EXPERIMENT 5

ORGANIC SYNTHESIS: FISCHER ESTERIFICATION

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.

\[
\begin{align*}
\text{R} & \text{C} \quad \text{O} \\
\text{O} & \quad \text{H} + \text{H}^{+} \quad \text{R}' \quad \text{C} \quad \text{O} \\
& \quad \text{R} \quad \text{O} \quad \text{R}' \quad \text{C} \quad \text{O} + \text{H}_2\text{O}
\end{align*}
\] (1)

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.)

\[
\begin{align*}
\text{CH₃} & \text{C} \quad \text{O} \\
\text{O} & \quad \text{H} + \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{H}_2\text{SO}_4 \quad \text{CH₃} & \quad \text{C} \quad \text{O} \\
& \quad \text{O-CH₂CH₂CH₂CH₃} + \text{H}_2\text{O}
\end{align*}
\] (2)

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

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1 Adapted 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$_2$SO$_4$ catalyst and H$_2$O 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$_2$SO$_4$ 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$_2$SO$_4$. 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**
3. 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!

4. Allow the mixture to reflux\(^2\) for 30 minutes. (Timed from the moment the solution starts boiling not from when you turned on the heat!)

5. 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.

6. Replace the heating mantle and raise it up to the flask with the ring and, after your instructor has checked the setup, distill the contents\(^3\) 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.

7. **Carefully** add the distillate to 50 mL of saturated aqueous sodium carbonate (Na\(_2\)CO\(_3\)) 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 (H\(_2\)CO\(_3\)) decomposes to H\(_2\)O and CO\(_2\) (eq 4).

\[
\begin{align*}
\text{CO}_3^{2-}(aq) & \quad + \quad 2 \text{H}^+(aq) \quad \longrightarrow \quad \text{H}_2\text{CO}_3(aq) \quad \quad \quad \quad \quad \text{(3)} \\
\text{H}_2\text{CO}_3(aq) & \quad \longrightarrow \quad \text{H}_2\text{O}(l) \quad + \quad \text{CO}_2(g) \quad \quad \quad \quad \quad \text{(4)}
\end{align*}
\]

8. Transfer the contents of the beaker to a separatory funnel (Figure 6-2) and drain off and discard the aqueous (lower) layer.

9. Extract\(^4\) the organic (upper) layer with 20 mL of saturated aqueous Na\(_2\)CO\(_3\). **CAREFUL:** CO\(_2\) 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.

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\(^2\)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.

\(^3\)Although 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 Na\(_2\)CO\(_3\)(aq), which forms a separate, lower layer. Substances (chiefly acids) that are more soluble in Na\(_2\)CO\(_3\)(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 Na$_2$CO$_3$ 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 (CaCl$_2$). Stir the mixture for 5-10 min. Any water present in the liquid will combine with the CaCl$_2$ 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 CaCl$_2$ 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 yield 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**

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

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The 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:

\[
\text{No. moles } n\text{-butyl acetate} \times 100 = \text{percent yield} \\
\text{No. moles limiting reactant} \times 100 = \text{_______ \%}
\]

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)
3. In this experiment, after the reaction mixture was refluxed for 30 min it contained $n$-butyl acetate, $n$-butyl alcohol, acetic acid, water, and sulfuric acid as major components. Your final product should have been pure $n$-butyl acetate. What becomes of the other components of the reaction mixture? (In each case indicate the principal way or ways the component was removed.)

a. $n$-butyl alcohol

b. acetic acid

c. sulfuric acid

d. water

4. Aside from improvements in laboratory technique, how might the percent yield of $n$-butyl acetate have been increased? (Hint: Consider the factors that control the equilibrium composition.) Whose principle is involved?

5. Using structural formulas write an equation for the synthesis of ethyl benzoate by the Fischer method.