

Organic Chemistry 3: Carboxylic Acids, Esters and Acyl Chlorides


To succeed in this topic you need to:-

- Have a good understanding of AS-level Organic Chemistry (Factsheets 15, 16, 17 and 27);
- Be confident in using organic nomenclature and structural formulae.

After working through this Factsheet you will:-

- Have been shown the necessary reactions for the carboxylic acids, esters and acyl chlorides;
- Have tried practice questions to gain experience in how knowledge of the chemistry of these functional groups can be called upon in examinations.

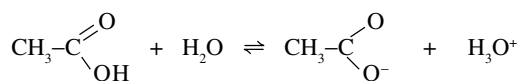
Carboxylic Acids

 **Functional group**

$$\text{R}-\text{C}\begin{matrix} \text{=O} \\ \text{OH} \end{matrix}$$

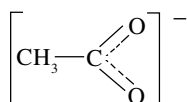
Reactions of the carboxylic acids are **not** simply those of the -OH and C=O groups put together.

The ionisation of the functional group is very significant.



Note the **acidic** property of donating a proton.

The resulting anion is stabilised by π -electrons and lone pair electrons (from the negative charge) forming a delocalised system.

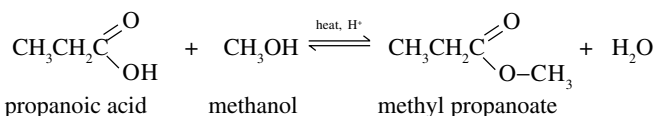


- The resulting structure is symmetrical; both C-O bonds are of equal length and strength.
- The presence of the C=O group means that the carbon atom is **electrophilic** in nature.

Reactions of Carboxylic Acids

1. Reaction of carboxylic acids with alcohols (esterification)

Carboxylic acid and an alcohol react to form an ester and water.



Reaction type: Substitution

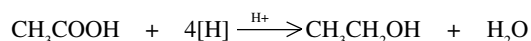
Conditions: Heat under reflux, add a few drops of conc. H_2SO_4

Mechanism: Nucleophilic

N.B. This reaction is reversible - see later reactions of esters.

2. Reaction with lithium tetrahydridoaluminate (III) - LiAlH_4

Carboxylic acids can be reduced to alcohols by LiAlH_4 dissolved in dry ether.



The 4[H] are supplied by the LiAlH_4 .

Reaction type: Reduction

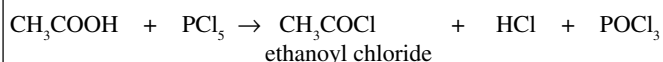
Conditions: LiAlH_4 dissolved in dry ether, followed by hydrolysis with $\text{H}^+(\text{aq})$

Mechanism: Nucleophilic

3. Reaction with PCl_5 to form acid chlorides

Carboxylic acids can be converted to acid chlorides (or "acyl chlorides") by reaction with phosphorus pentachloride.

The -OH group is replaced by a Cl^- nucleophile.



Reaction type: Substitution

Conditions: Dry - observation of steamy white fumes (HCl)

Mechanism: Nucleophilic

4. Reaction with sodium carbonate and sodium hydrogen carbonate



Reaction type: Neutralisation

Conditions: Aqueous

The reaction between NaHCO_3 and a carboxylic acid is a test for the -COOH group.


If NaHCO_3 is added and CO_2 gas is evolved, the -COOH group is present.



Reaction type: Neutralisation

Conditions: Aqueous

Esters

 **Functional group:** $\text{R}-\text{C}\begin{matrix} \text{=O} \\ \text{O}-\text{R}' \end{matrix}$

Where R and R' may be alkyl or aryl groups, and may be the same or different.

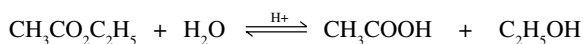
Practical Hint: Esters are characterised by their sweet "gluey" aroma.

Reactions of Esters**1. Hydrolysis of esters with acids and alkalis**

As shown earlier in this Factsheet, esters (and water) can be formed by the reaction of a carboxylic acid with an alcohol in acidic conditions.

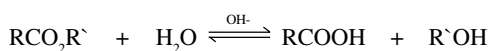
This is a reversible reaction, so can be looked at from the other direction, the hydrolysis of an ester to form a carboxylic acid and an alcohol.

The attainment of equilibrium in the system is catalysed by the presence of concentrated acid.

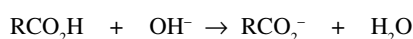


N.B. Using **acid** catalyst, equilibrium lies to the left in the above system, esterification is favoured over hydrolysis.

The same equilibrium is also catalysed by **alkaline** conditions.




When some RCOOH (acid molecules) have been formed, the OH⁻ ions react with them to form a salt.



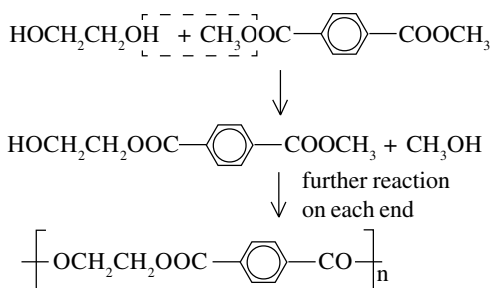
Salt formation removes RCO₂H from the equilibrium mixture. This moves the position of equilibrium to the right, the hydrolysis reaction therefore moving further towards completion in the presence of an alkali.

The alkali is not strictly a catalyst, as it gets used up in the reaction.

 Alkaline conditions are favoured for ester hydrolysis

2. The formation of polyesters.

Polyesters are formed when an acid with two carboxyl groups and an alcohol with two hydroxyl groups react to form a polymer.



Terylene: polyethane-1,2-diylbenzene-1,4-dicarboxylate

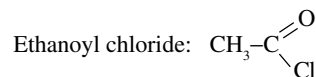
Reaction type: Substitution, polymerisation
Conditions: Acid
Mechanism: Nucleophilic

Because H₂O is liberated, this is called “condensation polymerisation”.

Polyesters have great tensile strength, and are used in fibre form in textiles.

Acid Chlorides - The Reactions of Ethanoyl Chloride.

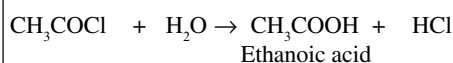
Acid chlorides are derivatives of carboxylic acids.



These are very reactive chemicals, prone to nucleophilic attack. The electronegative Cl atom attracts electrons from the already δ⁺ C atom, so the C–Cl bond is relatively easy to break, with the positive carbon left open to attack.

1. Reaction of ethanoyl chloride with water.

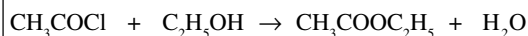
A violent reaction occurs, the mixture boils and clouds of HCl gas are evolved.



Reaction type: Substitution
Conditions: Room temperature
Mechanism: Nucleophilic

2. Reaction of ethanoyl chloride with alcohols.

A vigorous reaction at room temperature to form esters.

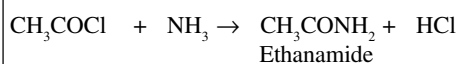


This is an excellent method of preparing esters, as unlike the reaction between a carboxylic acid and an alcohol, this reaction is not reversible - it goes quickly to completion.

Reaction type: Substitution
Conditions: Room temperature
Mechanism: Nucleophilic

3. Reaction of ethanoyl chloride with ammonia

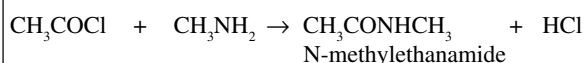
A violent reaction at room temperature, with an aqueous solution of ammonia, producing ethanamide.



Reaction type: Substitution
Conditions: Room temperature, aqueous
Mechanism: Nucleophilic

4. Reaction of ethanoyl chloride with primary amines.

Again a readily occurring reaction at room temperature, producing an amide.



Reaction type: Substitution
Conditions: Room temperature, aqueous
Mechanism: Nucleophilic

