CHAPTER 15: Carboxylic Acids & Esters

- Recognize the carboxyl group and classify compounds as acids or esters
- Explain how the structure of a carboxylic acid or ester affects its physical properties
- Identify neutralization, esterification, and hydrolysis/saponification reactions, and predict the resulting products
- Understand the biological importance of phosphate ester and anhydride bonding

Review §§ 9.2, 9.8, 9.9

15.1 NOMENCLATURE of CARBOXYLIC ACIDS

CARBOXYLIC ACIDS (IUPAC)

STEP 1. Identify the longest carbon chain that includes the carbonyl carbon [C-1]
STEP 2. Add the -oic acid suffix (and any multiplier prefix)
STEP 3. Identify branches

Common names reflect historic sources of acids

FATTY ACIDS: 3-20 (12-20) carbons

15.2 PHYSICAL PROPERTIES of CARBOXYLIC ACIDS

- bp's higher than alcohols of similar molecular weight

<table>
<thead>
<tr>
<th>Compound</th>
<th>bp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})</td>
<td>78</td>
</tr>
<tr>
<td>(\text{CH}_3\text{C}_2\text{H}_5\text{COOH})</td>
<td>100</td>
</tr>
<tr>
<td>(\text{HCOOH})</td>
<td>42</td>
</tr>
</tbody>
</table>

H-bonded dimers
• Highly polar
• Low- to medium-MW \((c_8\) acids soluble in \(H_2O\)
• Strong, often repellent odors
  - Crushed ants
  - Vinegar
  - Rancid butter
  - Goat body parts

15.3 ACIDITY of CARBOXYLIC ACIDS

\[ R-C-O-H \xrightleftharpoons{H_2O} R-CO_2^- + H^+ \]

- React with bases stronger than water:

\[ R-C-OH + NaOH \rightarrow R-CO_2^- Na^+ \]

LOW pH: \( R-COOH \)
HIGH pH: \( R-CO_2^- \)

15.4 SALTS of CARBOXYLIC ACIDS

<table>
<thead>
<tr>
<th>Carboxylate ion</th>
<th>( R-C-O^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>( R-C-O^- )</td>
</tr>
</tbody>
</table>

STEP 1. Identify acid
STEP 2. Replace -ic acid with -ate suffix
STEP 3. Identify cation

15.5 CARBOXYLIC ACID ESTERS

ESTER FORMATION

\[ R-C-OH + H-OR' \xrightarrow{H^+} R-C-O-OR' + H_2O \]

15.6 NOMENCLATURE of ESTERS

\[ R-C-O-R' \]

STEP 1. Identify the acid fragment
STEP 2. Replace -ic acid with the -ate suffix
STEP 3. Identify the R’ group
STEP 4. Combine: “R’ Group” + “Acid Fragment”

Examples:
- Isopentyl acetate
- Isoamyl acetate
- 3-Methylbutyl ethanoate
- Acetyl salicylic acid
- Methyl salicylate
- Salicylic acid from willow \((Salix)\) bark
PHYSICAL PROPERTIES of ESTERS

- Weakly polar (not as polar as ketones)
- Bp's like those of hydrocarbons of similar molecular weight

<table>
<thead>
<tr>
<th>Compound</th>
<th>bp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(CH₂)₄CH₂</td>
<td>69</td>
</tr>
<tr>
<td>CH₃(CH₂)₂OH</td>
<td>137</td>
</tr>
<tr>
<td>CH₃(CH₂)₂COOH</td>
<td>165</td>
</tr>
<tr>
<td>CH₃COOCH₂CH₃</td>
<td>77</td>
</tr>
</tbody>
</table>

No ester-ester H-bonding

- Solubility like that of ketones
- Floral, fruity odors

\[
\text{CH}_3\text{-C-O-CH}_2\text{CH}_2\text{CH}_2\text{(CH}_3\text{)}_2
\]
Banana oil

\[
\begin{array}{c}
\text{COOCH}_3 \\
\text{OH}
\end{array}
\]
Oil of wintergreen

GLYCEROL ESTERS

\[
3 \text{RCOOH} \rightarrow 3 \text{RCOOH} + \text{H}_2\text{O}
\]

Fatty acids

Fat (solid ester)
Oil (liquid ester)

TRIGLYCERIDE (TRIACYLGlycerol)
Fatty acid ester of glycerol

15.7 REACTIONS of ESTERS

ACID-CATALYZED HYDROLYSIS

\[
\begin{align*}
\text{R-C-OR} + \text{H}_2\text{O} &\rightleftharpoons \text{R-C-O}^- + \text{R'}\text{OH} \\
\text{R-C-O}^- + \text{H}^+ &\rightleftharpoons \text{R-COOH} + \text{H}_2\text{O}
\end{align*}
\]

HYDROLYSIS: Breakdown of a compound by reaction with water.

BASE-CATALYZED HYDROLYSIS

\[
\begin{align*}
\text{R-C-OR} + \text{OH}^- &\rightarrow \text{R-C-O}^- + \text{R'}\text{OH} \\
\text{R-C-O}^- + \text{H}^+ &\rightarrow \text{R-COOH} + \text{H}_2\text{O}
\end{align*}
\]

SAPONIFICATION

Reacting an ester with aqueous OH⁻ to produce an alcohol and a carboxylate salt
15.8 ESTERS of INORGANIC ACIDS

**PHOSPHATE ESTERS**

\[ \text{Phosphoric acid} + \text{R-OH} \xrightarrow{\text{enzyme}} \text{Phosphate monoester} \]

\[ \text{at physiological pH} \]

**ANHYDRIDES ("without water")**

\[ \text{enzyme} \quad \text{H}_2\text{O} \]

**ANHYDRIDE ESTERS**

**DI- and TRIPHOSPHATE ESTERS**

ARE ENERGY STORAGE BIOMOLECULES

**HIGH-ENERGY BOND!**