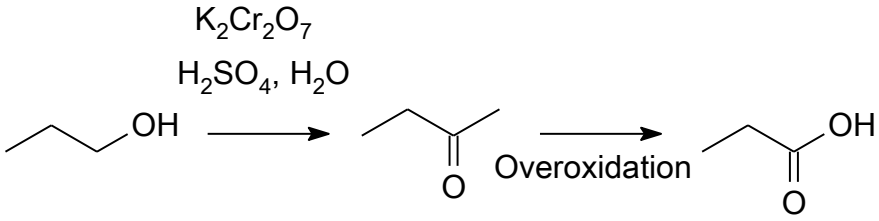
Organic chemistry – crib sheet

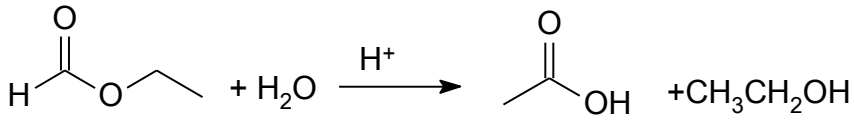
Carboxylic acids

General

Carboxylic acids are a group of compounds formed by the oxidation of an aldehyde



The second method of production is the hydrolysis (addition of water) of an ester to give the acid and alcohol.



Structure and bonding

Carboxylic acids will readily hydrogen bond with both water and themselves (when they bond with themselves it is known as dimerisation) as well as with other hydrogen containing compounds (such as alcohols).

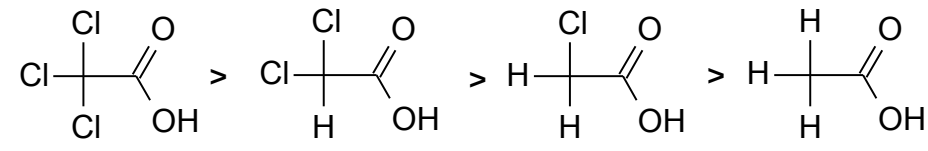
As they are acids, they have a dissociatable hydrogen, however as the hydrogen is strongly attracted to the oxygen, so they will have a low degree of dissociation and so are classed as “weak” acids.

When the hydrogen is lost, an oxonium ion is formed (O^-) which acts as a nucleophile.

The carbon with the OH group on also has a double bonded oxygen. The double bond can be treated the same as a carbon-carbon double bond in that it is open to electrophilic attack. The oxygen also has the lone pair of electrons which gives that a negative charge. In order for the molecule to stabilise itself, the central carbon “gives away” some of it's charge, making it slightly positive..

Due to the high degree of hydrogen bonding, carboxylic acids have relatively high melting and boiling points with all being liquid at room temperatures.

The acidity (as a measure of pKa) of the carboxylic acid is affected if it is acting as a 1º, 2º or 3º acid



pKa 0.7 1.48 2.86 4.76

Solubility

The solubility of the carboxylic acid depends on the length of the hydrocarbon chain. As with alcohols, the longer the hydrocarbon chain, the less soluble it will be.

Use of carboxylic acids

Carboxylic acids occur naturally and many creatures use them as a form of chemical weapon (such as methanoic acid by ants and wasps and oxalic acid in rhubarb leafs). Ethanoic acid is formed by the oxidation of ethanol (malt vinegar is whiskey that has gone "bad").

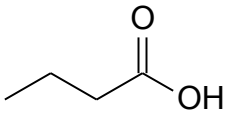
Carboxylic acids are also used to form esters when reacted with alcohols (esters are covered in another sheet) and reduced to give aldehydes and primary alcohols.

<u>Naming carboxylic acids</u>

An important feature of naming carboxylic acids is that they are known as "terminal" groups – that is that they can only appear at the end of a chain. They are also a high priority group, so counting along the chain starts from the acid group.

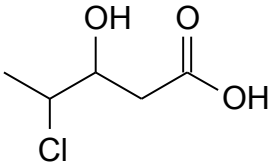
A secondary feature of carboxylic acids is that if there is an OH group on the chain, it becomes a hydroxy- group rather than an alcohol.

The naming rules are the same as with other carbonyl compounds, but to show it is a carboxylic acid, the ending becomes -oic acid.



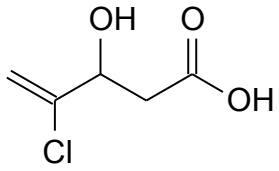
Number of carbons on the chain : 4, skeletal name = butan
Any other groups : no
Functional group : carboxylic acid
Any double bonds : no

Full name : butanoic acid



Number of carbons on the chain : 5, skeletal name = pentan
Any other groups : yes, OH and Cl
Any double bonds : no
Position of groups : OH on 3 and Cl on 4 (counting from the acid)
Functional group : carboxylic acid

Full name : 3-hydroxy, 4-chloro, pentanoic acid

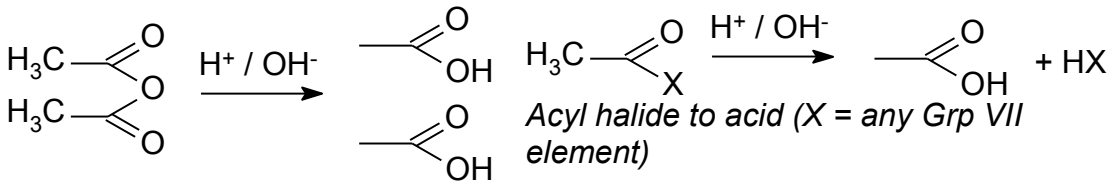


Number of carbons on the chain : 5, skeletal name = pentan
Any other groups : yes, OH and Cl
Any double bonds : yes
Position of groups : OH on 3, Cl on 4, double bond on 4 (counting from the acid)
Functional group : carboxylic acid

Full name : 3-hydroxy, 4-chloro-pentan-4-ene-oic acid

Preparation of a carboxylic acid

Other than the oxidation of an alcohol and ester hydrolysis, carboxylic acids can also be produced by the hydration of an acid anhydride or reaction between water and an acyl halide



Acid anhydride to acid

Acyl halide to acid (X = any Grp VII element)

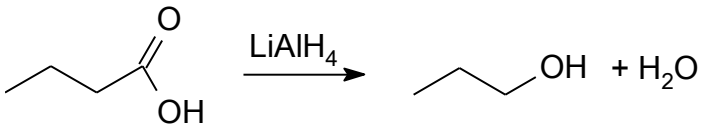
The reaction between the acyl halide and water is very vigorous with a large amount of heat generated (acyl halides and acid anhydrides are dealt with in another sheet)

Reactions of carboxylic acids

Reduction of a carboxylic acid to alcohol

Carboxylic acids are very stable compounds and do not readily undergo reduction reactions. To reduce the acid, a very strong reducing agent, such as $LiAlH_4$ (lithium aluminium hydride, the hydrogen here is in the -1 oxidation state making it very reactive).

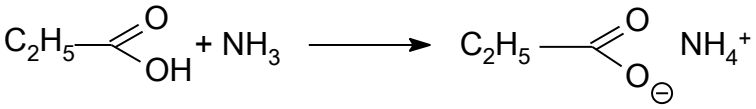
When the acid is reduced, the primary alcohol is formed



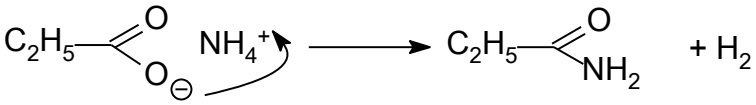
Amide formation

Amines and amides are compounds based around the ammonia molecule (NH_3). Nitrogen compounds are strong bases due to the lone pair of electrons on the nitrogen. When a carboxylic acid and amine react, the form amides. This is a 2 step process.

Step 1 : the H^+ reacts with the negatively charged N to form the ammonium ion leaving a negatively charged oxygen on the acid



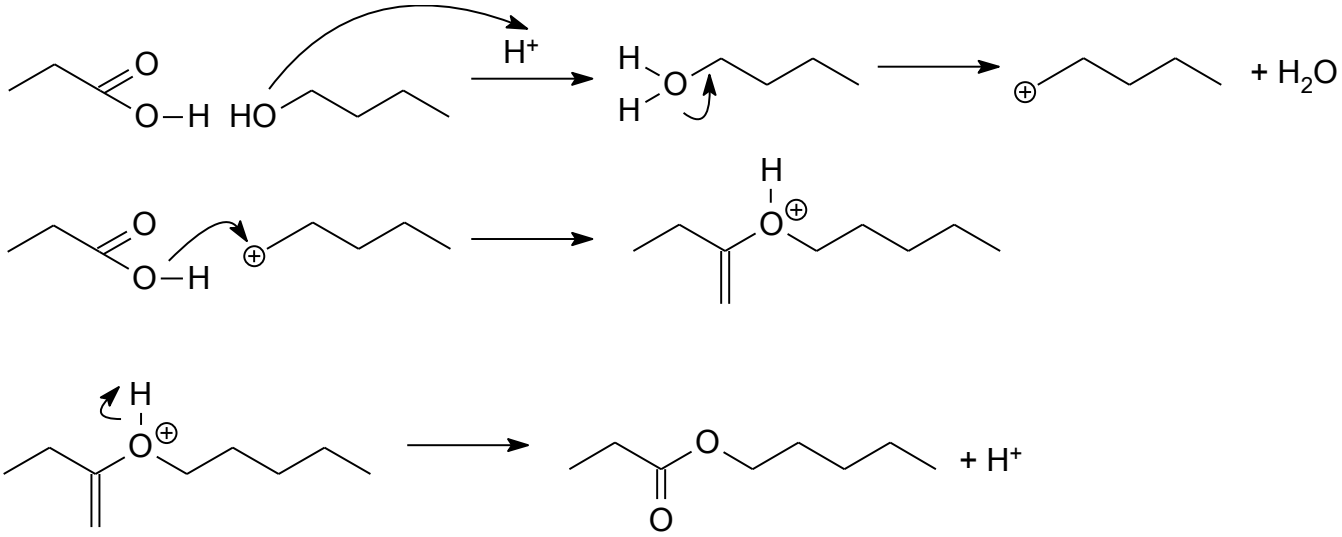
Step 2 : the negatively charged oxygen reacts with the ammonium group to form the amide and H_2



The chemistry of amines and amides are dealt with in another sheet.

Esterification

Esters are formed by the reaction of a carboxylic acid with an alcohol.



Here the acid reacts with the alcohol with an acid catalyst. The first part is the formation of the carbocation on the alcohol. A primary alcohol is much more prone to attack than the acid (the acid effectively “holds on” to the dissociatable H). The second step is the reaction between the acid and the carbocation to form the ester with the regeneration of the H+ catalyst.

Ester chemistry is dealt with in another sheet.