Experiment 7

Recrystallization: Purification of Crude Benzoic Acid and Phenanthrene

Reading: Handbook for Organic Chemistry Lab, section on Recrystallization (Chapter 12).

Recrystallization is the primary technique for the purification of compounds that are solids at room temperature. In the process of recrystallization, molecules are deposited from a saturated solution and are selected, according to their shapes, to fit into growing crystal lattices. The technique can be carried out by dissolving a compound to be purified in a hot solvent (or solvent mixture) and then allowing the solution to cool. If the solvent or solvent mixture is properly chosen, the compound has a decreased solubility at lower temperatures, and it will form crystals in the solution.

In this experiment, you will recrystallize both the benzoic acid and the phenanthrene that you separated during the previous experiment. The benzoic acid will be recrystallized from hexanes and the phenanthrene will be recrystallized from the solvent pair of ethanol and water.

Summary of the Steps in Recrystallization:

- Step 1: Dissolve the impure solid in a minimum amount of hot solvent.
  - If the solution is highly colored but you know that your product is not highly colored, go to Step 2.
  - If insoluble impurities are present, skip to Step 3.
  - Otherwise, skip to step 4.
- Step 2: Treat with decolorizing charcoal pellets (Norite) – about a quarter of a spatula tip's worth.
  - If color goes away, go to Step 3.
  - If color persists, add more Norite and wait five minutes. If color still persists, disregard it and go to Step 3.
- Step 3: If insoluble impurities are present, decant or gravity filter the hot solution, then proceed to Step 4.
- Step 4: Allow solution to cool slowly to room temperature.
- Step 5: Chill cooled solution by immersion in an ice bath – crystals should appear. If not, try scratching the bottom of the flask with a glass rod. Once crystals have formed, filter to isolate the product.

Safety Precautions

Ethanol and hexanes are highly flammable.

Procedure

You will work individually for this experiment. Before you begin, clean two NMR tubes and let them dry so they are ready to use later. If you did not isolate enough benzoic acid or phenanthrene during the previous experiment, you may take some from the recovery jars in the hood.

Recrystallization of Benzoic Acid

Weigh out 0.10 g of the benzoic acid that you isolated in the previous lab period. Place the benzoic acid in a small Erlenmeyer flask and add about 3 mL of hexanes. Swirl the contents of the flask and heat the solvent-solid mixture to the boiling point using a hot plate. (You can remove the aluminum heating block

from your stirring hotplate to get a level surface on which to rest the flask.) Intermittently add small portions of hexanes (about 1 mL), swirl, and heat to boiling until all soluble material has dissolved. If you have large chunks of product that are not going into solution, you may need to crush them with a glass stirring rod to help them dissolve. You should not use more than 10 mL of hexanes altogether; using more will make it difficult to isolate your crystals.

If your solution of benzoic acid is colored you should treat it with activated charcoal (Norite). First, remove the hot solution from the hot plate, and then add to it a small amount of pelletized Norite. Swirl and heat the mixture for up to 5 min or until the color disappears. If the solution is still colored after 5 min, add a little more Norite and repeat the process.

To remove the Norite, transfer the liquid to another flask. This can be accomplished by one of two methods:

1) Carefully decant the clear liquid to a clean flask
2) Transfer the clear liquid with a Pasteur pipet

Whichever method you choose, keep the solution warm during the process by placing the receiving flask on the hot plate as well.

Remove the solution of benzoic acid in hexanes from the hot plate and allow it to cool, undisturbed, at room temperature. You will probably see crystals growing in the solution after several minutes. After 15 min, cool the flask in an ice bath, whether or not crystal growth is apparent. If you still do not see any crystal growth after 10 min on ice, try scratching the bottom of the flask with a glass rod – this will sometimes product nucleation sites that allow crystals to begin growing. If you still do not see any crystals, you may need to return the solution to the hotplate and boil off about half the solvent volume, then slowly cool it again.

Isolate the crystals by vacuum filtration – remember to clamp your side-arm flask down so it doesn't flip over and break your Buchner funnel! Use a small amount of chilled hexanes to aid in the transfer of solids that adhere to the walls of the Erlenmeyer flask and to rinse the crystals. Allow the vacuum pump to suck air through the crystals for five min, then carefully transfer the crystals to a tared (pre-weighed) vial and allow to air dry for several minutes.

Determine the melting point and the weight of your purified benzoic acid. Submit a sample for NMR, using $CDCl_3$ as the solvent.

Recrystallization of Phenanthrene

To recrystallize phenanthrene, you will follow the procedure above for the recrystallization of benzoic acid, except that you will use a *solvent pair*. The solvent pair that you will use is ethanol and water. Phenanthrene is readily soluble in ethanol and is not soluble in water. Weigh out 0.1 g of phenanthrene, and then following the previous procedure, dissolve it into a minimal amount of hot ethanol. Next, add water in a dropwise fashion until the solution just remains cloudy, even while hot. Next, add a few drops of hot ethanol to the cloudy solution until it is again clear, and then remove the solution from the hot plate and cool undisturbed at room temperature. You should observe phenanthrene crystallizing out of the solution. During this time, place 6 mL of ethanol and 2 mL of water into an Erlenmeyer flask and chill it in an ice bath, to use for rinsing the crystals. This solvent mixture is close in composition to the solution is which your phenanthrene is currently dissolved, so it should work well for washing the crystals.

After 15 minutes, chill the phenanthrene solution in an ice bath, then isolate the crystals by vacuum filtration. Rinse the crystals on the filter paper with the chilled ethanol-water mixture. Determine the

melting point and the weight of your purified phenanthrene. Submit a sample for NMR, using $CDCl_3$ as the solvent.

Wastes

Organic Waste: All hexane filtrates.

Aqueous Waste: All ethanol/water filtrates.

Solid Chemical Waste: Used MP microcaps.

Recovery Jars: Place each purified compound in the appropriate recovery jar.

Lab Report

Your conclusions should include:

- How pure are the recovered compounds, based on NMR? What impurities are present?
- How pure are the compounds, based on melting point? Is this roughly in agreement with your NMR results?
- How does the purity before recrystallization (the results from your extraction lab) compare to the purity after recrystallization?
- What is the percent recovery for each compound?
- Where does product loss occur in a recrystallization?

Study Questions

1) What effect would each of the following operations have on the success of the recrystallization of benzoic acid from hexanes? Explain your answers.
   a. The hot solution containing the dissolved benzoic acid is immediately placed in an ice bath.

   b. After recrystallization has taken place, the cold solution is vacuum filtered and product crystals are collected on a Buchner funnel, then the crystals are washed with hot hexanes.

   c. After isolation of the benzoic acid crystals on a Büchner funnel, they are washed with diethyl ether.

2) A student crystallizes 5 g of a solid and isolates 3.5 g as the first crop. She then isolates a second crop of 1.2 g solid from the filtrate.
   a. What is the percent recovery in the first crop?

   b. What is the total percent recovery?

3) The solubility of acetanilide in hot and in cold water is given in the table below. What is the maximum percent recovery if 5.0 g of acetanilide is recrystallized from 100 mL of water?

Solubility (in 100 mL of water)	*Temperature*
5.5 g	100°C
0.53 g	0°C

4) The CRC lists the melting point for a compound as 182-183°C. You observe a melting point for this same compound isolated in your experiment as 177-181°C.What can you conclude about the compound isolated in your experiment?