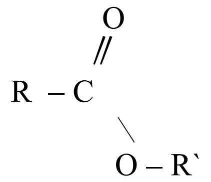
Preparation of Esters

When an organic acid reacts with an alcohol an ester is formed. Esters have pleasant odours and are frequently found in plants and fruits.
Esters are a class of compounds which are widely distributed in nature. They have the general formula:



R, R` = alkyl groups

Simple esters tend to have pleasant odours. In many cases the characteristics fragrances associated with flowers and fruits are due to simple compounds containing an ester as the functional group. Small structural changes give distinctly different fragrances.

For example, methyl butanoate, $CH_3CH_2CH_2COOCH_3$, is the major component responsible for the fragrance of apples while ethyl butanoate, $CH_3CH_2CH_2COOCH_2CH_3$, is characteristic of pineapples and propyl acetate, $CH_3COOCH_2CH_2CH_3$, of pears. Other examples of esters which are associated with common fruits are shown in the table below.

Natural fragrances are due to complex mixture of compounds which give fruits their unique flavours and fragrances. Food and beverages manufacturers use compounds prepared in the laboratory as food additives to enhance the appeal of their products. Good quality imitations or synthetic flavours are generally a combination of many compounds which attempt to mimic the natural fragrance.

Simple esters are usually prepared by “direct”esterification of an acid by an alcohol in the presence of an acidic catalyst:

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R`OH} \overset{H^{+1}}{\rightleftharpoons} \underset{\text{ester}}{RCOOR`} + \underset{\text{water}}{H_2O}$$

The rate of attainment of equilibrium may be speeded up by the addition of an acid catalyst, although this catalyst also catalyses the reverse reaction, (hydrolysis). However, direct esterification has the advantage of being a single-step synthesis, and the equilibrium may be shifted in the required direction by using an excess of the cheaper reactant or by removing one of the products.

The equilibrium constant is given by the law of mass action:

$$K = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]}$$

Due to the equilibrium character of the reaction, the yield can be significantly influenced by changing the proportions of the reactants.

It has been determined, for example that the reaction between ethanol and acetic acid, (ethanoic acid), to give ethyl acetate, (ethyl ethanoate), and water has an equilibrium constant, K = 4.00 (unitless, why?).

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{CH_3CH_2OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3} + \underset{\text{Water}}{H_2O}$$

Suppose that the experiment had begun with 1 mol each of ethanol and acetic acid.

At equilibrium, there would be x mol of ethylacetate, x mol of water, (1 - x) mol of ethanol and (1 - x) mol of acetic acid. Performing the calculation would give: x = 0.67 and thus the % yield of ethyl acetate is: $x \div 100 = 67\ \%$.

However, if one were to start with 2 mol of ethanol and 1 mol of acetic acid, the following situation would prevail at equilibrium:

[ethyl acetate] = x [water] = x [acetic acid] = 1 - x [ethanol] = 2 - x

Solution of the resulting quadratic equation gives: x = 0.845. Thus, under these conditions, using acetic acid as the limiting reactant, the yield is 85 %.

If initially, the concentration of ethanol is increased by five times, the yield of ethyl acetate at equilibrium based on acetic acid would approach 95 %.

There are generally no side reactions in esterification, if properly performed. As an example of a direct esterification, one of several simple esters will be prepared from the appropriate alcohol and acetic acid. These esters are ...

a) butyl acetate
b) isoamyl acetate or 3-methylbutyl acetate
c) propyl acetate

Procedure for making the above three esters:

Mix 5 cm^3 of one of the alcohols supplied with 6.0 cm^3 acetic acid in a test tube and add slowly 1.0 cm^3 concentrated H_2SO_4. Gently warm the mixture in a water bath for ~ 15 mins. Allow to cool and note the odour of the sweet-smelling product Pour the contents of the test tube into a boiling tube half-full of cold water, waft the odour. Dispose of the contents of the test tube in the organic waste disposal container.

Procedure for making methyl salicylate

1. Place 2 mL of methanol (CH_3OH) in a test tube.
2. Add 1 g of salicylic acid, (2-hydroxybenzoic acid).
3. Add 4 drops of concentrated sulphuric acid to the test tube. Put the test tube in a beaker of water on a hot plate. Bring the contents of the test tube to a boil,(~75^{O}C).
4. Smell the contents of the test tube as instructed (waft!). Identify the pleasant odour.
5. Once you detect the ester by its pleasant odour, examine the test tube carefully to see if there is one layer or two layers of liquid in the test tube.

Discussion Questions

1. Sulphuric acid acts as a catalyst for the making of the ester. Write a chemical equation showing the production of each of the above prepared ester. Use structural formulas in the equations. What are the uses of ethyl ethanoate?
2. For the ester, suggest what is present in the layer(s) of liquid in the test tubes once the ester have been formed.
3.a) Another ester, methyl butanoate, which smells like apples, can be made from methanol and butanoic acid. Write a structural equation for the preparation of methyl butanoate.
b)Another ester: isoamyl acetate, which smells like bananas, can be made from isoamyl alcohol and acetic acid. Write the structural equation for the preparation of isoamyl acetate
4.a) Given the equilibrium constant, K = 3.0 calculate how many moles of ester you would obtain, at equilibrium from 1 mol of pentan-3-ol and 1 mol of acetic acid, and express the result in terms of % yield.
b) What improvement in % yield, based on the alcohol employed, would result by tripling the amount of acetic acid in this experiment.