

EXPERIMENT 5

ORGANIC SYNTHESIS: FISCHER ESTERIFICATION¹

Materials Needed

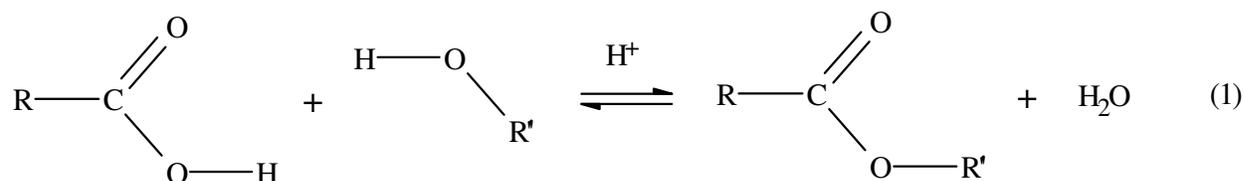
n-butyl alcohol, acetic acid, concentrated sulfuric acid
saturated aqueous sodium carbonate (sat Na₂CO₃(aq))
anhydrous calcium chloride pellets (CaCl₂(s))
distillation apparatus including thermometer
separatory funnel
boiling chips
litmus paper

Additional Reading Assignment

McMurry, Chap 17.1-17.4, Chap 7.5

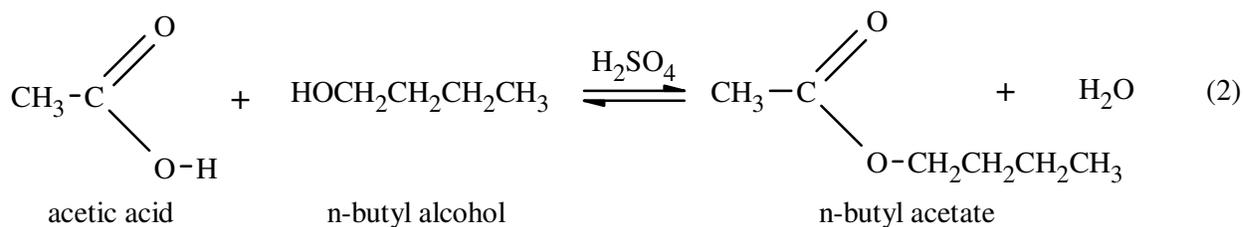
INTRODUCTION

A carboxylic acid and an alcohol react to form an ester and water as shown in equation 1 below.



This reaction is reversible but proceeds slowly in either direction unless a catalyst is added. Strong acids such as sulfuric acid (H₂SO₄), even in small amounts, catalyze the reaction (in both directions), consequently it attains equilibrium more rapidly if they are added. The presence of an acid, however, does not affect the amount of product present at equilibrium. (Why? See McMurry p 172) This procedure, which can be applied to a wide variety of acids and alcohols to produce many different esters, is generally called the Fischer ester synthesis in honor of Emil Fischer (1852-1919) who devised it.

In this experiment you will synthesize the ester, *n*-butyl acetate (bp 126.5°C), from acetic acid (bp. 118.1°C) and *n*-butyl alcohol (bp. 117.7°C) using sulfuric acid as a catalyst (equation 2). (In other words, you are carrying out equation 1 using R = methyl and R' = *n*-butyl.)



After mixing together the starting materials--carboxylic acid, alcohol, and H₂SO₄ catalyst--you will heat the

¹Adapted from S. C. Mohr, S. F. Griffin, W. J. Gensler *Laboratory Manual*, p. 225.

reaction mixture to boiling and maintain it at that temperature for 30 min. After 30 min of boiling, the reaction will have reached equilibrium, so that further heating will not increase the yield of the ester product. You will then follow a several-step procedure designed to isolate the ester product as a pure substance (free from acetic acid and butanol as well as the H_2SO_4 catalyst and H_2O side product). This is a typical, though relatively simple, organic synthesis.

PROCEDURE

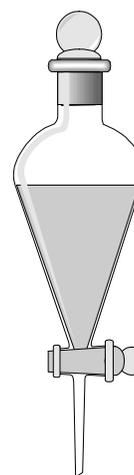
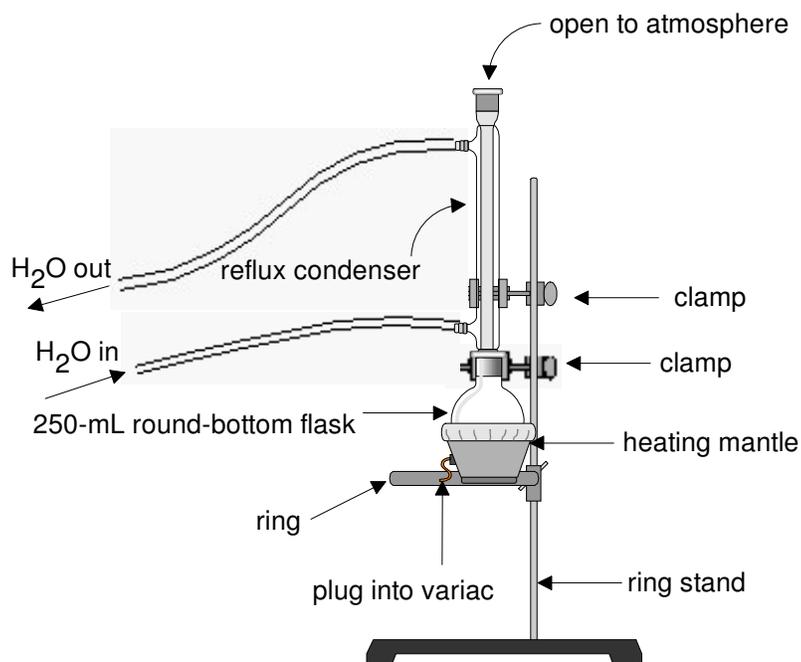
SAFETY PRECAUTIONS

- AVOID **BURNS**--PAY ATTENTION TO WHICH PARTS OF YOUR APPARATUS BECOME HOT.
- TREAT **CONCENTRATED H_2SO_4** WITH RESPECT--CLEAN UP ANY AND ALL SPILLS, HOWEVER SMALL. **RINSE EXPOSED AREAS OF YOUR SKIN IMMEDIATELY WITH LOTS OF WATER.**
- **DO NOT INHALE** ORGANIC VAPORS.
- KEEP REAGENT BOTTLES **CAPPED** WHEN NOT IN USE.
- DO NOT PUT BOILING CHIPS IN HOT SOLUTIONS.
- REMEMBER TO CAREFULLY **VENT** THE SEPARATORY FUNNEL.

1. In a 250-mL round-bottom flask, mix thoroughly 23 mL (18.5 g) of *n*-butyl alcohol, 18 mL (19 g) of acetic acid, and 2 mL of concentrated H_2SO_4 . To promote even boiling and prevent boil over, place 2-3 boiling chips in the flask. Use a large beaker to hold the flask until you attach it to the reflux condenser (step 2).
2. Clamp up a vertical reflux condenser on a ring stand (see Figure 6-1) and then place the 250-mL round-bottom flask in a heating mantle on top of a ring on the stand. Clamp the flask in place and then carefully lower the condenser onto the flask and **make sure you have an air-tight connection**. **Slowly** turn on the water for the condenser so as to give a gentle but steady flow. **CAUTION: A loose connection between the water hose and condenser can lead to a flood!** Note that you must position your equipment so as not to be too far from electrical and water outlets as well as a suitable drain. Have your instructor check and approve your setup **before** you go on to step 3.

Figure 6-1. Apparatus for reflux procedure

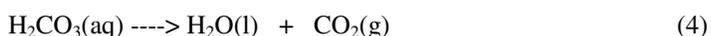
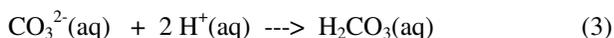
Figure 6-2. Separatory Funnel



- Bring the reaction mixture to boiling by turning on the Variac rheostat. (Initially a setting of 70 works well followed by about 50 once refluxing has begun.) If your reaction mixture fails to boil within 5-10 minutes, inform your instructor. **CAUTION:** Don't touch the flask or mantle because they become very hot!
- Allow the mixture to reflux² for 30 minutes. (Timed from the moment the solution starts boiling not from when you turned on the heat!)
- Carefully lower the ring and then remove the heating mantle and allow the flask to cool slightly. Fit a distilling head and thermometer onto the flask and arrange the condenser for distillation (same set up we used in experiment 4). Be sure that the cooling water enters the **lower** side arm of the condenser and leaves at the upper side arm. **CAUTION:** If for any reason after stopping reflux you add fresh boiling chips, be sure the solution is cool first--otherwise violent frothing may occur.
- Replace the heating mantle and raise it up to the flask with the ring and, after your instructor has checked the setup, distill the contents³ into a 250-mL Erlenmeyer flask. Record the temperature at which the first drop of distillate comes over. Stop the distillation when only approx. 5 mL of reddish-black liquid remains behind. (To see what this volume of liquid looks like, you may wish to put 5 mL of water in an empty 250-mL flask.) Record the temperature at which the distillation is stopped.

The distillate contains the *n*-butyl acetate plus the impurities; *n*-butyl alcohol, acetic acid, sulfurous acid (from reduction of some of the sulfuric acid--a side reaction), and water.

- Carefully** add the distillate to 50 mL of saturated aqueous sodium carbonate (Na₂CO₃) in a 250-mL beaker. Stir thoroughly and vigorously so as to mix the liquid layers. Sodium carbonate is a base and serves to neutralize acid impurities (i.e., sources of H⁺(aq)) in the mixture (eq 3). Carbon dioxide gas is given off as the intermediate carbonic acid (H₂CO₃) decomposes to H₂O and CO₂ (eq 4).



- Transfer the contents of the beaker to a separatory funnel (Figure 6-2) and drain off and discard the aqueous (lower) layer.
- Extract⁴ the organic (upper) layer with 20 mL of saturated aqueous Na₂CO₃. **CAREFUL:** CO₂ pressure may build up in the funnel. Your instructor will demonstrate the proper use of the separatory funnel. Drain off the aqueous (lower) layer and test it with litmus paper.

²**Reflux** (or flow back) refers to the process of boiling while leading the vapor into a cooling condenser mounted above the flask. The vapor condenses to the liquid state and drips back into the boiling mixture. In this way you can maintain a reaction mixture at a nearly constant high temperature (the boiling point) without loss of volatile material or excessive buildup of pressure.

³Although the pure ester has no color, the color of your crude product at this point may range from colorless to red or even black. Small amounts of (unknown) side products account for the coloration.

⁴**Extract** means to mix two immiscible liquids thoroughly in a separatory funnel and then separate them by draining the denser liquid layer through the stopcock. In this case the *n*-butyl acetate does not mix with the Na₂CO₃(aq), which forms a separate, lower layer. Substances (chiefly acids) that are more soluble in Na₂CO₃(aq) than they are in the organic layer are thereby extracted from the organic phase (*n*-butyl acetate) into the aqueous phase.

10. If the aqueous layer that you drained off in step #9 is basic to litmus then discard it, and extract the organic layer (which remains in the separatory funnel) with 15 mL distilled water. If the aqueous layer is acidic, then discard it, and repeat the Na₂CO₃ extraction (step #9) before extracting with 15 mL distilled water. After the distilled water layer has separated, drain it off and discard it.
11. Pour the organic layer, which now is mainly *n*-butyl acetate contaminated with small amounts of water, into a Erlenmeyer flask and dry it by adding approx. 5-10 g (enough to cover the bottom of the flask in a single layer) of calcium chloride pellets (CaCl₂). Stir the mixture for 5-10 min. Any water present in the liquid will combine with the CaCl₂ to form a solid hydrate, which is insoluble in organic liquids. By separating the liquid from the solid, the water originally present in the liquid will have been removed.
12. Decant the dried *n*-butyl acetate into a dry, previously weighed Erlenmeyer flask taking care to leave the solid CaCl₂ behind. Weigh the flask again and determine the yield of your reaction.

CALCULATIONS

The balanced equation for *n*-butyl acetate synthesis [equation 2] shows that the reaction requires the same number of moles of acetic acid as of *n*-butyl alcohol. Thus, complete conversion of the starting materials to product requires *equimolar* amounts of acid and alcohol. What would happen if the amounts taken for a particular reaction were not equal? Even if the equilibrium were somehow pushed as far as possible in the direction of the products, part of the reactant present in excess would have no choice but to remain left over and unchanged.

Clearly the reactant present in smaller molar amount (either acid or alcohol) limits the maximum amount of product that can be formed (the “theoretical yield”). This limiting reactant becomes the basis for calculating the percent yield⁵ obtained in your experiment. If the number of moles of butyl acetate formed comes out to be equal to the number of moles of limiting reactant, the yield is as high as it possibly could be and the percent yield is 100%. Put differently, a 100% yield corresponds to a number of moles of ester product equal to the number of moles of whichever reactant was present in short supply. Actual product yields are reported as the percentage of the number of moles of the limiting reactant. If you started with 0.33 mole of acetic acid and 0.50 mole of butanol, your limiting reactant would be acetic acid. If, from such a reaction, you isolated 0.22 mole of butyl acetate (i.e., your reaction yielded 0.22 mole of product), your percent yield would be

$$\frac{0.22 \text{ mole product}}{0.33 \text{ mole limiting reactant}} \times (100\%) = 67\%$$

OR

$$\frac{0.22 \text{ mole actual yield}}{0.33 \text{ mole theoretical yield}} \times (100\%) = 67\%$$

⁵The term “percent yield” is really short for “actual yield as a percent of the theoretical yield”. See Bettelheim and March, chap 4.6, p 122.

PRELABORATORY QUESTIONS

EXPERIMENT 5

ORGANIC SYNTHESIS: FISCHER ESTERIFICATION

Name _____ Section _____ Date _____

1. Define reflux.
2. What is the purpose of putting boiling chips in your flask?
3. What does it mean to *dry* an organic liquid such as your crude ester (step 11 of the experimental procedure)?
4. Give the structure of each of the following esters.
 - a. methyl formate
 - b. phenyl acetate
 - c. *n*-octyl pentanoate

LABORATORY DATA AND REPORT

EXPERIMENT 5

ORGANIC SYNTHESIS: FISCHER ESTERIFICATION

Name _____ Section _____ Date _____

Partners _____

1. Observations on the starting materials (**ASSESS ODORS CAREFULLY - DO NOT SNIFF!**)

n-butyl alcohol appearance and odor _____

acetic acid appearance and odor _____

Instructor' s Initials

2. Reflux set up approval _____

3. Distillation setup approval _____

4. Distillation Data

Temperature at which first distillate comes over _____ °C

Temperature at which distillation is stopped _____ °C

Handbook value for boiling point of *n*-butyl acetate _____ °C

Appearance and odor of distillate _____

5. Yield of *n*-butyl acetate (final product after extraction and drying)

Weight of empty dry flask _____ g

Weight of flask plus product _____ g

Net weight of *n*-butyl acetate _____ g

Appearance and odor of final product _____

6. Calculations

Molecular weight of *n*-butyl acetate _____ g/mole

Moles of *n*-butyl acetate yielded _____ moles

Weight of *n*-butyl alcohol used _____ g

Molecular weight of *n*-butyl alcohol _____ g/mole

Moles of *n*-butyl alcohol used _____ moles

Weight of acetic acid used _____ g

Molecular weight of acetic acid _____ g/mole

Moles of acetic acid used _____ moles

Identity of limiting reactant _____

Your percent yield:

$$\frac{\text{No. moles } n\text{-butyl acetate}}{\text{No. moles limiting reactant}} \times 100 = \text{percent yield}$$
$$\frac{\text{_____}}{\text{_____}} \times 100 = \text{_____ } \%$$

QUESTIONS

1. How many moles of water were formed by the esterification reaction in your experiment? Explain. [Hint: Base your answer on the number of moles of *n*-butyl acetate formed and the balanced equation for the reaction, equation 2]
2. Suppose that 1.8 g of *n*-butyl alcohol reacts with 0.50 g of decanoic acid in the presence of a small amount of sulfuric acid catalyst to give 0.49 g of the ester, *n*-butyl decanoate. (a) Write the balanced equation below.
(b) What is the limiting reactant in this esterification? (c) What is the percent yield? (Show your calculations for parts b and c)

