Carboxylic Acids and Esters

Chapter 17 Problems:
15, 21, 25, 35, 38, 49, 51

Carboxylic Acids

- The functional group of a carboxylic acid is a carboxyl group.
- Carboxyl with hydroxy
- represented in any one of three ways

\[
\begin{align*}
\text{O} & \quad \text{C-OH} \\
\text{O} & \quad \text{COOH} \\
\text{O} & \quad \text{CO_2H}
\end{align*}
\]

Nomenclature

- Drop the –e of the main chain name and add –oic acid.

<table>
<thead>
<tr>
<th>Condensed Structural Formulas</th>
<th>IUPAC Name</th>
<th>Common Name</th>
<th>Occurs In</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H-OH})</td>
<td>Methanoic acid</td>
<td>Formic acid</td>
<td>Ant and bee stings (Latin, Formica, “ant”)</td>
</tr>
<tr>
<td>(\text{CH_2-OH})</td>
<td>Ethanoic acid</td>
<td>Acetic acid</td>
<td>Vinegar (Latin, acetic, “vinegar”)</td>
</tr>
<tr>
<td>(\text{CH_3-C-OH})</td>
<td>Propanoic acid</td>
<td>Propionic acid</td>
<td>Dairy products (Greek, πρωθος, “pros,” “first”)</td>
</tr>
<tr>
<td>(\text{CH_3-CH_2-OH})</td>
<td>Butanoic acid</td>
<td>Butyric acid</td>
<td>Rancid butter (Latin, butyrum, “butter”)</td>
</tr>
</tbody>
</table>

Table 17.1 Names and Nomenclature of Carboxylic Acids
Nomenclature

- To name a dicarboxylic acid, add the suffix -dioic acid to the name of the parent alkane that contains both carboxyl groups.

Ethanedioic acid (Oxalic acid)
Propanedioic acid (Malonic acid)
Butanedioic acid (Succinic acid)
Pentanedioic acid (Glutaric acid)
Hexanedioic acid (Adipic acid)

Nomenclature: Substituents

- For common names, use the Greek letters alpha (α), beta (β), gamma (γ), and so forth to locate substituents.

4-Aminobutyric acid (γ-Aminobutyric acid; GABA)
2-Hydroxypropanoic acid (α-Hydroxypropionic acid; Lactic acid)

Physical Properties

- The carboxyl group contains three polar covalent bonds: C=O, C-O, and O-H
  - The polarity of these bonds determines the major physical properties of carboxylic acids.

- Label the partial positive and negative charges in carboxyl group.
Physical Properties

- The carbonyl group has a large dipole
- The hydroxy group is capable of hydrogen bonding.
- The molecules can H-bond to each other
- How does this affect boiling point?
  - Higher than aldehydes and ketones – no H-bonds
  - Higher than alcohols – H-bonds, not strong dipole

\[
\text{H}_3\text{C} = \overset{\delta^-}{\text{O}} - \overset{\delta^+}{\text{H}} - \overset{\delta^-}{\text{O}} = \text{CH}_3
\]

hydrogen bonding between two molecules

Physical Properties

- Carboxylic acids are more soluble in water than are alcohols, ethers, aldehydes, and ketones of comparable molecular weight

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Molecular Weight</th>
<th>Boiling Point (°C)</th>
<th>Solubility (g/100 mL H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COOH</td>
<td>acetic acid</td>
<td>60.1</td>
<td>118</td>
<td>infinite</td>
</tr>
<tr>
<td>CH₃CH₂CH₂OH</td>
<td>1-propanol</td>
<td>60.1</td>
<td>97</td>
<td>infinite</td>
</tr>
<tr>
<td>CH₃CH₂CHO</td>
<td>propanal</td>
<td>58.1</td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td>CH₃(CH₂)₂COOH</td>
<td>butanoic acid</td>
<td>88.1</td>
<td>163</td>
<td>infinite</td>
</tr>
<tr>
<td>CH₃(CH₂)₂CH₂OH</td>
<td>1-pentanol</td>
<td>88.1</td>
<td>137</td>
<td>2.3</td>
</tr>
<tr>
<td>CH₃(CH₂)₂CHO</td>
<td>pentanal</td>
<td>86.1</td>
<td>103</td>
<td>slight</td>
</tr>
</tbody>
</table>

Physical Properties

- Sharp and or sour odor/taste
  - Vinegar, rancid butter, sweat, sauerkraut
**Hydroxy Acids**

<table>
<thead>
<tr>
<th>Source</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid (Gigantia, sugar beet)</td>
<td><img src="structure_image" alt="Glycolic acid structure" /></td>
</tr>
<tr>
<td>Lactic acid (Sour milk)</td>
<td><img src="structure_image" alt="Lactic acid structure" /></td>
</tr>
<tr>
<td>Tartaric acid (Grapes)</td>
<td><img src="structure_image" alt="Tartaric acid structure" /></td>
</tr>
<tr>
<td>Maleic acid (Apples, grapes)</td>
<td><img src="structure_image" alt="Maleic acid structure" /></td>
</tr>
<tr>
<td>Citric acid (Citrus fruits, lemons, oranges, grapefruit)</td>
<td><img src="structure_image" alt="Citric acid structure" /></td>
</tr>
</tbody>
</table>

**Beta-hydroxy acid**

- **Salicylic Acid**
  - exfoliant
  - oil soluble – penetrates oil containing pores to remove dead skin cells
  - less irritating than alpha acids – anti-inflammatory of aspirin

**Reactions : Acid/Base**

- Carboxylic acids are weak acids
  - Give up the H bonded to O to water or base
  - values of $K_a$ for most unsubstituted aliphatic and aromatic carboxylic acids fall within the range $10^{-4}$ to $10^{-6}$ ($pK_a$ 4.0 - 5.0)
**Reaction With Bases**

- All carboxylic acids react with strong bases to form water-soluble salts

\[
\text{Carboxylic acid (slightly soluble in water)} + \text{NaOH} \rightarrow \text{Sodium salt} + \text{H}_2\text{O}
\]

**Benzoic acid**

- Sodium benzoate
  - Soluble in water
  - 60 g/100 mL water

**Ammonium benzoate**

- 20 g/100 mL water

**Reactions with bases**

- Salts of carboxylic acids
  - Drop the \(-\text{ic} \) acid
  - Change to \(-\text{ate} \)

- Sodium benzoate & monosodium glutamate
  - Food preservatives

**Esterification**

- Carboxylic acid + alcohol
- Ester
  - \(-\text{OR} \) of alcohol replaces \(-\text{OH} \) of acid
  - Reaction gives off water
Esters

- Name ester by naming alcohol and acid salt
  - Alcohol – 2 carbons – ethanol or ethyl alcohol
  - Acid – 2 carbons – ethanoic or acetic
  - Ethyl acetate

\[
\begin{align*}
\text{Ethyl acetate} & \quad \text{CH}_3\text{CO}\text{OCH}_2\text{CH}_3
\end{align*}
\]

Esters

- Fragrant molecules
- Can they H-bond to each other?
  - B.P. compared to acid/ alcohol
- Can they H-bond with water?
  - What happens as the number of carbons increases?

\[
\begin{align*}
\text{Ethanol} & \quad \text{CH}_3\text{CH}_2\text{OH} \\
\text{Acetic acid} & \quad \text{CH}_3\text{COOH}
\end{align*}
\]

Hydrolysis of Esters

- Hydrolysis of esters in aqueous acid is the reverse of Fischer esterification
- Products ____________ + ____________

\[
\begin{align*}
\text{Ethyl acetate} & \quad \text{CH}_3\text{COOCH}_2\text{CH}_3 \\
\text{H}_2\text{O} & \quad \text{H}^+ \\
\text{Acetic acid} & \quad \text{CH}_3\text{COOH} \\
\text{Ethanol} & \quad \text{CH}_3\text{CH}_2\text{OH}
\end{align*}
\]
**Ester Hydrolysis**

- If base is present, the carboxylic acid produces a salt.

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

**Ester Hydrolysis**

\[
\text{H}_3\text{C}^{-}\text{O}^{-}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{NaOH} \xrightarrow{} \text{H}_3\text{C}^{-}\text{OH} + \text{Na}^+\text{O}^{-}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

**Aspirin Synthesis**

- The chemical name for aspirin is acetyl salicylic acid.
- It is formed from reaction of acetic acid with salicylic acid.
  - What kind of reaction is this?
  - What kind of molecule is aspirin?

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

- What are the products of aspirin hydrolysis?
- Why does old aspirin smell like vinegar?

\[
\text{Aspirin} \xrightarrow{\text{H}_2\text{O, heat}} \text{Acetic acid} + \text{Formic acid}
\]

**Summary of Reactions**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Reagent</th>
<th>Product</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid</td>
<td>Water</td>
<td>Carboxylate anion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>base</td>
<td>Carboxylate salt</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alcohol</td>
<td>ester</td>
<td>esterification</td>
</tr>
<tr>
<td>Ester</td>
<td>water</td>
<td>Acid + alcohol</td>
<td>hydrolysis</td>
</tr>
<tr>
<td></td>
<td>base</td>
<td>Acid salt + alcohol</td>
<td>hydrolysis</td>
</tr>
</tbody>
</table>

**Examples**

- Label the molecules as carboxylic acids, esters, or acid salts.

\[
\text{Example 1: Carboxylic acid}
\]

\[
\text{Example 2: Ester}
\]

\[
\text{Example 3: Acid salt}
\]
Examples

- Ibuprofen and Naproxen work in a similar way as aspirin. Which part of the molecules do you think are important for function? (what parts are the same?)

![Chemical structures of Ibuprofen and Naproxen]