

15: ORGANIC ACIDS AND BASES AND SOME OF THEIR DERIVATIVES



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CHAPTER OVERVIEW

15: Organic Acids and Bases and Some of Their Derivatives

Organic acids have been known for ages. Prehistoric people likely made acetic acid when their fermentation reactions went awry and produced vinegar instead of wine. The Sumerians (2900–1800 BCE) used vinegar as a condiment, a preservative, an antibiotic, and a detergent. Citric acid was discovered by an Islamic alchemist, Jabir Ibn Hayyan (also known as Geber), in the 8th century, and crystalline citric acid was first isolated from lemon juice in 1784 by the Swedish chemist Carl Wilhelm Scheele. Medieval scholars in Europe were aware that the crisp, tart flavor of citrus fruits is caused by citric acid. Naturalists of the 17th century knew that the sting of a red ant's bite was due to an organic acid that the ant injected into the wound. The acetic acid of vinegar, the formic acid of red ants, and the citric acid of fruits all belong to the same family of compounds—carboxylic acids. Soaps are salts of long-chain carboxylic acids. Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays. The organic compounds that we consider in this chapter are organic acids and bases. We will also consider two derivatives of carboxylic acids: esters and amides. An ester is derived from a carboxylic acid and an alcohol. Fats and oils are esters, as are many important fragrances and flavors. An amide is derived from a carboxylic acid and either ammonia or an amine. Proteins, often called “the stuff of life,” are polyamides.

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15.0: Prelude to Organic Acids and Bases and Some of Their Derivatives

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15.1: Carboxylic Acids - Structures and Names

Learning Objectives

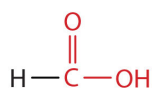
- Name carboxylic acids with common names.
- Name carboxylic acids according to IUPAC nomenclature.

Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure 15.1.1). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



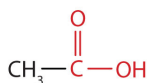
Figure 15.1.1: Carboxylic Acids in the Home. Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock

The simplest carboxylic acid, formic acid (HCOOH), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



Formic acid

The next higher homolog is acetic acid, which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Acetic acid

Pure acetic acid solidifies at 16.6°C , only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often “froze” on the storage shelf. For that

reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$), is seldom encountered in everyday life. The fourth homolog, butyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives. Models of the first four carboxylic acids are shown in Figure 15.1.2

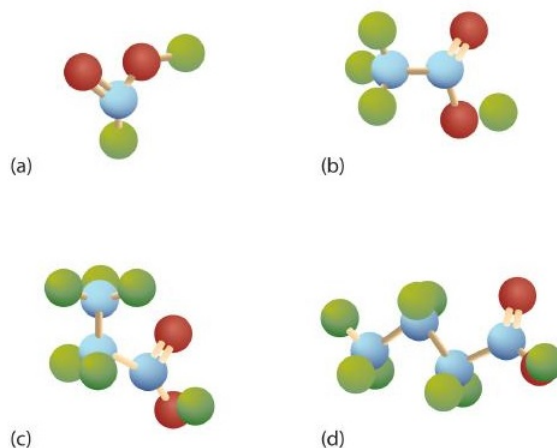
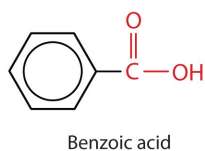
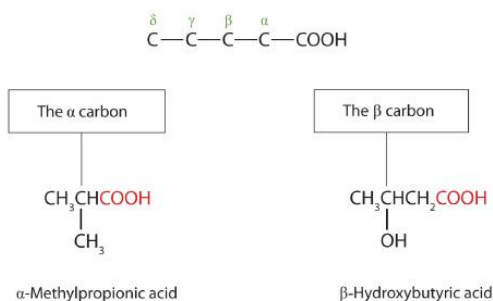


Figure 15.1.2: Ball-and-Stick Models of Carboxylic Acids. Carboxylic acids feature a carbon atom doubly bonded to an oxygen atom and also joined to an OH group. The four acids illustrated here are formic acid (a), acetic acid (b), propionic acid (c), and butyric acid (d).

The acid with the carboxyl group attached directly to a benzene ring is called benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$).



The common names of carboxylic acids use Greek letters (α , β , γ , δ , and so forth), not numbers, to designate the position of substituent groups in acids. These letters refer to the position of the carbon atom in relation to the carboxyl carbon atom.

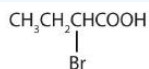
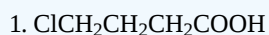


In the nomenclature system of the International Union of Pure and Applied Chemistry (IUPAC), the parent hydrocarbon is the one that corresponds to the longest continuous chain (LCC) containing the carboxyl group. The *-e* ending of the parent alkane is replaced by the suffix *-oic* and the word *acid*. For example, the carboxylic acid derived from pentane is pentanoic acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$). As with aldehydes, the carboxyl carbon atom is counted first; numbers are used to indicate any substituted carbon atoms in the parent chain.

Greek letters are used with common names; numbers are used with IUPAC names.

✓ Example 15.1.1

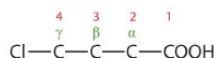
Give the common and IUPAC names for each compound.



2.

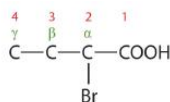
Solution

1. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The chlorine atom is attached to the γ -carbon in the common system or C4 in the IUPAC system. The compound is γ -chlorobutyric acid or 4-chlorobutanoic acid.

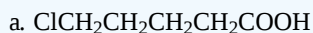
2. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The bromine (Br) atom is at the α -carbon in the common system or C2 in the IUPAC system. The compound is α -bromobutyric acid or 2-bromobutanoic acid.

? Exercise 15.1.1

Give the IUPAC name for each compound.



✓ Example 15.1.2

Write the condensed structural formula for β -chloropropionic acid.

Solution

Propionic acid has three carbon atoms: $\text{C}-\text{C}-\text{COOH}$. Attach a chlorine (Cl) atom to the parent chain at the beta carbon atom, the second one from the carboxyl group: $\text{Cl}-\text{C}-\text{C}-\text{COOH}$. Then add enough hydrogen atoms to give each carbon atom four bonds: $\text{ClCH}_2\text{CH}_2\text{COOH}$.

? Exercise 15.1.2

Write the condensed structural formula for 4-bromo-5-methylhexanoic acid.

Key Takeaways

- Simple carboxylic acids are best known by common names based on Latin and Greek words that describe their source (e.g., formic acid, Latin *formica*, meaning “ant”).
- Greek letters, not numbers, designate the position of substituted acids in the common naming convention.
- IUPAC names are derived from the LCC of the parent hydrocarbon with the *-e* ending of the parent alkane replaced by the suffix *-oic* and the word *acid*.

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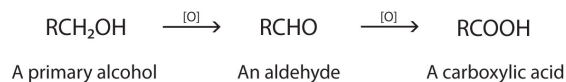
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15.2: The Formation of Carboxylic Acids

Learning Objectives

- To describe the preparation of carboxylic acids.

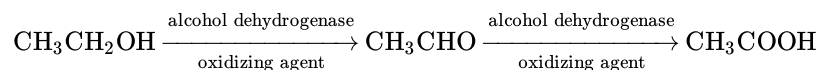
As we noted previously, the oxidation of aldehydes or primary alcohols forms carboxylic acids:



In the presence of an oxidizing agent, ethanol is oxidized to acetaldehyde, which is then oxidized to acetic acid.



This process also occurs in the liver, where enzymes catalyze the oxidation of ethanol to acetic acid.



Acetic acid can be further oxidized to carbon dioxide and water.

Summary

Whether in the laboratory or in the body, the oxidation of aldehydes or primary alcohols forms carboxylic acids.

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15.3: Physical Properties of Carboxylic Acids

Learning Objectives

- Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
- Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have “goaty” odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure 15.3.1). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$\text{CH}_3(\text{CH}_2)_4\text{COOH}$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

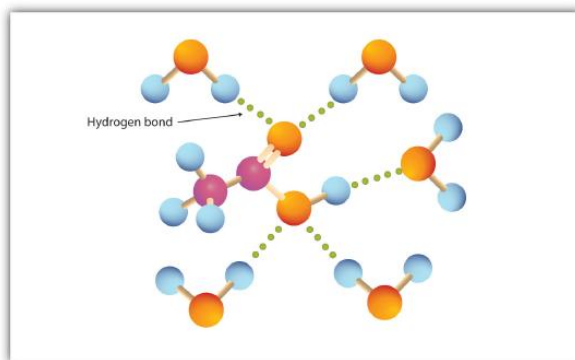


Figure 15.3.1: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 15.4.1 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table 15.3.1: Physical Constants of Carboxylic Acids

Condensed Structural Formula	Name of Acid	Melting Point (°C)	Boiling Point (°C)	Solubility (g/100 g of Water)
HCOOH	formic acid	8	100	miscible
CH ₃ COOH	acetic acid	17	118	miscible
CH ₃ CH ₂ COOH	propionic acid	-22	141	miscible
CH ₃ (CH ₂) ₂ COOH	butyric acid	-5	163	miscible
CH ₃ (CH ₂) ₃ COOH	valeric acid	-35	187	5
CH ₃ (CH ₂) ₄ COOH	caproic acid	-3	205	1.1
C ₆ H ₅ COOH	benzoic acid	122	249	0.29

Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

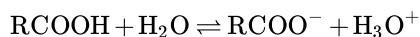
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15.4: Chemical Properties of Carboxylic Acids- Ionization and Neutralization

Learning Objectives

- Name the typical reactions that take place with carboxylic acids.
- Describe how carboxylic acids react with basic compounds.

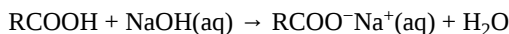
Water-soluble carboxylic acids ionize slightly in water to form moderately acidic solutions.



Their aqueous solutions exhibit the typical properties of acids, such as changing litmus from blue to red.

The anion formed when a carboxylic acid dissociates is called the *carboxylate* anion (RCOO^-).

Whether soluble in water or not, carboxylic acids react with aqueous solutions of sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate (NaHCO_3) to form salts:



In these reactions, the carboxylic acids act like inorganic acids: they neutralize basic compounds. With solutions of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions, they also form carbon dioxide gas.

Carboxylic acid salts are named in the same manner as inorganic salts: the name of the cation is followed by the name of the organic anion. The name of the anion is obtained by dropping the *-ic* ending of the acid name and replacing it with the suffix *-ate*. This rule applies whether we are using common names or International Union of Pure and Applied Chemistry (IUPAC) names:

$\text{CH}_3\text{COO}^-\text{Li}^+$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-\text{K}^+$	$\text{C}_6\text{H}_5\text{COO}^-\text{Na}^+$
Lithium acetate (lithium ethanoate)	Potassium butyrate (potassium butanoate)	Sodium benzoate

The salts of long-chain carboxylic acids are called soaps. We discuss the chemistry of soaps elsewhere.



Sodium palmitate (a soap)

✓ Example 15.4.1

Write an equation for each reaction.

- the ionization of propionic acid in water (H_2O)
- the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

Solution

Propionic acid has three carbon atoms, so its formula is $\text{CH}_3\text{CH}_2\text{COOH}$.

- Propionic acid ionizes in water to form a propionate ion and a hydronium (H_3O^+) ion. $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- Propionic acid reacts with $\text{NaOH}(\text{aq})$ to form sodium propionate and water. $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell)$

? Exercise 15.4.1

Write an equation for each reaction.

- the ionization of formic acid in water
- the ionization of *p*-chlorobenzoic acid in water

✓ Example 15.4.2

Write an equation for the reaction of decanoic acid with each compound.

- aqueous sodium hydroxide (NaOH)
- aqueous sodium bicarbonate (NaHCO₃)

Solution

- Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water (H₂O). $\text{CH}_3(\text{CH}_2)_8\text{COOH} + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3(\text{CH}_2)_8\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell)$
- With NaHCO₃, the products are a salt, H₂O, and carbon dioxide (CO₂). $\text{CH}_3(\text{CH}_2)_8\text{COOH} + \text{NaHCO}_3(\text{aq}) \rightarrow \text{CH}_3(\text{CH}_2)_8\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$

? Exercise 15.4.3

Write an equation for the reaction of benzoic acid with each compound.

- aqueous sodium hydroxide (NaOH)
- aqueous sodium bicarbonate (NaHCO₃)

📌 To Your Health: Organic Salts as Preservatives

Some organic salts are used as preservatives in food products. They prevent spoilage by inhibiting the growth of bacteria and fungi. Calcium and sodium propionate, for example, are added to processed cheese and bakery goods; sodium benzoate is added to cider, jellies, pickles, and syrups; and sodium sorbate and potassium sorbate are added to fruit juices, sauerkraut, soft drinks, and wine. Look for them on ingredient labels the next time you shop for groceries.



Calcium propionate



Potassium sorbate

Key Takeaways

- Soluble carboxylic acids are weak acids in aqueous solutions.
- Carboxylic acids neutralize bases to form salts.

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15.5: Esters - Structures and Names

Learning Objectives

- Identify the general structure for an ester.
- Use common names to name esters.
- Name esters according to the IUPAC system.

Esters have the general formula RCOOR' , where R may be a hydrogen atom, an alkyl group, or an aryl group, and R' may be an alkyl group or an aryl group but *not* a hydrogen atom. (If it were hydrogen atom, the compound would be a carboxylic acid.) Figure 15.5.1 shows models for two common esters.

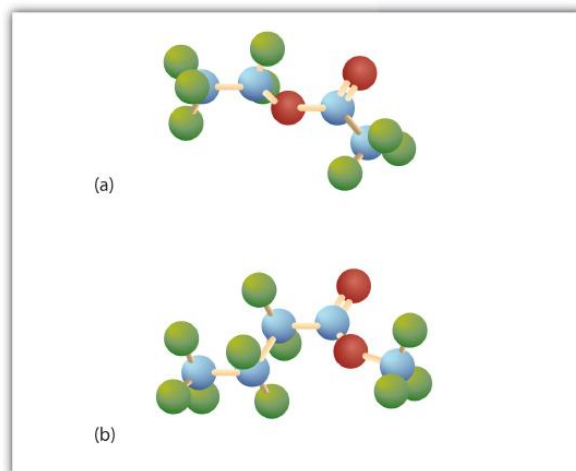


Figure 15.5.1: The Structure of Esters. Esters feature a carbon-to-oxygen double bond that is also singly bonded to a second oxygen atom, which is then joined to an alkyl or an aryl group. The esters shown here are ethyl acetate (a) and methyl butyrate (b).

Esters occur widely in nature. Unlike carboxylic acids, esters generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers. Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.

Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

Names of Esters

Although esters are covalent compounds and salts are ionic, esters are named in a manner similar to that used for naming salts. The group name of the alkyl or aryl portion is given first and is followed by the name of the acid portion. In both common and International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the *-ic* ending of the parent acid is replaced by the suffix *-ate* (Table 15.5.1).

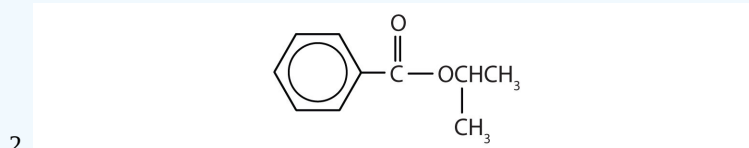
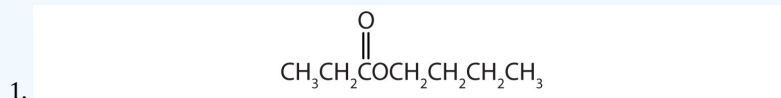
Table 15.5.1: Nomenclature of Esters

Condensed Structural Formula	Common Name	IUPAC Name
HCOOCH_3	methyl formate	methyl methanoate
$\text{CH}_3\text{COOCH}_3$	methyl acetate	methyl ethanoate
$\text{CH}_3\text{COOCH}_2\text{CH}_3$	ethyl acetate	ethyl ethanoate
$\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$	ethyl propionate	ethyl propanoate
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}(\text{CH}_3)_2$	isopropyl butyrate	isopropyl butanoate

Condensed Structural Formula	Common Name	IUPAC Name
	ethyl benzoate	ethyl benzoate

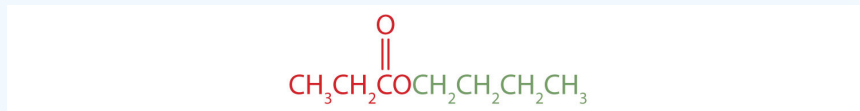
✓ Example 15.5.1

Give the common and IUPAC names for each compound.



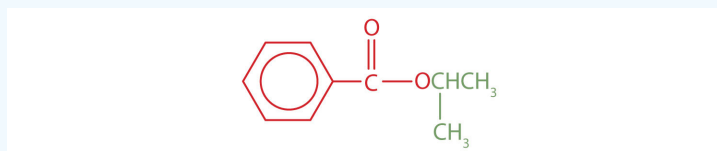
Solution

The alkyl group attached directly to the oxygen atom is a butyl group (in green).



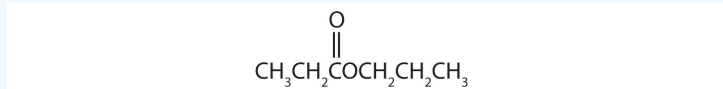
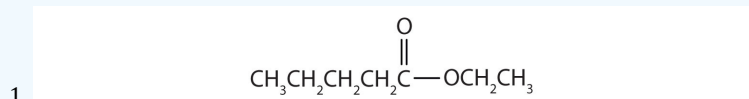
The part of the molecule derived from the carboxylic acid (in red) has three carbon atoms. It is called propionate (common) or propanoate (IUPAC). The ester is therefore butyl propionate or butyl propanoate.

1. An alkyl group (in green) is attached directly to the oxygen atom by its middle carbon atom; it is an isopropyl group. The part derived from the acid (that is, the benzene ring and the carbonyl group, in red) is benzoate. The ester is therefore isopropyl benzoate (both the common name and the IUPAC name).



? Exercise 15.5.1

Give the common and IUPAC names for each compound.

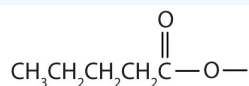


✓ Example 15.5.2

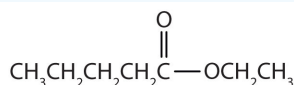
Draw the structure for ethyl pentanoate.

Solution

Start with the portion from the acid. Draw the pentanoate (five carbon atoms) group first; keeping in mind that the last carbon atom is a part of the carboxyl group.



Then attach the ethyl group to the bond that ordinarily holds the hydrogen atom in the carboxyl group.



? Exercise 15.5.2

Draw the structure for phenyl pentanoate.

Key Takeaway

- An ester has an OR group attached to the carbon atom of a carbonyl group.

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15.6: Physical Properties of Esters

Learning Objectives

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table 15.6.1 lists the physical properties of some common esters.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer “dries,” leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Table 15.6.1: Physical Properties of Some Esters

Condensed Structural Formula	Name	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Aroma
HCOOCH ₃	methyl formate	60	-99	32	
HCOOCH ₂ CH ₃	ethyl formate	74	-80	54	rum
CH ₃ COOCH ₃	methyl acetate	74	-98	57	
CH ₃ COOCH ₂ CH ₃	ethyl acetate	88	-84	77	
CH ₃ CH ₂ CH ₂ COOCH ₃	methyl butyrate	102	-85	102	apple
CH ₃ CH ₂ CH ₂ COOCH ₂ CH ₃	ethyl butyrate	116	-101	121	pineapple
CH ₃ COO(CH ₂) ₄ CH ₃	pentyl acetate	130	-71	148	pear
CH ₃ COOCH ₂ CH ₂ CH(CH ₃) ₂	isopentyl acetate	130	-79	142	banana
CH ₃ COOCH ₂ C ₆ H ₅	benzyl acetate	150	-51	215	jasmine
CH ₃ CH ₂ CH ₂ COO(C ₂ H ₅) ₄ CH ₃	pentyl butyrate	158	-73	185	apricot
CH ₃ COO(CH ₂) ₇ CH ₃	octyl acetate	172	-39	210	orange

Summary

Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

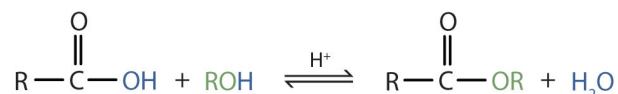
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15.7: Preparation of Esters

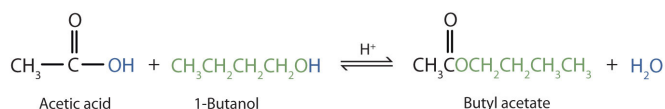
Learning Objectives

- To identify and describe the substances from which most esters are prepared.

Some esters can be prepared by esterification, a reaction in which a carboxylic acid and an alcohol, heated in the presence of a mineral acid catalyst, form an ester and water:



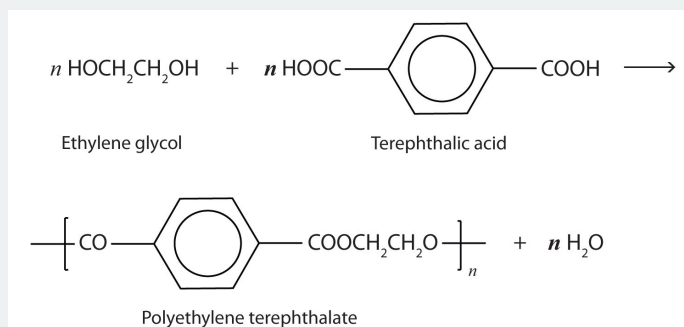
The reaction is reversible. As a specific example of an esterification reaction, butyl acetate can be made from acetic acid and 1-butanol.



A Closer Look: Condensation Polymers

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:



Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

Summary

Esters are made by the reaction of a carboxylic acid with an alcohol, a process that is called esterification.

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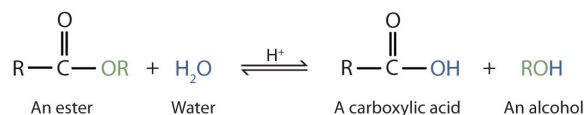
15.8: Hydrolysis of Esters

Learning Objectives

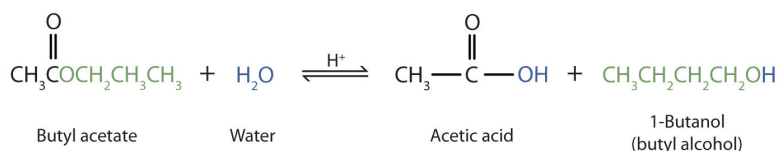
- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

Esters are neutral compounds, unlike the acids from which they are formed. In typical reactions, the alkoxy (OR') group of an ester is replaced by another group. One such reaction is hydrolysis, literally “splitting with water.” The hydrolysis of esters is catalyzed by either an acid or a base.

Acidic hydrolysis is simply the reverse of **esterification**. The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.



As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.

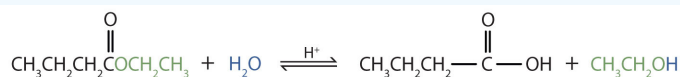


✓ Example 15.8.1

Write an equation for the acidic hydrolysis of ethyl butyrate ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$) and name the products.

Solution

Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:

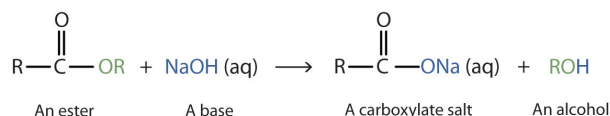


The products are butyric acid (butanoic acid) and ethanol.

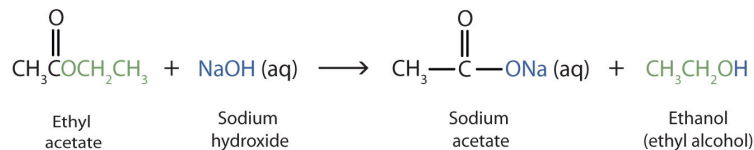
? Exercise 15.8.1

Write an equation for the acidic hydrolysis of methyl butanoate and name the products.

When a base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is used to hydrolyze an ester, the products are a carboxylate salt and an alcohol. Because soaps are prepared by the alkaline hydrolysis of fats and oils, alkaline hydrolysis of esters is called saponification (Latin *sapon*, meaning “soap,” and *facere*, meaning “to make”). In a saponification reaction, the base is a reactant, not simply a catalyst. The reaction goes to completion:



As a specific example, ethyl acetate and NaOH react to form sodium acetate and ethanol:

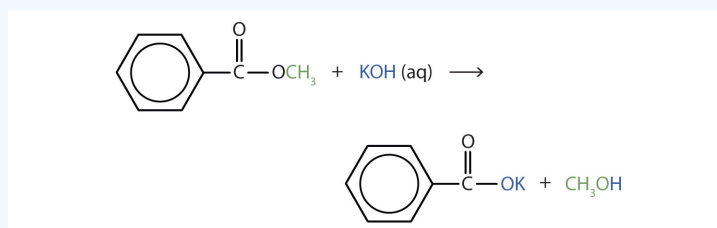


✓ Example 15.8.2

Write an equation for the hydrolysis of methyl benzoate in a potassium hydroxide solution.

Solution

In basic hydrolysis, the molecule of the base splits the ester linkage. The acid portion of the ester ends up as the *salt* of the acid (in this case, the potassium salt). The alcohol portion of the ester ends up as the free alcohol.



? Exercise 15.8.2

Write the equation for the hydrolysis of ethyl propanoate in a sodium hydroxide solution.

Summary

Hydrolysis is a most important reaction of esters. Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Basic hydrolysis of an ester gives a carboxylate salt and an alcohol.

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15.9: Esters of Phosphoric Acid

do, inorganic acids such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4) also form esters. The esters of phosphoric acid are especially important in . A phosphoric acid can form a monoalkyl, a dialkyl, or a trialkyl by reaction with one, two, or three molecules of an . . . The bonds between phosphate units in adenosine triphosphate (ATP) are called . These are high-bonds that store from the metabolism of foods. of ATP releases as it is needed for biochemical processes (for instance, for muscle contraction). Phosphate esters are also important structural constituents of phospholipids and nucleic acids. .

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15.10: Amines - Structures and Names

Learning Objectives

- Identify the general structure for an amine.
- Identify the functional group for amines.
- Determine the structural feature that classifies amines as primary, secondary, or tertiary.
- Use nomenclature systems to name amines.

Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three (Figure 15.10.1).

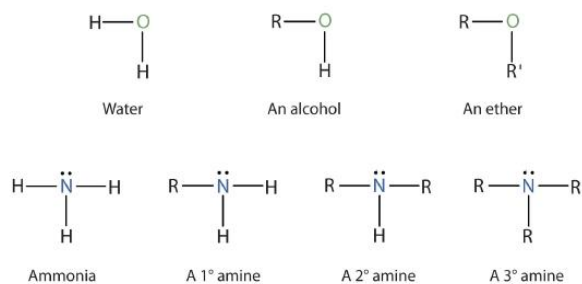
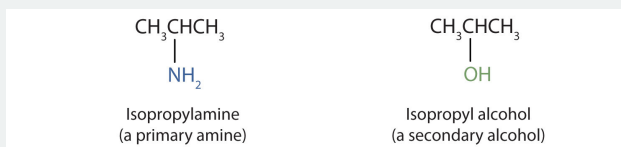


Figure 15.10.1: The Structure of Amines Compared to Water, an Alcohol, and an Ether

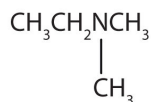
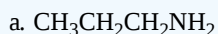
To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although isopropylamine looks similar to isopropyl alcohol, the former is a *primary* amine, while the latter is a *secondary* alcohol.



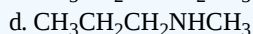
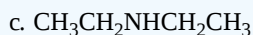
The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*. (Systematic names are often used by some chemists.) The amino group (NH_2) is named as a substituent in more complicated amines, such as those that incorporate other functional groups or in which the alkyl groups cannot be simply named.

✓ Example 15.10.1

Name and classify each compound.



b.



Solution

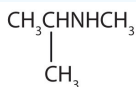
- a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.

- b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.
- c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.
- d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

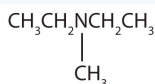
? Exercise 15.10.1

Name and classify each compound.

a.



b.



c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

d. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$

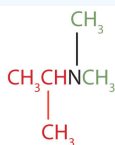
✓ Example 15.10.2

Draw the structure for each compound and classify.

- a. isopropyldimethylamine
- b. dipropylamine

Solution

- a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



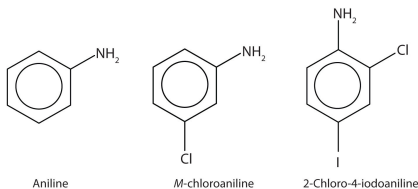
- b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$

? Exercise 15.10.2

Draw the structure for each compound and classify.

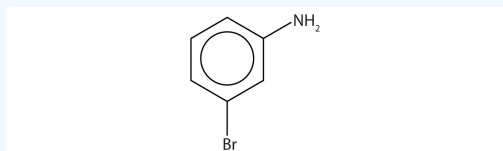
- a. ethylisopropylamine
- b. diethylpropylamine

The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—**aniline**. Aryl amines are named as derivatives of aniline.



✓ Example 15.10.3

Name this compound.

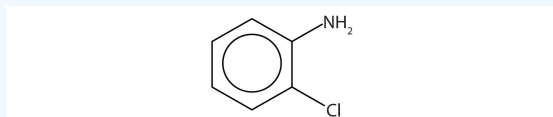


Solution

The benzene ring with an amino (NH₂) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

? Exercise 15.10.3

Name this compound.

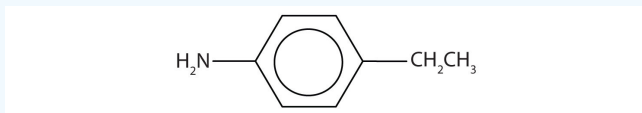


✓ Example 15.10.4

Draw the structure for *p*-ethylaniline and classify.

Solution

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino (NH₂) group.



? Exercise 15.10.4

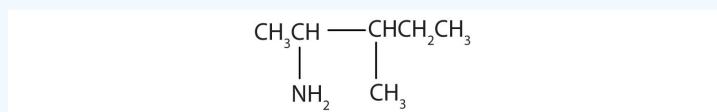
Draw the structure for *p*-isopropylaniline and classify.

✓ Example 15.10.5

Draw the structure for 2-amino-3-methylpentane.

Solution

Always start with the parent compound: draw the pentane chain. Then attach a methyl group at the third carbon atom and an amino group at the second carbon atom.



? Exercise 15.10.5

Draw the structure for 2-amino-3-ethyl-1-chloroheptane.

Ammonium (NH_4^+) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the NH_4^+ ion. For example, CH_3NH_3^+ is the methylammonium ion. The ion formed from aniline ($\text{C}_6\text{H}_5\text{NH}_3^+$) is called the anilinium ion.

✓ Example 15.10.6

Name each ion.

- CH_3NH_3^+
- $(\text{CH}_3)_2\text{NH}_2^+$
- $(\text{CH}_3)_3\text{NH}^+$
- $(\text{CH}_3)_4\text{N}^+$

Solution

The ions have one, two, three, and four methyl (CH_3) groups attached to a nitrogen atom. Their names are as follows:

- methylammonium ion
- dimethylammonium ion
- trimethylammonium ion
- tetramethylammonium ion

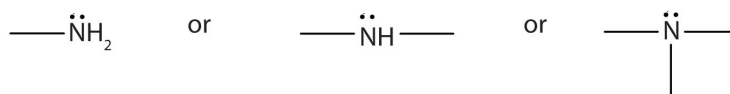
? Exercise 15.10.6

Name each ion.

- $\text{CH}_3\text{CH}_2\text{NH}_3^+$
- $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$
- $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2^+$
- $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$

Summary

An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The amine functional group is as follows:



Amines are classified as primary, secondary, or tertiary by the number of hydrocarbon groups attached to the nitrogen atom. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

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15.11: Physical Properties of Amines

Learning Objectives

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to a nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure 15.11.1), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2 ; -6°C) with those of ethane (CH_3CH_3 ; -89°C) and methanol (CH_3OH ; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table 15.11.1).

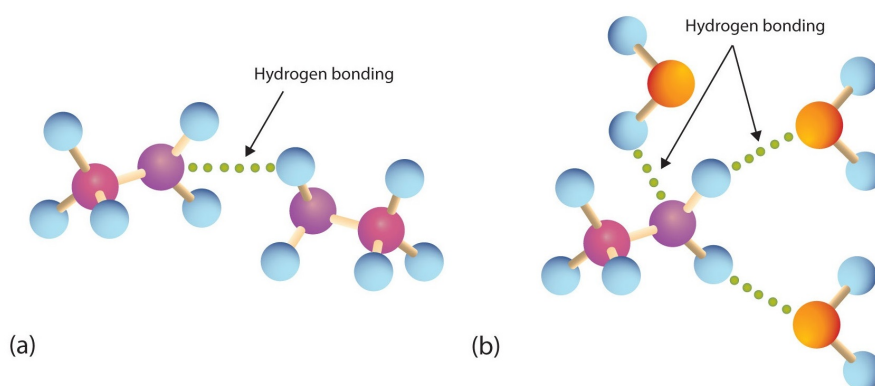


Figure 15.11.1: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

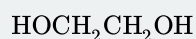
Table 15.11.1: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

Name	Condensed Structural Formula	Class	Molar Mass	Boiling Point ($^\circ\text{C}$)	Solubility at 25°C (g/100 g Water)
butylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	1°	73	78	miscible
diethylamine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	2°	73	55	miscible
butyl alcohol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	—	74	118	8
dipropylamine	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$	2°	101	111	4
triethylamine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	3°	101	90	14
dipropyl ether	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{O}$	—	102	91	0.25

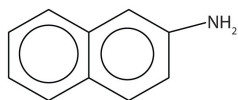
All three classes of amines can engage in hydrogen bonding with water (Figure 15.11.1b). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.



Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β -naphthylamine, are potent carcinogens.



Key Takeaways

- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

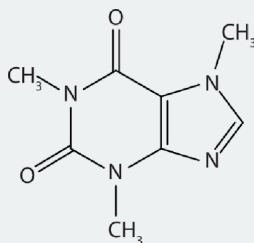
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Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means “like alkalis.” Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

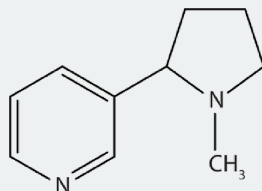
📌 To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



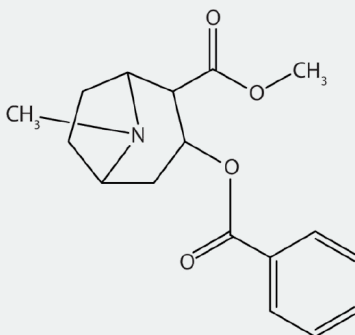
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



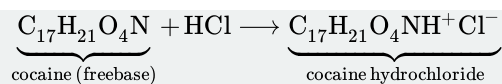
Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine’s “high” and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.



Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.



Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

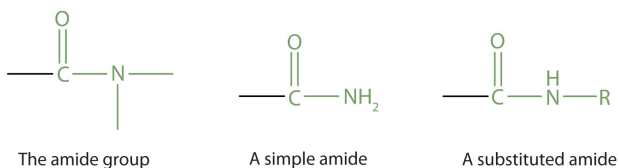
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15.13: Amides- Structures and Names

Learning Objectives

- Identify the general structure for an amide.
- Identify the functional group for an amide.
- Name amides with common names.
- Name amides according to the IUPAC system.

The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.



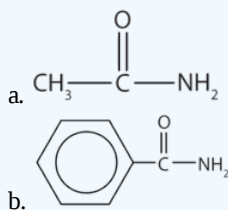
The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



✓ Example 15.13.1

Name each compound with the common name, the IUPAC name, or both.

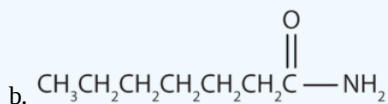
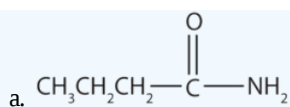


Solution

- This amide has two carbon atoms and is thus derived from acetic acid. The OH of acetic acid is replaced by an NH₂ group. The *-ic* from *acetic* (or *-oic* from ethanoic) is dropped, and *-amide* is added to give *acetamide* (or ethanamide in the IUPAC system).
- This amide is derived from benzoic acid. The *-oic* is dropped, and *-amide* is added to give benzamide.

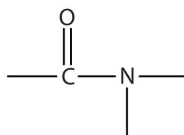
? Exercise 15.13.1

Name each compound with the common name, the IUPAC name, or both.



Key Takeaways

- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.
- The functional group for an amide is as follows:



- In names for amides, the *-ic acid* of the common name or the *-oic* ending of the IUPAC for the corresponding carboxylic acid is replaced by *-amide*.

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15.14: Physical Properties of Amides

Learning Objectives

- Compare the boiling points of amides with alcohols of similar molar mass.
- Compare the solubilities in water of amides of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

With the exception of formamide (HCONH_2), which is a liquid, all simple amides are solids (Table 15.14.1). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

Table 15.14.1: *Physical Constants of Some Unsubstituted Amides*

Condensed Structural Formula	Name	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)	Solubility in Water
HCONH_2	formamide	2	193	soluble
CH_3CONH_2	acetamide	82	222	soluble
$\text{CH}_3\text{CH}_2\text{CONH}_2$	propionamide	81	213	soluble
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$	butyramide	115	216	soluble
$\text{C}_6\text{H}_5\text{CONH}_2$	benzamide	132	290	slightly soluble

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure 15.14.1). (Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid [DNA], ribonucleic acid [RNA], and other giant molecules so important to life processes.

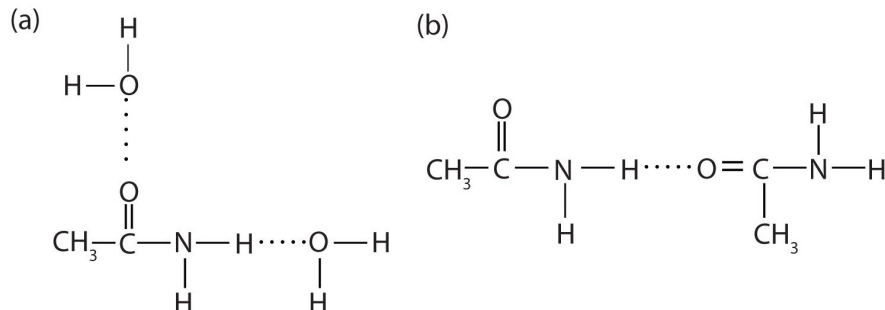


Figure 15.14.1: Hydrogen Bonding in Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.

Key Takeaways

- Most amides are solids at room temperature; the boiling points of amides are much higher than those of alcohols of similar molar mass.
- Amides of five or fewer carbon atoms are soluble in water?.

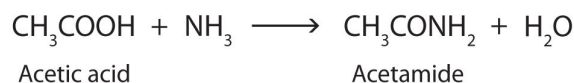
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15.15: Formation of Amides

Learning Objectives

- To describe the preparation procedure for amides.

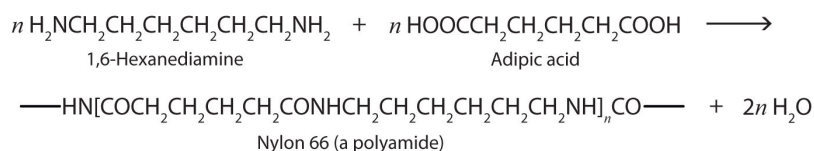
The addition of ammonia (NH₃) to a carboxylic acid forms an amide, but the reaction is very slow in the laboratory at room temperature. Water molecules are split out, and a bond is formed between the nitrogen atom and the carbonyl carbon atom.



In living cells, amide formation is catalyzed by enzymes. Proteins are polyamides; they are formed by joining amino acids into long chains. In proteins, the amide functional group is called a *peptide bond*.

Polyamides

Just as the reaction of a diol and a diacid forms a polyester, the reaction of a diacid and a diamine yields a polyamide. The two difunctional monomers often employed are adipic acid and 1,6-hexanediamine. The monomers condense by splitting out water to form a new product, which is still difunctional and thus can react further to yield a polyamide polymer.



Some polyamides are known as *nylons*. Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. They also can be molded into blocks for use in electrical equipment, gears, bearings, and valves.

Key Takeaway

- Amides are prepared by the reaction of a carboxylic acid with ammonia or an amine.

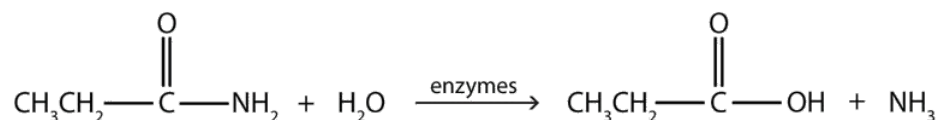
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15.16: Chemical Properties of Amides- Hydrolysis

Learning Objectives

- To identify the typical reaction that amides undergo.

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:



Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.

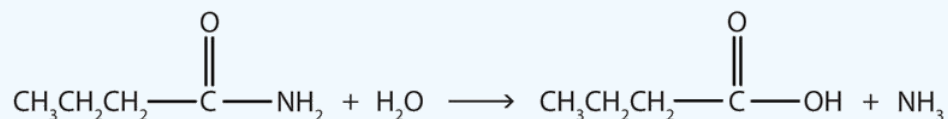
✓ Example 15.16.1

Write the equation for the hydrolysis of each compound.

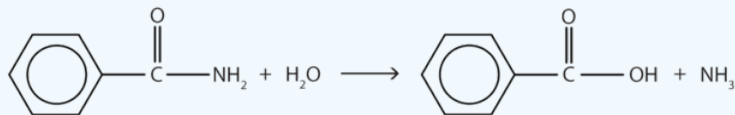
- butyramide
- benzamide

Solution

- The hydrolysis of a simple amide produces an organic acid and ammonia. Butyramide thus yields butyric acid and ammonia.



- The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.



? Exercise 15.16.1

Write the equation for the hydrolysis of each compound.

- propionamide (propanamide)
- hexanamide

📌 Career Focus: Athletic Trainer

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology,

chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

Key Takeaway

- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

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15.S: Organic Acids and Bases and Some of Their Derivatives (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.

A **carboxylic acid** (RCOOH) contains the functional group COOH , called the **carboxyl group**, which has an OH group attached to a carbonyl carbon atom. An **ester** (RCOOR') has an OR' group attached to a carbonyl carbon atom. An **amine** is derived from ammonia (NH_3), with one, two, or all three of the hydrogen atoms of NH_3 replaced by an alkyl (or an aryl) group. The **amide** functional group has a carbonyl group joined to a nitrogen atom from NH_3 or an amine.

There are many familiar carboxylic acids. The R group may be a hydrogen atom (as in formic acid, HCOOH), an alkyl group (as in acetic acid, CH_2COOH), or an aryl group (as in benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$). The location of substituents along the carbon chain is indicated by a Greek letter (for common names) or a number (for names from the International Union of Pure and Applied Chemistry).

A carboxylic acid is formed by the oxidation of an aldehyde with the same number of carbon atoms. Because aldehydes are formed from primary alcohols, these alcohols are also a starting material for carboxylic acids.

Carboxylic acids have strong, often disagreeable, odors. They are highly polar molecules and readily engage in hydrogen bonding, so they have relatively high boiling points.

Carboxylic acids are weak acids. They react with bases to form salts and with carbonates and bicarbonates to form carbon dioxide gas and the salt of the acid.

Esters are pleasant-smelling compounds that are responsible for the fragrances of flowers and fruits. They have lower boiling points than comparable carboxylic acids because, even though ester molecules are somewhat polar, they cannot engage in hydrogen bonding. However, with water, esters can engage in hydrogen bonding; consequently, the low molar mass esters are soluble in water. Esters can be synthesized by **esterification**, in which a carboxylic acid and an alcohol are combined under acidic conditions. Esters are neutral compounds that undergo **hydrolysis**, a reaction with water. Under acidic conditions, hydrolysis is essentially the reverse of esterification. When carried out under basic conditions, the process is called **saponification**.

Inorganic acids also react with alcohols to form esters. Some of the most important esters in biochemistry are those formed from phosphoric acid.

Amines are nitrogen-containing organic molecules derived from ammonia (NH_3). A **primary (1°) amine** (RNH_2) has one organic group bonded to the nitrogen atom, a **secondary (2°) amine** (R_2NH) has two organic groups bonded to the nitrogen atom, and a **tertiary (3°) amine** (R_3N) has three organic groups bonded to the nitrogen atom. Amines are basic compounds that react with strong acids to produce ammonium (NH_4^+) salts. A cyclic compound in which the ring contains one or more noncarbon atoms is called a **heterocyclic compound**. There are many heterocyclic amines, including many physiologically important ones. **Alkaloids** are heterocyclic amines found in many plants. Caffeine, nicotine, and cocaine are familiar alkaloids.

Organic compounds containing a carbonyl group bonded to a nitrogen atom are amides, and the carbon-to-nitrogen bond is an amide linkage (or a peptide linkage). Most amides are colorless and odorless, and the lighter ones are soluble in water. Because they are polar molecules, amides have comparatively high boiling points and melting points. Amides are synthesized from carboxylic acids and NH_3 or amines. Amides are neutral compounds. They resist hydrolysis in water, but acids, bases, and enzymes catalyze the reaction.

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