Lecture 17 – Carboxylic Acids
1. What do we call them?
2. Reactions: Acidity
3. Reactions: Redox
4. Reactions: Acid Chlorides
5. Soap
Previously – aldehydes and ketones

\[
\text{MgBr} \xrightarrow{\text{CO}_2} \text{OOH}
\]
The CO$_2$H group

This functional group has different properties to either the carbonyl (C=O) group or the alcohol group (OH).

Must consider the functional group ‘COOH’ as a whole.
Nomenclature

- Longest chain incl. COOH gives stem/ending: –anoic acid
- If substituents present, number so carboxyl group is C1

\[
\begin{align*}
\text{methanoic acid} & : \text{HCOOH} \\
\text{butanoic acid} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \\
\text{5-ethyl heptanoic acid} & : \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}
\end{align*}
\]

- Name conjugate base by replacing ‘–anoic acid’ with –anoate

\[
\text{sodium hexanoate} : \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^-\text{Na}^+
\]
– Some simple carboxylic acids have non-systematic names

- Methanoic acid
  a.k.a. Formic acid

- Ethanoic acid
  a.k.a. Acetic acid

- Propanoic acid
  a.k.a. Propionic acid

- Butanoic acid
  a.k.a. Butyric acid

- Benzoic acid
<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>Carboxylate anion</th>
<th>Acyl substituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃C⁻CH₂O⁻H</td>
<td>H₃C⁻CH₂O⁻⁻⁻⁻</td>
<td>H₃C⁻CH₂O⁻⁻⁻⁻</td>
</tr>
<tr>
<td>acetic acid</td>
<td>acetate</td>
<td>acetyl</td>
</tr>
<tr>
<td>(ethanoic acid)</td>
<td>(ethanoate)</td>
<td>(ethanoyl)</td>
</tr>
<tr>
<td>CH₃CH₂COOH</td>
<td>CH₃CH₂CO⁻⁻⁻⁻</td>
<td>CH₃CH₂CO⁻⁻⁻⁻</td>
</tr>
<tr>
<td>propionic acid</td>
<td>propioate</td>
<td>propionyl</td>
</tr>
<tr>
<td>(propanoic acid)</td>
<td>(propanoate)</td>
<td>(propanoyl)</td>
</tr>
<tr>
<td>C６H₅COOH</td>
<td>C₆H₅CO⁻⁻⁻⁻</td>
<td>C₆H₅CO⁻⁻⁻⁻</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>benzoate</td>
<td>benzoyl</td>
</tr>
</tbody>
</table>
Carb Quiz

Name the following carboxylic acids:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \]

Spectroscopy …

**Infrared:** Carboxylic acids show …

- a strong absorption \( \sim 1700 \text{ cm}^{-1} \) (C=O) and
- a broad absorption \( \sim 3000 \text{ cm}^{-1} \) (O-H)

**\(^{13}\text{C NMR}\):** The carboxylic carbon resonates around 180 ppm
Acids are ... acidic

For a weak acid the conjugate pair are in equilibrium
- The carboxylate ion is a resonance stabilised anion
- The equilibrium usually lies to the LHS (undissociated acid)

\[
\begin{align*}
R-OH & \quad \text{cf: alcohol} \\
& \quad \text{no resonance stabilisation, equilibrium lies very much to the left, alcohols have a neutral pH}
\end{align*}
\]
Carboxylates can dissolve in water

Carboxylic acids react with dilute aqueous sodium hydroxide solution to form the water soluble carboxylate ion

- Reaction of a weak acid (or base) with a strong base (or acid) goes to completion

\[
\text{C}_6\text{H}_5\text{COOH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{Na}^+ + \text{H}_2\text{O}
\]

- The reaction may be reversed

\[
\text{C}_6\text{H}_5\text{COO}^- + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{Cl}^-
\]

- Benzoic acid soluble in diethyl ether
- Sodium benzoate insoluble in diethyl ether (soluble in NaOH solution)
Carboxylic acids are formed by an oxidation reaction

- There are many oxidising agents
  - eg $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$, $\text{MnO}_4^-/\text{H}^+$, $\text{CrO}_3$, $\text{O}_3$, $\text{Ag}^+$
- Primary alcohols and aldehydes are oxidised to carboxylic acids

$$\begin{align*}
\text{primary alcohol} & \xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+} \text{carboxylic acids} \\
\text{aldehydes not} & \text{ normally isolated} \\
\text{3-methylhexanol} & \xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+} \text{carboxylic acids}
\end{align*}$$
Alcohols from Carbs

Reduction to a primary alcohol

- Two step reaction - lithium aluminium hydride then aqueous acid

\[
\text{R-C} \quad \text{OH} \quad \xrightarrow{1) \text{LiAlH}_4} \quad \text{R-C} \quad \text{H} \quad \xrightarrow{2) \text{H}^+} \quad \text{R-C} \quad \text{H} \quad \text{OH}
\]

carboxylic acids

alcohol

3-propylhexanoic acid
Conversion to Acyl Halides is Useful

Substitution of the OH group

- Thionyl chloride reacts to form an acid chloride

\[
\text{H}_3\text{C}\overset{\text{O}}{\text{C}}\overset{\text{O}}{\text{H}} + \text{Cl}_2\overset{\text{S}}{\text{O}}\overset{\text{Cl}}{\text{Cl}} \rightarrow \text{H}_3\text{C}\overset{\text{C}}{\text{C}}\overset{\text{Cl}}{\text{Cl}} + \text{H}_2\text{Cl} + \text{SO}_2
\]

- Acetic acid (ethanoic acid)
- Acetyl chloride (ethanoyl chloride)
- Sulfur dioxide

Benzoic acid

\[\text{SOCl}_2\]

More on this later...
Fatty Acids

- **Fatty acids** are long chain carboxylic acids ($C_8 - C_{20}$)

  - Saturated fatty acids have alkane chain (e.g., coconut, animal fats, butter)
    - Monounsaturated fatty acids contain one double bond (e.g., olive oil)
    - Polyunsaturated fatty acids contain two or more double bonds (e.g., soya)

Fats are esters of fatty acids and an alcohol
Soap

Sodium salt of long chain fatty acids
- Combination of hydrophobic chain and polar hydrophilic carboxylate group \( \Rightarrow \) grease can be removed into water

\[
\text{Sodium stearate} \\
\text{hydrocarbon} \quad \checkmark \\
\text{non-polar and hydrophobic} \quad \checkmark \\
\text{dissolves in fatty things} \quad \checkmark \\
\text{carboxylate salt} \\
\text{polar, hydrophilic} \\
\text{dissolves in water} \\
\]
Soap – how it works
Commercial soaps

- Soap is made by heating fats with conc. NaOH
- Synthetic analogues are widely used in detergents

![](image)

- Cheaper to make and stronger grease penetrating power
Carb Quiz

Suggest reagents …

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{OH} & \quad \text{O} \\
\text{Cl} & \quad \text{O}
\end{align*}
\]
You should now be able to

1. Recognise a carboxylic acid and name simple examples
2. Understand the acid / base reactions of a carboxylic acid
3. Understand the Redox reactions leading to and from carboxylic acids
4. Convert a carboxylic acid into an acid chloride
5. Recognise the role of long chain fatty acids in soap

Next: Carboxylic acids are all very well, but what are they good for?