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# **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  $R-C \xrightarrow{O} OH$ 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.

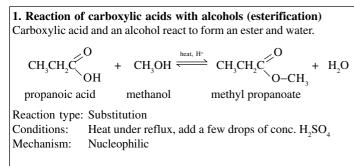
$$CH_3 - C \bigcirc O + H_2 O \rightleftharpoons CH_3 - C \bigcirc O + H_3 O$$

Note the acidic property of donating a proton.

The resulting anion is stabilised by  $\pi$ -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**



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

**2. Reaction with lithium tetrahydridoaluminate (III) - LiAlH**<sub>4</sub> Carboxylic acids can be reduced to alcohols by  $\text{LiAlH}_4$  dissolved in dry ether.

 $CH_3COOH + 4[H] \xrightarrow{H_+} CH_3CH_2OH + H_2O$ 

The 4[H] are supplied by the  $LiAlH_4$ .

 Reaction type:
 Reduction

 Conditions:
 LiAlH<sub>4</sub> dissolved in dry ether, followed by hydrolysis with H<sup>+</sup>(aq)

 Mechanism:
 Nucleophilic

**3. Reaction with PCl<sub>5</sub> 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<sup>-</sup> nucleophile.

 $\begin{array}{rrrr} \mathrm{CH_{3}COOH} &+& \mathrm{PCl_{5}} \rightarrow & \mathrm{CH_{3}COCl} &+& \mathrm{HCl} &+& \mathrm{POCl_{3}} \\ && \text{ethanoyl chloride} \end{array}$ 

Reaction type:SubstitutionConditions:Dry - observation of steamy white fumes (HCl)Mechanism:Nucleophilic

4. Reaction with sodium carbonate and sodium hydrogen carbonate

 $2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COO^-Na^+ + CO_2 + H_2O$ Reaction type: Neutralisation

Conditions: Aqueous

The reaction between NaHCO<sub>3</sub> and a carboxylic acid is a test for the -COOH group.

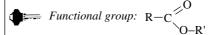
If NaHCO<sub>3</sub> is added and CO<sub>2</sub> gas is evolved, the -COOH group is present.

 $CH_{3}COOH + NaHCO_{3} \rightarrow CH_{3}COO^{-}Na^{+} + CO_{2} + H_{2}O$ 

Reaction type: Neutralisation

Conditions: Aqueous

# Esters



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.

 $CH_3CO_2C_2H_5 + H_2O \iff CH_3COOH + C_2H_5OH$ 

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.

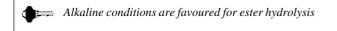
 $RCO_2R$ ` +  $H_2O \xrightarrow{OH} RCOOH$  + ROH

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

 $RCO_{2}H + OH^{-} \rightarrow RCO_{2}^{-} + H_{2}O$ 

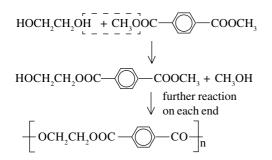
(e.g.)  $CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$ 

Salt formation removes  $\text{RCO}_2\text{H}$  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.



#### 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

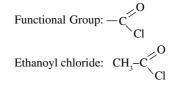
Reaction type:Substitution, polymerisationConditions:AcidMechanism:Nucleophilic

Because H<sub>2</sub>O is liberated, this is called "condensation polymerisation".

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

# Acid Chlorides - The Reactions of Ethanoyl Chloride.

Acid chlorides are derivatives of carboxylic acids.



Theses are very reactive chemicals, prone to nucleophilic attack. The electronegative Cl atom attracts electrons from the already  $\delta$ + 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.

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$$
  
Ethanoic acid

Reaction type:SubstitutionConditions:Room temperatureMechanism:Nucleophilic

**2. Reaction of ethanoyl chloride with alcohols.** A vigorous reaction at room temperature to form esters.

$$CH_3COCI + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

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.

CH <sub>3</sub> COCl	+	$\rm NH_3 \rightarrow$	$CH_3CONH_2 +$	HCl
			Ethanamide	

Reaction type:SubstitutionConditions:Room temperature, aqueousMechanism:Nucleophilic

# 4. Reaction of ethanoyl chloride with primary amines. Again a readily occuring reaction at room temperature, producing an amide. $CH_{3}COCl + CH_{3}NH_{2} \rightarrow CH_{3}CONHCH_{3} + HCl$ N-methylethanamide

Reaction type:SubstitutionConditions:Room temperature, aqueousMechanism:Nucleophilic

### **Questions** 1. Explain:

- (a) Why the –COOH group is acidic.
- (b) Why the resulting anion (-COO<sup>-</sup>) is stable.
- 2. The following reaction is reversible:

 $\begin{array}{rll} CH_3COOH &+& CH_3OH \rightleftharpoons CH_3COOCH_3 &+& H_2O\\ State the conditions which favour:\\ (a) Esterification.\\ (b) Ester hydrolysis. \end{array}$ 

3. For the following reaction scheme:

 $CH_3COOH \xrightarrow{step 1} CH_3COCI \xrightarrow{step 2} CH_3CONH_2$ 

Give the reaction equations and conditions for:(a) Step 1.(b) Step 2.

4. For the following reaction scheme:

Give the reaction equations and conditions for:

- (a) Step 1.
- (b) Step 2.

# Answers

- 1. (a) It is a proton  $(H^+)$  donator.
  - (b) Delocalisation of electrons over the -COO<sup>-</sup> system means negative charge is less localised, so the species is more stable.
- 2. (a) Acidic.
  - (b) Alkaline.
- 3. (a)  $CH_3COOH + PCl_5 \rightarrow CH_3COCl + HCl + POCl_3$

Conditions: Dry.

(b)  $CH_3COCl + NH_3 \rightarrow CH_3ONH_2 + HCl$ 

Conditions: Room temperature, aqueous.

4. (a)  $CH_3CH_2COOH + 4[H] \rightarrow CH_3CH_2CH_2OH + H_2O$ 

Conditions:  $LiAlH_4$  in dry ether, hydrolysis with dilute acid.

(b)  $CH_3CH_2COOH + NaHCO_3 \rightarrow CH_3CH_2COONa + CO_2 + H_2O$ 

Conditions: Room temperature, aqueous.

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