid contact with skin, eyes and clothing.

Experimental

A. Dehydration of 2-Butanol

Assemble the gas collection apparatus shown in **figure 1** below ***before the reactants are mixed*** by carrying out the following steps:

(**1**) Fit the collection tube with a septum stopper in one end.
(**2**) Fill the collection tube with water,
(**3**) Insert the end of the Teflon tubing that is coming out from the top of the septa into the collection tube all the way up to reach the stopper.
(**4**) Place your index finger over the top end of the tube and invert it (water should remain in the tube.)

(**5**) Place the tube, with the open end down, into a 250-mL beaker half-filled with water.
(**6**) Remove your finger (the column of water should remain in the tube.)
(**7**) In the reaction tube, place 2 drops of concentrated sulfuric acid. Add a boiling stone, then place a rubber septum on top.
(**9**) Connect the other end of the Teflon tubing to the reaction tube as shown in **figure 1**.

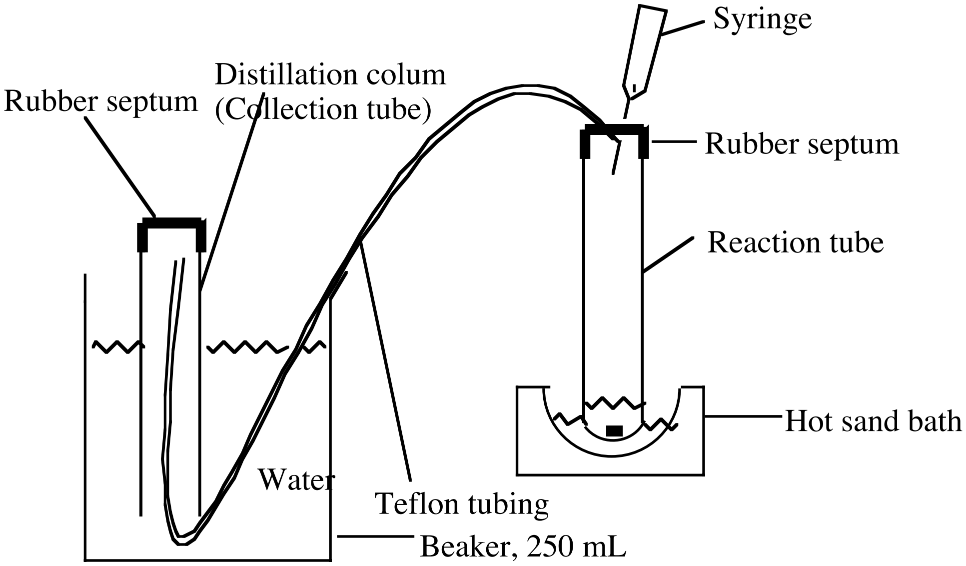


Fig. 1: Assembly for the Generation of Gaseous Products

After the assembly is complete, add 0.2 mL of 2-butanol to the reaction tube using a syringe and heat the mixture in a preheated sand bath. Generation of gaseous product can be observed by watching the rapid decrease of the water level in the collection tube. **Keep heating until no more bubbles escape from the bottom of the collection tube.** Remove the Teflon tubing from the gas collection tube, and then from the beaker, before removing the reaction tube from the heat. Use this sequence of steps in shutting down the reaction to prevent water from being sucked back into the hot reaction tube while it is cooling down. Label the beaker containing the collection tube kept in the water and submit it for the gas chromatographic analysis.

The butenes have been determined to elute from the non-polar column (SE30) in the following order: 1-butene, *trans*-2-butene, and *cis*-2-butene. Determine the relative amount (% composition) of the three components of gas products, assuming that the amount of each substance in the gaseous mixture is proportional to the area under its corresponding GC peak. Assume that these areas are equal to the peak height (mm) × the peak width at a half-height (mm).

B. Dehydrobromination of 2-Bromobutane

Assemble the gas collection apparatus shown in **figure 2** below ***before the reactants are mixed*** by carrying out the following steps:

(**1**) Fit the collection tube with a septum stopper in one end.
(**2**) Fill the collection tube with water,
(**3**) Insert the end of the Teflon tubing that is coming out from the top of the septa into the collection tube all the way up to reach the stopper.
(4) Place your index finger over the top end of the tube and invert it (water should remain in the tube.)
(**5**) Place the tube, with the open end down, into a 250-mL beaker half-filled with water.
(**6**) Remove your finger (the column of water should remain in the tube.)
(**7**) In a10 mL round-bottom flask equipped with a water-cooled condenser, place 5 mL of 1*M* potassium *t*-butoxide (*or* 575 mg of potassium *t*-butoxide powder and 5 mL of *t*-butanol) using the Automatic pipette. Add a boiling stone to the flask.
(**9**) Connect the other end of the Teflon tubing to the top of the water-cooled condenser as shown in figure 2.

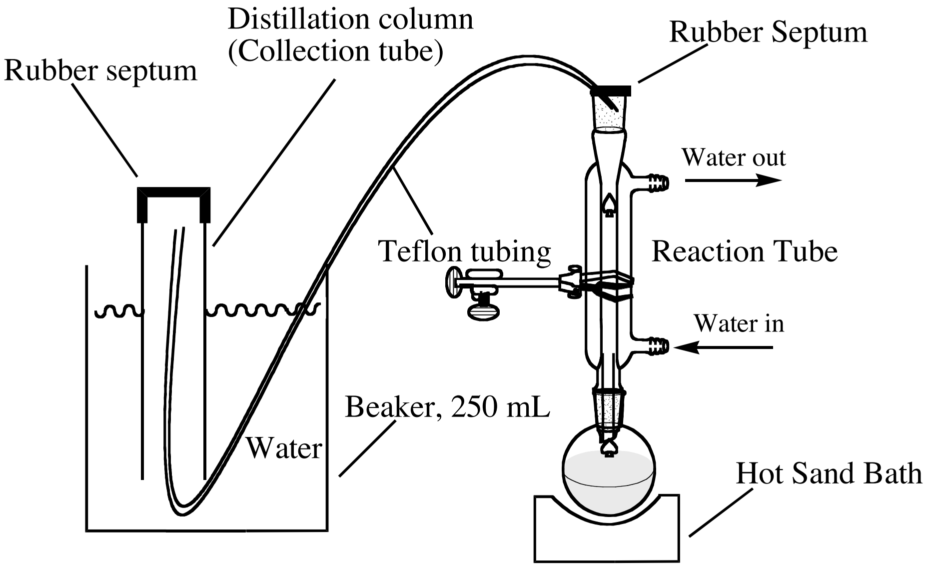


Fig. 2: Assembly for the Generation of Gaseous Products

After the assembly is complete, add 0.5 mL of 2-bromobutane to the 10 mL round bottom flask using a syringe, and heat the mixture in a preheated sand bath. Generation of gaseous product can be observed by watching the rapid decrease of the water level in the collection tube. **Keep heating until no more bubbles escape from the bottom of the collection tube.** Remove the Teflon tubing from the gas collection tube, and then from the beaker, before removing the reaction tube from the heat. Use this sequence of steps in shutting down the reaction to prevent water from being sucked back into the hot reaction tube while it is cooling down. Label the beaker containing the collection tube kept in the water and submit it for the gas chromatographic analysis.

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In your lab write-up, construct a data table with the percent composition of each of the three products for both reactions. Discuss the difference of the product composition from both reactions. If the GC plot did not match what you predicted, provide an explanation as to what might have happened.

Post-lab Questions:

1. Write the structure of the three alkenes produced by the dehydration of 3-methyl 3-pentanol. Which one would you expect to be the major product?
2. Write the structure of the three alkenes produced by reaction of tert-butoxide with 3-methyl-3-bromopentane. Which would you expect to be the major product? What would be the major product if the base was changed to ethoxide ion?
3. A student wished to prepare ethylene gas by dehydration of ethanol at 140^{o}C using sulfuric acid as the dehydrating agent. A low-boiling liquid was obtained instead of ethylene. What was the liquid, and how might the reaction conditions be changed to give ethylene?
4. From your knowledge of the dehydration of tertiary alcohols, which alkene should predominate in the product of the dehydration of 2-methyl-2-butanol and why?
5. What is the maximum volume *(at STP)* of the butene mixture that could be obtained by the dehydration of 91 mg of 2-butanol?
6. The percentages of each alkene calculated from the GC peak areas in this experiment are reasonably close the true percentages, but not 100% accurate. How would you increase the accuracy of these percentages *(hint: remember experiment 4 last quarter?)*