

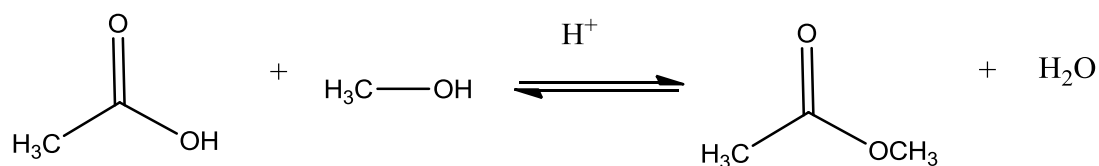
CHM230 - Preparation of Methyl Benzoate

Preparation of Methyl Benzoate

Introduction

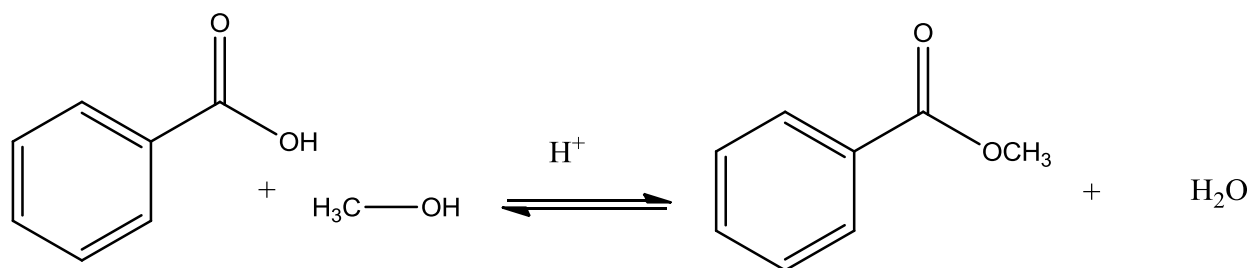
The ester group is an important functional group that can be synthesized in a number of different ways. The low-molecular-weight esters have very pleasant odors and indeed are the major components of the flavor and odor aspects of a number of fruits. Although the natural flavor may contain nearly a hundred different compounds, single esters approximate the natural odors and are often used in the food industry for artificial flavors and fragrances.

Esters can be prepared by the reaction of a carboxylic acid with an alcohol in the presence of a catalyst such as concentrated sulfuric acid, hydrogen chloride, *p*-toluenesulfonic acid, or the acid form of an ion exchange resin:



This Fischer esterification reaction reaches equilibrium after a few hours of refluxing. The position of the equilibrium can be shifted by adding more of the acid or of the alcohol, depending on cost or availability. The mechanism of the reaction involves initial protonation of the carboxyl group, attack by the nucleophilic hydroxyl, a proton transfer, and loss of water followed by loss of the catalyzing proton to give the ester.

In this experiment you will prepare methyl benzoate by reacting benzoic acid with methanol using sulfuric acid as a catalyst. Since this is a reversible reaction, it will reach an equilibrium that is described by the equilibrium constant, K_{eq} .



For this experiment, you will isolate the product, methyl benzoate, and any unreacted benzoic acid. Using this data, you will calculate the equilibrium constant for the reaction (see calculation section below).

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Procedure

A. Reflux

1. Add 0.1 mole of benzoic acid to a 100 mL round bottom flask.
2. Add 40 mL of methanol
3. Add 3.0 mL of concentrated sulfuric acid
4. Mix all reactants and add boiling stones
5. Attach a water cooled reflux condenser
6. Reflux for one hour

B. Separation

1. Cool the mixture to room temperature
2. Decant the mixture into a separatory funnel
3. Rinse the round bottom flask with 10 mL of methylene chloride into the funnel
4. Add 40 mL of methylene chloride and 40 mL of water to the funnel
5. Extract the methyl benzoate into the methylene chloride layer by shaking
6. Separate the organic and aqueous phases

C. Washing (do not discard any materials during this step)

1. Wash the organic layer with 20 mL of R. I. water
2. Wash the organic layer with 20 mL of 5% sodium carbonate
3. Repeat step 2
4. Wash the organic layer with water
5. Drain the organic layer into a dry erlenmeyer flask and dry with magnesium sulfate
6. The aqueous layer from the **sodium carbonate wash** should be acidified with concentrated HCl. When this aqueous material is made strongly acidic with hydrochloric acid, unreacted benzoic acid may be observed. The unreacted benzoic acid should precipitate. Remove the solvent by vacuum filtration. Collect and dry the solid benzoic acid and let it air-dry until the next lab period. You will need this weight for the K_{eq} calculations.

D. Distillations

1. Transfer the dried product (minus the solids) and methylene chloride to a round bottom flask large enough to accommodate the total volume
2. Attach a three way adapter and short condenser and thermometer
3. Distill off the solvent, methylene chloride.
4. Transfer the residue from step 3 into a preweighed container. If needed, transfer the residue from step 3 to a small round bottom flask as possible, reattach the adapter and condenser and thermometer and distill the product into a preweighed container

E. Analysis

1. Determine the actual yield of the product and the unreacted (recovered) benzoic acid.
2. Determine the refractive index of the product
3. Obtain an IR spectrum of the product (reference spectrum are at the end of this document)
4. Calculate K_{eq}
5. Calculate theoretical yield and determine % yield (two different ways, see calculation section below).

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Calculations

Calculation of the Equilibrium Constant, K_{eq} - Calculate a value for the equilibrium constant K_{eq} based upon your weight of recovered benzoic acid. In addition, calculate the percent yield of your synthesis based upon the amount of starting benzoic acid used, and another percent yield based upon the amount of benzoic acid that actually reacted (as determined by the weight of recovered benzoic acid).

Calculation of the Equilibrium Constant K_{eq} :



$$K_{eq} = \frac{[C_6H_5CO_2CH_3][H_2O]}{[C_6H_5CO_2H][CH_3OH]}$$

Since the volume of the reaction mixture is the same for each component, we can use moles instead of molarities as the units in our K_{eq} expression. Let B_i = initial moles of benzoic acid, let M_i = initial moles of methanol, and let X = final moles of methyl benzoate produced at equilibrium.

Based upon the stoichiometry of equation 1, we can conclude three things about X , namely that X = final moles of water produced at equilibrium, X = moles of benzoic acid consumed when equilibrium is established, and X = moles of methanol consumed when equilibrium is established. Using our definitions, equation 2 becomes:

$$K_{eq} = \frac{(X)(X)}{(B_i - X)(M_i - X)}$$

We know B_i and M_i . All we need to do before we can calculate K_{eq} is to Put X in terms of something known, like the amount of benzoic acid recovered. Let B_f = final moles of benzoic acid present at equilibrium. Thus $B_f = B_i - X$, or $X = B_i - B_f$. Substituting $(B_i - B_f)$ for X in equation 3 gives:

$$K_{eq} = \frac{(B_i - B_f)(B_i - B_f)}{(B_i - (B_i - B_f))(M_i - (B_i - B_f))} \quad \text{or} \quad K_{eq} = \frac{(B_i - B_f)^2}{B_f(M_i - (B_i - B_f))}$$

We can now calculate K_{eq} by entering the appropriate values of the moles of benzoic acid used (B_i), the moles of methanol used (M_i), and the moles of benzoic acid recovered (B_f) into equation 5.

Calculation of the % Yield based upon initial amount of benzoic acid used:

Let E = moles of methyl benzoate ester obtained. **Note that this** calculation is valid only if benzoic acid is the limiting reagent.

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$$\begin{aligned}\% \text{ yield} &= \frac{(\text{moles methyl benzoate obtained})(100)}{(\text{Initial moles benzoic acid})} \\ &= \frac{E(100)}{B_i}\end{aligned}$$

Calculation of the % Yield based upon amount of benzoic acid that is consumed:

$$\begin{aligned}\% \text{ yield} &= \frac{(\text{moles methyl benzoate obtained})(100)}{(\text{moles benzoic acid consumed})} \\ &= \frac{E(100)}{X} = \frac{E(100)}{(B_i - B_f)}\end{aligned}$$

Lab Report Guidance

In addition to the requirements listed in the syllabus for creating a lab report, your report should contain the following information:

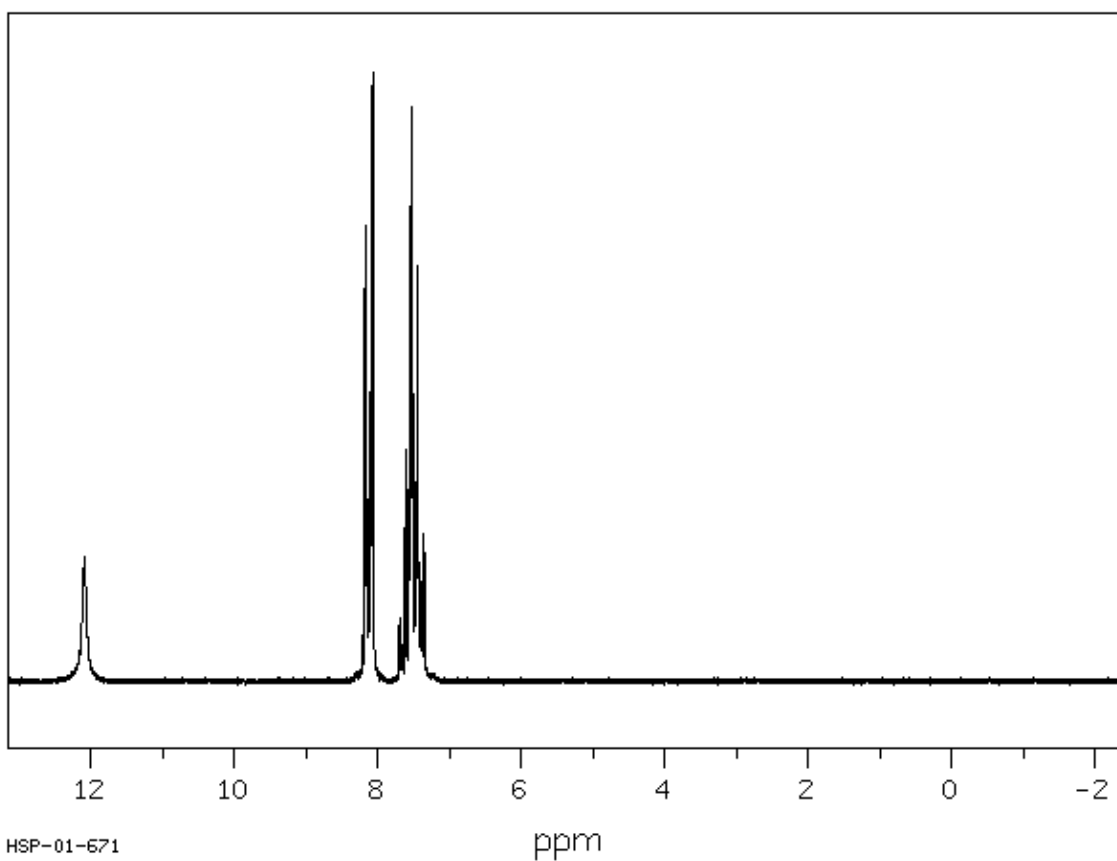
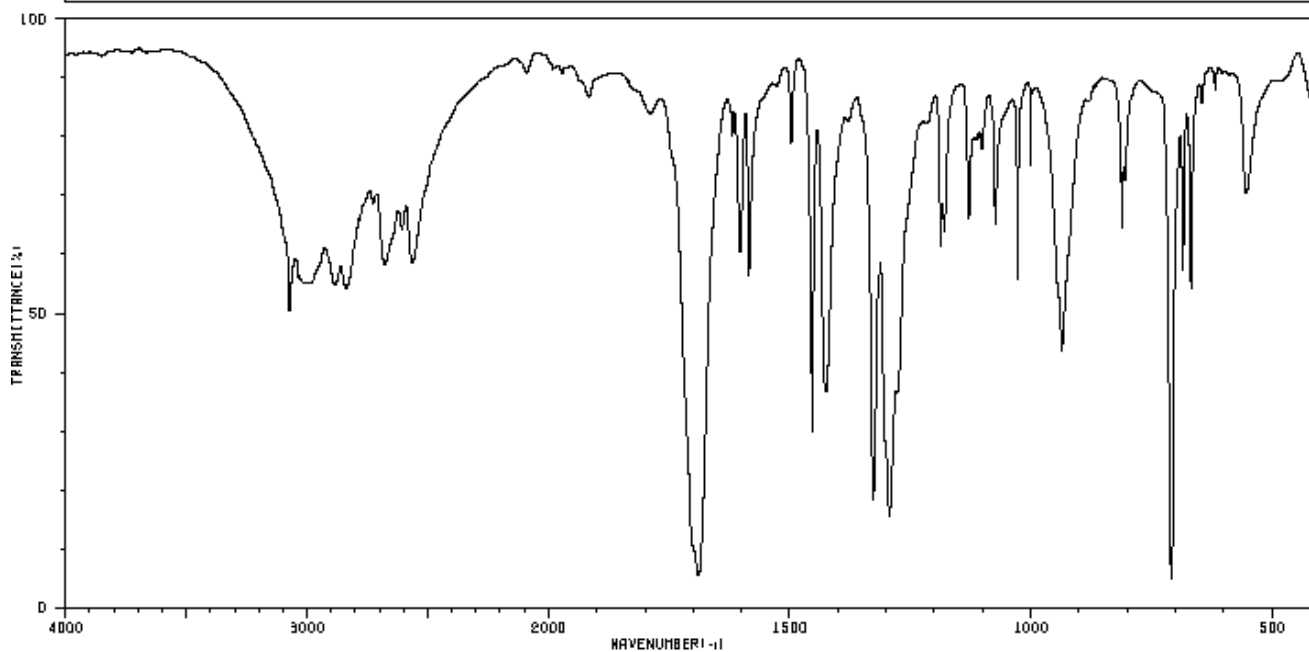
1. Reference to procedure with any changes noted
2. Equation of the reaction showing structures of reactants and products. Below each reactant, list the molecular weight, and amount used in grams (or mLs) and moles. Below each product, list the theoretical yield in grams and moles.
3. The complete mechanism showing all intermediates and arrows to demonstrate electron movement
4. Flow chart for the isolation of methyl benzoate and unreacted benzoic acid
5. Weight of recovered benzoic acid
6. Weight and boiling point of methyl benzoate
7. Calculations
 - a. percent yield based on amount of benzoic acid with which you started
 - b. percent yield based on amount of benzoic acid consumed
 - c. Calculate the equilibrium constant.
8. Interpretation of data and conclusion. Explain what was done in this experiment to drive the reaction toward ester formation.

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Reference Spectrum

IR and proton NMR of Benzoic Acid

HIT-NO=1081	SCORE= ()	SDBS-NO=673	IR-NIDA-6334D : KBR DISC
BENZOIC ACID			
<chem>C7H6O2</chem>			



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HIT-NO=1155	SCORE= ()	SDBS-NO=725	IR-NIDA-00428 : LIQUID FILM
METHYL BENZOATE			
$C_8H_8O_2$			

