Chapter 5
Carboxylic Acids and Esters

6 C Carbon 12.011 8 O Oxygen 15.9994

Chapter Objectives:

- Learn to recognize the carboxylic acid, ester, and related functional groups.
- Learn the IUPAC system for naming carboxylic acids and esters.
- Learn the important physical properties of the carboxylic acids and esters.
- Learn the major chemical reaction of carboxylic acids and esters, and learn how to predict the products of ester synthesis and hydrolysis reactions.
- Learn some of the important properties of condensation polymers, especially the polyesters.

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Organic and Biochemistry for Today (Seager & Slabaugh)
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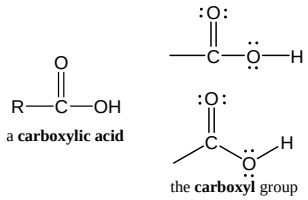
Carboxylic Acids

- **Carboxylic acids** are weak organic acids which contain the **carboxyl group** (RCO_2H):



a **carboxylic acid**

the **carboxyl** group

RCOOH RCO_2H

condensed ways of writing the carboxyl group

- The tart flavor of sour-tasting foods is often caused by the presence of carboxylic acids.

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Nomenclature of Carboxylic Acids

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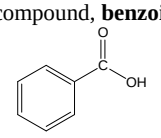
Nomenclature of Carboxylic Acids

- Select the longest carbon chain containing the carboxyl group. The **-e** ending of the parent alkane name is replaced by the suffix **-oic acid**.
- The carboxyl carbon is always numbered "1" but the number is not included in the name.
- Name the substituents attached to the chain in the usual way.
- Aromatic carboxylic acids (i.e., with a CO_2H directly connected to a benzene ring) are named after the parent compound, **benzoic acid**.



Benzoic acid

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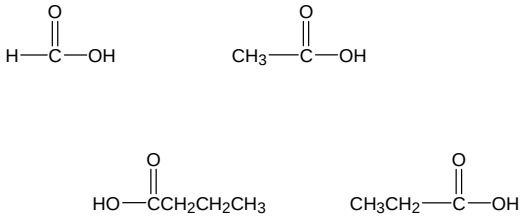
Examples: Naming Carboxylic Acids

- Name the following compounds:



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Examples: Naming Carboxylic Acids

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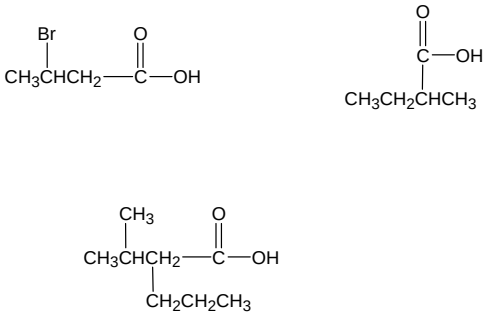

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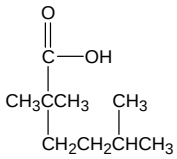
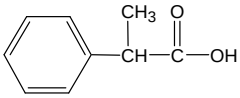
Examples: Naming Carboxylic Acids

- Name the following compounds:





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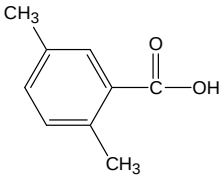
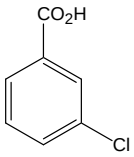
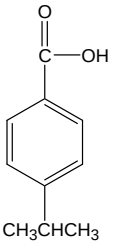
Examples: Naming Carboxylic Acids

- Name the following compounds:







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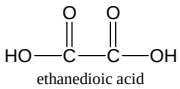
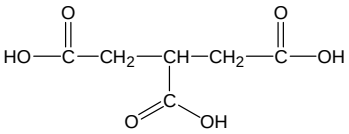
More Complicated Acids

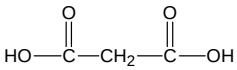
- For molecules with two carboxylic acid groups the carbon chain in between the two carboxyl groups (including the carboxyl carbons) is used as the longest chain; the suffix **-dioic acid** is used.
- For molecules with more than two carboxylic acid groups, the carboxyl groups are named as *carboxylic acid substituents*.



ethanedioic acid



propane-1,2,3-tricarboxylic acid



propanedioic acid

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Examples: Drawing Carboxylic Acids

- Draw structural formulas for the following molecules:
  - 2-methylpropanoic acid
  - 2,2,5-trimethylhexanoic acid
  - 4,5-dimethyl-3-nitrooctanoic acid

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Examples: Drawing Carboxylic Acids

- Draw structural formulas for the following molecules:
  - *para*-bromobenzoic acid
  - 2,4,6-trinitrobenzoic acid
  - 4-ethylpentanedioic acid (what's wrong with this name?)

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Physical Properties of Carboxylic Acids

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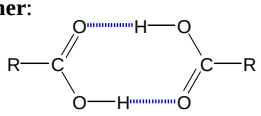
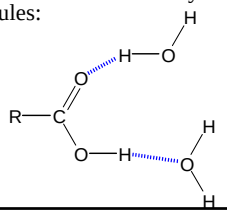
Physical Properties of Carboxylic Acids

- Carboxylic acids hydrogen bond to themselves to form a **dimer**:



- Carboxylic acids also form hydrogen bonds to water molecules:



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Physical Properties of Carboxylic Acids

- Since carboxylic acids can form more than one set of hydrogen bonds, their boiling points are usually higher than those of other molecules of the same molecular weight (MW).
- Low-MW carboxylic acids are generally liquids at room temp. (often, they are somewhat oily); higher-MW carboxylic acids are generally waxy solids.
- Carboxylic acids with 12 to 20 carbon atoms are often referred to as **fatty acids**, since they are found in the triglycerides in fats and oils (more later).
- Short-chain carboxylic acids are also generally more soluble in water than compounds of similar MW, since they can hydrogen bond to more than one water molecule.

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Physical Properties of Carboxylic Acids

- As the number of carbons in a carboxylic acid series becomes greater, the boiling point increases and the solubility in water decreases.
- Many carboxylic acids that are liquids at room temperature have characteristically sharp or unpleasant odors.
  - Ethanoic acid/acetic acid is the main ingredient in vinegar.
  - Butanoic acid is partially responsible for the odor of locker rooms and unwashed socks.
  - Hexanoic acid is responsible for the odor of Limburger cheese.
- Like most acids, carboxylic acids tend to have a sour taste (e.g., vinegar, citric acid, etc.)

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Table 5.2 Physical properties of some carboxylic acids

Common Name	Structural Formula	BP (°C)	MP (°C)	Solubility (g/100 mL H_2O)
Formic acid	H—CO_2H	101	8	Infinite
Acetic acid	CH_3—CO_2H	118	17	Infinite
Propionic acid	CH_3CH_2—CO_2H	141	-21	Infinite
Butyric acid	$CH_3(CH_2)_2$—CO_2H	164	-5	Infinite
Valeric acid	$CH_3(CH_2)_3$—CO_2H	186	-34	5
Caproic acid	$CH_3(CH_2)_4$—CO_2H	205	-3	1
Caprylic acid	$CH_3(CH_2)_6$—CO_2H	239	17	Insoluble
Capric acid	$CH_3(CH_2)_8$—CO_2H	270	32	Insoluble
Lauric acid	$CH_3(CH_2)_{10}$—CO_2H	299	44	Insoluble
Myristic acid	$CH_3(CH_2)_{12}$—CO_2H	Dec.	58	Insoluble
Palmitic acid	$CH_3(CH_2)_{14}$—CO_2H	Dec.	63	Insoluble
Stearic acid	$CH_3(CH_2)_{16}$—CO_2H	Dec.	71	Insoluble

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Boiling Points of Various Functional Groups

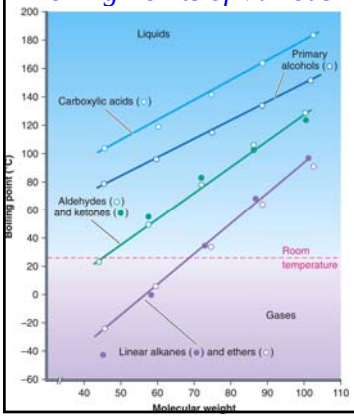

Figure 5.4
The boiling points of carboxylic acids compared to 1° alcohols, aldehydes and ketones, ethers and alkanes.

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Comparing Physical Properties

Boiling Point:
- Carboxylic acid
- Alcohols
- Aldehydes/Ketones
- Ethers
- Alkanes

Water Solubility:
- Carboxylic acid
- Alcohols
- Aldehydes/Ketones
- Ethers
- Alkanes

Name	Molecular weight	Boiling point	Solubility in water
Pentane	72 g/mol	35°C	Insoluble
Diethyl ether	74 g/mol	35°C	Insoluble
Butanal	72 g/mol	76°C	7.1 g / 100 mL H_2O
1-Butanol	74 g/mol	118°C	9.1 g / 100 mL H_2O
Propanoic acid	74 g/mol	141°C	Infinite

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Examples: Predicting Physical Properties

- Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.)
  - 1-pentanol
  - hexane
  - butanoic acid
  - pentanal
- Which member of each of the following pairs of compounds would you expect to have a higher solubility in water?
  - 2-butanone *or* propanoic acid
  - hexanoic acid *or* ethanoic acid

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Some Important Carboxylic Acids

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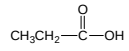
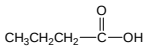
Important Carboxylic Acids

Methanoic acid (Formic acid)
(from Latin *formica,* ant)
A component of the venom of ants and caterpillars; produced in the body when methanol is consumed

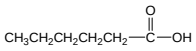
Ethanoic acid (Acetic acid)
(from Latin *acetum*, vinegar)
Vinegar is a 5% solution of acetic acid dissolved in water; acetic acid is also responsible for the taste of sour wine (from the oxidation of ethanol) and sourdough bread



Propanoic acid (Propionic acid)
Found in Swiss cheese; salts of this acid are used as mold inhibitors



Butanoic acid (Butyric acid)
(from Latin *butyrum,* butter)
This acid has a foul, rancid odor; produced from the breakdown of soft triglycerides in butter



Hexanoic acid (Caproic acid)
Responsible for the odor of Limburger cheese.

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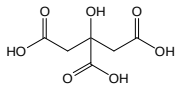
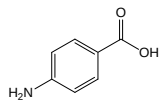
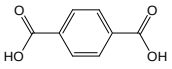


2-hydroxy-1,2,3-propanetricarboxylic acid (Citric acid)
Found in citrus fruits (lemons, grapefruit, oranges, etc.); commonly used in buffering solutions with sodium citrate



para-Aminobenzoic aid (PABA)
Used in sunscreens; absorbs short-wavelength UV light. It is also required by bacteria for the production of folic acid, needed to maintain the growth of healthy cell walls; sulfa drugs block the uptake of PABA by bacteria, causing them to be unable to manufacture folic acid, and thus preventing the bacteria from multiplying

Oxalic acid
Found in many leafy green plants such as rhubarb and spinach; combines with calcium ions in the body to produce insoluble salts, which form kidney stones



Terephthalic acid
A white, crystalline solid; used in the manufacture of some polyesters

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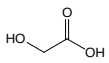
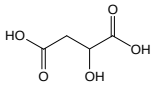


Glycolic acid
An **alpha-hydroxy acid** used in cosmetics and skin creams; alpha-hydroxy acids are thought to loosen the cells of the epidermis and accelerate the flaking off of dead skin; however these compounds can increase the skin's sensitivity to UV light



Malic acid
Responsible for the sharp taste of apples (genus *Malus*)

2-hydroxypropanoic acid (Lactic acid)
Produced from the fermentation of sugars under anaerobic conditions; found in sweat, sour milk, fermented pickles, sauerkraut, and yogurt; produced in muscles from glucose under anaerobic conditions (the buildup of lactic acid leads to a heavy, weak feeling, and muscle cramps); produced after death during the breakdown of sugars in the body by bacteria, inactivating the enzymes that allow the transport of calcium ions, causing rigor mortis

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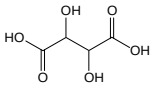
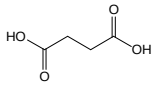
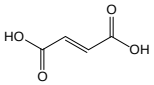
Niacin
A water-soluble, B-Complex vitamin obtained from fish, green vegetables, lean meat, poultry, whole-grain and enriched bread and cereal; produced in the body from tryptophan; essential for growth, healthy tissues, the production of energy from carbohydrates, and the production of fats



Tartaric acid
Found naturally in wine, and is responsible for some of the sharp taste of wine; it is added to many sour-tasting sweet foods. The potassium salt, *cream of tartar*, has many cooking applications; the potassium-sodium salt, *Rochelle salt*, is a mild laxative.



Succinic acid
An intermediate along the citric acid cycle



Fumaric acid
Occurs naturally in many plants, and is essential for vegetable and animal tissue respiration; used in baking powders, and in some fruit drinks as a replacement for citric acid

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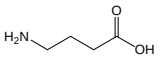
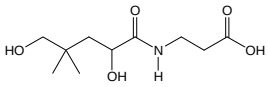
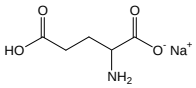


Gamma-aminobutanoic acid (GABA)
A *inhibitory neurotransmitter*; ethanol binds to the same protein as GABA at a neighboring location, distorting the protein so that GABA binds more easily, further inhibiting the cell from firing; benzodiazepines such as Valium also bind to the same protein but at a different site, inhibiting the cell still further, and sometimes with deadly consequences



Pantothenic acid
A water-soluble B-complex vitamin; converted by the body into Coenzyme A, which helps the body produce energy from food



Monosodium Glutamate (MSG)
The sodium salt of the amino acid glutamate; produced in meat during the decomposition of proteins; with inosine monophosphate (IMP), one of the major substances responsible for the flavor of meat; MSG is also added to some foods to enhance their meaty flavor

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Chemical Properties of Carboxylic Acids

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Acids and Bases

- **Acids:**
  - have a sour taste.
  - react with active metals to produce H_2 gas.
  - turn blue litmus red.
- **Bases:**
  - have a bitter taste and a slippery feel.
  - turn red litmus blue.
- When they react with each other, acids and bases cancel each others properties in a **neutralization reaction**:

acid + base → salt + water

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Acids

- An **acid** gives a **proton (H^+)** to another species. Acids produce **hydronium ions**, **H_3O^+**, when they are dissolved in water:

$$H{-}A + H_2O \rightarrow A^- + H_3O^+$$

- A **strong acid** is one that *completely dissociates* in water (i.e., every molecule of the acid splits apart):

$$H{-}Cl + H_2O \rightarrow Cl^- + H_3O^+$$

- A **weak acid** is one in which only a small percentage of the molecules are dissociated at any one time (in other words, there is also a backwards reaction, where the acid molecule is regenerated):

$$H{-}F + H_2O \rightleftharpoons F^- + H_3O^+$$

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The pH Scale

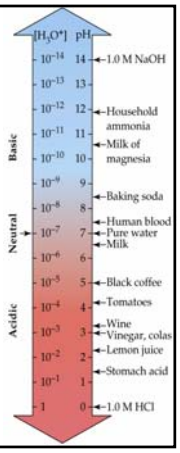
- The acidity of a solution is measured using the **pH scale**. The pH of a solution is defined as

pH = - log[H_3O^+]

Acidic: **pH < 7.00** [H_3O^+] > [OH^-]

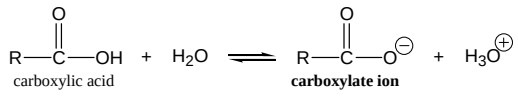
Basic: **pH > 7.00** [H_3O^+] < [OH^-]

Neutral: **pH = 7.00** [H_3O^+] = [OH^-]

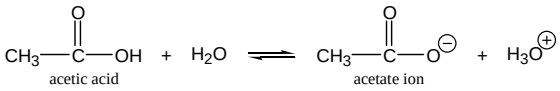


The Acidity of Carboxylic Acids

- Carboxylic acids are weak acids; in water, they dissociate to produce hydronium ions and **carboxylate ions**:



- A 1.0 *M* solution of acetic acid is about 0.5% dissociated into hydronium and **acetate** ions:



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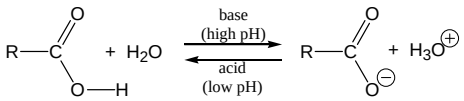
The Acidity of Carboxylic Acids

- The dissociation of a carboxylic acid is a reversible reaction, and the position of the equilibrium can be affected by the addition of acid (low pH) or by adding base (high pH):



- At the *physiological pH* of 7.4 (the pH of most body fluids) the carboxylate form of most carboxylic acids is the predominate form.

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Carboxylate Salts

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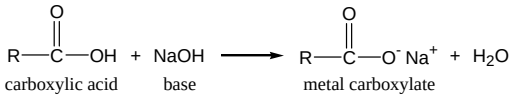
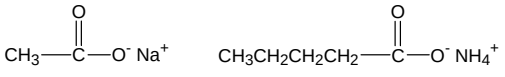
Carboxylate Salts

- Carboxylic acids react with strong bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) to produce **carboxylate salts**.
- Carboxylate salts are named by naming the metal first, and changing the **-ic acid** ending of the carboxylic acid name to **-ate**.





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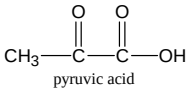
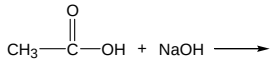
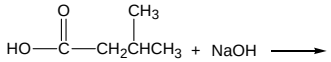
Examples: Carboxylate Salts

- Draw the structure of pyruvate, the form of pyruvic acid which is found as an intermediate in energy conversion reactions in living organisms.



- Complete the following reactions and name the carboxylate salt products.





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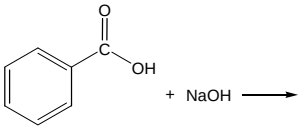
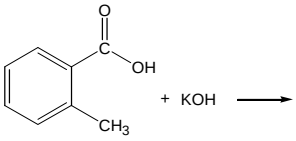
Examples: Carboxylate Salts

- Complete the following reactions and name the carboxylate salt products.





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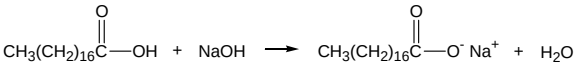
Physical Properties of Carboxylate Salts

- Carboxylate salts are ionic compounds, and are typically solids at room temperature.
- Because they contain charges, carboxylate salts are typically much more soluble in water than the carboxylic acids from which they are derived.
  - This is important in the formation of *soaps* (more later).



Stearic acid (octadecanoic acid)
insoluble in water
found in beef fat and some butters

Sodium stearate (sodium octadecanoate)
soluble in water

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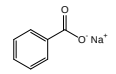
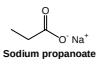
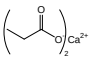
Important Carboxylate Salts



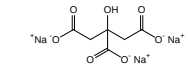
Sodium benzoate
Found in cranberries and prunes; commonly used as a preservative in baked goods, ketchup, carbonated beverages, etc.



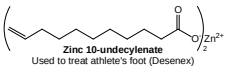
Sodium propanoate



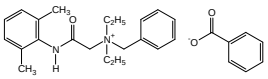
Calcium propanoate
Commonly used preservatives; found in bread, cakes, and cheeses



Sodium citrate
The sodium salt of citric acid, sodium citrate, is used in buffers with citric acid to maintain desirable characteristics of foams and gels (jelly, ice cream, candy, whipped cream, etc.) by controlling the pH of the product; also used in medicines and blood for transfusions; also functions as an anticoagulant in blood



Zinc 10-undecylenate
Used to treat athlete's foot (Desenex)



Denatonium benzoate ('Bitrex')
Benzyl diethyl ((2,6-xylylcarbamoyl)methyl) ammonium benzoate
Discovered in 1958, this is the bitterest-tasting compound known; as little as ten parts per million make substances unbearably bitter to most humans. It is used as an *aversive agent*, an additive that prevents accidental ingestion of a toxic substance. It is used to denature ethanol, methanol, and rubbing alcohol, and well as solvents, paints, arnishes, antifreeze, etc.

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