

# CAIE Chemistry A-level

## 33: Carboxylic Acids and Derivatives (A-level only)

### Notes

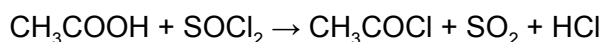
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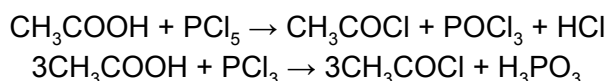
## Carboxylic Acids

### Formation of acyl chlorides

**Acyl chlorides** can be formed from carboxylic acids using **sulfur dichloride oxide** ( $\text{SOCl}_2$ ). In this reaction, sulfur dioxide, hydrogen chloride and an acyl chloride are produced. The products are relatively easy to separate since  $\text{SO}_2$  and  $\text{HCl}$  are both gases.



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

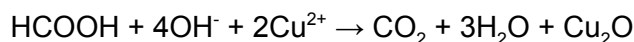


## Further Oxidation of Carboxylic Acids

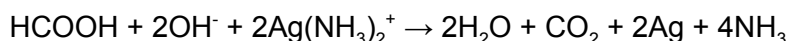
### Oxidation of methanoic acid

**Methanoic acid** can be further **oxidised** to produce **carbon dioxide** and **water**. This reaction can be carried out using Fehling's or Tollen's reagent.

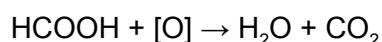
*Using Fehling's reagent:* red precipitate is observed



*Using Tollen's reagent:* silver mirror is observed on test tube



The overall equation for the oxidation of methanoic acid is:

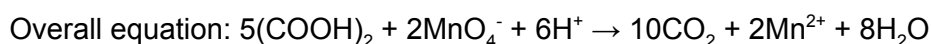
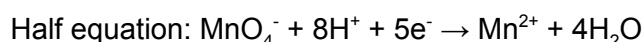
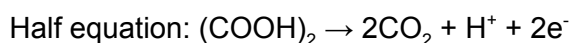


### Oxidation of ethanedioic acid

**Ethanedioic acid** can be further **oxidised** to produce **carbon dioxide** and **water**. This reaction can be carried out using **warm acidified potassium manganate(VII)**.

This is a **redox** reaction and can be used to **standardise potassium manganate(VII)** solution. A standard solution of ethanedioic acid is **titrated** with warm potassium manganate(VII) until the solution stops decolourising and has a faint pink colour. The concentration of potassium manganate(VII) can then be calculated.

The overall equation can be written using the two half equations:



## Relative Acidities of Carboxylic Acids, Phenols and Alcohols

The relative acidities are as follows: **carboxylic acids > phenols > alcohols**

- **Carboxylic acids** are the **most acidic** due to the structure of the carboxylate ion ( $\text{RCOO}^-$ ) which forms in solution. In the carboxylate ion, a **delocalised pi system** develops over the  $-\text{COO}^-$  group because the lone pair on the negatively charged oxygen overlaps with the p orbitals of the carbon atom. This delocalised system distributes the negative charge through the  $-\text{COO}^-$  group, making the **carboxylate ion more stable**.
- **Phenols** are more acidic than alcohols because the **phenoxide ion** is **relatively stable**. The lone pair on the oxygen atom is delocalised into the pi system meaning the negative charge is dispersed among the carbon atoms. This means that phenol is more likely to donate a hydrogen ion compared with alcohols.
- **Alcohols** are the **least acidic** because of the **positive inductive effect**. In the **alkoxide ion**, the alkyl groups “**push**” **electrons** away from themselves towards the oxygen, increasing the electron density of the oxygen, making it more likely to bond to a hydrogen ion again and reform an alcohol.

### Acidities of Chlorine-Substituted Ethanoic Acids

Chlorine-substituted ethanoic acid is a stronger acid than pure ethanoic acid. Chlorine is very **electronegative**. As described above, the  $-\text{COO}^-$  group has a **delocalised electron system** which distributes the negative charge through the group. When chlorine is bonded to ethanoic acid, the negative charge is distributed even more throughout the molecule. This makes the chlorine-substituted ethanoate ion **less likely to attract a hydrogen ion** making the ion **more stable** than the ethanoate ion.



The two **equilibria** for ethanoic acid and chlorine-substituted ethanoic acid are shown below. The position of equilibrium for the chlorine-substituted ethanoic acid (equation 2) will be further to the right as the **carboxylate ion** is **more stable**.



The **more chlorines that are substituted** on to ethanoic acid, the **stronger the acid** will be so the further the position of equilibrium will lie to the right.

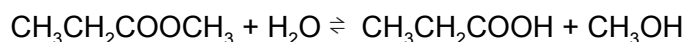


## Esters

### Acid and Base Hydrolysis of Esters

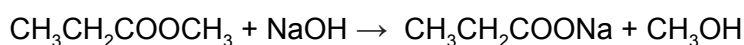
#### Acid hydrolysis

When esters react with water an **acid catalyst** is required. This reaction is **reversible** so **excess water** must be used to ensure the position of equilibrium is shifted as far towards the products as possible. This reaction can occur when the ester is mixed with dilute acid.



#### Alkali hydrolysis

An ester can be hydrolysed by **heating it under reflux** with a dilute alkali (such as sodium hydroxide). These reactions are not reversible so the products are easier to separate.



To convert the carboxylate salt product into a **carboxylic acid**, **excess strong dilute acid** can be added to the salt (after the alcohol has been removed from the products by distillation).

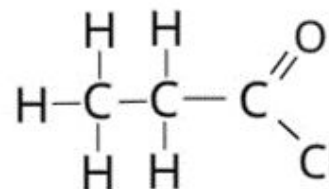
### Commercial Uses of Esters

Esters are commonly used commercially as **solvents**, **perfumes** and **flavourings**. Many foods contain esters to artificially create the smell and taste of fruit.

## Acyl Chlorides

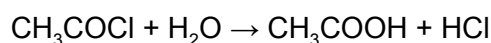
Acyl chlorides, also known as acid chlorides are **acid derivatives**. They have a similar structure to carboxylic acids, with the -OH group being replaced by a chlorine atom.

Acyl chlorides have the suffix **-oyl chloride**, e.g. propanoyl chloride.



### Hydrolysis of Acyl Chlorides

Hydrolysis occurs when an acyl chloride reacts with water. The products of hydrolysis are hydrochloric acid and a carboxylic acid. The reaction between ethanoyl chloride and water is shown below:

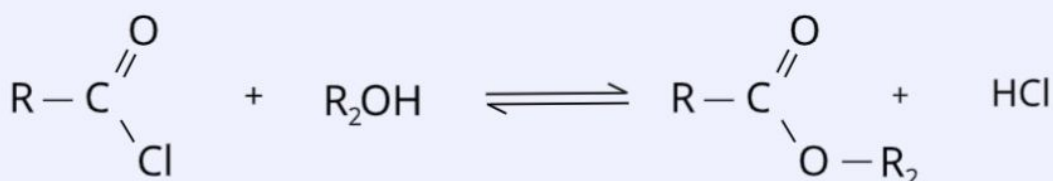


## Reactions of Acyl Chlorides

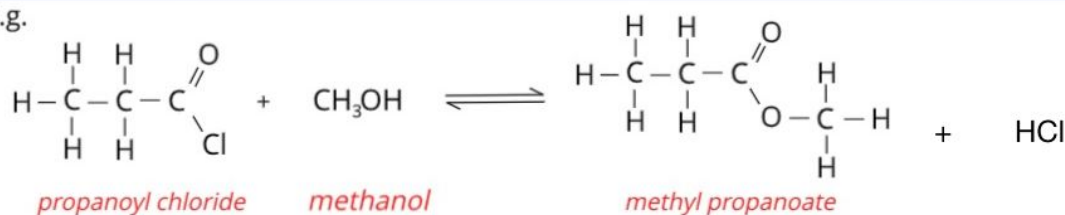
### Reactions with alcohols

Esters are produced when **alcohols** and **acyl chlorides** react together. When an alcohol reacts with an acyl chloride, a vigorous reaction takes place and steamy fumes of hydrochloric acid are produced. This is a method of producing **esters**.

#### GENERAL EQUATION

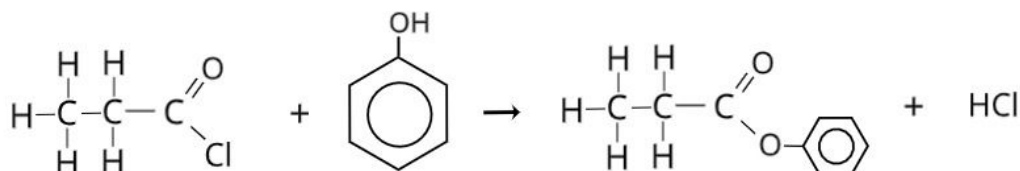


E.g.



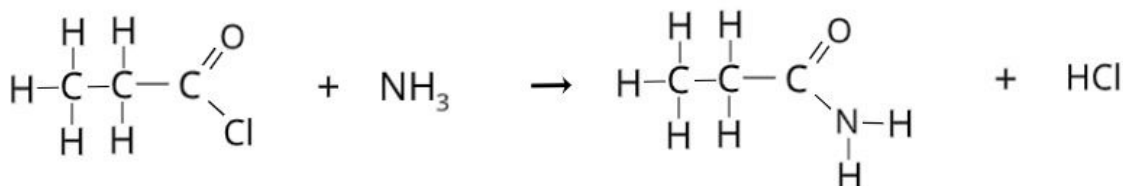
### Reactions with phenols

**Phenols** are aromatic compounds with an alcohol group bonded to the benzene ring. The reaction between phenols and acyl chlorides produces an **aromatic ester**.

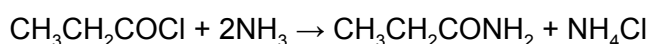


### Reactions with ammonia

When acyl chlorides react with ammonia, an **amide** and **hydrogen chloride** gas is produced. Amides are organic compounds containing the group **-CONH<sub>2</sub>**. Amides are given the suffix **-amide** so in the reaction below, the product is **propanamide**.

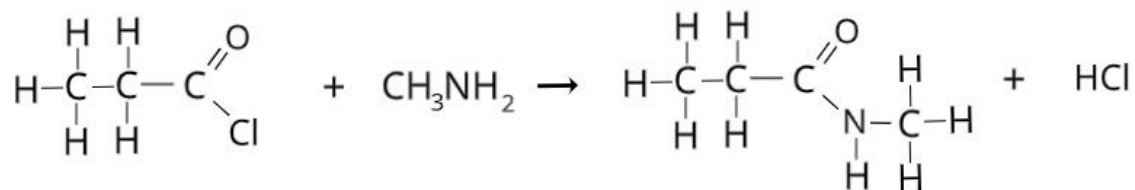


The hydrogen chloride produced reacts with the **excess ammonia** to produce ammonium chloride. The overall equation can be written as:

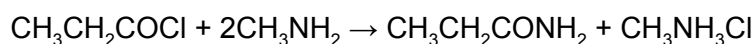


### Reactions with primary amines

A **primary amine** contains an  $\text{-NH}_2$  group bonded to an alkyl group. Methylamine has the formula  $\text{CH}_3\text{NH}_2$ . When a primary amine reacts with an acyl chloride, an **N-substituted amide** is produced. In the reaction below, N-methylpropanamide is formed ('methyl' comes from the alkyl group on the primary amine).



The hydrogen chloride produced reacts with the excess primary amine so the overall equation for the reaction can be written as:



### **Relative Ease of Hydrolysis of Acyl Chlorides, Alkyl Chlorides and Aryl Chlorides**

- **Acyl chlorides** contain the group  $\text{-COCl}$ .
- **Alkyl chlorides** are chloroalkanes containing  $\text{C-Cl}$ .
- **Aryl chlorides** are aromatic compounds with a chlorine atom bonded to a benzene ring

When the chlorides above undergo hydrolysis (reaction with water or hydroxide ions), nucleophilic substitution occurs.

#### Hydrolysis with water

- **Acyl chlorides** react vigorously with cold water to produce a carboxylic acid and hydrogen chloride gas. E.g.  $\text{CH}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HCl}$ .
- **Alkyl chlorides** have almost no reaction with water.
- **Aryl chlorides** have no reaction with water.

#### Hydrolysis with sodium hydroxide

- **Acyl chlorides** react vigorously with hydroxide ions to produce salts and water:  

$$\text{CH}_3\text{COCl} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{NaCl} + \text{H}_2\text{O}$$
- **Alkyl chlorides** react with hydroxide ions to produce an alcohol and a salt:  

$$\text{CH}_3\text{Cl} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaCl}$$
- **Aryl chlorides** generally have no reaction with hydroxide ions.

The reactions above show that the relative ease of hydrolysis is **acyl chlorides > alkyl chlorides > aryl chlorides**. Acyl chlorides are hydrolysed the easiest while aryl chlorides are the least likely to undergo hydrolysis.



**Aryl chlorides are unreactive** because the C-Cl bond is stronger than in an alkyl chloride. This is because the benzene electron system forms interactions with the lone pairs on the chlorine atom, strengthening the bond. Aryl chlorides do not undergo hydrolysis with hydroxide ions because the high electron density of the benzene ring repels the negatively charged hydroxide ions.

**Acyl chlorides are reactive** because the electronegative chlorine and oxygen cause the attached carbon to become slightly positively charged. This slight positive charge attracts a nucleophile, causing a reaction.

Condensation (addition-elimination) mechanism for hydrolysis of acyl chlorides:

