Chapter 13  Carboxylic Acids, Esters, Amines, and Amides

13.1  Carboxylic Acids

A carboxylic acid contains a carboxyl group, which
• is a carbonyl group (C=O) attached to a hydroxyl group (—OH).
• is found on carbon 1 in carboxylic acids.

\[
\begin{align*}
\text{CH}_3 - &\quad \text{hydroxyl group} \\
&\quad \text{or CH}_3\text{COOH} \\
&\quad \text{carbonyl group}
\end{align*}
\]

IUPAC Names

In the IUPAC names of carboxylic acids
• the -e in the alkane name is replaced with -oic acid.

\[
\begin{align*}
\text{CH}_4 &\quad \text{Methane} &\quad \text{HCOOH} &\quad \text{Methanoic acid} \\
\text{CH}_2=\text{CH}_2 &\quad \text{Ethane} &\quad \text{CH}_3=\text{COOH} &\quad \text{Ethanoic acid}
\end{align*}
\]

• substituents are numbered from the carboxyl carbon 1.

\[
\begin{align*}
\text{CH}_3 &\quad \text{3-methylbutanoic acid}
\end{align*}
\]

Names and Sources of Some Carboxylic Acids

Common Carboxylic Acids

methanoic acid (formic acid)

\[
\begin{align*}
\text{O} &\quad \text{H—C—OH}
\end{align*}
\]

ethanoic acid (acetic acid)

\[
\begin{align*}
\text{O} &\quad \text{CH}_3—\text{C—OH}
\end{align*}
\]

Aromatic Carboxylic Acids

Benzoic acid

• is the aromatic carboxylic acid.
• locates substituents by numbering the ring from carbon 1 in the carboxyl group.

\[
\begin{align*}
\text{CH}_3 &\quad 1-\text{methylbenzoic acid} \\
\text{OH} &\quad \text{Benzoic acid}
\end{align*}
\]
Learning Check

Give the IUPAC names of each compound.

A. \( \text{CH}_3\text{─CH}_2\text{─COOH} \)

\( \text{CH}_3\)  

B. \( \text{CH}_3\text{─CH─CH}_2\text{─COOH} \)

C. \( \text{O} \)

\( \text{C} \)

\( \text{Br} \)

Solution

A. \( \text{CH}_3\text{─CH}_2\text{─COOH} \) propanoic acid

\( \text{CH}_3\)  

B. \( \text{CH}_3\text{─CH─CH}_2\text{─COOH} \) 3-methylbutanoic acid

C. \( \text{O} \)

\( \text{C} \)

\( \text{OH} \)

\( \text{Br} \)

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13.2 Properties of Carboxylic Acids

Polarity of Carboxylic Acids

Carboxylic acids

• are strongly polar.

• have two polar groups:
  - hydroxyl (\(-\text{OH}\)) and
  - carbonyl (\(\text{C}=C\text{O}\)).

Polarity of Carboxylic Acids

Carboxylic acids

• form dimers in which hydrogen bonds form between two carboxyl groups.

\[ \begin{array}{c}
\text{O} \quad \text{H} \quad \text{O} \\
\text{CH}_3\text{─C} \quad \text{C} \quad \text{CH}_3
\end{array} \]

A dimer of acetic acid

• have higher boiling points than alcohols, ketones, and aldehydes of similar mass.

Comparison of Boiling Points

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Mass</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O} )</td>
<td>58</td>
<td>49 °C</td>
</tr>
<tr>
<td>( \text{CH}_2\text{─CH}_2\text{─C─H} )</td>
<td>60</td>
<td>97 °C</td>
</tr>
<tr>
<td>( \text{CH}_2\text{─CH}_2\text{─CH}_2\text{─OH} )</td>
<td>60</td>
<td>118 °C</td>
</tr>
<tr>
<td>( \text{CH}_2\text{─C─OH} )</td>
<td>60</td>
<td>118 °C</td>
</tr>
</tbody>
</table>
Solubility in Water

Carboxylic acids:
- form hydrogen bonds with many water molecules.
- with 1-4 carbon atoms are very soluble in water.

Acidity of Carboxylic Acids

Carboxylic acids
- are weak acids.
- ionize in water to produce carboxylate ions and hydronium ions.

\[
\begin{align*}
\text{CH}_3\text{C}-\text{OH} + \text{H}_2\text{O} & \rightleftharpoons \text{CH}_3\text{C}-\text{O}^- + \text{H}_3\text{O}^+ \\
\end{align*}
\]

Neutralization of Carboxylic Acids

Carboxylic acid salts
- are a product of the neutralization of a carboxylic acid with a strong base.

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

(carboxylic acid salt)
- are used as preservatives and flavor enhancers.

Learning Check

Write the equation for the reaction of propanoic acid with
A. water.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}-\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CH}_2\text{C}-\text{O}^- + \text{H}_3\text{O}^+ \\
\end{align*}
\]

B. KOH.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}-\text{OH} + \text{KOH} & \rightarrow \text{CH}_3\text{CH}_2\text{C}-\text{O}^- \text{K}^+ + \text{H}_2\text{O} \\
\end{align*}
\]

Solution

Write the equation for the reaction of propanoic acid with
A. water.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}-\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CH}_2\text{C}-\text{O}^- + \text{H}_3\text{O}^+ \\
\end{align*}
\]

B. KOH.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}-\text{OH} + \text{KOH} & \rightarrow \text{CH}_3\text{CH}_2\text{C}-\text{O}^- \text{K}^+ + \text{H}_2\text{O} \\
\end{align*}
\]
13.3 Esters

In an ester, the H in the carboxyl group is replaced with an alkyl group.

\[
\text{CH}_3\text{—C—O—CH}_3
\]
ester group

Esterification

Esterification is the reaction of 
• a carboxylic acid and alcohol in the presence of an acid catalyst to produce an ester.

\[
\text{CH}_3\text{—C—OH} + \text{H—O—CH}_2\text{—CH}_3 \xrightarrow{\text{H}^+} \text{CH}_3\text{—C—O—CH}_2\text{—CH}_3 + \text{H}_2\text{O}
\]
Ethyl acetate (an ester)

Learning Check

Write the equation for the reaction of propanoic acid and methanol in the presence of an acid catalyst.

Solution

Write the equation for the reaction of propanoic acid and methanol in the presence of an acid catalyst.

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

Ester Products

Aspirin
• is used to relieve pain and reduce inflammation.
• is an ester of salicylic acid and acetic acid.

Oil of wintergreen
• is used to soothe sore muscles.
• is an ester of salicylic acid and methanol.
Naming Esters

The name of an ester contains the names of:
• the alkyl group from the alcohol.
• the carbon chain from the acid with -ate ending.

methyl ethanoate (acetate)

CH₃—O—C—CH₃

IUPAC: methyl ethanoate
common: methyl acetate

Esters in Plants

Esters give pleasant fragrances and flavors to many fruits and flowers.

Learning Check

Give the IUPAC and common names of the following compound, which is responsible for the flavor and odor of pears.

O

CH₃—C—O—CH₂—CH₂—CH₃

Learning Check

Give the IUPAC and common names of the following compound, which is responsible for the flavor and odor of pears.

O

CH₃—C—O—CH₂—CH₂—CH₃

Solution

Give the IUPAC and common names of the following compound, which is responsible for the flavor and odor of pears.

from 1-propanol

O

CH₃—C—O—CH₂—CH₂—CH₃

propyl ethanoate (IUPAC)
propyl acetate (common)
Solution

A. 3-bromobutanoic acid
\[ \text{CH}_3\text{CH} = \text{CH}_2\text{COOH} \]

B. Ethyl propionate
\[ \text{CH}_3\text{CH}_2\text{C} = \text{O} - \text{CH}_2\text{CH}_3 \]

Acid Hydrolysis of Esters

In acid hydrolysis
- an ester reacts with water to produce a carboxylic acid and an alcohol.
- an acid catalyst is required.

\[ \text{H} - \text{C} = \text{O} - \text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \xrightleftharpoons{\text{H}^+} \text{H} - \text{C} = \text{O} - \text{H} + \text{H} - \text{O} - \text{CH}_2\text{CH}_3 \]

Base Hydrolysis (Saponification)

Base hydrolysis or saponification,
- is the reaction of an ester with a strong base.
- produces the salt of the carboxylic acid and an alcohol.

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

Base Hydrolysis of Fatty Acids Produces Soaps

Base Hydrolysis of Fatty Acids

Cleaning Action of Soap

A soap
- contains a nonpolar end that dissolves in nonpolar fats and oils, and a polar end that dissolves in water.
- forms groups of soap molecules called micelles that dissolve in water and are washed away.

Learning Check

Write the organic products when methyl acetate reacts with
A. water and an acid catalyst.
B. KOH.
Solution

Write the organic products when methyl acetate reacts with
A. water and an acid catalyst.
\[ \text{CH}_3-\text{C}==\text{O} \ \text{OH} \ + \ \text{HO--CH}_3 \]
B. KOH.
\[ \text{CH}_3-\text{C}--\text{O}^- \text{K}^+ \ + \ \text{HO--CH}_3 \]

Amines

Amines are derivatives of ammonia, NH\(_3\).
- contain N attached to one or more alkyl or aromatic groups.

\[
\begin{align*}
\text{CH}_3 \\ 
\text{CH}_3-\text{NH}_2 & \quad \text{CH}_3-\text{NH} & \quad \text{CH}_3-\text{N--CH}_3 \\
\end{align*}
\]

Classification of Amines

Amines are classified as primary, secondary, or tertiary.
- In a primary (1°) amine, one carbon group is bonded to the nitrogen atom.
- A secondary (2°) amine has two carbon groups bonded to the nitrogen atom.
- A tertiary (3°) amine has three carbon groups bonded to the nitrogen atom.

\[
\begin{align*}
\text{CH}_3 & \quad \text{N--H} \\
\text{CH}_3 & \quad \text{N--H} \\
\text{CH}_3 & \quad \text{N--CH}_3 \\
\end{align*}
\]

Models of Amines

The 3-dimensional models show the shapes of amine molecules with one or more alkyl groups bonded to the nitrogen atom.

Naming Amines

Simple amines
- are named as alkylamines.
- list the names of the alkyl groups bonded to the N atom in alphabetical order in front of amine.

\[
\begin{align*}
\text{CH}_3-\text{CH}_2-\text{NH}_2 & \quad \text{Ethylamine} \\
\text{CH}_3-\text{NH}-\text{CH}_3 & \quad \text{Dimethylamine} \\
\text{CH}_3-\text{N--CH}_2-\text{CH}_3 & \quad \text{Ethyltrimethylamine} \\
\end{align*}
\]
Give the common name and classify as primary, secondary, or tertiary.

A. \( \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2 \) propylamine, 1°

B. \( \text{CH}_3-\text{CH}_2-N-\text{CH}_3 \) ethyldimethylamine, 3°

The amine of benzene is named aniline. Alkyl groups on the N use the prefix \( \text{N}^- \) with alkyl name.

A. \( \text{CH}_3-\text{NH}-\text{CH}_2-\text{CH}_3 \) ethylmethylamine

B. \( \text{CH}_3-\text{CH}_2-N-\text{CH}_2-\text{CH}_3 \) diethylmethylamine

C. \( \text{NH}_2 \) aniline

The N–H bond provides hydrogen bonding in 1° and 2° amines, but not in 3° amines. It is not as polar as the O–H bonds in alcohols.
Solubility in Water

Amines
• with 1-6 carbon atoms are soluble in water.
• form hydrogen bonds with the polar O-H bond in water.

Learning Check

Consider the following compounds.
1) CH₃—CH₂—CH₂—NH₂
2) CH₃—CH₂—NH—CH₃
3) CH₃—CH₂—CH₂—CH₃

A. Which compound has the highest boiling point?
B. Which compound is soluble in water?

Solution

Consider the following compounds.
1) CH₃—CH₂—CH₂—NH₂
2) CH₃—CH₂—NH—CH₃
3) CH₃—CH₂—CH₂—CH₃

A. Which compound has the highest boiling point?
1) CH₃—CH₂—CH₂—NH₂

B. Which compound is soluble in water?
1) CH₃—CH₂—CH₂—NH₂
2) CH₃—CH₂—NH—CH₃

Amines React as Bases

Like ammonia, amines are weak bases in water.

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{ammonium hydroxide}
\]

\[
\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{OH}^- \quad \text{methylammonium hydroxide}
\]

Neutralization Forms Amine Salts

An amine salt
• forms when an amine is neutralized by acid.
• is named by replacing the amine part of the name with ammonium, followed by the name of the negative ion.

\[
\text{CH}_3\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{NH}_3^+ \text{Cl}^- \quad \text{methylamine methylammonium chloride}
\]

Properties of Amine Salts

Amine salts are
• solids at room temperature.
• soluble in water and body fluids.
• the form used for drugs.
Alkaloids

Alkaloids are
• physiologically active nitrogen-containing compounds.
• obtained from plants.
• used as anesthetics, antidepressants, and in stimulants such as caffeine.
• often addictive.

Cocaine

Cocaine (from coca leaves) is
• sold illegally as the amine salt.
• reacted with NaOH to produce the free amine form known as “crack.”

Caffeine

Caffeine
• is a stimulant of the central nervous system.
• is found in coffee beans, tea, chocolate, and soft drinks.

Nicotine

Nicotine
• increases the adrenaline level in the blood.
• causes addiction to tobacco.

Morphine and Codeine

Morphine and codeine are
• alkaloids.
• obtained from the oriental poppy plant.
• used as painkillers.
• modified to make heroin.

Learning Check

Write the structural formula for
A. methylpropylamine
B. 2-chloroaniline
Solution

A. methylpropylamine  \( \text{CH}_3\text{–CH}_2\text{–CH}_2\text{–NH–CH}_3 \)
B. 2-chloroaniline

Chapter 13  Carboxylic Acids, Esters, Amines, and Amides

13.5 Amides

Amides

In amides,
- an amino group (–NH\(_2\)) replaces the –OH group of carboxylic acids.

\[
\text{CH}_3\text{–C–OH} \quad \text{Carboxylic acid} \quad \text{CH}_3\text{–C–NH}_2 \quad \text{Amide}
\]

Aromatic Amide

The aromatic amine is benzamide.

\[
\text{O} \\
\text{O} \\
\text{C} \\
\text{NH}_2 \\
\text{Benzamide}
\]

Preparation of Amides

Amides are produced
- by reacting a carboxylic acid with ammonia or an amine (1° or 2°).
- using heat.

\[
\text{CH}_3\text{–C–OH} + \text{NH}_3 \xrightarrow{\text{Heat}} \text{CH}_3\text{–C–NH}_2 + \text{H}_2\text{O}
\]

\[
\text{O} \\
\text{O} \\
\text{H–C–NH}_2 \quad \text{Methanamide (IUPAC)}
\]

\[
\text{O} \\
\text{O} \\
\text{CH}_3\text{–CH}_2\text{–C–NH}_2 \quad \text{Propionamide (IUPAC)}
\]

Naming Amides

Amides are named as alkanamides.
- IUPAC replaces –oic acid ending with –amide.
- Common names replace -ic acid ending with –amide.

\[
\text{O} \\
\text{O} \\
\text{H–C–NH}_2 \quad \text{Formamide (common)}
\]

\[
\text{O} \\
\text{O} \\
\text{CH}_3\text{–CH}_2\text{–C–NH}_2 \quad \text{Propanamide (common)}
\]
An alkyl group bonded to the N atom is named as \textit{N-alkyl} in front of the amide name.

\[
\begin{align*}
\text{CH}_3\text{–C–N–CH}_3 & \quad \text{\textit{N-methylethanamide} (IUPAC)} \\
\text{CH}_3\text{–CH}_2\text{–C–N–CH}_2\text{–CH}_3 & \quad \text{\textit{N-ethylpropanamide} (IUPAC)} \\
\end{align*}
\]

\[
\begin{align*}
\text{N-ethylacetamide (common)} \\
\text{N-methylacetamide (common)}
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{CH}_3\text{–CH}_2\text{–CH}_2\text{–C–NH}_2 & \quad \text{butanamide; butryamide} \\
\text{O} & \quad \text{H} \\
\text{CH}_3\text{–C–N–CH}_2\text{–CH}_3 & \quad \text{\textit{N-ethylethanamide}; \textit{N-ethylacetamide}}
\end{align*}
\]

\[
\begin{align*}
\text{A.} & \quad \text{CH}_3\text{–CH}_2\text{–CH}_2\text{–C–NH}_2 \\
\text{B.} & \quad \text{CH}_3\text{–C–N–CH}_2\text{–CH}_3
\end{align*}
\]

Some Amides in Health and Medicine

- Urea is the end product of protein metabolism.
- Saccharin is an artificial sweetener.
- Some amides such as phenobarbital, Nembutal\textsuperscript{TM} and Seconal\textsuperscript{TM} are barbiturates.
- Acetaminophen is used to reduce fever and pain.
Some Amides in Health and Medicine

Physical Properties of Amides

Amides

- that are primary (−NH₂) or secondary (−NH−) form hydrogen bonds.
- that are primary have higher melting points than secondary.
- that are tertiary (no H on N) do not form hydrogen bonds and have lower melting points.
- all form hydrogen bonds with water.
- with 1-5 carbon atoms are soluble in water.

Hydrogen Bonding of Amides

Amides undergo

- acid hydrolysis to produce a carboxylic acid and an ammonium salt.
- base hydrolysis to produce the salt of a carboxylic acid and an amine or ammonia.

Hydrolysis of Amides

Hydrolysis Reactions

Learning Check

Write the products of the hydrolysis of N-ethylpropanamide with NaOH.
Solution

Write the products of the hydrolysis of N-ethylpropanamide with NaOH.

\[ \text{CH}_3\text{—CH}_2\text{—C—O—Na}^+ + \text{CH}_3\text{—CH}_2\text{—NH}_2 \]