

17: CARBOXYLIC ACIDS AND THEIR DERIVATIVES



CHAPTER OVERVIEW

17: Carboxylic Acids and their Derivatives

17.1: Carboxylic Acids and Their Derivatives- Properties and Names

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17.1: Carboxylic Acids and Their Derivatives- Properties and Names

Learning Objectives

- Objective 1
- Objective 2

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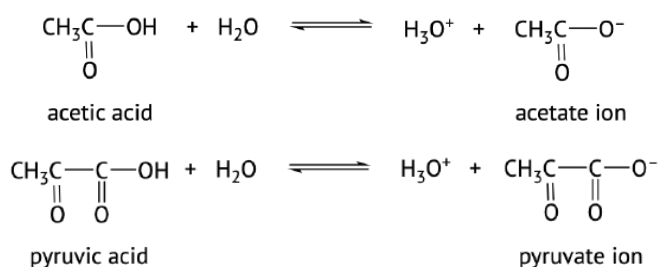
17.2: Acidity of Carboxylic Acids

Learning Objectives

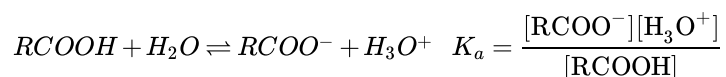
- Define pK_a and use it to determine acidity of different carboxylic acids.
- Describe the reactions between carboxylic acids and strong bases.

Ionization of Carboxylic Acids

Carboxylic acids are named such because they tend to be more acidic than other functional groups in organic chemistry. In dilute aqueous solutions, they act as *weak acids* that partially dissociate to produce the corresponding **carboxylate anion** and hydronium cation (H_3O^+). Carboxylate anions are named by replacing the *-ic acid* ending from the carboxylic acid with *-ate*, see examples below.



The extent of dissociation of these weak acids in water is described by K_a values. Remember that a compound with a smaller K_a value will be a weaker acid.



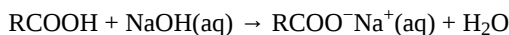
When comparing the acidity of organic and biomolecules, it is useful (and more preferable) to use pK_a values instead of K_a values, which are calculated by taking the negative log of K_a : $pK_a = -\log K_a$. When using the pK_a scale, it is important to know that *weaker acids* have *larger* and more positive pK_a values, this is opposite of K_a values. The pK_a values of some typical carboxylic acids are listed in Table 17.2.1. (Remember that pK_a is a log expression, which means that every 1 pK_a unit represents a 10-fold change in acidity.)

Table 17.2.1: Comparisons of Carboxylic Acid K_a and pK_a Values

| Name | Compound | K_a | pK_a |
|----------------------|--|----------------------|--------|
| formic acid | HCOOH | 1.8×10^{-4} | 3.74 |
| acetic acid | CH ₃ COOH | 1.8×10^{-5} | 4.74 |
| propanoic acid | CH ₃ CH ₂ COOH | 1.3×10^{-5} | 4.89 |
| butanoic acid | CH ₃ CH ₂ CH ₂ COOH | 1.5×10^{-5} | 4.82 |
| chloroacetic acid | ClCH ₂ COOH | 1.4×10^{-3} | 2.85 |
| trichloroacetic acid | Cl ₃ CCOOH | 2.3×10^{-1} | 0.64 |
| hexanoic acid | CH ₃ (CH ₂) ₄ COOH | 1.3×10^{-5} | 4.89 |
| benzoic acid | C ₆ H ₅ COOH | 6.5×10^{-5} | 4.19 |
| oxalic acid | HOOC-COOH | 5.4×10^{-2} | 1.27 |
| | ⁻ OOC-COOH | 5.2×10^{-5} | 4.28 |
| glutaric acid | HOOC(CH ₂) ₃ COOH | 4.5×10^{-5} | 4.35 |
| | ⁻ OOC(CH ₂) ₃ COOH | 3.8×10^{-6} | 5.42 |

Neutralization of Carboxylic Acids

Carboxylic acids will react with bases such as sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), and sodium bicarbonate (NaHCO₃) to form water and a **carboxylic acid salt**:



In these reactions, the carboxylic acids act like inorganic acids: they neutralize basic compounds. With solutions of carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) 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:

| | | |
|--|---|--|
| CH ₃ COO ⁻ Li ⁺ | CH ₃ CH ₂ CH ₂ COO ⁻ K ⁺ | C ₆ H ₅ COO ⁻ Na ⁺ |
| Lithium acetate (lithium ethanoate) | Potassium butyrate (potassium butanoate) | Sodium benzoate |

Note

The salts of long-chain carboxylic acids are called soaps.



Sodium palmitate (a soap)

Example 17.2.1

Write an equation for each reaction.

- the ionization of propionic acid in water (H₂O)
- the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

Solution

Propionic acid has three carbon atoms, so its formula is CH₃CH₂COOH.

- Propionic acid ionizes in water to form a propionate ion and a hydronium (H₃O⁺) ion. CH₃CH₂COOH(aq) + H₂O(ℓ) → CH₃CH₂COO⁻(aq) + H₃O⁺(aq)
- Propionic acid reacts with NaOH(aq) to form sodium propionate and water. CH₃CH₂COOH(aq) + NaOH(aq) → CH₃CH₂COO⁻Na⁺(aq) + H₂O(ℓ)

Exercise 17.2.1

Write an equation for each reaction.

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

Example 17.2.2

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

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

Solution

- a. Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water (H₂O). $\text{CH}_3(\text{CH}_2)_8\text{COOH} + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3(\text{CH}_2)_8\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell)$
- b. 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 17.2.3

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

- a. aqueous sodium hydroxide (NaOH)
 b. aqueous sodium bicarbonate (NaHCO₃)

📌 Note 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

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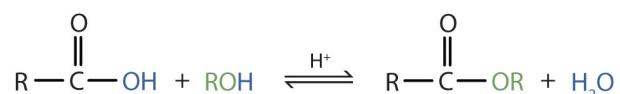
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation

Learning Objectives

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

Carboxylic acids will react with alcohols and amines following a similar pattern. In both cases, the $-OH$ group of the carboxylic acid will be replaced by a different group to form either an ester or an amide, with water formed as a by-product. When the reaction involves an alcohol, the $-OH$ of the acid is replaced by the $-OR'$ of the alcohol. When the reaction involves an amine, the $-OH$ of the acid is replaced by the $-NH_2$, or $-NHR'$, or $-NR'_2$ of the amine.

Ester formation

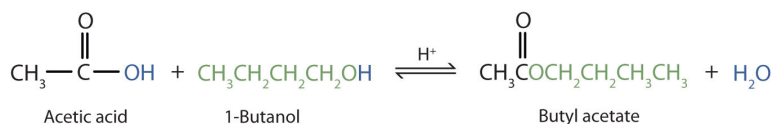


Amide formation



Esterification

Esters are prepared by **esterification**, a reaction in which a carboxylic acid and an alcohol are heated in the presence of an acid catalyst:

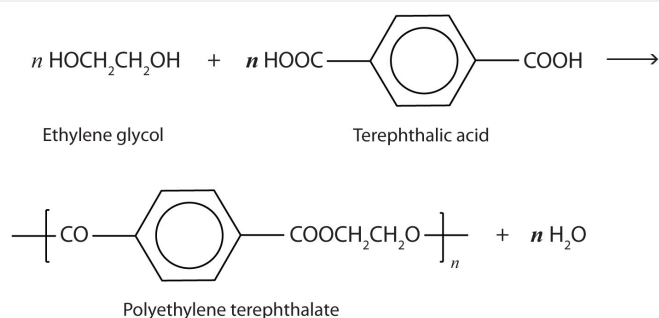


The reaction is reversible and will reach equilibrium with approximately equivalent amounts of reactants and products. Using excess amounts of alcohol and continuously removing a product, can drive the reaction towards the product side as per LeChatelier's principle.

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.

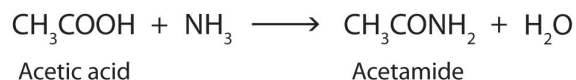
The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:



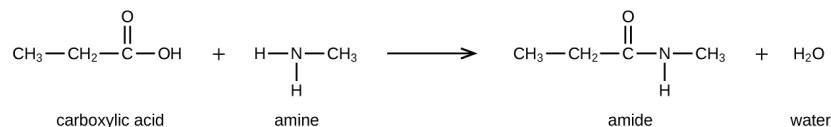
Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called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

Amide Formation

When a carboxylic acid reacts with ammonia (NH₃) a *primary amide* is formed:



When a carboxylic acid reacts with primary or secondary amines, secondary or tertiary amides are produced, respectively.



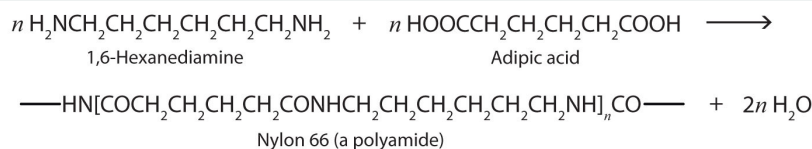
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Tertiary amines do not have a hydrogen attached to the nitrogen and therefore do not form amides when mixed with carboxylic acids. However, an acid-base reaction does occur with the amine accepting a proton (acts as a base) and the carboxylic acid donating a proton. In this case the ammonium and carboxylate salts are formed:

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Note 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.

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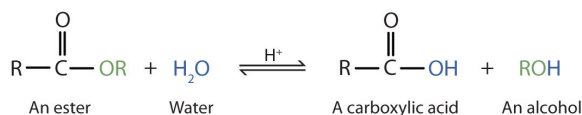
17.4: Hydrolysis of Esters and Amides

Learning Objectives

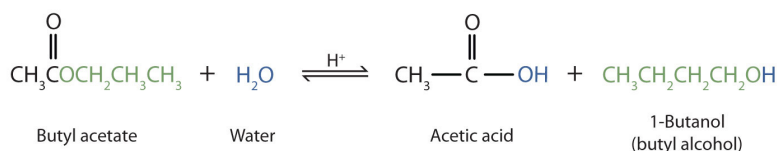
- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

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.

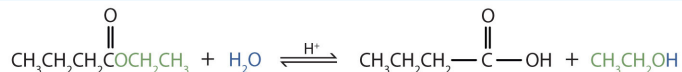


✓ Example 17.4.1

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:

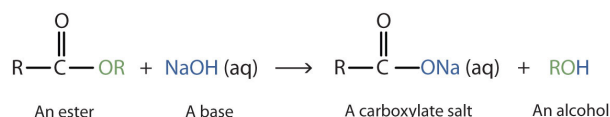


The products are butyric acid (butanoic acid) and ethanol.

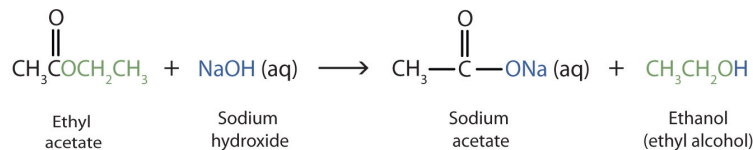
? Exercise 17.4.1

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:

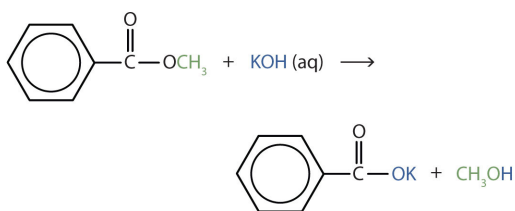


✓ Example 17.4.2

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.

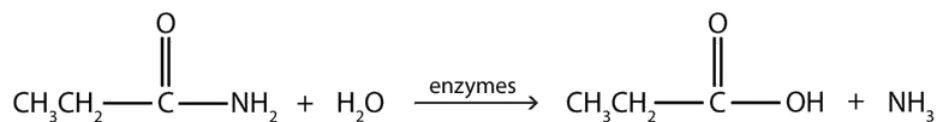


? Exercise 17.4.2

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

Hydrolysis of Amides

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.

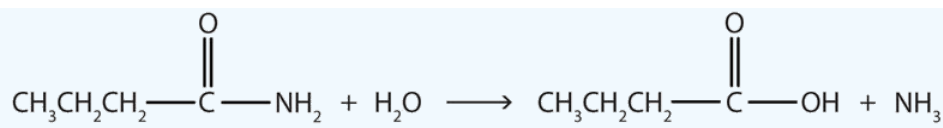
✓ Example 17.4.1

Write the equation for the hydrolysis of each compound.

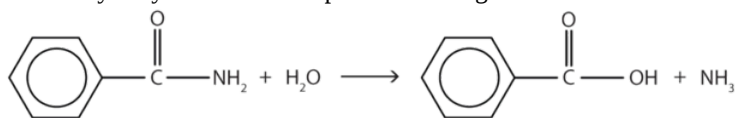
- butyramide
- benzamide

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 17.4.1

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.

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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17.5: Polyamides and Polyesters

Learning Objectives

- Describe how polyamides and polyesters are formed.

Animal intestines and silk were used for all guitar strings for centuries, until modern technology and changes in musical taste brought about significant changes. There are two major types of guitar strings in use today. Steel strings (first developed around 1900) are found on acoustic and electric guitars. They have a bright, crisp sound that lends itself well to diverse music such as jazz, rock 'n' roll, and bluegrass. Nylon strings are a more recent development. During World War II, the silk and animal products needed to manufacture steel guitar strings were not available. Nylon quickly proved to be a more-than-adequate substitute. Now nylon strings are found on all classical guitars. Their sound is somewhat softer than the steel strings, making the tone quality well-suited for the classical genre of music.

Polymerization - Condensation Polymers

A condensation polymer is a polymer formed by condensation reactions. Monomers of condensation polymers must contain two functional groups so that each monomer can link up with two other monomers. One type of condensation polymer is called a polyamide.

One pair of monomers that can form a *polyamide* is that of adipic acid and hexanediamine. Adipic acid is a carboxylic acid with two carboxyl groups on either end of the molecule. Hexanediamine has amino groups on either end of a six-carbon chain. When these molecules react with each other, a molecule of water is eliminated, classifying it as a condensation reaction (see figure below).

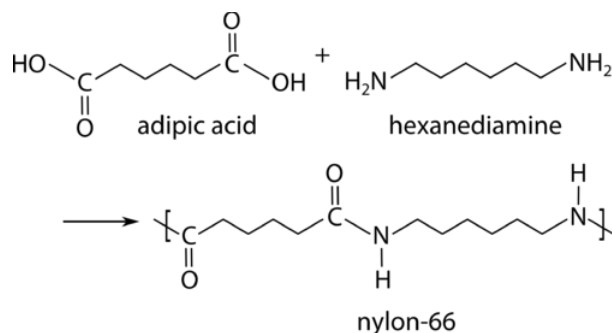


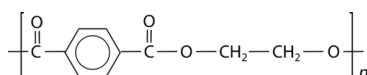
Figure 17.5.2: Nylon synthesis.

The polymer that results from the repetition of the condensation reaction is a polyamide called nylon-66. Nylon-66 was first invented in 1935 and has been used in all sorts of products. Polyamides, including Nylon-66, are commonly found in fibers and clothing, cooking utensils, fishing line, and carpeting—among many other applications.



Figure 17.5.3: Nylon spatula.

Polyester is another common type of condensation polymer. Recall that esters are formed from the reaction of an alcohol with a carboxylic acid. When both the acid and alcohol have two functional groups, the ester is capable of being polymerized. One such polyester is called polyethylene terephthalate (PET) and is formed from the reaction of ethylene glycol with terephthalic acid. The structure of PET is shown below.



PET is used in tires, photographic film, food packaging, and clothing. Polyester fabric is used in permanent-press clothing. Its resistance to wrinkling comes from the cross-linking of the polymer strands.

Summary

- A condensation polymer is a polymer formed by condensation reactions.
- Polyamides and polyesters are common types of condensation polymers.

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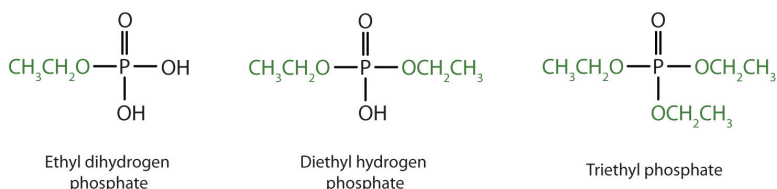
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17.6: Phosphoric Acid Derivatives

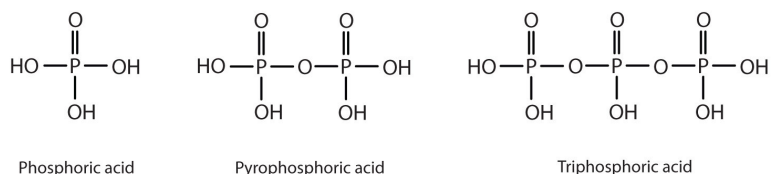
Learning Objectives

- Objective 1
- Objective 2

Just as carboxylic acids 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 biochemistry. A phosphoric acid molecule can form a monoalkyl, a dialkyl, or a trialkyl ester by reaction with one, two, or three molecules of an alcohol.

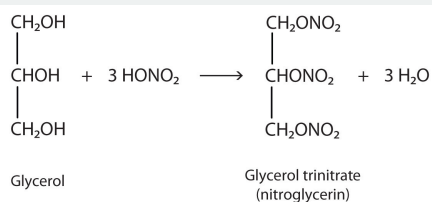


Esters of pyrophosphoric acid and triphosphoric acid are also important in biochemistry.



Esters of these acids are present in every plant and animal cell. They are biochemical intermediates in the transformation of food into usable energy. The bonds between phosphate units in adenosine triphosphate (ATP) are called *phosphoanhydride* bonds. These are high-energy bonds that store energy from the metabolism of foods. Hydrolysis of ATP releases energy as it is needed for biochemical processes (for instance, for muscle contraction). Phosphate esters are also important structural constituents of phospholipids and nucleic acids.

The explosive nitroglycerin (glyceryl trinitrate) is an ester formed from glycerol and nitric acid. It is used in medicine to relieve chest pain in heart disease.



Summary

Inorganic acids such as H_3PO_4 form esters. The esters of phosphoric acid are especially important in biochemistry.

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