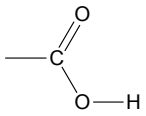
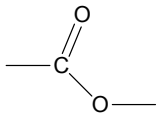
Carboxylic Acids, Esters and Acyl Chlorides

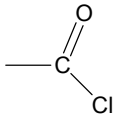
Carboxylic acids contain the –COOH functional group, attached to an alkyl stem. They are widely found in nature, from the methanoic acid in ants, the ethanoic acid in vinegar to the citric acid in citrus fruits.



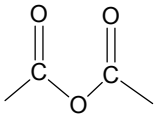
Esters contain the –COO- functional group, with an alkyl group attached to either side. Esters are widely used in perfumes and flavourings since they are responsible for the flavours of many foods and the scents of flowers.



Acyl chlorides contain the –COCl functional group, attached to an alkyl stem.



Acid anhydrides contain the –COOCO- functional group, attached to two alkyl groups. They can be considered as two carboxylic acid molecules joined together by a condensation with elimination of a water molecule.

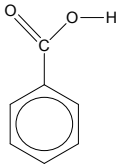


Naming

carboxylic acids

- name the alkyl group, then replace the final 'e' with 'oic acid'.
- remember that the carbon in the -COOH group is part of the alkyl chain for naming purposes, so:

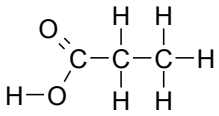
HCOOH	is methanoic acid
CH_3COOH	is ethanoic acid etc.
C_6H_5COOH	is benzoic acid



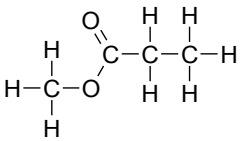
- the -COOH group can only go on the end of a chain, so no numbering is required to identify its position. Like in an aldehyde, the carbon in the –COOH group becomes number 1 in the chain.

esters

Esters can be considered as derivatives of carboxylic acids, where the hydrogen in the –COOH group has been replaced with an alkyl group. The ester name starts with the name of this alkyl group, then the name from the carboxylic acid, with the '-oic acid' ending replaced with '-oate'.



propoanoic acid



methyl **propano**ate

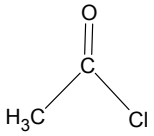
e.g. $CH_3COOC_3H_7$ is propyl ethanoate

$CH_3CH_2COOCH_3$ is methyl propanoate etc.

$CH_3COOC_6H_5$ is phenyl ethanoate
$C_6H_5COOC_6H_5$ is phenyl benzoate

acyl chlorides

These are similarly named as derivatives of carboxylic acids. The '-oic acid' suffix is replaced with '-oyl chloride'. Hence:

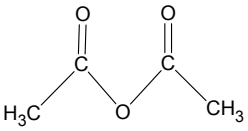


CH_3COCl is ethanoyl chloride (pronounced -o-ile, not –oil!)
CH_3CH_2COCl is propanoyl chloride
C_6H_5COCl is benzoyl chloride

acid anhydrides

These too are named as derivatives of carboxylic acids. The two alkyl groups are the same, so we simply remove the '-oic acid' suffix and replace with '-oic anhydride'.

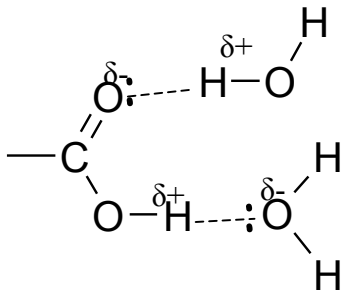
$CH_3COOCOCH_3$ is ethanoic anhydride etc.



Solubility of carboxylic acids

Short chain carboxylic acid (1 – 4 carbons) are readily soluble in water. They can dissolve in water because the highly polar C=O and O-H groups in the carboxylic acid functional group can form hydrogen bonds to the water molecules. The alkyl group is non-polar and does not interact with the water molecules.

Diagram:



As the size of the alkyl group increases the solubility decreases, as the non-polar alkyl group has a greater effect on the overall polarity of the molecule.

Dicarboxylic acids, with two –COOH groups on either end of the chain are readily soluble in water, having two polar carboxyl groups to form hydrogen bonds with the water molecules.

Acid Reactions of Carboxylic Acids

- Carboxylic acids reacting with metals and bases (metal oxides, hydroxides and carbonates) to form salts. These salts are IONIC; the metal providing the positive ion and the carboxylic acid forming a negative carboxylate ion.

- Carboxylic acids are **weak acids** (partially dissociated in aqueous solution). This means that carboxylic acids react **more slowly** than strong acids of the same concentration, as the concentration of H^+ in the solution is lower.

$$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$$

1) with reactive metals

carboxylic acid + metal → metal carboxylate (salt) + hydrogen

e.g. $CH_3COOH + Na \rightarrow CH_3COO^-Na^+ + ½\ H_2$

ethanoic acid sodium ethanoate

Observations:

- effervescence
- the metal dissolves

Evaporation of the resulting solution will give white crystals of sodium ethanoate

2) with alkalis (metal hydroxides/ammonia solution)

carboxylic acid + metal hydroxide → metal carboxylate (salt) + water

e.g. $CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$

Observations:

- none - no fizzing etc.

This is a neutralisation reaction.
An indicator would be needed to see when the solution had become neutral.
Crystals of the salt can be obtained by evaporation.

3) with metal carbonates

carboxylic acid + metal carbonate → metal carboxylate + water + carbon dioxide

e.g. $2\ CH_3COOH + Na_2CO_3 \rightarrow 2\ CH_3COO^-Na^+ + CO_2 + H_2O$

Observations:

- fizzing
- (solid) metal carbonate dissolves

This is a neutralisation reaction.
Crystals of the salt can be obtained by evaporation.

*NOTE: The reaction with carbonates provides a **test for carboxylic acids**. Other acidic organic molecules such as phenols are not sufficiently reactive to react with carbonates.*

4) with metal oxides

carboxylic acid + metal oxide → metal carboxylate + water

e.g. $2\ CH_3COOH + CuO \rightarrow (CH_3COO^-)_2Cu^{2+} + H_2O$

Observations:

- metal oxide dissolves

This is a neutralisation reaction.
Crystals of the salt can be obtained by evaporation.

Practice:

Write balanced equations to show the reactions of butanoic acid with:

magnesium, calcium hydroxide, strontium carbonate, lithium oxide

Reactions of carboxylic acids – esterification

Esterification is the reaction of a carboxylic acid with and alcohols to form an ester.
Esters have fruity smells and are found naturally in fruits.

butyl butanoate – pineapple
3-methylbutyl ethanoate – pear
ethyl 2-methylbutanoate - apple

Esters are used to make artificial flavourings and perfumes. Combinations of esters can be used to mimic some of the more complex mixtures found in nature.

Conditions:

Warm the carboxylic acid with the alcohol in the presence of a small amount of concentrated sulphuric acid as a catalyst. The reaction mixture needs to be refluxed because the reaction is fairly slow.

Separating the product:

The reaction is **reversible** and at equilibrium there will be products and reactants both present. Distillation is used to remove the impure ester from the reaction mixture, before purification.

Equations:

e.g. $CH_3CH_2COOH + CH_3OH \overset{\textbf{conc.}\ \text{sulphuric acid catalyst}}{\rightleftharpoons} CH_3CH_2COOCH_3 + H_2O$

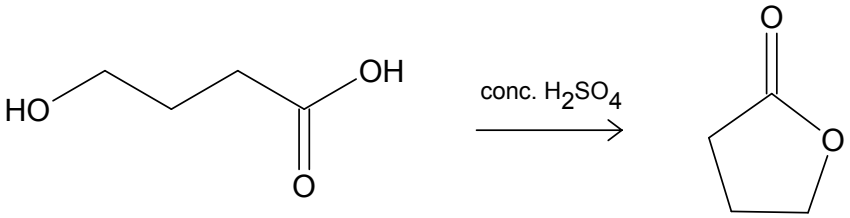
propanoic acid + methanol ⇌ methyl propanoate + water

How it works:

The H- from the alcohol's OH group and the –OH from the carboxylic acid are removed to make water. The O from the alcohol joins to the C=O of the carboxylic acid to form an ester link.

$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

Note: It is also possible for a molecule containing both an alcohol and a carboxyl group to react with itself, forming a cyclic ester, so long as the two reacting groups are not too close together that the resulting ring would be too strained.



4-hydroxybutanoic acid

Practice:

i) Using displayed formulae, write an equation for the reaction between butanoic acid and ethanol in the presence of an acid catalyst; name the ester formed in this reaction

ii) write an equation for the ester formed when 5-hydroxyhexanoic acid is warmed with an acid catalyst

Reactions of Esters

Esters can be hydrolysed to form a carboxylic acid (or its salt) and an alcohol.

Definition: Hydrolysis is a reaction with water or hydroxide ions that breaks a chemical compound into two compounds

i) Acid hydrolysis

Conditions: heat under reflux
dilute sulphuric acid or hydrochloric acid catalyst

Reaction: e.g. $CH_3COOCH_2CH_2CH_3 + H_2O \overset{HCl_{(aq)}}{\rightleftharpoons} CH_3COOH + HOCH_2CH_2CH_3$
propyl ethanoate + water ethanoic acid + propan-1-ol

ii) Alkaline hydrolysis

Conditions: heat under reflux
aqueous sodium or potassium hydroxide

The reaction in this case is not reversible, and leads to the formation of the sodium salt of the carboxylic acid.

$CH_3COOCH_2CH_2CH_3$ + NaOH → $CH_3COO^-Na^+$ + $HOCH_2CH_2CH_3$
propyl ethanoate + sodium hydroxide sodium ethanoate + propan-1-ol

This is the reaction that is done in soap-making to turn fats into soaps – called **saponification**.

Practice: Butyl hexanoate can be hydrolysed with aqueous acid or with aqueous alkali.
- draw the structure of butyl hexanoate
- write equations for the acid and alkaline hydrolysis

Reactions of Acyl Chlorides

- Acyl chlorides are very reactive. They are useful in organic synthesis as they react to form carboxylic acid derivatives: esters, amides etc. with good yields.
- Acyl chlorides react with nucleophiles undergoing substitution reactions in which the carbonyl group is retained, and a chloride ion eliminated.

Preparation of acyl chlorides:
Acyl chlorides are made from the corresponding carboxylic acids by reacting them with thionyl chloride, $SOCl_2$. The other products are HCl and SO_2, which as gases which can be allowed to escape (harmful! - in a fume cupboard) leaving the acyl chloride product.

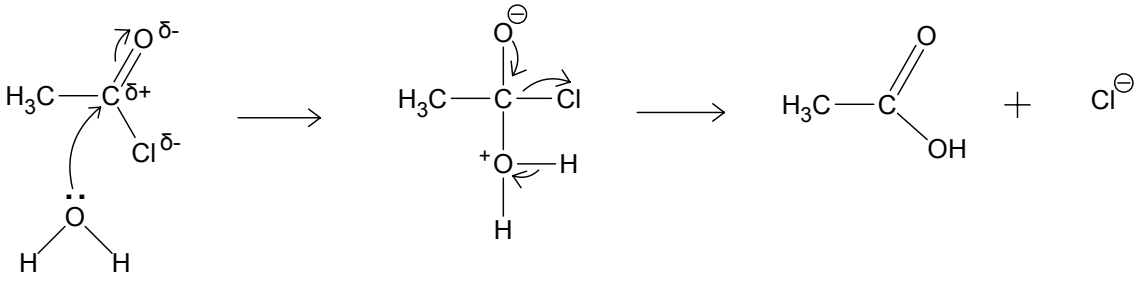
e.g. CH_3CH_2COOH + $SOCl_2$ → CH_3CH_2COCl + SO_2 + HCl
propanoic acid thionyl chloride propanoyl chloride

Reaction with water:
When water is added to an acyl chloride, a violent reaction takes place with the release of steamy fumes of hydrogen chloride. A carboxylic acid is formed.

e.g. CH_3COCl + H_2O → CH_3COOH + HCl
ethanoyl chloride ethanoic acid

Mechanism:
In the first stage:
- Nucleophiles are lone-pair donors. The lone pair on the nucleophile is used to form a dative bond to the δ+ carbon of the carbonyl group, an addition step.
- At the same time the pi-bond of the C=O breaks heterolytically, forming $C\text{-}O^-$.

In the second stage:
- The C=O bond reforms using a lone pair from the oxygen of the $C\text{-}O^-$.
- The C-Cl bond breaks heterolytically, eliminating a chloride ion, Cl^-.



Reaction with alcohols:
An ester is formed when an acyl chloride reacts with an alcohol.

e.g. CH_3CH_2COCl + $HOCH_3$ → $CH_3CH_2COOCH_3$ + HCl
propanoyl chloride methanol methyl propanoate hydrogen chloride

Reaction with phenols:
An ester is also formed when an acyl chloride reacts with a phenol. Carboxylic acids are not reactive enough to form esters in reactions with phenols, but being much more reactive, phenyl esters can be formed using acyl chlorides.

e.g. CH_3COCl + HOC_6H_5 → $CH_3COOC_6H_5$ + HCl
ethanoic acid phenol phenyl ethanoate hydrogen chloride

Reaction with ammonia and amines:
Acyl chlorides will also react with ammonia and amines to form amides. These reactions will be covered in the topic on Amino Acids, Amides and Chirality.

Reactions of Acid Anhydrides

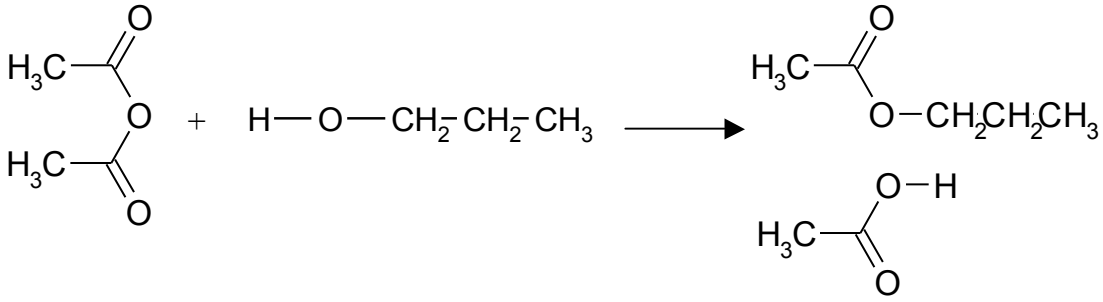
Acid anhydrides react in a similar way to acyl chlorides with alcohols, phenols, water, ammonia and amines. They are less reactive than acyl chlorides, and so useful in laboratory preparations where the reactivity of acyl chlorides might be too hazardous.

In particular, acid anhydrides are used in reactions with alcohols and phenols to form esters because, unlike esterification, the reaction is not reversible so the yield is much better. The other product from the acid anhydride is the corresponding carboxylic acid.

Conditions:
The reaction mixture is gently heated.

Equation:

e.g.



ethanoic anhydride + propan-1-ol → propyl ethanoate + ethanoic acid

Practice:

i. Write an equation using displayed formulae for the reaction between an acid anhydride and an alcohol which would allow you to make the ester methyl propanoate.

ii. Write an equation using skeletal formulae for the reaction between 4-methylphenol and propanoic anhydride to form 4-methylphenyl propanoate.