CHM 112 Lab Procedure 5:

ESTERIFICATION REACTIONS

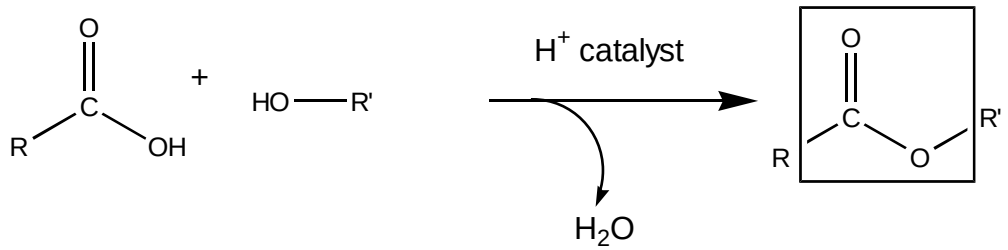
Objectives:

(a) to demonstrate how an ester can be made by the interaction of a carboxylic acid and an alcohol, in the presence of a sulfuric acid catalyst.

(b) to verify that the esterification reaction has taken place by a change in solubility and the distinctive change in odors.

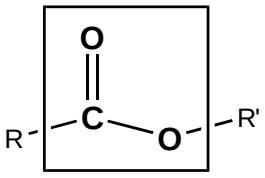
In this procedure, you will perform several esterification reactions, which are the interaction of a carboxylic acid with an alcohol, aided by an inorganic acid catalyst. In this procedure the catalyst is sulfuric acid.

The reaction (EQ 1) that takes place is:



carboxylic acid alcohol ester

The portion of the product (the ester) that has a box around it is the “ester link” or the “ester bond”. It is the group of the carbon atom that is double-bonded to one oxygen and single-bonded to another oxygen. Both oxygens are bonded to the same carbon.



the ester link

The opposite of the esterification reaction is called **<u>hydrolysis</u>** – the addition of water to the ester link and breaking apart of the ester into the carboxylic acid and the alcohol. Hydrolysis also requires the presence of a catalyst (either acid or base).

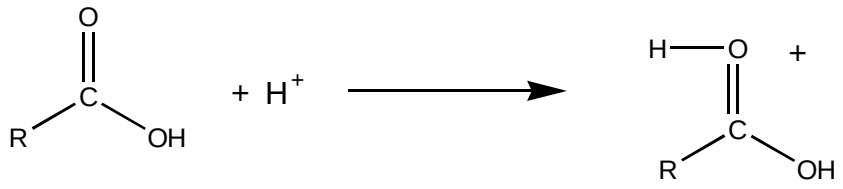
Evidence for the esterification reaction is twofold. One clue is the change in solubility. The alcohol in each of these cases is soluble, and the acids are also soluble – although salicylic acid is only marginally soluble. The products are an ester and water – and the ester is usually not soluble. Therefore, after the reaction has occurred, the solution in the tube will separate into two layers – the top layer is the ester. The other clue to the reaction is a distinctive change in odor. The alcohols and acids usually have sharp and unpleasant odors. The ester products, on the other hand, have pleasant odors, and often smell like certain

fruits. Sometimes these ester products are used as ingredients in certain consumer products, to make them smell better. That berry-scented shampoo that smells so great in the shower is likely due to a synthesized ester! However, you must realize that the odor of natural products – like fruits – is not due to a single ester. A number of esters blend their odors to give strawberries/oranges/any other fruit their rich, luscious smell. So, the single ester that is created in the lab may **resemble** the odor of the fruit, but is not the entire picture.

At equilibrium, only about 60%-70% of the potential yield of ester has formed, the bottom layer is likely to contain unreacted alcohol and carboxylic acid. The trick to forming more ester is to utilize Le Châtelier's Principle and shift the equilibrium to the right by adding excess alcohol, (or by removing water). If hydrolysis is the preferred reaction, the reaction can be shifted to the left by an excess of water. If the reaction is incomplete, the odors of acid and the alcohol may confuse or mask the odor of the ester product.

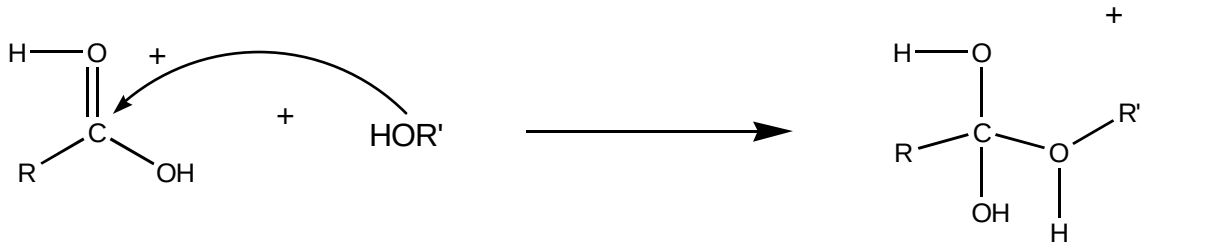
The function of the acid catalyst is rather complicated, the following steps occur:

1) The carboxylic acid accepts a proton from the acid catalyst – it binds to the carbonyl oxygen atom. Since the inorganic acid is a strong acid, it forces the weaker carboxylic acid to act as a base and accept the proton.



positive ion

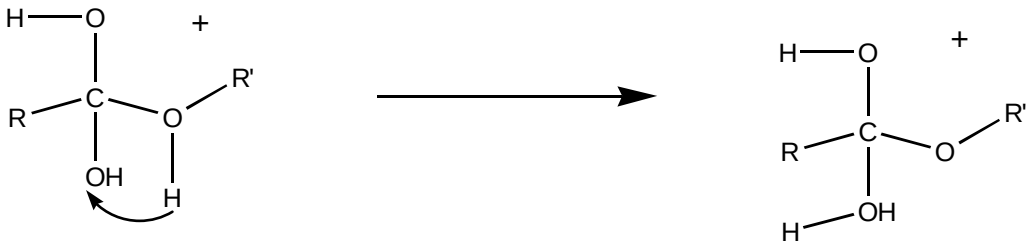
2) A lone pair of electrons on the alcohol oxygen atom attacks the carbon atom and forms a tetrahedral intermediate.



positive ion

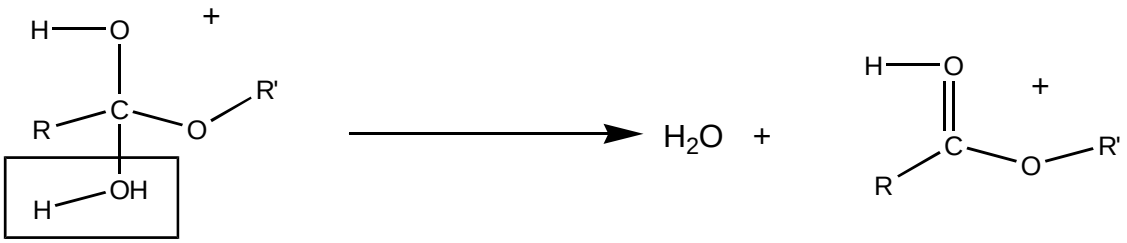
a tetrahedral positive ion

3) A hydrogen shifts from one oxygen atom to another (the chemistry involved is pretty complicated – just know that it <u>does</u> shift – don't worry so much how or why at this point)

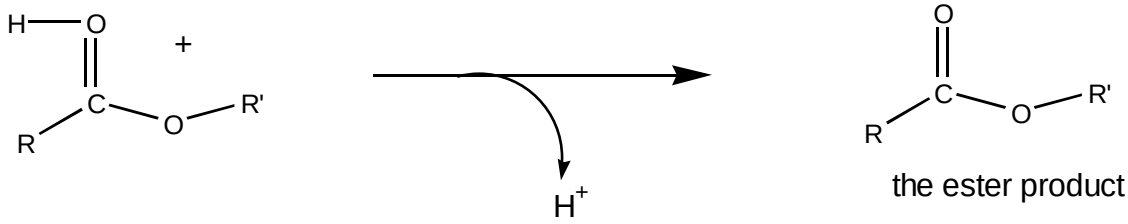


a tetrahedral positive ion

4) The water molecule leaves



5) That proton that's just been bonded to the carbonyl oxygen atom leaves – regenerating the catalyst and releasing the ester molecule.



the ester product

Procedure:

Work in pairs in this entire procedure unless your instructor directs you to do otherwise.

Write out each reaction and the odor of each product in your laboratory notebook. When you are satisfied with the results, transfer them to the final report sheet.

When writing out the reactions, use STRUCTURES and be sure to write out the OTHER molecule that forms in the reaction along with the ester.

1. Prepare a hot water bath using a 600 mL beaker (fill the beaker about ½ full so that it doesn't take forever to heat!) and a hot plate, and maintain its temperature at 60-70 °C.

2. Use test tubes that are clean and dry.

3. You will be performing five esterification reactions. Using one tube per reaction, label each tube:
    a) 1-butanol and acetic acid (remember that acetic acid is the COMMON name of this acid; the bottles may be labeled with an IUPAC name – what is the IUPAC name for acetic acid?)
    b) 1-pentanol and acetic acid
    c) methanol and salicylic acid
    d) 3-methyl-1-butanol (isoamyl alcohol) and acetic acid
    e) 1-octanol and acetic acid

4. Place 3 mL of each alcohol into the appropriately labeled tube. **Cautiously smell the odors of the alcohols by wafting.** A reminder about wafting – bring the container near your nose and use your free hand to gently fan (waft) the vapors toward your nose. Inhale slowly and cautiously – **do not place your nose directly over the vessel; do not inhale deeply.**

5. **Cautiously smell the odors of the acids by wafting.** If the acid is liquid, place about 1 mL of the acid into the appropriately labeled tube. If the acid is a solid, measure about 0.5 g acid and add to the alcohol. Solid acids may have to be stirred with a stirring rod to dissolve. Stir all reactions to homogenize any layers that may form. Rinse off stirring rod with deionized water each time a different solution is stirred.

6. Into each tube, cautiously add 5 drops concentrated sulfuric acid, drop-by-drop, and stir to dissolve. Rinse off stirring rod with deionized water each time a different solution is stirred.

7. Place the test tubes in the water bath and allow it to remain there for at least ten minutes. Some of the esters form quickly; the formation of other esters requires more time. If, at the end of 10 minutes, the odor of either the acid or the alcohol remains, heat for another 5 minutes.

8. Remove a few drops from the top layer with a **clean** dropper and place them on a watch glass. Waft the odor toward your nose and attempt to identify the odor. Sometimes, the odor may be more easily identified if the reaction contents are poured into a small beaker containing 20 mL of hot water (about 60-70 °C). Again, attempt to identify the odor.

9. Using the Equation 1 (EQ 1) at the beginning of the procedure for the formation of an ester, write out the reactions that are occurring in each tube, using the correct formulas of the acids and alcohols for each reaction.

Lab partner(s) _____ Notebook points/initials _____

Date:_____ **Name:**_____

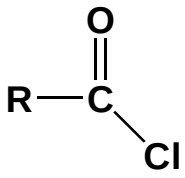
REPORT FOR LAB PROCEDURE 5: ESTERIFICATION REACTIONS

For each of the five esters, give the odor and write the equation for each specific reaction. Use structural formulas for all compounds.

REACTANTS	ODOR OF ESTER	REACTION EQUATION
1-Butanol and acetic acid		
1-Pentanol and acetic acid		
Methanol and salicylic acid		
3-Methyl-1-butanol and acetic acid		
1-Octanol and acetic acid		

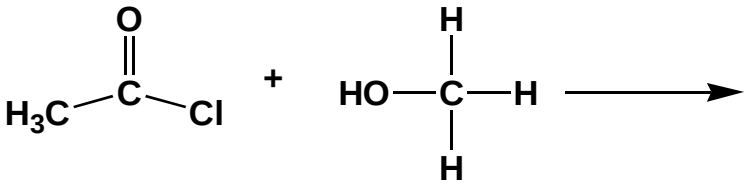
Study questions:

1. An **acid chloride** is a derivative of a carboxylic acid; a chlorine atom (-Cl) replaces the hydroxyl (-OH) group of the carboxylic acid. The acid chloride functional group looks like:

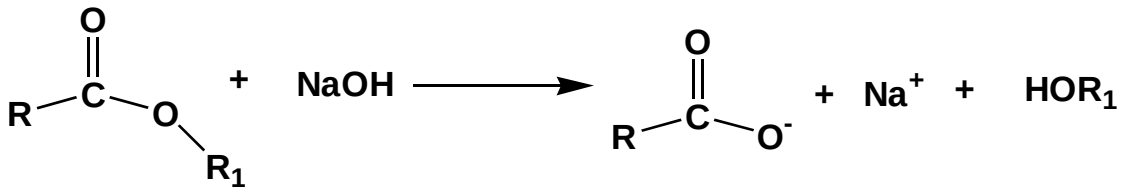


an acid chloride

Acid chlorides also can react with alcohols to form an ester, by the same mechanism as the reaction of a carboxylic acid with an alcohol. Write out the structures of the **<u>two molecules</u>** formed in this reaction of methyl alcohol and acetyl chloride (the acid chloride equivalent of acetic acid.)



2. An ester may be **hydrolyzed** (the bond cleaved with the addition of a water molecule) in the reversal of the ester formation reaction (done in an excess of water). This reaction is called **saponification** and is performed by the addition of a strong base, and cleaves the ester into the alcohol and the carboxylate salt.



sodium carboxylate salt

+ alcohol

Write the structures of the reactants and saponification products when **ethyl butanoate** (the common name is **ethyl butyrate)** is saponified in the presence of the strong base, KOH (potassium hydroxide). By the way, ethyl butyrate is an ester that smells like pineapples.