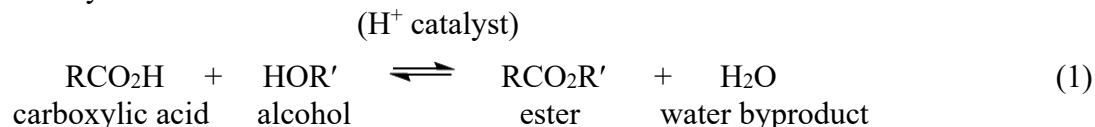


SYNTHESIS OF ESTERS USING ACETIC ANHYDRIDE¹

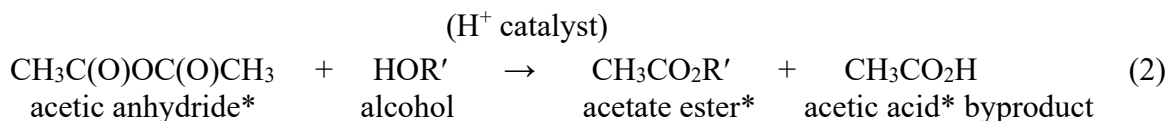
Introduction

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. (Equation 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 esters -- benzyl acetate, decyl acetate, hexyl acetate, isopentyl acetate, isopropyl acetate, n-octyl acetate, propyl acetate -- and synthesize it by reacting acetic anhydride with the appropriate alcohol. *Be sure to draw out these structures completely in your notebook (you can use ROH/OR to represent the unknown alcohol/ester).



After mixing together the starting materials -- acetic anhydride, an alcohol (either benzyl alcohol, 1-decanol, hexyl alcohol, isoamyl alcohol, isopropanol, 1-octanol, or 1-propanol depending on the specific ester being prepared) and H₂SO₄ 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, that is free from any leftover starting materials and acetic acid side product. This is a typical, though relatively simple, organic synthesis procedure. The mass 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.

Safety and Waste Precautions

- ▶ Treat concentrated H₂SO₄ with respect! Clean up any and all spills, however small. Rinse exposed areas of your skin and clothing immediately with lots of water.
- ▶ Acetic anhydride is corrosive and has harmful fumes. Avoid breathing it and measure it out in a fume hood, using the provided graduated cylinder (keep the graduated cylinder in the hood).
- ▶ Wear gloves throughout the experiment (at least up to procedure step 7).
- ▶ Do not inhale organic vapors.
- ▶ Keep reagent bottles capped when not in use.
- ▶ Dispose of all waste in proper waste container in hood.

¹ Adapted from Gilbert and Martin, Experimental Organic Chemistry, 6th Ed., pp. 770-71.

Materials Provided

- 2.0 mL (premeasured) of an alcohol to be chosen from the following: 1-dodecanol, (n-dodecyl alcohol), 1-propanol (*n*-propyl alcohol), 3-methyl-1-butanol (isoamyl alcohol, isopentyl alcohol), 1-octanol (n-octyl alcohol), phenylmethanol (benzyl alcohol), isopropanol (2-propanol), 1-hexanol (*n*-hexyl alcohol), 1-decanol (*n*-decyl alcohol).
- 2-3 mL acetic anhydride available in buret in hood
- 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 (15 mL or more), several small test tubes, 1 screw-cap vial, Pasteur pipettes

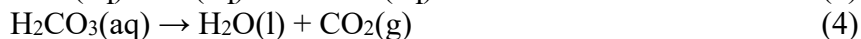
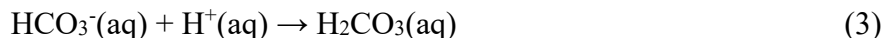
Procedure

ester chosen	volume of acetic anhydride (mL)
dodecyl acetate	1.0
benzyl acetate	2.3
decyl acetate	1.2
hexyl acetate	1.9
isopentyl (isoamyl) acetate	2.2
isopropyl acetate	3.1
<i>n</i> -octyl acetate	1.5
propyl acetate	3.2

1. Place the volume of acetic anhydride indicated in the above table in a 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 approximately 5 minutes 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. 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, the 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 it 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. Transfer the liquid to the vial with a Pasteur pipet. To recover as much liquid as possible, place the tip of the pipet against the bottom of the test tube while withdrawing liquid. Cap the vial and weigh it. Investigate 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-known odors you have experienced in everyday life. Do not merely describe it as having a chemical odor!
11. Take IR and refractive index. Compare your sample to literature data to identify your ester.

Lab Report

The Results section of your notebook should include the following:

- Balanced chemical equation with your specific alcohol and ester (using complete structures/line drawings, rather than condensed formulas).
- Report the volume of ester produced.
- Calculate the theoretical yield and the percent yield.
- Consider the purification process when discussing error and yield.
- Conclusion: provide evidence that you synthesized the specific ester drawn.