

EXPERIMENT 7

SYNTHESIS OF ESTERS USING ACETIC ANHYDRIDE¹

Materials Needed

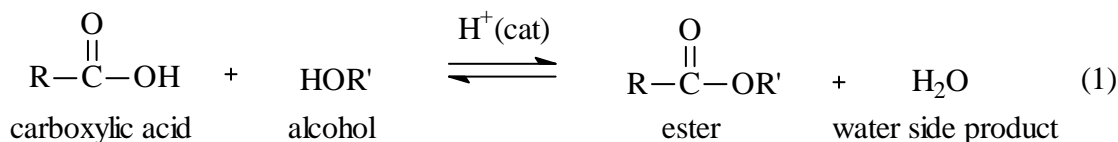
- 2.0 mL of an alcohol to be chosen from the following: 1-propanol (*n*-propyl alcohol), 3-methyl-1-butanol (isoamyl alcohol, isopentyl alcohol), 1-octanol (*n*-octyl alcohol), phenylmethanol (benzyl alcohol)
- 2-3 mL acetic anhydride
- 3 drops concentrated sulfuric acid
- saturated aqueous sodium chloride (sat NaCl(aq))
- saturated aqueous sodium bicarbonate (NaHCO₃(aq))
- anhydrous calcium chloride pellets (CaCl₂(s))
- 1 very large test tube, several small test tubes, 1 screw-cap vial, Pasteur Pipettes

Additional Reading Assignment

Bettelheim, Chapter 19

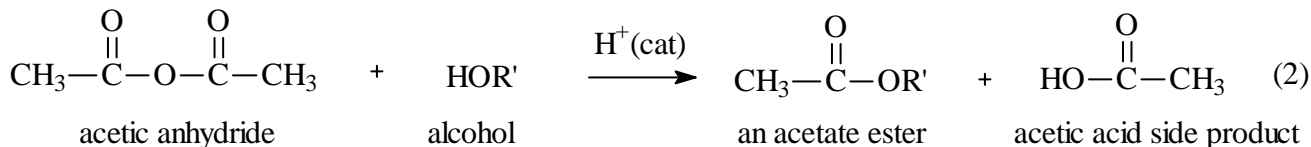
INTRODUCTION

A carboxylic acid and an alcohol react in the presence of an acid catalyst to form an ester and water as shown in equation 1. This reaction, termed Fischer esterification in honor of its discoverer, can be used to prepare a variety of esters.



There are problems with this reaction however. The esterification reaction is reversible with an equilibrium constant that favors the products only slightly. Excess of either the carboxylic acid or the alcohol must be used to drive the equilibrium to the right (Le Chatelier's Principle) in order to get a decent yield of the ester product. The reaction is also rather slow (even at elevated temperatures with the acid catalyst added), too slow to allow us to carry it out in a two-hour laboratory period.

Esters of acetic acid (i.e., alkyl acetates) can be prepared in a more efficient manner by using acetic anhydride (rather than acetic acid) as the non-alcohol reactant (eq 2). Like Fischer esterification, this reaction is catalyzed by acid, but unlike Fischer esterification, it is very fast and irreversible. In this experiment you will choose one of the following four esters -- propyl acetate, isopentyl acetate, benzyl acetate, *n*-octyl acetate -- and synthesize



it by reacting acetic anhydride with the appropriate alcohol.

¹Adapted from Professor Steim's Chemistry 25 Laboratory Experiment #2 at Brown University (<http://www.chem.brown.edu/chem25/labs/experiment2.pdf>)

After mixing together the starting materials--acetic anhydride, an alcohol (either 1-propanol, 3-methyl-1-butanol, benzyl alcohol, or 1-octanol depending on the specific ester being prepared) and H_2SO_4 catalyst--you will heat the reaction mixture briefly to make sure the reaction has gone to completion. You will then follow a several-step procedure designed to isolate the ester product as a pure substance (free from any leftover starting materials and acetic acid side product). This is a typical, though relatively simple, organic synthesis procedure. The weight of the product obtained (i.e. the yield) will be measured and the percent yield determined. The synthesized esters will also be assessed for their fragrance.

PROCEDURE

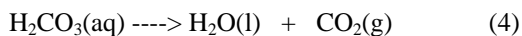
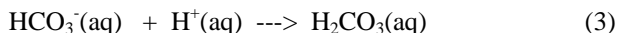
SAFETY PRECAUTIONS

- **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.**
- **ACETIC ANHYDRIDE IS CORROSIVE AND HAS HARMFUL FUMES.** AVOID BREATHING IT AND KEEP THE CONTAINER COVERED WHILE YOU TRANSPORT IT TO YOUR FUME HOOD.
- **WEAR GLOVES** THROUGHOUT THE EXPERIMENT (AT LEAST UP TO PROCEDURE STEP 7)
- **DO ALL OPERATIONS IN THE HOOD.**
- KEEP REAGENT BOTTLES **CAPPED** WHEN NOT IN USE.

ester chosen	volume of acetic anhydride (mL)
propyl acetate	3.1
isopentyl acetate	2.2
benzyl acetate	2.3
<i>n</i> -octyl acetate	1.5

1. Place the volume of acetic anhydride indicated in the above table in a **very large dry** test tube, add 3 drops of concentrated sulfuric acid and mix thoroughly. Obtain 2.0 mL of one of the alcohols in a dry small test tube.
2. Hold the large test tube containing the acetic anhydride in cold water (to cool the reaction), and add the alcohol to it in several increments; mixing between additions. Without cooling, the strongly exothermic reaction could become too vigorous. Then place the tube in hot water at about 70° C for 5 min to complete the reaction.
3. Add eight drops of water using a Pasteur pipet. Mix briefly after each drop. The purpose is to hydrolyze any excess unreacted acetic anhydride remaining after the esterification is complete.
4. Cool the reaction mixture to near room temperature and transfer it to a smaller test tube. Add 6 mL half-saturated sodium chloride solution (3 mL saturated NaCl plus 3 mL distilled water) to the test tube. Mix thoroughly and vigorously, then set the tube aside until upper and lower layers form. (The salt helps to break emulsions; if water alone were used, two layers would not separate easily.) The upper layer is the ester, which is a water-insoluble volatile liquid. In the propyl acetate and isoamyl acetate syntheses, the layers separate cleanly within a minute or two. The octyl acetate and benzyl acetate produce milky emulsions which should be given five minutes to separate; for these two esters, both layers remain cloudy even after separation.
5. The lower layer is a water solution of sulfuric and acetic acids, and should be removed and discarded. Use a Pasteur pipet to remove it, but save it temporarily in another container before throwing it away. The last portion of the lower layer can be removed by placing the tip of the Pasteur pipet against the bottom of the tube, and watching carefully as you slowly withdraw the liquid. Do not be concerned if a few drops remain behind. Do not remove the upper layer (the ester) from the test tube.
6. Add 6.0 mL of saturated sodium bicarbonate to the upper layer in the test tube, mix vigorously, and allow

up to 5 minutes for the layers to separate. The base neutralizes remaining acids (eq 3 and 4), and helps to remove traces of acetic acid. Remove and discard the lower layer. Retain the upper layer.



7. Again wash the upper layer with 6.0 mL of half-saturated NaCl. (Repeat steps #4 and 5)
8. Wash the upper layer with 6.0 mL saturated sodium chloride. Mix thoroughly, and allow the layers to separate. The upper layer (the ester) should not be cloudy at this point. Again remove and discard the lower layer, but this time try to remove every drop of it (without, of course, removing a significant amount of the ester). The concentrated salt solution helps to remove dissolved water from the upper layer (i.e. it dries the ester). Use a Pasteur pipet to transfer the upper layer to a small *dry* test tube.
9. Dry the ester over CaCl_2 . (Add anhydrous CaCl_2 pellets to a height of approximately 0.5 cm in the test tube, and stir occasionally with a spatula for about 10 minutes.)
10. Weigh a small vial and cap, and transfer the liquid to it with a Pasteur pipet. To recover as much liquid as possible, place the tip of the pipet against the bottom of the test tube. Cap the vial and weigh it and then store it in your locker. Check out the odor before storing the ester. Do not stick your nose nearly into the vial! This would overwhelm your olfactory sensing mechanism. Instead, place a drop or two on a piece of paper and gently waft the delightful fragrance in the direction of your nose. Try not to be too critical - describe the odor by comparing it to well-know odors you have experienced in every day life. (Don't merely describe it as having a chemical odor!) Save this vial in your lab drawer for a later experiment.

CALCULATIONS

The balanced equation for acetate ester synthesis [equation 2] shows that the reaction requires the same number of moles of acetic anhydride as of the alcohol used. Thus, complete conversion of the starting materials to product requires *equimolar* amounts of anhydride and alcohol. What would happen if the molar amounts taken for a particular reaction were not equal? Even if the reaction went 100% to completion, 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 yield² obtained in your experiment. If the number of moles of ester obtained 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 anhydride and 0.50 mole of alcohol, 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

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

²The term "percent yield" is really short for "actual yield as a percent of the theoretical yield".

PRELABORATORY QUESTIONS

EXPERIMENT 7

SYNTHESIS OF ESTERS USING ACETIC ANHYDRIDE

Name _____ Section _____ Date _____

1. What does it mean to *dry* an organic liquid such as your crude ester (step 9 of the experimental procedure)?

4. Give the structure of each of the following.

a. n-octyl acetate

b. isopentyl acetate

c. acetic anhydride

IN-LAB OBSERVATIONS/DATA

EXPT 7 - SYNTHESIS OF ESTERS USING ACETIC ANHYDRIDE

Names _____ Section _____ Date _____

Ester chosen _____ Alcohol used _____

1. Observations on the starting materials

alcohol _____

acetic anhydride _____

2. Observations on the reaction (steps 1-3)

appearance of solution before heating _____

appearance of solution after heating _____

observations upon addition of water _____

3. Observations during the purification procedures (steps 4-9)

observations on first wash (NaCl) (step 4) _____

observations on 2nd wash (NaHCO₃) (step 6) _____

observations on 3rd wash (NaCl) (step 7) _____

observations on 4th wash (sat NaCl) (step 8) _____

observations on drying (CaCl₂) (step 9) _____

4. Observations on the final product

appearance _____

odor _____

5. Yield of final product

Weight of empty vial and cap _____ g

Weight of capped vial with product _____ g

Yield _____ g

REPORT: EXPT 7 - SYNTHESIS OF ESTERS

1. Equation for Synthesis Reaction Carried Out:

2. Results Tables (fill in all of the empty cells!)

Reactant	Volume used (mL)	Literature density (g/ml)	Mass used (g)	Molar mass (g/mol)	Moles Used
	2.0				
acetic anhydride		1.08		102.1	

limiting reactant = _____

Product	Mass yielded (g)	Molar mass (g/mol)	Moles yielded	Description of Odor

3. Calculations - show your calculations below

Calculation of Masses of Reactants (use the volume and the literature density to calculate the mass) (you need to look up the literature value for the density of your alcohol)

Calculation of Moles of Reactants and Product (use the mass and the molar mass to calculate the number of moles) (the molar mass can be calculated from the molecular formula and/or looked up in a handbook)

Percent Yield Calculation

$$\frac{\text{moles of product}}{\text{moles of limiting reactant}} \times 100 = \text{percent yield}$$

$$\text{_____} \times 100 = \text{_____}$$

