Experiment V-C: Synthesis of Fumaric Acid

Background Reading

McMurry, J. Organic Chemistry, 8^{th} Ed. Figure 3.5 (sigma bond rotation),
Figure 6.3 (carbocation intermediates), Figures 7.3 and 7.4 (cis-trans isomerism),
Figure 11.21 (elimination mechanism), and Section 20.2 (carboxylic acid dimers).
Zubrick, J. W. The Organic Chem Lab Survival Manual.
The Heating Mantle (in Ch 18) and *Standard Reflux* (in Ch 23, note Figure 23.1).

Key Words

isomerization, hydrogen bond, dimer, polymer, reflux, sublimation

Experimental Data

- Include both net chemical equation and reaction's carbocation mechanism in your report.
- Refer to background reading for mechanism, as well as for principles.
- Include a labeled diagram with a caption for the reflux apparatus.
- Provide product mass and yield % calculation in your data section.
  Calculate yield % on both a mole basis and a mass basis.
- Determine MP's of both reactant and product, and compare them with reference values.

Substances

1 g maleic acid
15 mL deionized water
8 mL concentrated (18 M) $HCl_{(aq)}$

Apparatus

Items in kit
25-mL round-bottom flask
reflux condenser

Items not in kit
heating mantle
55-mm filter paper and Büchner funnel
250-mL vacuum flask
watch glass
capillary tubes

Procedure

1. Obtain 1 g of maleic acid. Grind the solid in a hood with a mortar and pestle. Weigh solid *after* grinding. Place solid in a 25-ml round-bottom flask, along with 8 ml of deionized water and one boiling stone.

   Caution – Grinding, weighing, and transferring to flask are all performed in a hood because airborne acid particles are irritants.

   Place a stir-plate underneath the flask and a stir-bar in the flask. Then, stir until all of the solid has dissolved. Essentially, you will need to dissolve all of the solid in order to obtain a complete reaction.

2. Set up a reflux apparatus with the flask, and clamp both the flask and the condenser to a stand. Connect water hoses with the inlet (from tap) at the bottom and the outlet (to drain) at the top. Turn the water on with a low to moderate flow rate. Do not ever put a stopper on the top of the condenser during a reflux.

3. Carefully, and slowly, pour 8 ml of concentrated hydrochloric acid into the reflux assembly through the top of the condenser. Use a small glass funnel if necessary.

   Caution – Concentrated HCl solutions and vapors are corrosive and cause acid burns.
   Use gloves and avoid all contact with skin, eyes, and nose.
   Clean up all spills immediately with gloves and wet paper towels.

4. Place a heating mantle sized for either 25 or 50-ml flasks underneath the flask. Press the flask firmly into the bottom of the fabric basket to ensure that it has good contact with the heating surface. If the mantle and its controller are separate components, be sure to plug the mantle into a controller, and not directly into an electrical outlet. Then, heat the reflux assembly with a gentle boil for 15 minutes.

5. While the solution is refluxing, determine the melting range of solid maleic acid. Prepare the solid and the capillary tubes in the hood only. Place the used capillary tubes in the broken glass container.

6. When the reflux is complete, turn off the heat and allow the glassware to cool for two minutes. Then, place the flask in an ice-water bath to crystallize the product. The condenser can be removed, but the flask need to remain clamped to the stand.

   The product, fumaric acid, is less soluble than the reactant due to intermolecular bonding. Fumaric acid molecules can form long, hydrogen-bonded chains, which are insoluble, whereas maleic acid molecules generally form dimers, which are smaller and soluble.

7. Collect product crystals by vacuum filtration using 55-mm filter paper in a Büchner funnel with a 250-ml vacuum flask.

8. Rinse the round-bottom flask with up to 5 ml of cold (5 ^{o}C) deionized water to collect any remaining crystals. Dispose of all filtrate in the appropriately-labeled waste jar.

9. Place filter paper with crystals on a weighed watch glass. Dry the crystals in the oven at 100 ^{o}C for at least 10 minutes. Weigh the dried product.

10. Obtain the melting range of the product. Sealed capillary tubes must be used because fumaric acid can sublime. That is, the solid becomes a gas with a normal (1 atm) sublimation point of approximately 200 ^{o}C. The melting range in a sealed capillary (at a higher pressure) is above 280 ^{o}C. Work with instructor to seal capillary tubes for two trials using a Bunsen burner . Place the used capillary tubes in the broken glass container. Dispose of product crystals in the labeled waste jar. The filter paper may be placed in a trash receptacle after all of the crystals have been scraped off of it.

    Caution - Do not use a glass thermometer in the Mel-Temp for this step.
    The melting range is above the thermometer's range and it can shatter.
    Use the digital thermometer only.

Post-Lab Q's

1. Explain why maleic acid is weighed after grinding, rather than before. Also, describe the grinding procedure and location.

2. Decolorizing carbon, a solid which was used in the recrystallization experiment, works by bonding with polar compounds. Predict the consequences if it is used to purify the crystallized fumaric acid product (polar) in step 7.

3. If the product crystals are not completely dried when determining the melting point, describe the particular (erroneous) phase change temperature that might be observed.

4. Explain, in terms of rate laws, why the product's low solubility favors the forward reaction over the reverse. In this case, the forward rate law is rate = k[maleic acid]^{n} and the reverse rate law is rate = k[fumaric acid]^{n}, where the brackets denote concentrations. Consider how the reverse rate law is affected by the low solubility.

5. Review steps 4 and 7, as well as the background reading (cis-trans and carboxylic acid dimers). Draw skeleton structures showing the intermolecular hydrogen bonding of maleic acid (dimer) and fumaric acid (polymer). Explain, based on your drawings, how the intermolecular bonding results in different structures for the two isomers. Explain their relative solubilities and melting points in terms of these intermolecular structures.