# WJEC Chemistry A-level

# 4.5: Carboxylic Acids and their Derivatives

## Detailed Notes

### Welsh Specification

## Relative Acidities

Consider acids as substances which **donate hydrogen ions** to any other substance. Carboxylic acids, alcohols, phenol and water are all **weakly acidic**. This means they all only partially dissociate in water. In order of increasing acidity, we have:

**Alcohol < water < phenol < carboxylic acid**

An **equilibrium** of the form

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$
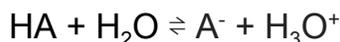
is set up for each compound, and it is the **nature of the negative A⁻ ion** which determines the **degree of acidity** of each compound.

1. Carboxylic acid
   A carboxylic acid dissociates to form a **carboxylate ion**. In the carboxylate ion, one of the **lone pairs** on the negative oxygen ends up o**verlapping with the p orbitals** on the carbon and oxygen in the C=O bond. This leads to a **delocalised pi system** over the COO⁻ group and, due to the electronegativity of oxygen, the delocalised system is **distorted** towards the **region of oxygen** atoms. The more the charge is spread, the **more stable** the ion becomes as it is less attractive for a hydrogen ion. This distribution of charge means the carboxylate ion is **less likely to reform** the carboxylic acid.

2. Phenol
   Phenol dissociates to form a **phenoxide ion**. In this ion, one of the **lone pairs** on the oxygen atom overlaps with the **delocalised electron system** on the **benzene** ring. This **distributes** the negative charge, making the ion more stable.

3. Water
   Water dissociates to form an OH⁻ ion and a H⁺ ion, showing how water can act as both an **acid** and a **base**. The negative charge on the OH⁻ ion **attracts hydrogen ions** very easily so the water molecules only **partially dissociate**.

4. Alcohol
   An alcohol dissociates to form a negative ion (below, left) which has **alkyl groups** bonded to the negative oxygen. In the negative ion, there is **no delocalisation** of the negative charge so the oxygen remains **very electronegative**. This means the oxygen is still **highly attractive to hydrogen ions**, so the alcohol will reform immediately.
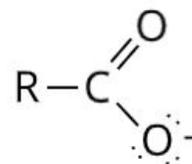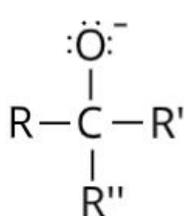


INCREASING STABILITY

### The difference in acidity between carboxylic acids and phenol

In the **carboxylate ion**, the charge is spread and **distorted** between **two oxygens**. In the **phenoxide ion**, the oxygen atom is still the **most electronegative part** of the ion. Therefore, in the phenoxide ion, the oxygen atom is still very negatively charged and so will **readily attract hydrogen atoms**. This means **phenol will reform** from the phenoxide ion **more readily** than a carboxylic acid will reform from a carboxylate ion - making a **carboxylic acid more acidic** than phenol.

### The difference in acidity between alcohols and water

**Alcohols** are **less acidic** than **water** due to the **alkyl groups**. Alkyl groups are **'electron pushing'**, since the alkyl groups tend to **donate electrons** towards the electronegative oxygen. This **increases** the **electron density** around the oxygen, making it **more attractive** to hydrogen ions.

The **relative acidities** of these four compounds can be observed by their reactions with compounds such as **sodium hydrogen carbonate** and **sodium hydroxide**. The **more acidic** compounds, such as a **carboxylic acid**, will react with these bases, whereas generally an **alcohol** is not a strong enough acid for a reaction to take place.

## Formation of Carboxylic Acids

Carboxylic Acids are recognised by the **functional group -COOH** which contains a carbonyl group (C=O) and an -OH group. They are produced from the **oxidation of primary alcohols** under **reflux** conditions. When a primary alcohol undergoes oxidation, first the alcohol is oxidised to an **aldehyde** and then **further oxidation** of an aldehyde produces a **carboxylic acid. Reflux** ensures that any **aldehyde products are bypassed** and only the secondary oxidation product forms.

**Acidified potassium dichromate(VI)** is commonly used as the **oxidising agent**. As the oxidation occurs, the **orange solution** will turn **green**.

*Example: Oxidation of a primary alcohol to an aldehyde*
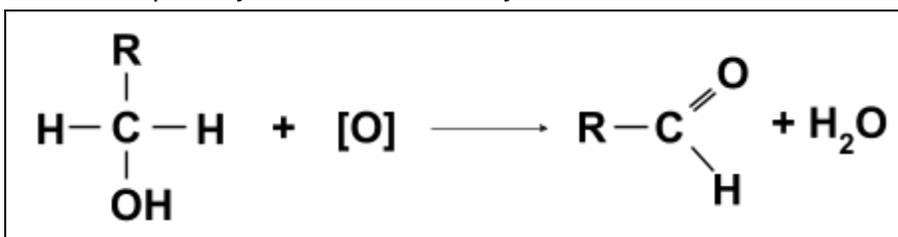
Aldehydes can also be **oxidised further** to produce carboxylic acids.

*Example: Oxidation of an aldehyde to a carboxylic acid*
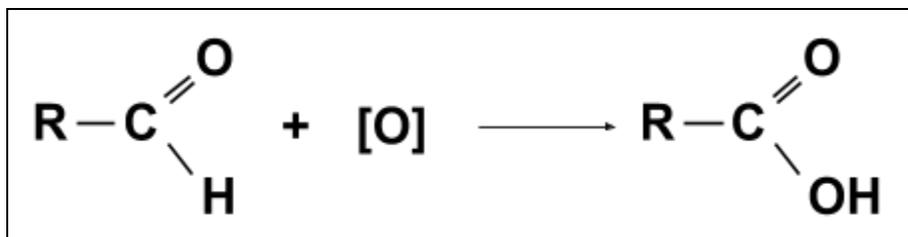


## Aromatic Carboxylic Acids

Aromatic carboxylic acids contain a **benzene ring** and can be produced from the **oxidation of methyl side chains** on benzene. **Alkaline potassium manganate**, followed by **dilute sulfuric acid** to acidify the mixture, is commonly used as the **oxidising agent** in this reaction.

*Example:*
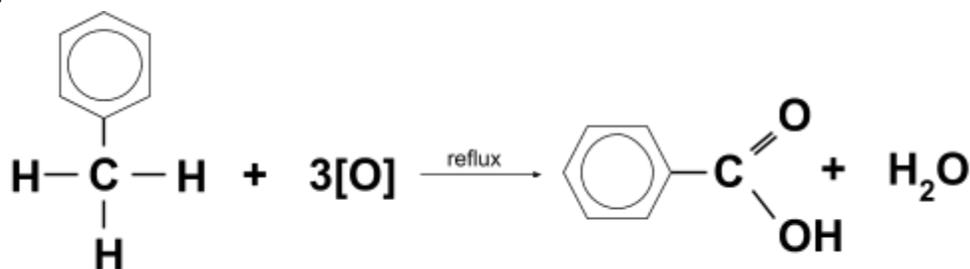


Regardless of the **length of the side chain**, all side chains are **oxidised to a -COOH group**. This means that compounds such as **propylbenzene** or **ethylbenzene** will still be oxidised to **benzoic acid**.

## Reduction

**Carboxylic acids** can be **reduced** back to **primary alcohols** in the presence of the reducing agent, **LiAlH$_4$** in **aqueous conditions.** Due to the bonding of this reducing agent, it provides the H$^-$ ion necessary for reduction. **NaBH$_4$** is commonly used to **reduce aldehydes and ketones** but this reducing agent is **not strong enough** to reduce a **carboxylic acid**. The reactions are written using [H] to represent the reducing hydrogen.

*Example:*
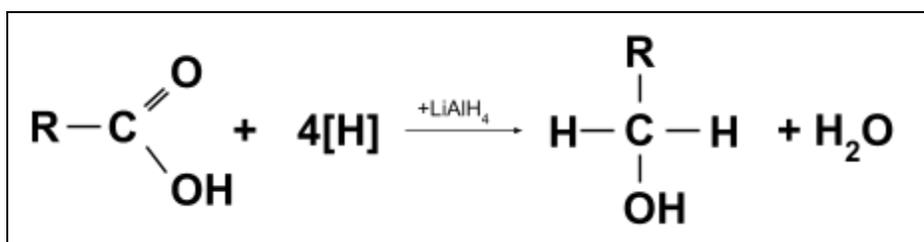
## Decarboxylation

This is the process by which the **-COOH functional group** of a carboxylic acid or the **-COO⁻Na⁺ group** of a carboxylate salt is **removed** from the molecule and is **replaced by a hydrogen** atom.

The **carboxylic acid** or **carboxylate salt** is heated with **soda lime,** which contains **sodium hydroxide** (NaOH).

*Example: reaction of sodium ethanoate with soda lime*

$$CH_3COO^-Na^+ + NaOH \rightarrow CH_4 + Na_2CO_3$$

The process can also be carried out on **aromatic carboxylic acids** where the **-COOH group** is on a **side chain**. In this reaction, **water** is also produced as an additional product.

*Example: reaction of benzoic acid with soda lime*
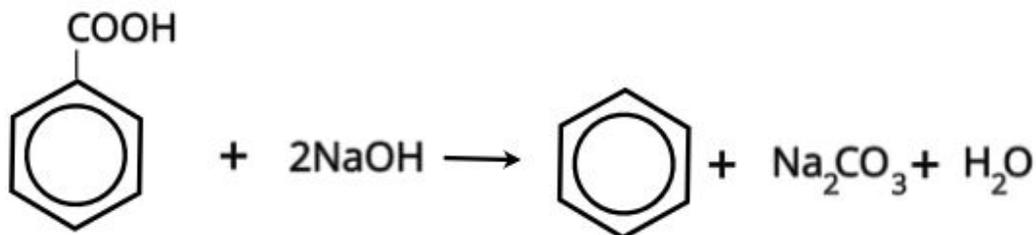


## Esterification

**Carboxylic acids** can react with **alcohols** in the presence of a **strong acid catalyst** to form **esters**. **Concentrated sulfuric acid** is commonly used as the acid catalyst. This reaction, esterification, is a form of **hydrolysis** and is carried out under **reflux**.

*Example:*
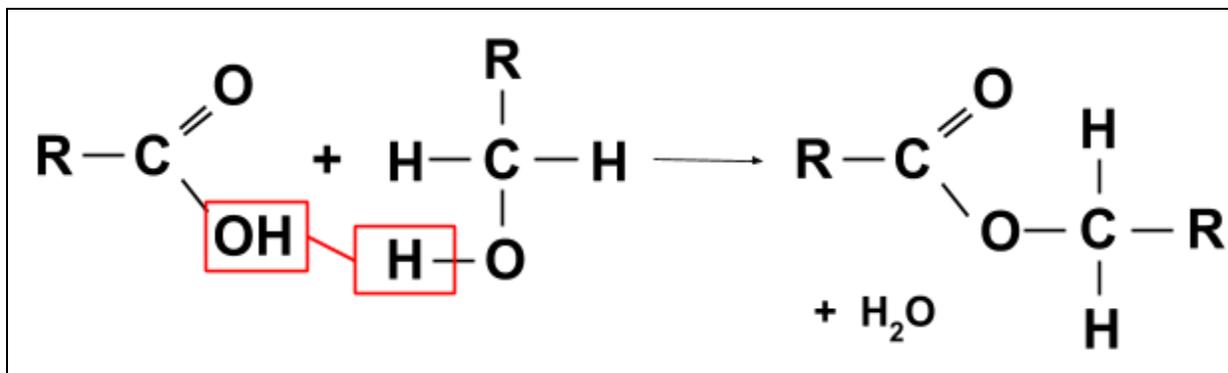


*A method for remembering the reaction is: remove the -OH from the acid and the hydrogen from the alcohol to make water. Then combine the acid and alcohol.*

Esters are **sweet smelling compounds** used in **food flavourings** and **perfumes**. They have **low boiling points** and also make **good solvents** for other polar molecules.

### Acyl Chlorides
**Acyl chlorides** have the functional group **-COCl**.

$$R-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{<}}$$
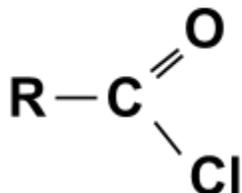
They can be formed from carboxylic acids using **sulfur dichloride oxide** ($SOCl_2$). In this reaction, sulfur dioxide, hydrogen chloride and an acyl chloride are produced. The **products** are relatively **easy to separate** since $SO_2$ and HCl are both gases. This makes **$SOCl_2$** the **preferred reagent** for producing acyl chlorides from carboxylic acids.

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$
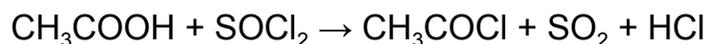
Acyl chloride can also be produced from carboxylic acids by using **phosphorus(V) chloride** or **phosphorus(III) chloride**.

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$
$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$
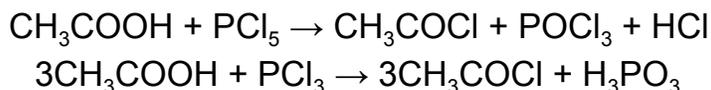
**Acyl chlorides** are very **polar molecules** due to the **strong electronegativity of chlorine**. Therefore, acyl chlorides can go one to **react violently** in various reactions. In particular,  the **hydrolysis** of acid chlorides is much **more rapid** than the hydrolysis of esters.

## Nitriles and Amides

### Conversion of Carboxylic acids to Nitriles and Amides
**Carboxylic acids** can react to form **nitriles**. These nitriles can then undergo **further reactions** to form **amides**.
First, **ammonium carbonate** is added to **excess of the carboxylic acid** until the **ammonium salt** is formed. Then the ammonium salt is heated to undergo **dehydration**. This produces an **amide**.

To **produce the nitrile** from the amide, the **amide is heated** with **phosphorus(V) oxide** ($P_4O_{10}$) so that it undergoes **dehydration**.

## Nitriles

**Nitriles** can be formed from the addition of a **:CN⁻ nucleophile** to a **halogenoalkane** in the mechanism of **nucleophilic substitution**. It is an organic synthesis reaction as it leads to an extension of the carbon chain. To produce the cyanide ion, **potassium cyanide** is added to **sulfuric acid**.

*Example:*
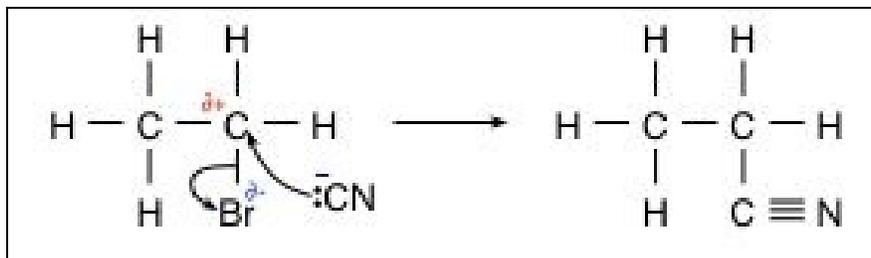


## Hydroxynitriles

**Hydroxynitriles** can be formed from **aldehydes and ketones** by the addition of a :CN⁻ nucleophile in an **addition-elimination** reaction. **KCN** (potassium cyanide) is often used as the reagent to provide the nucleophile instead of HCN (hydrogen cyanide). This is because **HCN** is a **very poisonous gas** and is difficult to store.

*Example:*
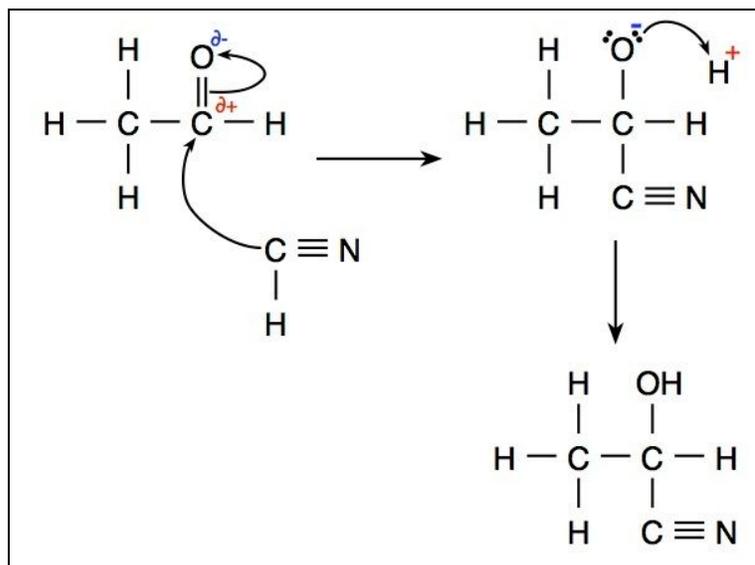


**Hydroxynitriles** commonly contain a **chiral carbon centre** meaning optical isomers of the product exist. This is because the **:CN- nucleophile** can attack from either above or below the **planar C=O** double bond, which produces the two **different enantiomers**.

### Reduction of nitriles
**Nitriles** can be reduced to **amines** by **reducing agent LiAlH$_4$,** in **aqueous** conditions. Due to the bonding of this reducing agent, it provides the **H$^-$ ion** necessary for reduction. The reactions are often written using **[H]** to represent this reducing hydrogen.
Reduction of propanenitrile to propylamine:

$$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$$
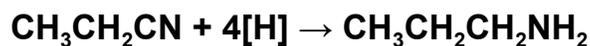
## Amides

### Primary amides
In these compounds, the **-OH group** of a carboxylic acid is **replaced by** the **-NH$_2$ group**. Primary amides can be formed from **carboxylic acids** or **acyl chlorides** on the addition of **ammonia**. An **addition-elimination** reaction takes place to produce an amide and water or hydrochloric acid.

*Example: addition elimination to form ethanamide*
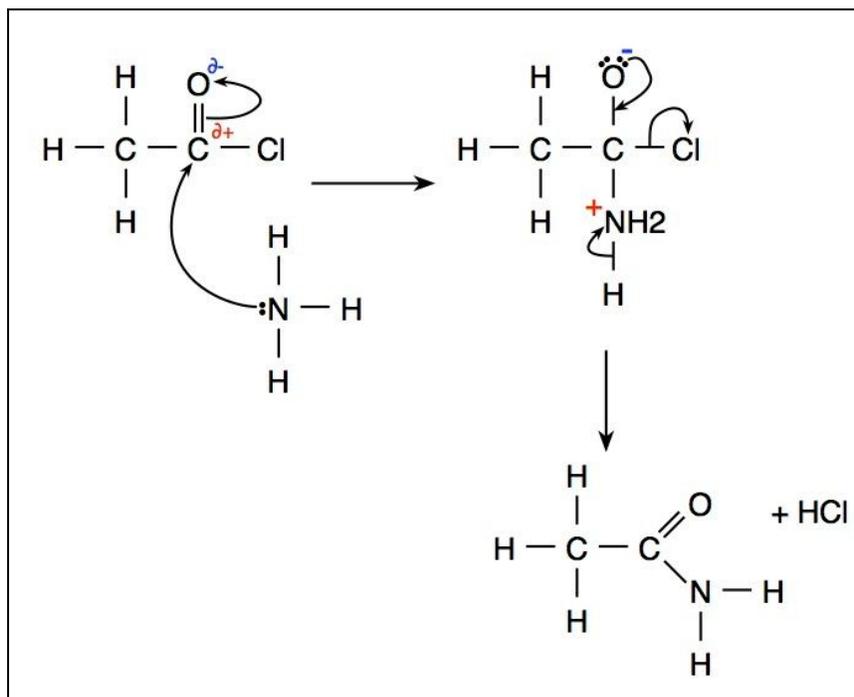
### N-Substituted Amide

When an **amine compound** is combined with a **carboxylic acid**, an **addition-elimination reaction** will occur, producing an **N-substituted amide**. These molecules have the functional group -CONHR where the R group is a carbon chain of any length.

*Example: addition-elimination to form N-methyl ethanamide*
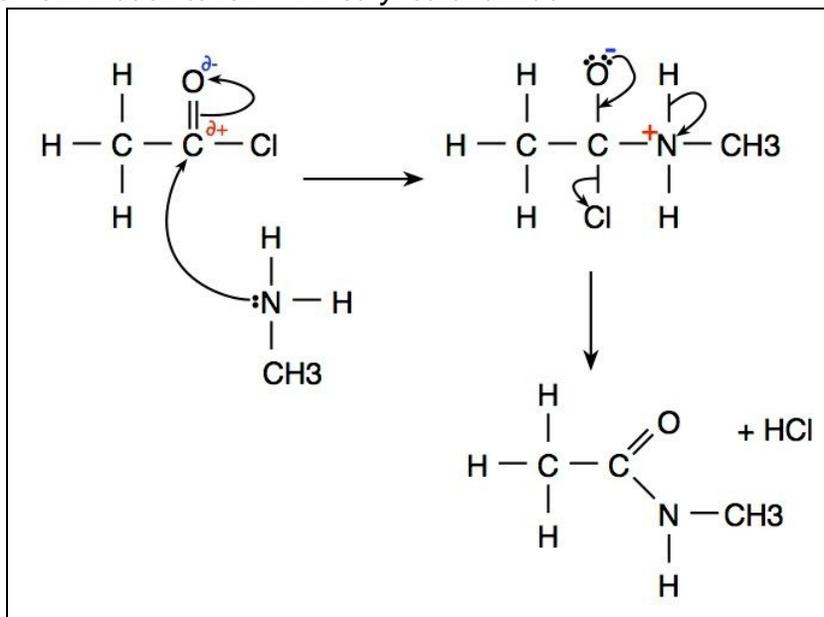


## Hydrolysis of amides and nitriles

Both **amides** and **nitriles** can undergo **hydrolysis** reactions when in **aqueous conditions**. The reaction is considered to be the opposite to the formation reaction, often called dehydration.

This process occurs in **two main stages**. Firstly, **nitriles** react with **water** to produce **amides**. Then the amides undergo **further hydrolysis** and react with water to form either a **carboxylic acid or a carboxylate salt**, depending on the reaction **conditions**.

### Acidic Hydrolysis

The hydrolysis of an amide by a **dilute acid** will lead to the formation of a **carboxylic acid**. For example, **ethanenitrile** would form **ethanamide** which would then react to form **ethanoic acid**. This occurs because the ethanoate ions react with hydrogen ions to produce the weak, carboxylic acid.

*Example:*

$$CH_3CN + 2H_2O + HCl \longrightarrow CH_3COOH + NH_4Cl$$

**Alkaline Hydrolysis**

In more **basic conditions** containing **sodium hydroxide** instead of water, the nitrile undergoes hydrolysis to produce a **carboxylate salt** and **ammonia**. For example, **ethanenitrile** would form **ethanamide,** which would then form **sodium ethanoate**.

*Example:*

$$CH_3CN + H_2O + NaOH \longrightarrow \boxed{CH_3COO^- Na^+} + NH_3$$

<span style="color:red">Sodium<br>Carboxylate salt</span>
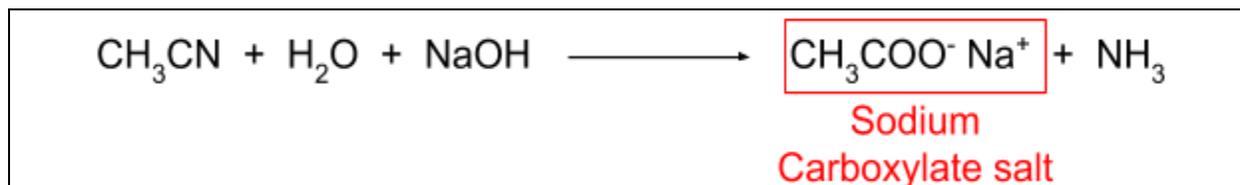
This process can also be called **saponification** as sodium carboxylate salts are used in the production of soaps and lubricants.