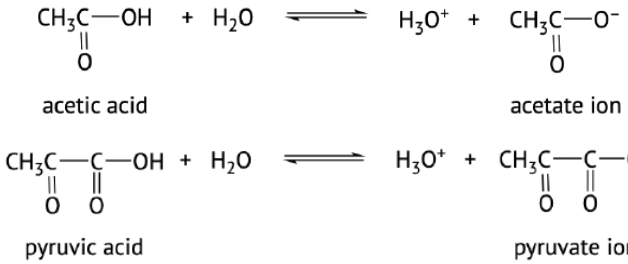
17.2: Acidity of Carboxylic Acids

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.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \quad K_a = \frac{[\mathrm{RCOO^-}][\mathrm{H_3O^+}]}{[\mathrm{RCOOH}]}$$

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 X 10^{-4}	3.74
acetic acid	CH_3COOH	1.8 X 10^{-5}	4.74
propanoic acid	CH_3CH_2COOH	1.3 X 10^{-5}	4.89
butanoic acid	$CH_3CH_2CH_2COOH$	1.5 X 10^{-5}	4.82
chloroacetic acid	$ClCH_2COOH$	1.4 X 10^{-3}	2.85
trichloroacetic acid	Cl_3CCOOH	2.3 X 10^{-1}	0.64
hexanoic acid	$CH_3(CH_2)_4COOH$	1.3 X 10^{-5}	4.89
benzoic acid	C_6H_5COOH	6.5 X 10^{-5}	4.19
oxalic acid	HOOCCOOH	5.4 X 10^{-2}	1.27
	$^-$OOCCOOH	5.2 X 10^{-5}	4.28
glutaric acid	$HOOC(CH_2)_3COOH$	4.5 X 10^{-5}	4.35
	$^-OOC(CH_2)_3COOH$	3.8 X 10^{-6}	5.42

Neutralization of Carboxylic Acids

Carboxylic acids will react with bases such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$) to form water and a **carboxylic acid salt**:

$$RCOOH + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + H_2O$$

$$2RCOOH + Na_2CO_3(aq) \rightarrow 2RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

$$RCOOH + NaHCO_3(aq) \rightarrow RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

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:

$CH_3COO^-Li^+$	$CH_3CH_2CH_2COO^-K^+$	$C_6H_5COO^-Na^+$
Lithium acetate (lithium ethanoate)	Potassium butyrate (potassium butanoate)	Sodium benzoate

Note

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

$CH_3(CH_2)_{13}CH_2COO^-Na^+$

Sodium palmitate (a soap)

Example 17.2.1

Write an equation for each reaction.

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

Solution

Propionic acid has three carbon atoms, so its formula is CH_2CH_2COOH.

1. Propionic acid ionizes in water to form a propionate ion and a hydronium (H_3O^+) ion. $CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$
2. Propionic acid reacts with NaOH(aq) to form sodium propionate and water. $CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COO^-Na^+(aq) + H_2O(\ell)$

Exercise 17.2.1

Write an equation for each reaction.

a. the ionization of formic acid in water
b. the ionization of *p*-chlorobenzoic acid in water

Example 17.2.2

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

a. aqueous sodium hydoxide (NaOH)
b. aqueous sodium bicarbonate ($NaHCO_3$)

Solution

a. Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water (H_2O). $CH_3(CH_2)_8COOH + NaOH(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell)$
b. With $NaHCO_3$, the products are a salt, H_2O, and carbon dioxide (CO_2). $CH_3(CH_2)_8COOH + NaHCO_3(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell) + CO_2(g)$

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 ($NaHCO_3$)

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.