Acid-Catalyzed Hydration of 1-Hexene

Objectives

- Synthesis of 2-hexanol from 1-hexene using acid as a catalyst
- Identify products that follow Markovnikov's rule

Background

Acid-Catalyzed Hydration of Alkenes

The hydration reaction of a double bond in an organic molecule uses the addition of a water molecule to the organic molecule, resulting in the formation of an alcohol. The general mechanism involves the addition of a hydrogen cation, forming a carbocation intermediate. The carbocation then reacts with a water molecule, which is subsequently deprotonated to give the alcohol, as shown in Figure 1.

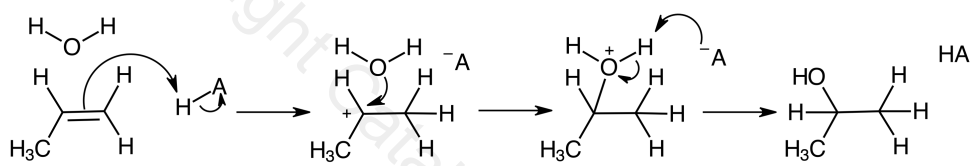

Figure 1 General mechanism of acid-catalyzed hydration of an alkene

Role of the Acid Catalyst

The hydration of an alkene requires a strong acid catalyst for the reaction to occur. The added acid is classified as a catalyst as it is regenerated throughout the reaction mechanism. First, the hydrogen cation of the acid is attacked by the electrons in the double bond, adding a hydrogen on one carbon of the double bond and a cation on the other carbon. After water attacks the carbocation, the conjugate base of the acid deprotonates the water, forming the alcohol and regenerating the acid.

The first step of the reaction is essentially a protonation of an alkene, which is only possible with a strong acid. A sulfuric acid solution is an ideal catalyst as it is a strong acid, and water is added as the solvent. Other strong acids, such as hydrochloric or hydrobromic acid, are not used because the small conjugate base ions could participate in a competing nucleophilic attack on the carbocation intermediate.

Markovnikov's Rule for Product Regioselectivity

If an alkene is not symmetrical, there are two different locations where the alcohol could end up during hydration. The regioselectivity of electrophilic addition follows the pattern of Markovnikov's rule, which states that the new substituent will end up on the more substituted carbon, as demonstrated in Figure 2. In the case of the alkene hydration in this lab, Markovnikov's rule stipulates that the product alcohol should be as substituted as possible. Therefore, the hydration of 1-hexene results in 2-hexanol, the secondary alcohol, rather than the possible primary alcohol.

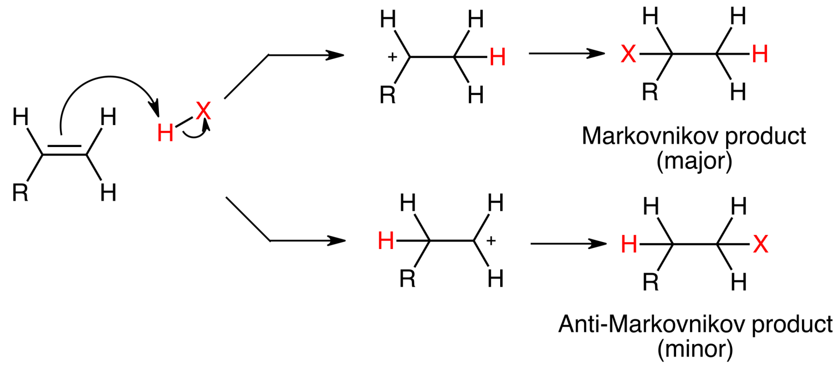

Figure 2 Markovnikov product for addition of an electrophile to an alkene

The basis for Markovnikov's rule is the stability of the carbocation formed in the intermediate. A carbocation is more stable on a more substituted carbon, so that carbocation location is more likely to form. Then, the nucleophile attacks the carbocation on the more substituted carbon, placing the new substituent on that carbon.

Markovnikov's rule does not apply to all addition reactions. Additions that follow different pathways or do not involve carbocations can lead to an anti-Markovnikov product, with the substituent on the less substituted carbon.

Materials

- 1-hexene
- 85% phosphoric acid
- 9M NaOH
- Boiling chips
- Solid NaCl
- Diethyl ether
- Saturated NaCl solution
- Anhydrous potassium carbonate
- Ice bath
- Microscale glassware kit
- Hot plate
- Aluminum foil
- FTIR

Safety goggles are required!

All work should be performed in the fume hood.

1-hexene is a flammable irritant. Sulfuric acid is oxidizing and toxic; avoid contact with skin and clothing. Sodium hydroxide is corrosive and toxic. Diethyl ether is highly flammable and toxic. Anhydrous potassium carbonate (K_2CO_3) can be an irritant.

Procedure

Acid-Catalyzed Hydration of 1-Hexene

1. Place 1.0 mL of 85 % sulfuric acid (H_2SO_4) in a 3 mL screw top vial.
2. Add 0.5 mL of 1-hexene and a magnetic stir bar to the vial and cap the vial.
3. Clamp the vial to a ring stand above a stir plate and start the stirring at the highest setting that allows the stir bar to turn smoothly.
4. Stir the solution at the high setting for 20 minutes.
5. Add another 0.5 mL of 1-hexene and continue stirring for another 20 minutes.
6. Transfer the solution to a 10 mL Erlenmeyer flask.
7. Cool the flask down for 5 minutes in an ice bath.
8. Measure 4 mL of 9 M NaOH in a graduated cylinder.
9. Use a Pasteur pipet to transfer 1 mL (approximately 20 drops) of 9 M NaOH to the vial that had contained the reaction mixture and swirl it to rinse.
10. Transfer the rinse mixture dropwise to the flask in the ice bath, swirling and replacing the flask in the ice bath after each addition.
11. Add the remaining measured 9 M NaOH to the flask dropwise, swirling and replacing the flask in the ice bath after each addition.
12. Transfer the liquid in the flask to a short neck round bottom flask, making sure all solid is left in the original flask.
13. Add a couple of boiling chips to the round bottom flask.

14. Use a Sharpie to mark the level of the liquid in the flask. Do not mark on the paint on the flask.
15. Assemble the distillation apparatus using a 15 mL Erlenmeyer flask as a receiving vessel.
16. Wrap the distillation column with aluminum foil and place the apparatus in a heating block on the hot plate.
17. Heat the solution to a rapid boil. Do not allow the solution to boil over or foam up into the distillation head.
18. Collect the 2-hexanol/water mixture that distills between 85 – 100^{o} C.
19. Stop the collection when the temperature has remained at 100 ^{o}C for 1 minute. **NOTE:** If the liquid volume in the round bottom flask drops below 2 mL before 100 ^{o}C is reached for one minute, add water to the flask to bring the level back to the mark.
20. Add approximately 160 mg of NaCl to the receiver flask and swirl to dissolve the salt.
21. Add 2.0 mL of diethyl ether to the receiver flask.
22. Mix the layers in the receiver flask with a Pasteur pipet by drawing the mixture into the pipet and rapidly expelling it.
23. Remove the bottom aqueous layer from the receiver flask and place the layer in a beaker for later disposal.
24. Wash the remaining ether solution with aqueous saturated NaCl solution by mixing with a Pasteur pipet as previously described and then removing the bottom aqueous layer.
25. Dry the ether solution by adding 0.100 g of anhydrous potassium carbonate and allowing the solution to stand for 5 to 7 minutes, swirling occasionally.
26. Transfer the dried ether solution to a clean 15 mL Erlenmeyer flask using a Pasteur pipet, making sure not to transfer any of the K_2CO_3.
27. Rinse the remaining potassium carbonate with 1.0 mL of ether and add the rinse to the flask containing the ether solution.
28. In the fume hood, heat the flask with your hands to evaporate the ether from the 2-hexanol.
29. Determine the mass of your final product.
30. Use one drop of your final product to run a sample for an FTIR spectrum.
31. The aqueous layer should go into the **halogenated** waste. The product will go in the non-halogenated waste. Put away all chemicals and clean up the hood, bench space and balance area.

Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. What should you do if H_2SO_4 contacts your skin?

2. When should you stop the distillation process for this procedure?

3. With 85 % H_2SO_4 by volume in water being used in the reaction, how many moles of water will be added to the reaction when 1.25 mL of 85 % H_2SO_4 is added?

4. What peaks in the IR spectrum would indicate the loss of 1-hexene and the formation of 2-hexanol?

Lab 2: Acid-Catalyzed Hydration of 1-Hexene Report Sheet

Name ______________________ Section ______________________

Date ______________________ Instructor ______________________

Acid-Catalyzed Hydration of 1-Hexene

Amount of reactant used (grams) ____________________________

Amount of reactant used (moles) ____________________________

Space for calculations:

Product obtained (grams) ____________________________

Product obtained (moles) ____________________________

Space for calculations:

Product theoretical yield ____________________________

Space for calculations:

Product percent yield ____________________________

Space for calculations:

Write the equation for the reaction.

Post-lab Questions

1. Is your percent yield within reason of what you would expect? Explain your answer.

2. How can the IR spectrum be used to show that there is not starting material left and that the products are alcohols?

3. Can the IR spectrum be used to determine a mixture of 2-hexanol and 1-hexanol? Explain your answer.