

# Cambridge (CIE) A Level Chemistry



Your notes

## Carboxylic Acids

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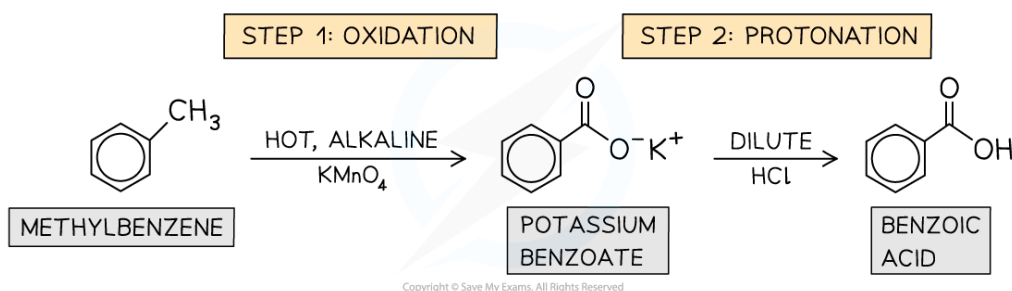
# Production of Benzoic Acid

- **Benzoic acids** are the simplest **aromatic carboxylic acids** with the molecular formula of  $C_6H_5COOH$
- Benzoic acids and their derivatives are often used as reagents in the synthesis of **esters**
- The compounds can be produced from the **oxidation** of **alkylbenzenes**

## Oxidation of alkylbenzenes

- The alkyl side-chain in alkylbenzenes, such as methylbenzene, can be oxidised to a **carboxylic acid**
- The alkylbenzene is **heated under reflux** with a solution of **hot alkaline  $KMnO_4$**  (this is the **oxidising agent**)
  - The **purple** colour of the  $Mn^{7+}$  ions disappears as they are **reduced** to  $Mn^{4+}$  ions
  - A **brown precipitate** of  $MnO_2$  is formed
- The mixture is then **acidified** with **dilute acid** (such as hydrochloric acid) to **protonate** the organic product form and produce a benzoic acid

## Making benzoic acid from methylbenzene



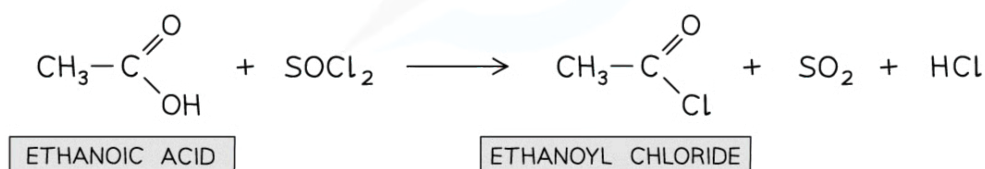
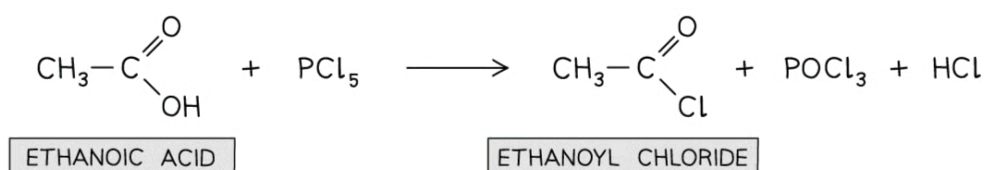
*Alkylbenzenes such as methylbenzene undergo oxidation to form benzoic acid*



# Reactions of Carboxylic Acids to Produce Acyl Chlorides

- **Acyl chlorides** are compounds with the functional group  $\text{-COCl}$
- They look similar in structure to **carboxylic acids** but have a Cl atom instead of an  $\text{-OH}$  group attached to the carbonyl ( $\text{C=O}$ )
- Acyl chlorides are **more reactive** than their corresponding carboxylic acids and are therefore often used as **starting materials** in the production of organic compounds such as **esters**
- They can be prepared from the reaction of carboxylic acids with:
  - **Solid** phosphorus(V) chloride ( $\text{PCl}_5$ )
  - **Liquid** phosphorus(III) chloride ( $\text{PCl}_3$ ) and heat
  - **Liquid** sulfur dichloride oxide ( $\text{SOCl}_2$ )
- For example, the acyl chloride **ethanoyl chloride** can be formed from **ethanoic acid** in the above reactions

## Using ethanoic acid to form ethanoyl chloride



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*Ethanoic acid can be used to produce ethanoyl chloride with different by-products depending on the reagent used*

# Further Oxidation of Carboxylic Acids



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- **Carboxylic acids** can be formed from the **oxidation** of primary alcohols
- The primary alcohols are firstly oxidised to **aldehydes** and then further oxidised to **carboxylic acids**
- Some carboxylic acids can get even **further oxidised**

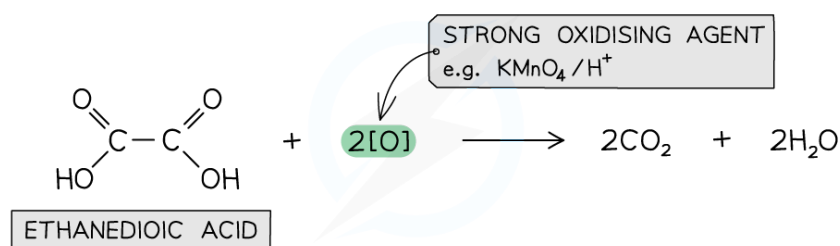
## Methanoic acid

- **Methanoic acid** is a **strong reducing agent** and gets **further oxidised** to **carbon dioxide** ( $\text{CO}_2$ )
- The oxidation of methanoic acid can occur by:
  - Warming methanoic acid with **mild oxidising agents** such as **Fehling's** or **Tollens'** reagent
    - In a Fehling's solution, the  $\text{Cu}^{2+}$  ion is **reduced** to  $\text{Cu}^+$  ion which **precipitates** as **red**  $\text{Cu}_2\text{O}$
    - With Tollens' reagent, the  $\text{Ag}^+$  is **reduced** to  $\text{Ag}$
  - Using **stronger** oxidising agents such as **acidified  $\text{KMnO}_4$**  or **acidified  $\text{K}_2\text{Cr}_2\text{O}_7$** 
    - The **purple**  $\text{KMnO}_4$  solution turns **colourless** as  $\text{Mn}^{7+}$  ions are **reduced** to  $\text{Mn}^{2+}$  ions
    - The **orange**  $\text{K}_2\text{Cr}_2\text{O}_7$  solution turns **green** as the  $\text{Cr}^{6+}$  ions are reduced to  $\text{Cr}^{3+}$  ions

## Ethanedioic acid

- Another carboxylic acid that can get further oxidised is **ethanedioic acid**
- A **strong oxidising agent** such as **warm acidified  $\text{KMnO}_4$**  is required for the oxidation of ethanedioic acid to **carbon dioxide**

## Oxidation of ethanedioic acid



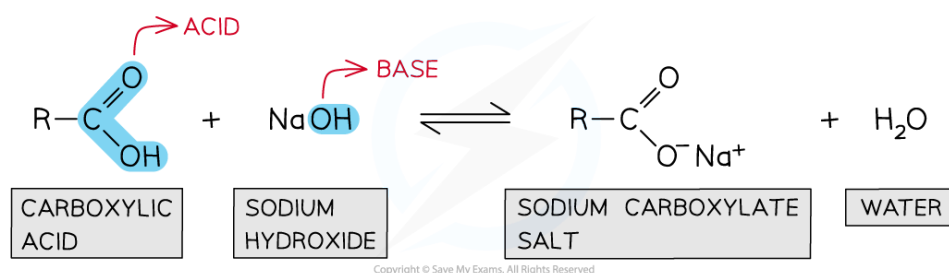
*Ethanedioic acid is a dicarboxylic acid that can get further oxidised to carbon dioxide*



# Relative Acidities of Carboxylic Acids, Phenols & Alcohols

- Carboxylic acids are compounds with a  $\text{-COOH}$  functional group
- They can act as **acids** and lose a proton ( $\text{H}^+$  ion) in an aqueous solution to form **carboxylate salts** and **water**

## Carboxylic acids forming carboxylate salts



*Carboxylic acids dissociate in aqueous solutions to form carboxylate salts and water*

- However, carboxylic acids are only **weak acids** as the **position of equilibrium** lies well over to the **left-hand side**
- The  $\text{pK}_a$  values of carboxylic acids, phenols, and alcohols suggest that carboxylic acids are **stronger acids** than alcohols and phenols
  - The  $\text{pK}_a$  is a measure of the relative strength of a species as an acid
  - The smaller the  $\text{pK}_a$  value, the stronger the acid

## Relative acidity of ethanol, phenol & carboxylic acids table

Acid	Dissociation	$\text{pK}_a$ at $25^\circ\text{C}$
Ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{aq}) \rightleftharpoons \text{C}_2\text{H}_5\text{O}^-(\text{aq}) + \text{H}^+(\text{aq})$	16
Phenol	$\text{C}_6\text{H}_5\text{OH}(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{O}^-(\text{aq}) + \text{H}^+(\text{aq})$	10
Ethanoic acid	$\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$	4.8
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$	4.2

- This order of relative acidities can be explained by looking at the **strength** of the O-H bond and the stability of the **conjugate bases** of the acids

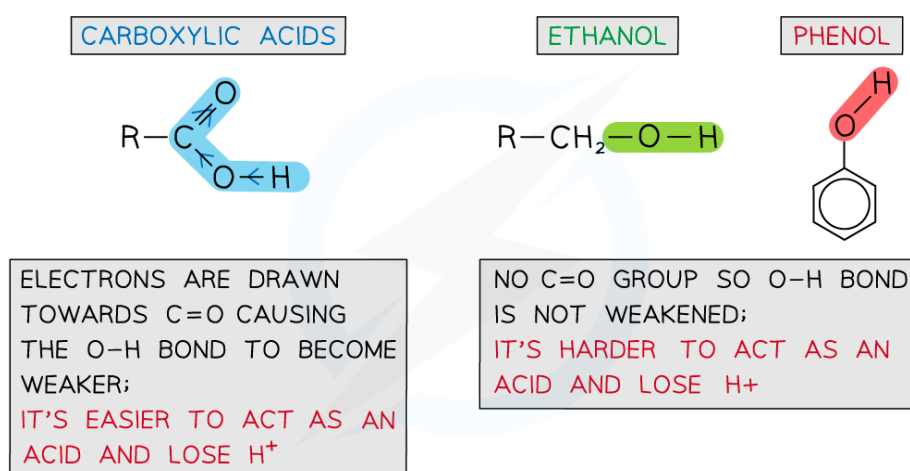


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## Strength of O-H bond

- In carboxylic acids, the electrons in the O-H bond are drawn towards the C-O bond
- The electrons in the C-O bond are drawn towards the C=O bond
- Overall, the O-H bond is **weakened** due to the **carbonyl** (C=O) group removing electron density from it and drawing it towards itself
- Carboxylic acids can therefore more easily **lose** a proton compared to phenols and alcohols which **lack** this electron-withdrawing carbonyl group

## Comparing OH bond strength of carboxylic acids, ethanol and phenol



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*The carbonyl group in carboxylic acids draws the electrons away from the O-H bond causing it to become weaker compared to the O-H bond in phenols and alcohols*

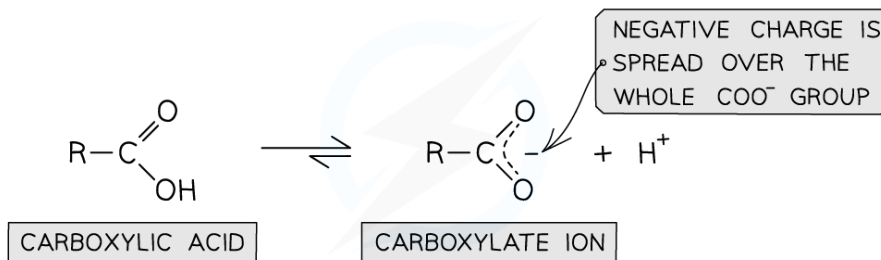
## Stability of carboxylate ions

- The **conjugate base** of carboxylic acids is the **carboxylate ion**
- The **charge density** on the oxygen atom is **spread out** over the carboxylate ion
- This is because the charge is **delocalised** on an **electronegative carbonyl oxygen atom**
- As a result, the electrons on the oxygen atom are **less available** for bond formation with an H<sup>+</sup> ion to reform the **undissociated** acid molecule with -COOH group
- The position of the dissociation equilibrium lies more to the right compared to alcohols and phenols

## The equilibrium position of a carboxylic acid and its carboxylate ion



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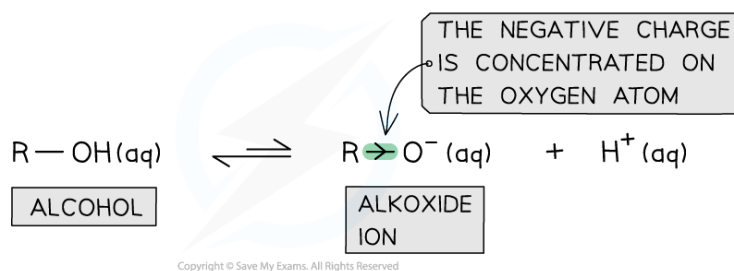


*The carboxylate ion is stable due to the delocalisation of the charge density on the electronegative oxygen*

## Stability of alkoxide ions

- The **conjugate base** of alcohols is the **alkoxide ion**
- The **alkyl** group in the ion is an **electron-donating** group that donates electron density to the oxygen atom
- As a result, the electron density on the oxygen atom is **more readily available** for bond formation with an  $\text{H}^+$  ion
- Alkoxide ions also **lack** the ability to delocalise the charge density on the entire ion
- The conjugate bases of alcohols are therefore less stable than the alcohols themselves and are more likely to reform the alcohol
- This means that alcohols are **weaker acids** compared to carboxylic acids and phenols
- The position of the dissociation equilibrium lies more to the left

## The equilibrium position of an alcohol and its alkoxide ion



*The electron-donating alkyl groups in alkoxide ions increase the electron density on the oxygen atom which is, therefore, more likely to bond with a  $\text{H}^+$  ion and reform the alcohol*

## Stability of phenoxide ions

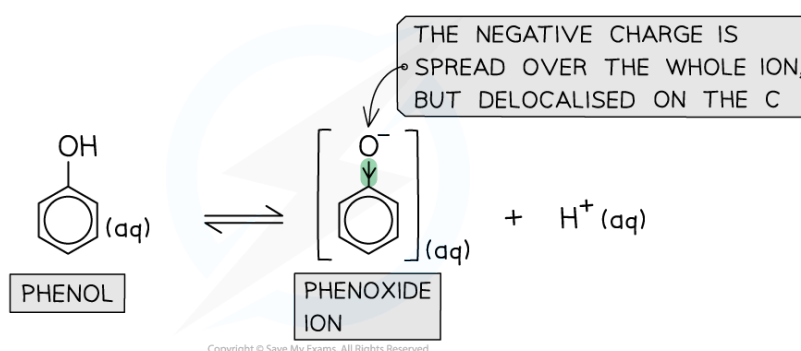
- In the **phenoxide ion** (which is the conjugate base of phenol) the charge density on the oxygen atom is **spread out** over the entire ion
- This delocalisation of electrons **stabilises** the phenoxide ion



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- As a result, the electrons on the oxygen atom are **less available** for bond formation with a proton ( $\text{H}^+$  ion)
- The **conjugate base** of phenols is therefore **more stable** than phenol
- However, since the delocalisation of charge density is on carbon atoms and not on electronegative oxygen atoms like in the carboxylate ion, phenoxide ions are **less stable** than carboxylate ions
- Therefore, phenols are **weaker acids** relative to carboxylic acids
- The position of the dissociation equilibrium lies more to the right compared to alcohols and more to the left compared to carboxylic acids

## The equilibrium position of phenol and the phenoxide ion



*The charge density is delocalised on the entire benzene ring in the phenoxide ions*





# Relative Acidities of Chlorine-Substituted Carboxylic Acids

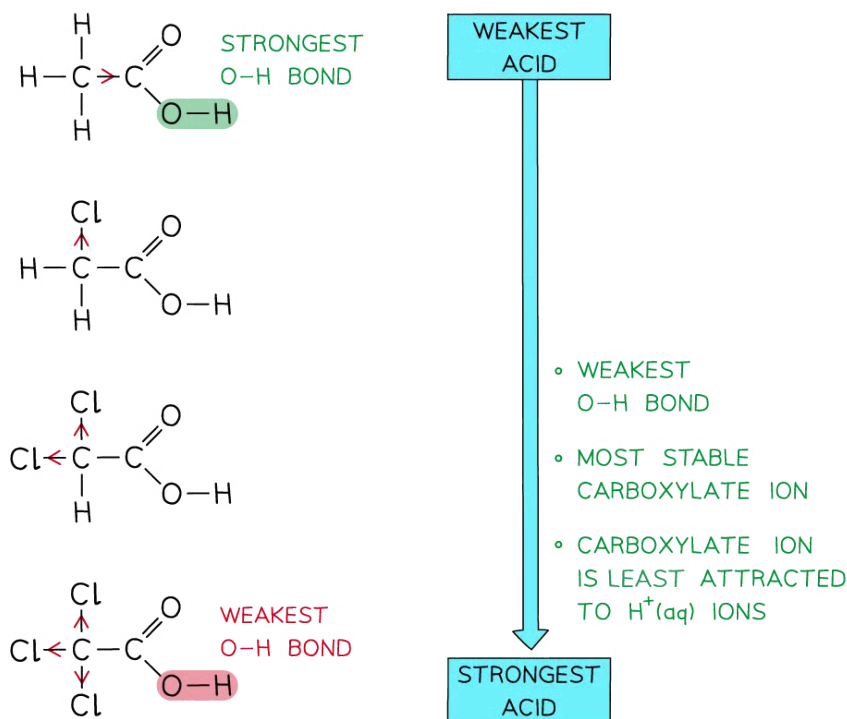
- **Electron-withdrawing** groups bonded to the carbon attached to the  $\text{-COOH}$  group make the carboxylic acids **stronger acids**
- This is because the  $\text{O-H}$  bond in the **undissociated acid molecule** is even further weakened as the electron-withdrawing group draws even more electron density away from this bond
- Furthermore, the electron-withdrawing groups extend the **delocalisation** of the negative charge on the  $\text{-COO}^-$  group of the carboxylate ion
- The  $\text{-COO}^-$  group is now even more stabilised and is less likely to bond with an  $\text{H}^+$  ion
- **Chlorine-substituted carboxylic acids** are examples of carboxylic acids with electron-withdrawing groups

## $\text{pK}_a$ values of ethanoic acid and chlorine-substituted derivatives table

Acid	$\text{pK}_a$ at $25^\circ\text{C}$
Ethanoic acid, $\text{CH}_3\text{COOH}$	4.8
Chloroethanoic acid, $\text{CH}_2\text{ClCOOH}$	2.9
Dichloroethanoic acid, $\text{CHCl}_2\text{COOH}$	1.3
Trichloroethanoic acid, $\text{CCl}_3\text{COOH}$	0.6

- The  $\text{pK}_a$  values of ethanoic acid and **chloro-substituted derivatives** show that the **more** electron-withdrawing groups there are on the carbon attached to the  $\text{-COOH}$  group, the **stronger** the acid

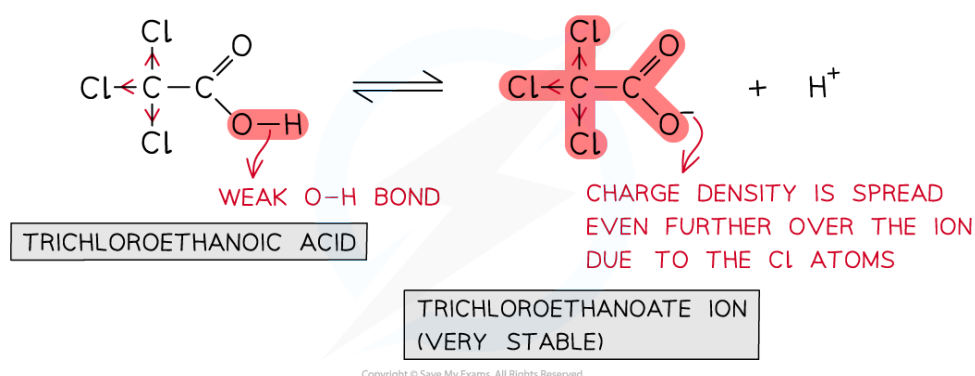
## Comparing the relative acidities of chlorine substituted derivatives of ethanoic acid



**The more chlorine atoms there are in the carboxylic acids, the stronger the acid is**

- Trichloroethanoic acid is the **strongest acid** as:
  - The O-H bond in  $CCl_3COOH$  is the **weakest** since there are **three** very strong electronegative Cl atoms withdrawing electron density from the  $-COOH$  group
  - When the O-H is broken to form the carboxylate ( $-COO^-$ ) ion, the charge density is further spread out by the three electron-withdrawing Cl atoms
  - The carboxylate ion is so **stabilised** that it is less attracted to  $H^+$  ions

## The equilibrium of trichloroethanoic acid and the trichloroethanoate ion



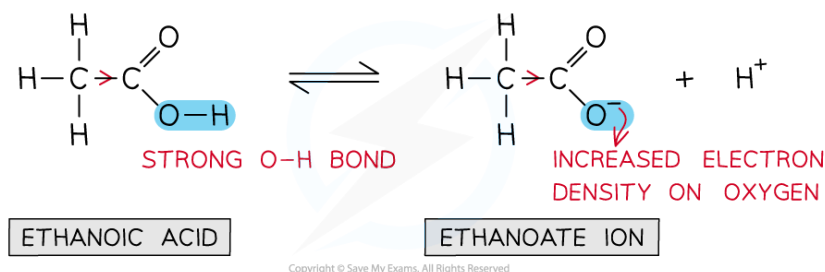
**Relative acidity of trichloroethanoic acid**

- Ethanoic acid is the **weakest acid** as:
  - It contains an **electron-donating** methyl group which **strengthens** the O-H bond
  - The methyl group **donates** negative charge towards the  $\text{-COO}^-$  group which becomes more likely to accept an  $\text{H}^+$  ion



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## The equilibrium of ethanoic acid and the ethanoate ion



*Relative acidity of ethanoic acid*