# *DEHYDRATION OF AN ALCOHOL*

**OVERVIEW:** The purposes of this experiment are to demonstrate the acid-catalyzed dehydration of an alcohol to produce a mixture of alkene isomers; to analyze the products of the reaction by gas chromatography; and to interpret the results in terms of the mechanism of the reaction.

**BACKGROUND:** Dehydration of 3-methyl-3-pentanol with 85% phosphoric acid yields a mixture of alkenes. The reaction proceeds by a mechanism that is the reverse of the acid-catalyzed Markovnikov hydration of an alkene. The relative amounts of each of the alkenes produced can be determined by gas chromatography. These results suggest which isomer is more stable and is, therefore, the preferred reaction product. In addition, an unexpected product suggests the importance of rearrangements in reactions involving carbocations.

**SAFETY:** Phosphoric acid is corrosive to skin and clothing. Use gloves and a face shield when handling phosphoric acid. Use sodium bicarbonate solution to neutralize a spill. Quickly wash any affected skin with lots of soap and water. The alcohol and alkenes are volatile and flammable liquids. Use only a heating mantle for heating and distilling the reaction. Work in the hood at all times, and collect the products in an ice bath to prevent loss or product by evaporation.

**LAB NOTEBOOK:** In your notebook, be sure to have a balanced equation showing the reactants and <u>all possible products</u> of dehydration. Include structural formulas for all reactants and products. Use a data table to show molar masses and moles of reactants and to calculate theoretical yield (moles and grams) of products (the total amount of alkenes expected).

**PROCEDURE:** Place approximately 2.0 g of 3-methyl-3-pentanol, approximately 0.5 g of 85% phosphoric acid, and a boiling chip into a 5-mL round-bottom vial from the microscale glassware kit. Use the microscale kit to construct a distillation apparatus that includes the reaction vial, a short column packed with stainless steel sponge (for use as a fractionating column), a distilling head (with thermometer), a condenser, a curved collection nozzle, and a 5-mL graduated vial as the distillate receiver. Clamp the distillation apparatus on a ring stand and set it in a heating mantle. Place the receiving vial into a beaker of ice to prevent loss of the volatile alkene products. Turn the water on very gently to the condenser. Heat the reaction slowly until it begins to boil. As the reaction proceeds, the alkene products will begin to distill. When the residue in the reaction flask stops boiling, all the reactant

alcohol has been consumed, and the reaction is completed. Turn the heating mantle off and remove the distillation apparatus from the heating mantle. Remove the receiving vial containing the products.

Add a small amount of NaCl to the distillate to begin to absorb any water present. Then add approximately 1 mL of saturated sodium bicarbonate solution to remove any residual acid. Put a screw cap on the vial and shake several times, venting the cap each time. Carefully remove the aqueous layer. (*Which layer is this? How would you determine this as you are adding the aqueous bicarbonate solution?*) Discard the aqueous layer. Dry the organic phase with magnesium sulfate. (Use enough $MgSO_4$ until it remains free flowing in the vial.) Carefully decant the liquid into a clean pre-weighed vial. Weigh the vial with product to determine the actual yield of your reaction. Cap the vial tightly and leave it setting in ice to minimize loss of products.

**ANALYSIS OF PRODUCTS:**

**Gas chromatography:** Inject a 1 μL sample of your products onto the "B" (non-polar) column of the gas chromatograph. (*Why do you use the non-polar column? How polar (or non-polar) are your products? Would your products have an affinity for the polar stationary phase in the other column? What would you expect to be the result of using a polar column for these compounds?*) Observe the number of product peaks on the chromatogram. Is this the number of peaks (products) that you expected? If not, what additional product(s) is(are) formed that you had not originally considered? Attempt to measure the areas of the peaks and determine the relative amounts of each of the alkenes present.

Look up the boiling points of all of the isomers produced. If molecules have very similar structures, they will normally elute from a gas chromatograph in order of increasing boiling point. Assuming this is true, which isomer is formed in the largest amount in your reaction?

It is normally observed in reactions in which alkenes are formed that the more stable alkene is formed as the major product. This observation is called *Zaitsev's Rule* (or Saytsev or Saytzev, depending on which book you read). Does the product distribution that you determined from your gas chromatogram conform to Zaitsev's rule? (Is the more stable product formed in greatest amount? Is the least stable isomer formed in the smallest amount? (*How do you determine the relative stability of alkene isomers?*))

**Infrared Spectroscopy:** Take your alkene sample to the IR lab. Add 2 drops of your alkene mixture onto one NaCl plate. Place the second plate on top to "sandwich" your sample between the plates. Mount the NaCl plates into the spectrometer so that the sample is in the beam of the IR laser. Follow the directions mounted on the cabinet above the spectrometers to obtain an infrared spectrum of your products. Be sure all the peaks are labeled, and then print the spectrum. Clean the plates with acetone (NOT water!) when you have finished. Also take a spectrum of the alcohol that was the starting material in the reaction (there is a small dropper bottle of the alcohol in the IR lab). Compare the two spectra. What peaks indicate that the reaction has proceeded as expected? (*Based on the IR spectra, how do you know that the starting material is an alcohol? Is the product still an alcohol? What other functional group is indicated in the product spectrum?*)

**DISPOSAL**: Dispose of the alkene products in the labeled waste jars in the side hood. The remaining phosphoric acid solution in the reaction vial should be carefully neutralized with sodium bicarbonate and then discarded in the sink with lots of water.

**LAB REPORT**: Your lab report should include calculations of theoretical and percent yield of alkene products. Attach your gas chromatogram and include your calculations of areas and relative amounts of the alkene isomers. Label your IR spectra showing the important peaks that identify the functional groups in the reactant and product molecules. Of course, also include a brief statement of purpose, chemical equations showing structural formulas, a brief narrative procedure, and a discussion of your results. The discussion should include the mechanism of the reaction showing explicitly how all the product isomers are formed in the reaction.