



WJEC Chemistry A-Level

OA2.3: Carboxylic Acids and their Derivatives

Detailed Notes

English Specification

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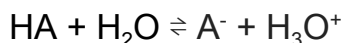


Relative Acidities

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:



An **equilibrium** of the form



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 **overlapping 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

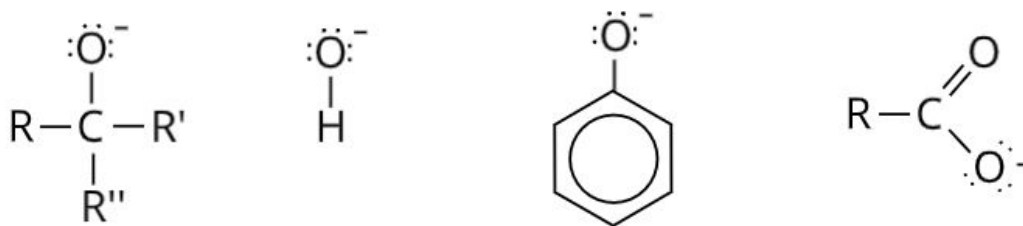
Phenol dissociates to form a **phenoxide ion**. In this ion, one of the **lone pairs** on the oxygen atom overlaps with the **delocalised electron system** on the **benzene** ring. This **distributes** the negative charge, making the ion more stable.

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.

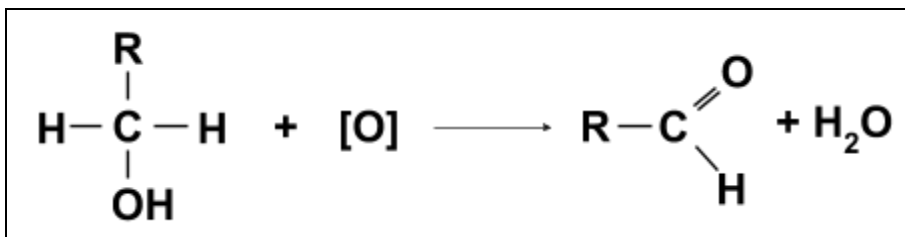
The **relative acidities** of these four compounds can be observed by their reactions with compounds such as **sodium hydrogen carbonate** and **sodium hydroxide**. The **more acidic** compounds, such as a **carboxylic acid**, will react with these bases, whereas generally an **alcohol** is not a strong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

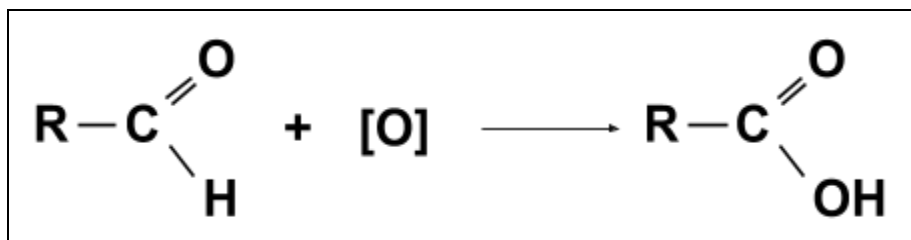
Example: Oxidation of a primary alcohol to an aldehyde





Aldehydes can also be **oxidised further** to produce carboxylic acids.

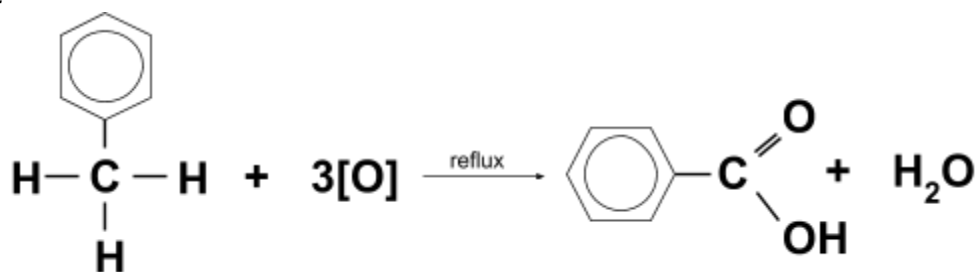
Example: Oxidation of an aldehyde to a carboxylic acid



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:

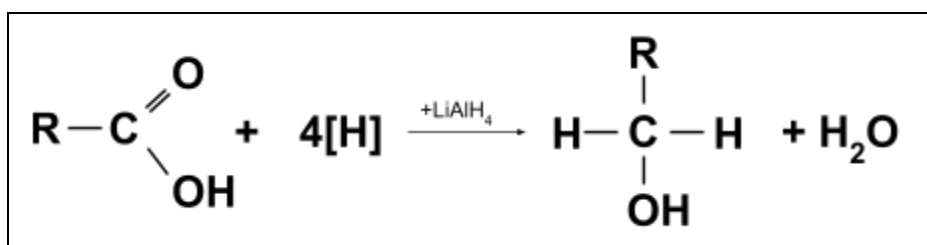


Regardless of the **length of the side chain**, all side chains are **oxidised to a -COOH group**. This means that compounds such as **propylbenzene** or **ethylbenzene** will still be oxidised to **benzoic acid**.

Reduction

Carboxylic acids can be **reduced** back to **primary alcohols** in the presence of the reducing agent, **LiAlH₄** in **aqueous conditions**. Due to the bonding of this reducing agent, it provides the H⁻ ion necessary for reduction. **NaBH₄** 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**.

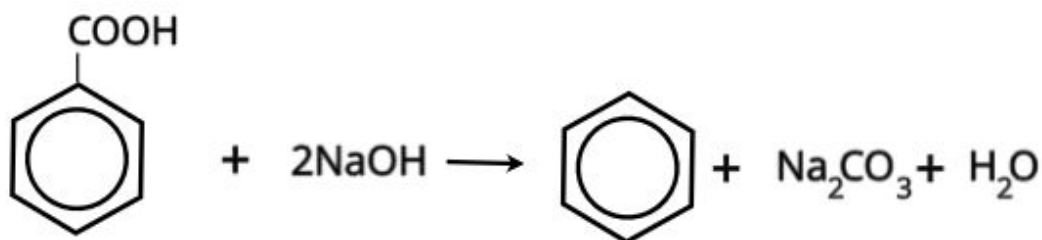
The **carboxylic acid** or **carboxylate salt** is heated with **soda lime**, which contains **sodium hydroxide** (NaOH).

Example: reaction of sodium ethanoate with soda lime



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.

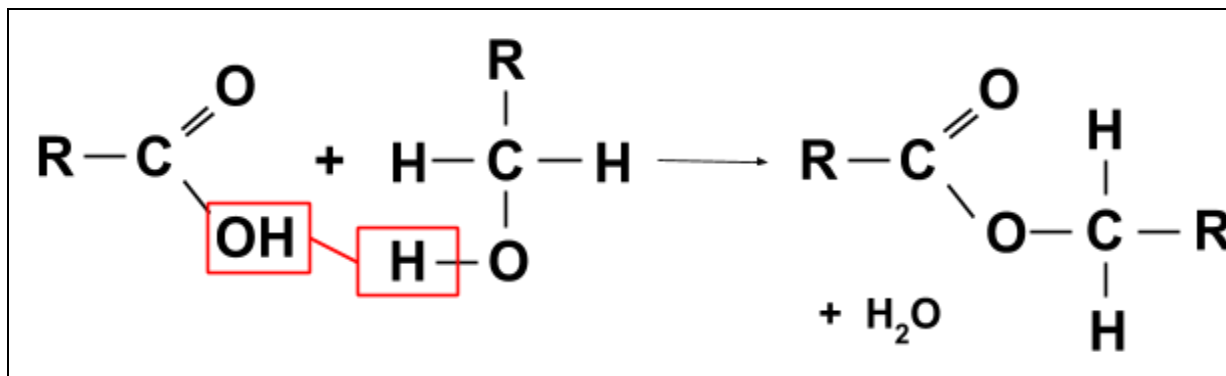
Example: reaction of benzoic acid with soda lime



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:



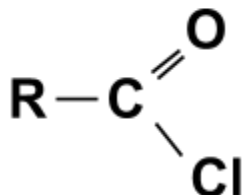
A method for remembering the reaction is: remove the -OH from the acid and the hydrogen from the alcohol to make water. Then combine the acid and alcohol.



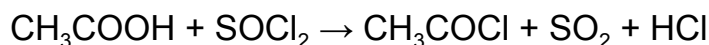
Esters are **sweet smelling compounds** used in **food flavourings** and **perfumes**. They have **low boiling points** and also make **good solvents** for other polar molecules.

Acyl Chlorides

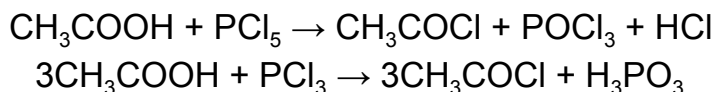
Acyl chlorides have the functional group **-COCl**.



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.



Acyl chloride can also be produced from carboxylic acids by using **phosphorus(V) chloride** or **phosphorus(III) chloride**.



Acyl chlorides are very **polar molecules** due to the **strong electronegativity of chlorine**. Therefore, acyl chlorides can go on 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**.



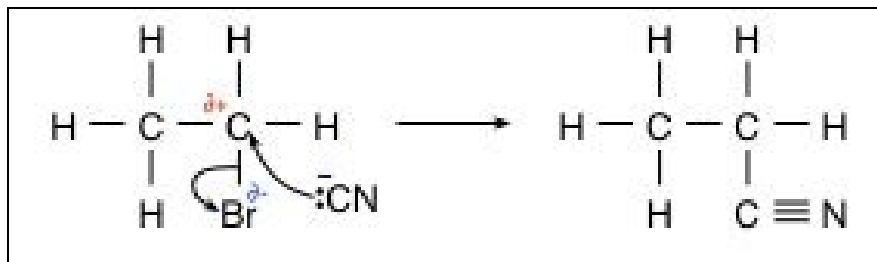


To **produce the nitrile** from the amide, the **amide is heated** with **phosphorus(V) oxide** (P_4O_{10}) so that it undergoes **dehydration**.

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**.

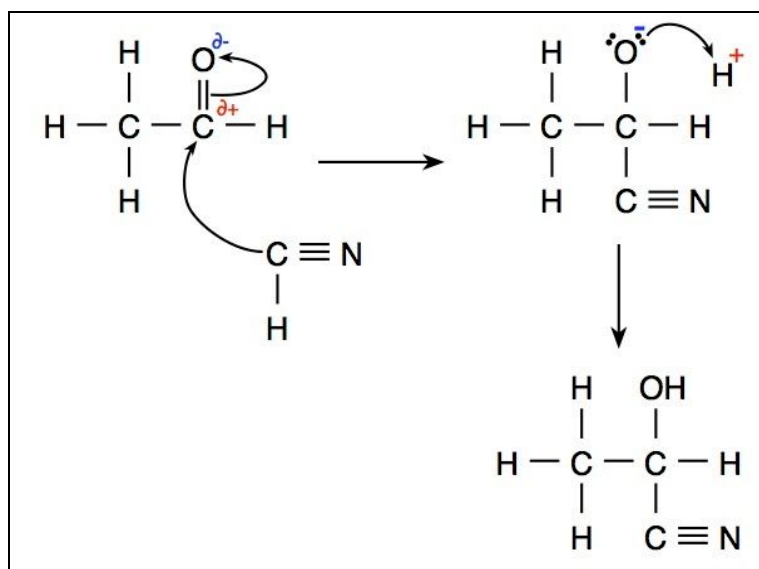
Example:



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**.

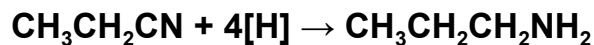




Reduction of nitriles

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 **$[\text{H}]$** to represent this reducing hydrogen.

Reduction of propanenitrile to propylamine:

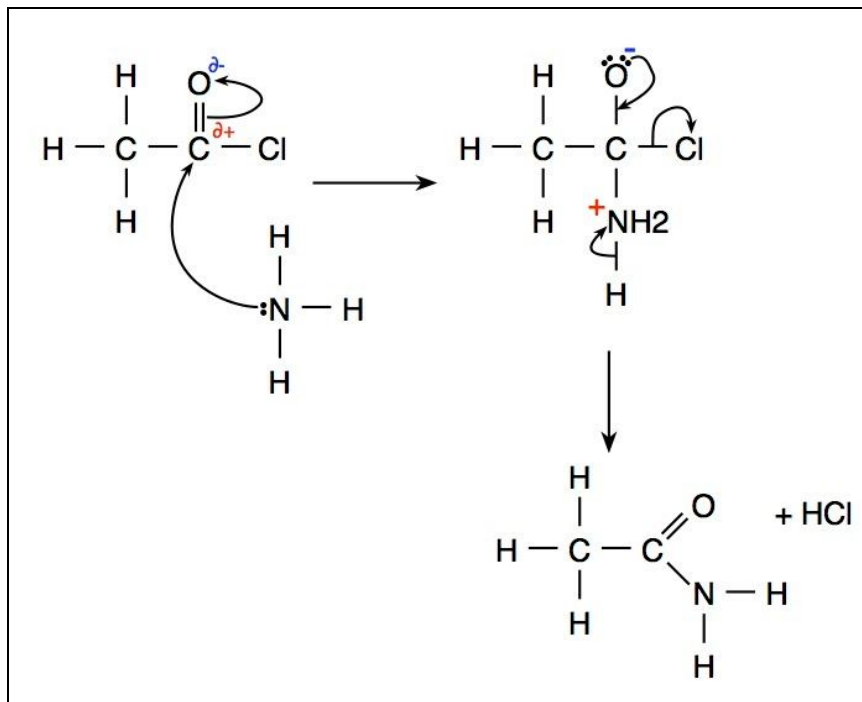


Amides

Primary amides

In these compounds, the **$-\text{OH}$ group** of a carboxylic acid is **replaced by the $-\text{NH}_2$ 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

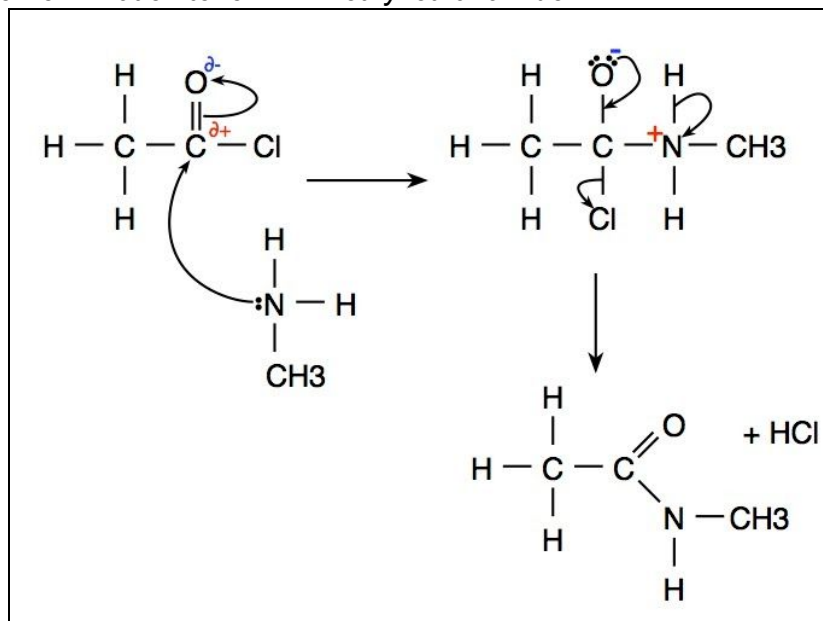




N-Substituted Amide

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:

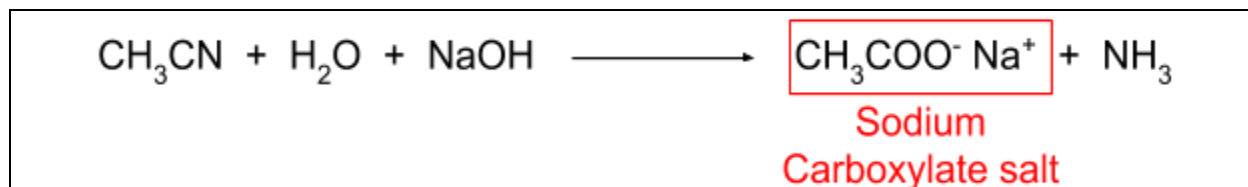




Alkaline Hydrolysis

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:



This process can also be called **saponification** as sodium carboxylate salts are used in the production of soaps and lubricants.

