

EXPERIMENT 7

ORGANIC SYNTHESIS: MICROWAVE-ASSISTED FISCHER ESTERIFICATION

Materials Needed

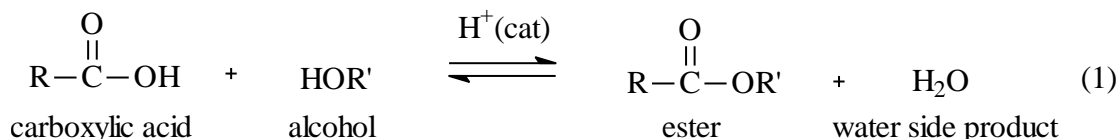
- 1.0-2.0 mL of an alcohol to be chosen from the following: 3-methyl-1-butanol (isoamyl alcohol, isopentyl alcohol), 1-octanol (*n*-octyl alcohol), phenylmethanol (benzyl alcohol)
- 2.0 mL acetic acid
- 10 drops concentrated sulfuric acid
- 0.2 g silica beads
- saturated aqueous sodium chloride (sat NaCl(aq))
- 10% aqueous sodium bicarbonate (NaHCO₃(aq))
- anhydrous sodium sulfate pellets (Na₂SO₄(s))
- 10 mL diethyl ether
- 1 GlassChem™ pressure vessel and torque tool for tightening cap
- 1 very large test tube, several small test tubes, 1 screw-cap vial, Pasteur Pipettes

Textbook Reading Assignment

Smith, Chapter 13.6

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.



The esterification reaction is reversible with an equilibrium constant that favors the products only slightly. Therefore, in order to get a decent yield of the ester product, an excess of one of the reactants is usually used to drive the equilibrium to the right (Le Chatelier's Principle). In addition, a drying agent, such as silica beads can be used to absorb the water side product as it is formed and again drive the equilibrium toward the products.

However, this reaction is rather slow (even at elevated temperatures with the acid catalyst added); too slow to allow us to carry it out in a 2-hour lab period using standard heating methods. Luckily, WSU recently purchased a Microwave Assisted Reaction System (MARS) which will allow us to use microwave heating to speed the process.

In this experiment you will choose one of the following three esters -- isopentyl acetate, benzyl acetate, *n*-octyl acetate -- and synthesize it by reacting acetic acid with the appropriate alcohol (3-methyl-1-butanol, benzyl alcohol, or 1-octanol) under microwave irradiation at 130 °C for 15 minutes. Concentrated H₂SO₄ will be used as a catalyst and silica beads added to absorb the water side product and drive the equilibrium.

Once the reaction period is over you will need to carry out a several-step procedure designed to isolate the ester product as a pure substance (free from any leftover starting materials). 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. RINSE EXPOSED AREAS OF YOUR SKIN **IMMEDIATELY** WITH LOTS OF WATER.
- ACETIC ACID IS CORROSIVE AND HAS HARMFUL FUMES. AVOID BREATHING IT AND KEEP THE CONTAINER COVERED WHILE YOU TRANSPORT IT TO YOUR FUME HOOD.
- DIETHYL ETHER IS EXTREMELY FLAMMABLE AND HAS HARMFUL FUMES. KEEP IT IN THE FUME HOOD AT ALL TIMES.
- WEAR GLOVES THROUGHOUT THE EXPERIMENT.
- DO ALL OPERATIONS IN THE HOOD.
- KEEP REAGENT BOTTLES CAPPED WHEN NOT IN USE.

ester chosen	volume of alcohol (mL)
isopentyl acetate	1.4
benzyl acetate	1.2
n-octyl acetate	1.9

1. Determine the name of the alcohol you will be using as a reactant. Place the indicated volume (see table) of your alcohol into a 20-mL GlassChem™ vessel. (When adding material to the GlassChem™ vessel take care to not get the material on the screw threads of the vessel.)
2. Also add 2.0 mL of glacial acetic acid, 0.20 g silica beads, and 10 drops of sulfuric acid to the GlassChem™ vessel.
3. Cap your GlassChem™ vessel with the provided screw cap and tighten it with the special torque tool. Label your tube with a Sharpie™ or wax pencil toward the top of the glass. Place the vessel in the MARS turntable and note the slot number you used.
4. The instructor will place the turntable into the MARS apparatus and demonstrate how to program the unit. The unit will be programmed to heat the contents of the tubes to 130 °C and then hold that temperature for 15 min. The tubes will then be allowed to cool to 50 °C before you will be allowed to retrieve yours.
5. Carefully open your reaction vessel making sure to point it away from you toward the back of the fume hood as you do. Use a Pasteur pipet to transfer the liquid contents to a 50 mL beaker containing 10 mL of 10% $NaHCO_3$ solution. Stir the mixture in the beaker with a glass rod to promote mixing. (The $NaHCO_3$ acts as a base and neutralizes remaining acids (eq 2 and 3), and helps to remove left over acetic acid and sulfuric acid.)
$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \quad (2)$$
$$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g) \quad (3)$$
6. Once effervescence has completely subsided, add water to the solution until any visible solids completely dissolve. Now transfer the contents to a separatory funnel and add 10 mL diethyl ether. Use the separatory funnel to thoroughly mix the contents (the instructor will demonstrate), then allow the layers to separate before draining off the bottom aqueous layer (mainly contains $NaHSO_4$ and $NaCH_3CO_2$).
7. Wash the organic layer with 10 mL 10% $NaHCO_3$. To accomplish this, simply leave the top layer (the organic layer) in the separatory funnel and add 10 mL 10% $NaHCO_3$. Use the separatory funnel to mix the contents and then drain off the lower undesired aqueous layer.

8. Now wash the upper layer with 10 mL of saturated NaCl using same type of procedure as in the previous step.
9. Dry the organic layer by transferring it to an Erlenmeyer flask and adding enough anhydrous Na₂SO₄ to form a thin layer across the bottom of the flask. Allow the solution to dry for at least 10 min.
10. Weigh a 25-mL round bottom flask and transfer the dried organic liquid to it with a Pasteur pipet. The instructor or TA will assist you in evaporating off the ether solvent by using a rotary evaporator.
11. After the ether has been removed weigh the flask containing your product. Determine the yield of the product by simple subtraction.
12. Assess the fragrance of your 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!)
13. Cap the flask with a ground glass stopper, parafilm the outside of the cap and store it in your drawer. We will use the product for Expt 8.

% YIELD CALCULATION

The balanced equation for acetate ester synthesis [eq 1] shows that the reaction requires the same number of moles of acetic acid as of the alcohol used. Thus, complete conversion of the starting materials to product requires equal moles of acid and alcohol. What would happen if the moles used were not equal? Even if the reaction went 100% to completion, part of the reactant present in excess would have to remain left over and unchanged.

Clearly the reactant present in smaller molar amount (in this case either the 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 yield¹ obtained in your experiment. If the number of moles of ester obtained 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 alcohol, your limiting reactant would be acetic acid. If, from such a reaction, you isolated 0.22 mole of ester product (i.e., your reaction yielded 0.22 mole of product), your percent yield would be

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

OR

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

¹The term "percent yield" is really short for "actual yield as a percent of the theoretical yield".

PRELABORATORY QUESTIONS

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Name _____ Section _____ Date _____

1. What does it mean to **dry** an organic liquid such as your crude ester (step 9 of the experimental procedure)?
2. Give the structure of each of the following.
 - a. octyl acetate
 - b. benzyl acetate
 - c. acetic acid

IN-LAB OBSERVATIONS/DATA

ORGANIC SYNTHESIS: MICROWAVE-ASSISTED FISCHER ESTERIFICATION

Names _____ Section _____ Date _____

Ester chosen _____ Alcohol used _____

1. Data and Observations on the starting materials

alcohol _____

acetic acid _____

Sulfuric Acid _____

Silica Beads _____

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

appearance of solution before heating _____

appearance of solution after heating _____

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

observations when added to NaHCO_3 (step 5) _____

observations on ether extraction (step 6) _____

observations on wash with NaHCO_3 (step 7) _____

observations on wash with NaCl (step 8) _____

observations on drying with Na_2SO_4 (step 9) _____

4. Observations on the final product

appearance _____

fragrance _____

5. Yield of final product

Weight of empty flask _____ g

Weight of flask with product _____ g

Yield _____ g

EXPT 7. MICROWAVE-ASSISTED FISCHER ESTERIFICATION

1. Equation for Specific 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
alcohol: _____					
acetic acid	2.0	1.049			

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

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

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

QUESTIONS

1. Explain why it was necessary to use different volumes of alcohol in the different ester syntheses even though the same volume of acetic acid was used for each?

2. How was the unreacted acetic acid side removed from the product solution so as to afford pure ester as the final product? Explain using a chemical equation as part of your explanation.

3. How were the final residual traces of water removed from the ester after the various aqueous washes were performed?

4. You most likely did not obtain a 100% yield in your synthesis. In fact, a 100% yield is hardly ever achieved in a chemical synthesis. One reason for this is that some of the product is inevitably lost in the process of trying to purify it. Look at the purification steps in this experiment and identify some places where the product ester was lost. Explain thoroughly.
5. Use the Smith textbook, the Sigma-Aldrich Flavors & Fragrances Catalog, or the Internet to look up what your ester's fragrance is supposed to resemble. Compare your assessment of its odor to the literature description and try to rationalize any differences.
6. Please comment on the lab overall. If you have any suggestions as to how this lab could be improved in the future please write them here (extra credit will be given for good constructive suggestions.)