CARBOXYLIC ACIDS

Carboxyl group:

\[ \text{O:} \]
\[ \text{—C—\text{OH}} \]

**Nomenclature** —

<table>
<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
<th>IUPAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-COOH</td>
<td>formic acid, methanoic acid</td>
<td></td>
</tr>
<tr>
<td>CH₃-COOH</td>
<td>acetic acid, ethanoic acid</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂-COOH</td>
<td>propionic acid, propanoic acid</td>
<td></td>
</tr>
<tr>
<td>CH₃(CH₂)₂-COOH</td>
<td>butyric acid, butanoic acid</td>
<td></td>
</tr>
<tr>
<td>CH₃(CH₂)₃-COOH</td>
<td>valeric acid, pentanoic acid</td>
<td></td>
</tr>
<tr>
<td>CH₃(CH₂)₄-COOH</td>
<td>caproic acid, hexanoic acid</td>
<td></td>
</tr>
</tbody>
</table>

Positions along the chain are indicated by Greek letters (common names) or numbers (IUPAC).

\[ \begin{array}{c}
\text{Br} \\
\text{CH₃CHCH₂CH₂C—OH} \\
5 \quad 4 \quad 3 \quad 2 \quad 1 \\
\delta \quad \gamma \quad \beta \quad \alpha \\
\end{array} \]

\[ \gamma \text{-bromovaleric acid} \]

\[ \begin{array}{c}
\text{Br} \\
\text{CH₃CHCH₂CH₂C—OH} \\
5 \quad 4 \quad 3 \quad 2 \quad 1 \\
\delta \quad \gamma \quad \beta \quad \alpha \\
\end{array} \]

\[ 4 \text{-bromopentanoic acid} \]
Dicarboxylic acids —

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<thead>
<tr>
<th>Structure</th>
<th>Common Name</th>
<th>IUPAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOOC-COOH</td>
<td>oxalic acid,</td>
<td>ethanedioic acid</td>
</tr>
<tr>
<td>HOOC-CH₂-COOH</td>
<td>malonic acid,</td>
<td>propanedioic acid</td>
</tr>
<tr>
<td>HOOC-(CH₂)₂-COOH</td>
<td>succinic acid,</td>
<td>butanedioic acid</td>
</tr>
<tr>
<td>HOOC-(CH₂)₃-COOH</td>
<td>glutaric acid,</td>
<td>pentanedioic acid</td>
</tr>
<tr>
<td>HOOC-(CH₂)₄-COOH</td>
<td>adipic acid,</td>
<td>hexanedioic acid</td>
</tr>
</tbody>
</table>

Aromatic acids —

\[\text{benzoic acid} \quad \text{phthalic acid} \quad \text{isophthalic acid} \quad \text{terephthalic acid}\]

Salts —

Name cation followed by acid name with -ic changed to -ate, eg

\[\text{sodium benzoate}\]
Physical Properties —

Lower molecular weight acids are soluble in H₂O: hydrogen bonding. Usually soluble in organic solvents.

Sodium and potassium salts of lower molecular weight acids are soluble in H₂O and not soluble in organic solvents of low polarity. The salts of long-chain carboxylic acids are soaps. Sodium and potassium soaps form micelles in water.

Carboxylic acids form dimers (pronounced die'-mers) in the liquid phase ---

These dimers also exit to some extent in the gas phase, consequently, carboxylic acids have high boiling points for a given molecular weight.
**Acidity**

\[
\begin{align*}
\text{RCOOH} + \text{H}_2\text{O} &\rightleftharpoons \text{RCOO}^- + \text{H}_3\text{O}^+ \\
K_{eq} &= \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]} \\
K_a &= \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]} \\
pK_a &= -\log K_a
\end{align*}
\]

Compare acidity of carboxylic acids with alcohols:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} &\rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}^+, K_a \sim 10^{-16} \\
\text{CH}_3\text{COOH} &\rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+, K_a \sim 10^{-5}
\end{align*}
\]
Reason —

Carboxylate anion is more stable compared to carboxylic acid than alkoxide ion is compared to alcohol.

Neither alcohol nor alkoxide ion are stabilized by resonance, but the situation is different for a carboxylic acid and its anion; in this case the anion is stabilized more than the acid:

![Chemical structures showing resonance stabilization](image)

Substituent groups —

Those which stabilize the anion more than its conjugate acid (electron withdrawing) increase acid strength. Those which destabilize anion more than acid (electron donating) decrease acid strength.
Synthesis of Carboxylic Acids —

Oxidation of Primary Alcohols or Alkylbenzenes ---

\[ \text{RCH}_2\text{OH} \xrightarrow{\text{KMnO}_4, \text{heat}} [\text{RCHO}] \xrightarrow{} \text{RCOOH} \]

\[ \text{Ar-R} \xrightarrow{\text{KMnO}_4, \text{heat}} \text{Ar-COOH, where R is 1º or 2º} \]

Grignard Synthesis ---

\[ \text{C} + \text{R} \xrightarrow{} \text{C}\text{R} \xrightarrow{\text{HX}} \text{C}\text{R} + \text{MgX}_2 \]

\[ \text{eg} \]

\[ \text{MgBr} + \text{CO}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{COOH} \]

This method results in a product which has one carbon more than the reactant.
Nitrile Hydrolysis —

May be carried out under acidic or basic conditions – conditions used may depend on other functional groups present.

\[
R\text{—C≡N:} \xrightarrow{\text{heat}} \begin{cases} \text{H}_2\text{O}, \text{H}_2\text{SO}_4 & \rightarrow \text{RCOOH} + (\text{NH}_4)_2\text{SO}_4 \\ \text{H}_2\text{O}, \text{NaOH} & \rightarrow \text{RCOO}^- \text{Na}^+ + \text{NH}_3 \end{cases}
\]

Mechanism ---

Acidic Hydrolysis:
Basic Hydrolysis:

![Chemical equation diagram]

**Aliphatic Nitrile Synthesis**

\[ RX + K^+CN^- \xrightarrow{\text{DMSO}} \text{RC}≡\text{N} + K^+X^- \]

Best if R is primary, a disaster if it is tertiary.

*eg*  
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{CN}^- \xrightarrow{\text{DMSO}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \]

*but*  
\[ \text{H}_3\text{C}\text{C}\text{C}\text{Br} + \text{CN}^- \xrightarrow{\text{DMSO}} \text{H}_2\text{C}\text{C} + \text{HCN} \]
* Aromatic Nitrile Synthesis —

\[
\begin{align*}
\text{NO}_2 & \xrightarrow{\text{Sn, HCl}} \text{HCl, 0 oC } \xrightarrow{\text{NaOH}} \text{NH}_2 \\
\text{NaNO}_2 & \xrightarrow{\text{HCl, 0 oC}} \text{HCl, 0 oC } \xrightarrow{\text{CuCN}} \text{CN} \\
\text{Sandmeyer reaction}
\end{align*}
\]

Reactions of Carboxylic Acids —

Reduction to Primary Alcohols —

\[
\begin{align*}
\text{R-COOH} & \xrightarrow{1. \text{LiAlH}_4 \text{ or BH}_3 \text{ in THF}} \text{R-CH}_2\text{OH} \\
\text{(or Ar)} & \xrightarrow{2. \text{H}_3\text{O}^+} \\
\end{align*}
\]

BH\text{\textsubscript{3}} has the advantage that most other groups will not be affected if an excess of the reagent is not used. LiAlH\text{\textsubscript{4}} will reduce nitro, nitrile, and various carbonyl groups, among others.
Hunsdiecker Reaction —

In this reaction the carboxylic acid is decarboxylated to a bromide or iodide, having one less carbon.

\[
\text{R-COOH (or Ar)} \xrightarrow{\text{HgO or Pb(OAc)}_4 \text{ or Ag}_2\text{O and Br}_2 \text{ or I}_2 \text{ in CCl}_4} \text{R-X} + \text{CO}_2
\]

Mechanism —

\[
\begin{align*}
\text{O} & \\
\text{R}^+\text{C}^-\text{O}^-&\text{Ag}^+ + \text{Br}_2 \xrightarrow{\text{heat}} \text{R}^\cdot\text{C}^-\text{O}^-\text{Br} + \text{AgBr} \\
\text{O} & \\
\text{R}^\cdot\text{C}^-\text{O}^-&\text{Br} \xrightarrow{\text{heat}} \text{R}^\cdot\text{C}^-\text{O}^- + \cdot\text{Br} \\
\text{O} & \\
\text{R}^\cdot\text{C}^-\text{O}^-& \xrightarrow{\text{heat}} \text{R}^\cdot + \text{CO}_2 \\
\text{O} & \\
\text{R}^\cdot\text{C}^-\text{O}^-&\text{Br} + \text{R}^\cdot \xrightarrow{\text{heat}} \text{R}^\cdot\text{C}^-\text{O}^- + \text{R-Br}
\end{align*}
\]