

Verification of Esterification

PA State Standards for Science and Technology Addressed:

3.4.10.A Explain concepts about the structure and properties of matter.

Apply knowledge of mixtures to appropriate separation techniques.

3.7.10.A Identify and safely use a variety of tools, basic machines, materials and techniques to solve problems and answer questions.

Apply advanced tool and equipment manipulation techniques to solve problems.

3.7.12.A Apply advanced tools, materials and techniques to answer complex questions.

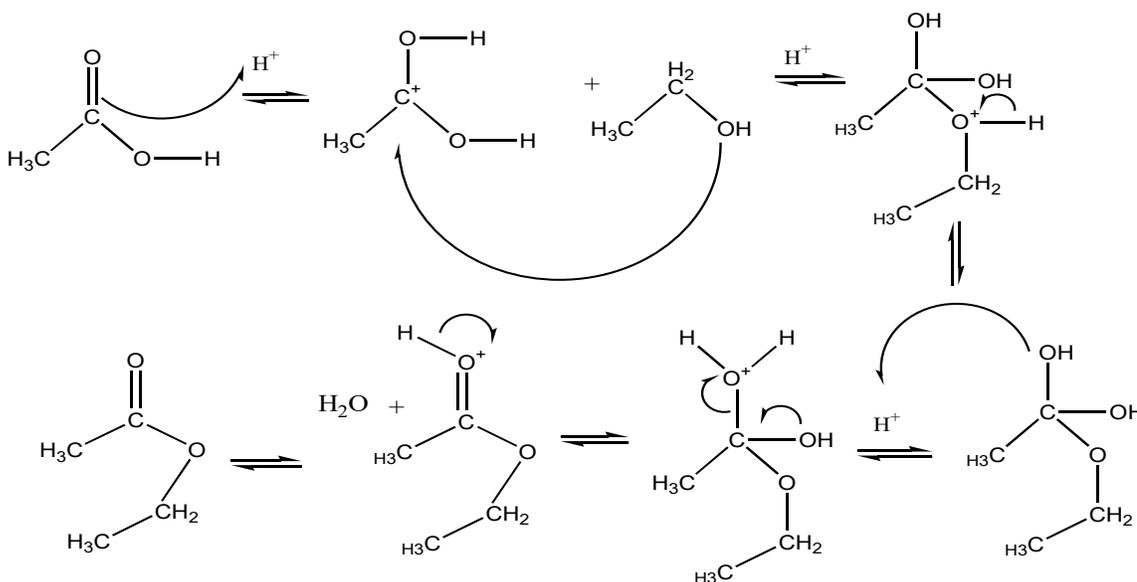
Demonstrate the safe use of complex tools and machines within their specifications.

Introduction:

Many of the flavors and odors one tastes and smells are compounds called esters. Many esters occur naturally in plants and can be isolated using chemical means. They can also be prepared synthetically for use in food additives for flavors and synthetic fragrances. Solvents such as ethyl acetate (fingernail polish remover) or even the starting compounds of plastics are also examples of esters.

Esterification is the process of producing esters. It involves a reaction between an alcohol and an acid (either an organic or an inorganic acid). Some catalysts, such as a small amount of concentrated hydrochloric or sulfuric acid or an ion exchange resin, are used to start or accelerate the reaction.

At first glance, the esterification reaction may appear to be an acid-base neutralization reaction. However, there is no formation or reaction of ions in esterification. The following mechanism shows the reaction:



The esters are named as salts of the carboxylic acids. The alkyl or aromatic groups of the alcohol are named first followed by the acid with an -ate ending instead of the -ic ending.

Some Common Esters

| Alcohol | Acid | Ester | Odor |
|---------|-----------|-------------------|-------------|
| methyl | acetic | methyl acetate | sweet |
| ethyl | acetic | ethyl acetate | fruity |
| isoamyl | acetic | isoamyl acetate | banana |
| isoamyl | butyric | isoamyl butyrate | pear |
| methyl | salicylic | methyl salicylate | wintergreen |

Purpose:

The purpose of this experiment is to synthesize ethyl acetate and to verify the formation of the product with a gas chromatograph.

Equipment/Materials:

| | |
|-------------------------------|-------------------|
| Glacial acetic acid | Droppers |
| Ethanol | Hot plate |
| Ethyl acetate | Labeling tape |
| Methanol | Syringe |
| Dowex 50x2 ion exchange resin | Kimwipes |
| Microscale kit | Gas chromatograph |
| 250mL beaker | Computer |
| Microscale thermometer | Printer |

Safety:

- Keep the chemicals away from open flames.
- Wear safety glasses.
- Glacial acetic acid is a **strong** irritant to the skin and eyes.
- Locate the eyewash and acid safety stations in the laboratory.

Procedure:

PART I: Retention Times for Standards

1. Turn on the GC and start the Peak Sample software. A data acquisition system popup should appear with phrases like initializing, waking up, signing on, setting modes, and calibrating. If you get a popup saying can't wake – check power and cable, try one of the following options.
 - a. Check to make sure that the cable between the GC and computer is properly attached and that the GC is on.
 - b. Close the program. Unplug the USB cord from the computer, then plug it in again. Restart the program. If it still won't wake, try the next option.
 - c. Click on the Edit Menu, then select Overall. In the COM Port/USB device number box, try a number from 1 – 5. Keep trying until the data acquisition system begins to function.

2. Click on edit menu, then select channels. Under Channel 1, pick Temperature. Click on the numbers to highlight them, then click Change. Change the numbers as follows:
 - Start 150°C
 - Hold 20 minutes
 - Ramp 0 degree / min
 - Until the temperature is 150°C
 3. Be sure the time scale starts at zero and ends at 16 min. Use the arrows to adjust.
 4. Obtain a microliter syringe and vials of ethanol, glacial acetic acid, and ethyl acetate.
 5. Clean the syringe by rinsing it 10 -- 15 times with one of the standards. With the plunger fully depressed, place the needle into the sample. Slowly draw up the plunger to obtain a sample in the syringe. Remove the syringe from the sample. Discharge this sample into the sink or onto a Kimwipe. Depress the plunger, and put the syringe needle back into the sample. Draw up a second sample and discharge it. Repeat. **Do not push on the plunger when the needle is inside a sample.**
 6. Place the syringe needle back into the sample and withdraw over 1 microliter. Remove the needle from the sample bottle, then depress the plunger to the 1 microliter line. Wipe the needle with a Kimwipe.
 7. Click on the Z or θ button on the run screen to zero the current.
 8. Insert the needle carefully into the injection port of the GC until the entire needle is inside the instrument.
 9. Inject the sample and start the data collection simultaneously by depressing the syringe plunger and pressing the space bar on the computer at the same time.
 10. When the sample peak of a standard returns to baseline, the run may be stopped by pressing the end button on the computer. After pressing end, print the graph. Be sure to label the graphs.
 11. Repeat steps 5-10 for the other 2 standards.
- Note: Proceed to Part II and work on it while running standards to save time.**

PART II: Esterification

1. Fill a 250mL beaker half-full with water and place it on a hotplate near a wall. Place a microscale thermometer in the water. Monitor the temperature – it should stay between 70 – 80°C.
2. Use a microspatula to place a small amount of ion-exchange resin (about equal to two garden peas) into three microscale test tubes. The test tubes may be placed in microscale Erlenmeyer flasks, which will act as stands for the test tubes.
3. Add 25 drops glacial acetic acid and 25 drops ethanol to each of the test tubes.

4. Place all three test tubes into the hot water. Aim the tubes at a wall in case the chemicals boil and spurt out of the test tube.
5. **Monitor the water temperature.** If it drops below 70° C, turn up the heat; if it rises above 80 °C, turn the heat down or off and add some cold water. At the end of ten minutes remove and label one of the test tubes.
6. At the end of twenty minutes, remove and label another test tube.
7. At the end of thirty minutes, remove and label the third test tube.
8. Allow all three test tubes and contents to cool. When the test tubes are cool enough to handle, procede to Part III.

PART III: Verification of Esterification

1. Following the procedure learned in Part I, run the contents of each of the 3 test tubes in the GC. Inject 2 microliters of each sample. These samples will have peaks for each of the standards. **Do not stop the run until peaks for ethanol, glacial acetic acid, and ethyl acetate have all been obtained.**
2. After injecting the last sample, rinse the syringe well with methanol.

Data and Calculations:

Part I:

| Sample | Retention time in min. |
|---------------------|------------------------|
| ethanol | |
| glacial acetic acid | |
| ethyl acetate | |

Part III:

| Sample | Retention Time | Area | Identity | % Composition |
|---------------------|----------------|------|----------|---------------|
| Test Tube 1, peak 1 | | | | |
| Test Tube 1, peak 2 | | | | |
| Test Tube 1, peak 3 | | | | |
| Test Tube 2, peak 1 | | | | |
| Test Tube 2, peak 2 | | | | |
| Test Tube 2, peak 3 | | | | |
| Test Tube 3, peak 1 | | | | |
| Test Tube 3, peak 2 | | | | |
| Test Tube 3, peak 3 | | | | |

Questions:

1. What was the purpose of running the standards on the gas chromatograph?
2. Why was the sample size increased to 2 microliters for the test tube samples?
3. Explain how gas chromatography could be used to determine when a system has reached equilibrium.
4. Compare the various chromatograms and write observations and conclusions in sentence form. Be sure to compare the percent composition of the ester at $T = 10$, $T = 20$, and $T = 30$ minutes.