Carboxylic Acids and Esters

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IR Spectrum for Carboxylic acids

O-H absorption
C=O absorption

Butanoic acid
Solubility in Water

- The smaller carboxylic (up to C4) acids dissolve in water in all proportions but after this the solubility rapidly reduces. They dissolve because they can hydrogen bond to the water molecules.

Acidity

The carboxylic acid are only weak acids in water and only partially dissociate, but they are strong enough to displace carbon dioxide from carbonates.

\[
\text{CH}_3\text{CO}_2\text{H(aq)} \rightleftharpoons \text{CH}_3\text{CO}_2^-\text{(aq)} + \text{H}^+\text{(aq)}
\]

The carboxylic acid salts are stabilised by delocalisation, which makes the dissociation more likely.
Delocalisation

- The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.

The pi charge cloud has delocalised and spread out. The delocalisation makes the ion more stable and therefore more likely to form. This means it is a stronger acid than phenol.

Strength of Carboxylic acids

- Increasing chain length pushes electron density on to the COO\(^-\) ion, making it more negative and less stable. This makes the acid less strong.

<table>
<thead>
<tr>
<th>Alkyl groups electron releasing</th>
<th>Chlorine electron withdrawing</th>
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<tbody>
<tr>
<td>Propanoic acid less acidic than ethanoic acid</td>
<td>Chloroethanoic acid more acidic than ethanoic acid</td>
</tr>
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</table>
Examples of salt formation reactions

carboxylic acids can form salts with sodium, sodium hydroxide and sodium carbonate.

\[
\text{acid} + \text{metal (Na)} \rightarrow \text{salt} + \text{hydrogen}
\]

\[
\text{CH}_3\text{CO}_2\text{H} + \text{Na} \rightarrow \text{CH}_3\text{CO}_2\cdot\text{Na}^+ + \text{H}_2
\]

\[
\text{acid} + \text{alkali (NaOH)} \rightarrow \text{salt} + \text{water}
\]

\[
\text{CH}_3\text{CO}_2\text{H} + \text{NaOH} \rightarrow \text{CH}_3\text{CO}_2\cdot\text{Na}^+ + \text{H}_2\text{O}
\]

\[
\text{acid} + \text{carbonate (Na}_2\text{CO}_3) \rightarrow \text{salt} + \text{water} + \text{CO}_2
\]

\[
2\text{CH}_3\text{CO}_2\text{H} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{CO}_2\cdot\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2
\]

Reaction with sodium hydroxide

Carboxylic acids neutralise sodium hydroxide. The pH stays steady when small amounts of NaOH are added then rapidly jumps as neutralisation occurs.

Before neutralisation has occurred a buffer solution is present as there is a mixture of a weak acid and its salt present:

\[
\text{ethanoic acid} + \text{NaOH} \rightarrow \text{sodium ethanoate} + \text{water}
\]
**PH of ethanoate ion**

- Sodium ethanoate solution is slightly alkaline so \( \text{OH}^- \) ions must be present.

Explanation:
- Water dissociates into \( \text{H}^+ \) and \( \text{OH}^- \) ions.
  \[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \]
- The ethanoate ions can accept \( \text{H}^+ \) ions and form ethanoic acid, leaving an imbalance in \( \text{H}^+ \) and \( \text{OH}^- \) (extra \( \text{OH}^- \)).
  \[ \text{CH}_3\text{CO}_2^- + \text{H}^+ \rightarrow \text{CH}_3\text{CO}_2\text{H} \]

**Oxidation of methanoic acid**

Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group.

\[
\begin{array}{c}
\text{H} - \text{C} - \text{O} - \text{H} + \text{[O]} \rightarrow \\
\text{H} - \text{O} - \text{C} - \text{O} - \text{H}
\end{array}
\]

It forms carbonic acid (\( \text{H}_2\text{CO}_3 \)) which can decompose to give \( \text{CO}_2 \).
Reduction of carboxylic acid

Carboxylic acids can be reduced to alcohols by LiAlH₄, lithium tetrahydridoaluminate.

\[
\text{CO}_2\text{H} \quad \xrightarrow{\text{LiAlH}_4} \quad \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}
\]

benzoic acid \quad \text{phenylmethanol}

The LiAlH₄ acts as a nucleophile since H⁻ ions are present. LiAlH₄ can also be used to reduce carbonyls to alcohols.

NaBH₄ is not strong enough a reducing agent to reduce carboxylic acids but can reduce carbonyls to alcohols.

It is not possible to partially reduce a carboxylic acid to a carbonyl.

Esterification

Carboxylic acids react with alcohols to form esters and water.

An Ester

Esters have two parts to their names, eg methyl propanoate.

The bit ending in –yl comes from the alcohol that has formed it and is next to the single bonded oxygen.

The bit ending in –anoate comes from the carboxylic acid.
**Ester formation**

Carboxylic Acid + Alcohol $\xrightarrow{\text{H}^+}$ Ester + water

The reaction is reversible. The reaction is quite slow and needs heating under reflux, (often for several hours or days). Low yields (50% ish) are achieved. An acid catalyst ($\text{H}_2\text{SO}_4$) is needed.

\[
\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}
\]

Ethanoic acid Ethanol Ethyl Ethanoate

---

**Draw and name the esters formed from the reacting the following alcohols and carboxylic acids**

1. Methanol + Butanoic acid
   - Methyl Butanoate

2. Propan-1-ol + Ethanoic acid
   - Propyl Ethanoate

3. Ethanol + Propanoic acid
   - Ethyl Propanoate
IR Spectrum for an Ester

Mechanism for Esterification

There are two possibilities for the mechanism. Does the single bonded oxygen come from the alcohol or the carboxylic acid?

Experiments were done where a radioactive isotope of oxygen $O^{18}$ was inserted in an alcohol that was used to make an ester.

There are two possible results and esters
Result 1

\[
\text{Result 1} \quad \text{PhCO}^{18}\text{O} \text{CH}_3 + \text{H}_2\text{O}
\]

Result 2

\[
\text{Result 2} \quad \text{PhCOO} \text{CH}_3 + \text{H}_2^{18}\text{O}
\]

A mass spectrometer showed that the oxygen was found in the ester and not in the water. Result 1 occurs.

These bonds must therefore be broken.

Mechanism:
Addition - Elimination

Extra:
Uses of Esters: Solvents

• Although polar, they do not form hydrogen bonds (reason: there is no hydrogen bonded to a highly electronegative atom)
  – thus, much lower b.p. than the hydrogen-bonded carboxylic acids they came from. They are also almost insoluble in water

They will act as solvents, however, for other polar organic substances

e.g. Ethyl ethanoate is used as a solvent in glues and printing inks

Uses of Esters: Plasticisers

• Often pure polymers have limited flexibility because the polymer chains cannot move over each other.
• Incorporating some plasticiser into the polymer allows the chains to move more easily and the polymer can become more flexible.

To make PVC ‘mock leather’ material up to 50% by weight plasticiser must be added.

The plasticiser may evaporate over time making the plastic more brittle as it ages.
Uses of Esters: food flavourings

Esters are sweet smelling compounds that can be used in perfumes and flavourings.

For use in perfumes they need to be non toxic, soluble in solvent such as ethanol, volatile (turns into gas easily), and not react with water.

Hydrolysis of esters

Esters can be hydrolysed and split up by either heating with acid or with sodium hydroxide.

i) with acid reagents: dilute acid (HCl)
conditions: heat under reflux

This reaction is the reverse reaction of ester formation. When an ester is hydrolysed a carboxylic acid and an alcohol are formed.

\[
\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
\]

ethylethanoate – pineapple smell

This reaction is reversible and does not give a good yield of the products.
ii) with sodium hydroxide
reagents: dilute sodium hydroxide
conditions: heat under reflux

\[ \text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2^- \text{Na}^+ + \text{CH}_3\text{OH} \]

methyl propanoate         sodium propanoate         methanol

The carboxylic acid salt product is the anion of the carboxylic acid.
The anion is resistant to attack by weak nucleophiles such as alcohols, so the reaction is not reversible.
This reaction goes to completion.
Converting between carboxylic acids and their salts.

NaOH

Carboxylic acid $\rightleftharpoons$ carboxylic acid salt

HCl

After an ester is hydrolysed by reacting with sodium hydroxide, the carboxylic acid salt can be turned into the carboxylic acid by adding hydrochloric acid.

Fats and oils

Fats and oils are ESTERS of glycerol and long chain carboxylic acids (fatty acids)

The molecular formula shown above suggests that the fat molecule is shaped like an E, but the molecule is actually shaped more like this:
Hydrolysis of fats

\[
\text{Hydrolysis of fats} \\
\text{Boil with KOH}
\]

Hydrolysing fats to make Soap

Both the soap and glycerol are useful products

Glycerol form hydrogen bonds very easily. It is used in cosmetics, food and in glues
**Soap Molecule**

Sodium palmitate

\[
\begin{align*}
\text{Non polar} & : & \text{polar} \\
\text{H}_3\text{C} & - & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{CH}_2 \\
& & \text{C} \\
& & \text{O} \\
& & \text{O}^{-} \\
\end{align*}
\]

Non polar

**Biodiesel**

biodiesel is a mixture of methyl esters of long chain carboxylic acids

Vegetable oils can be converted into biodiesel by reaction with methanol in the presence of a (strong alkali) catalyst

\[
\text{CH}_2\text{O}--\text{C}--(\text{CH}_2)_{14}\text{CH}_3 + 3\text{CH}_3\text{OH} \rightarrow \text{H}_2\text{C}--\text{OH} + 3\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{CH}_3 \text{ biodiesel}
\]