

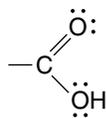
INTERCHAPTER R

Carboxylic Acids

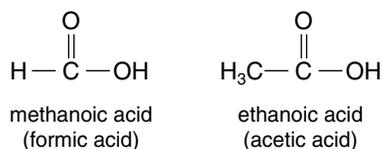


A fruit market in Portugal. The carboxylic acids citric acid $\text{CH}_2\text{COHCH}_2(\text{COOH})_3(s)$, malic acid, $\text{CH}_2\text{CHOH}(\text{COOH})_2(s)$, and tartaric acid, $(\text{CHOH})_2(\text{COOH})_2(s)$, are all found in fruit. Citric acid is particularly abundant in lemons, limes, oranges, and other citrus fruits. It plays a major role in our metabolism and is added to food and beverages to provide an acidic or sour flavor. Malic acid is found in apples, pears, plums, and cherries and gives unripe fruit and some candies their sour taste. Tartaric acid is found mostly in grapes, bananas, and tamarinds and is one of the main acids present in wine. Esters, which are derived from the reaction of carboxylic acids and alcohols, are responsible for the characteristic odors of many fruits.

Organic molecules that have the functional group



(abbreviated —COOH) are called **carboxylic acids**. Carboxylic acids occur both in nature and in the laboratory. Vinegar, for example, is a dilute solution of acetic acid, $\text{CH}_3\text{COOH}(aq)$; butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}(aq)$, is responsible for the rancid odor of spoiled butter; and hexanoic acid, $\text{CH}_3(\text{CH}_2)_4\text{COOH}(aq)$, is partially responsible for the characteristic odor of goats. In fact, hexanoic acid is often called caproic acid from the Latin name for goat, *capra*. The two simplest carboxylic acids are



Methanoic acid and ethanoic acid are generally referred to by their common names, formic acid and acetic acid, respectively.

Being acids, carboxylic acids donate a proton to

water to become carboxylate ions, $\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \parallel \\ \text{—C—} \\ \diagdown \\ \text{:}\ddot{\ominus}\text{O}\text{:} \end{array}$ and react

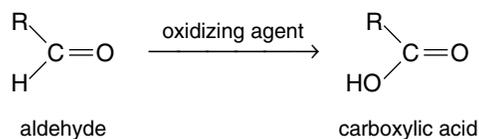
with bases to form carboxylate salts. Generally, carboxylic acids are weak acid. As we shall see below, carboxylic acids can be produced by the oxidation of aldehydes. Carboxylic acids react with alcohols to form a class of often fragrant compounds called esters and with polyalcohols to form oils and fats.



Figure R.1 Formic acid is responsible for the irritants in certain plants, such as stinging nettles. Formic acid is a colorless, fuming liquid that is very soluble in water. It is the major irritant in ant bites and was first isolated by the distillation of ants.

R-1. Carboxylic Acids Can Be Produced by the Oxidation of Aldehydes

One important use of aldehydes is in the production of carboxylic acids:

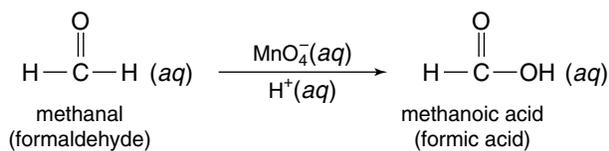


For example, the two simplest carboxylic acids, formic acid (Figure R.1) and acetic acid (Figure R.2),

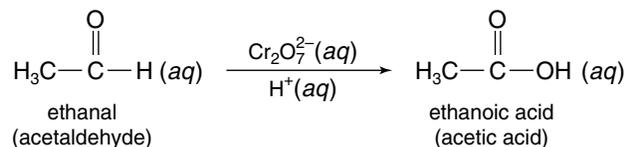


Figure R.2 Acetic acid is a clear, colorless liquid with a pungent odor. Household vinegar is an approximately 5% acetic acid solution. The pure compound is commonly called glacial acetic acid because it freezes at 18°C . Acetic acid is used in the manufacture of plastics, pharmaceuticals, dyes, insecticides, photographic chemicals, acetates, and many other organic chemicals.

can be formed from formaldehyde and acetaldehyde, respectively, according to

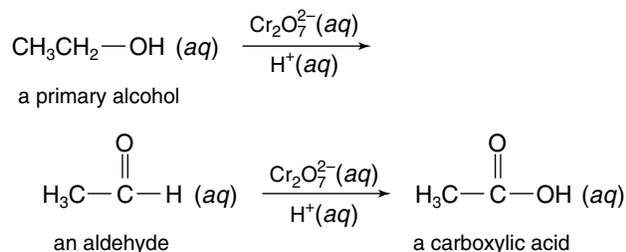


and

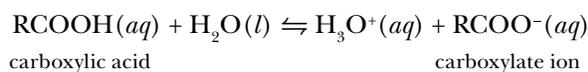


The oxidizing agent in these reactions effectively inserts an oxygen atom between the carbon atom and the hydrogen atom in the aldehyde group. The $-\text{COOH}$ group is called the **carboxyl group** and is the functional group that is characteristic of organic acids (carboxylic acids).

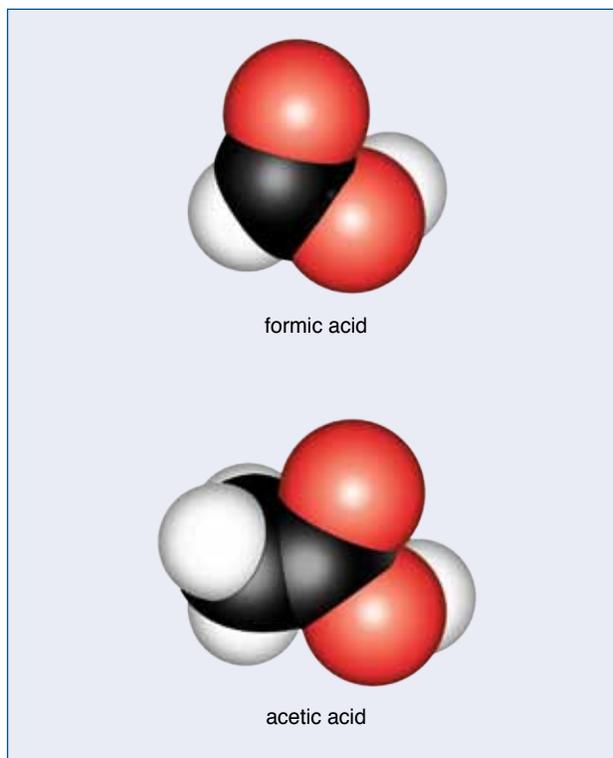
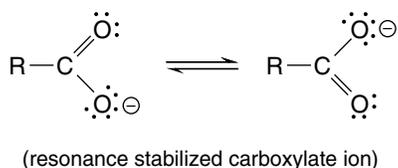
We can also obtain carboxylic acids by the direct oxidation of primary alcohols. In the oxidation, the aldehyde occurs as an intermediate species:



Being acids, carboxylic acids donate a proton to a water molecule according to



Typical acid dissociation constants of carboxylic acids are of the order of 10^{-3} M to 10^{-5} M (see Table 20.4). For example, the $\text{p}K_a$ value of acetic acid is 4.74, or $K_a = 1.8 \times 10^{-5}$ M. The acidic nature of carboxylic acids is due to the relative stability of the carboxylate anion, which can delocalize its negative charge over its two oxygen atoms according to the two resonance forms:



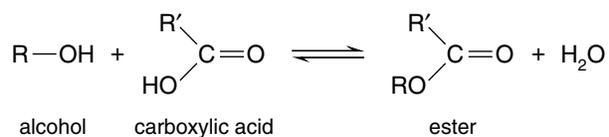
The IUPAC name of a carboxylic acid is formed by replacing the $-e$ from the end of the alkane name of the longest chain of carbon atoms containing the $-\text{COOH}$ group with the suffix $-oic\ acid$. For example, the IUPAC name for formic acid, $\text{HCOOH}(aq)$, is methanoic acid, and that for acetic acid, $\text{CH}_3\text{COOH}(aq)$, is ethanoic acid. Table R.1 lists the

TABLE R.1 Structural formulas and IUPAC names of some carboxylic acids

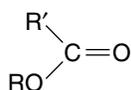
Structural formula	IUPAC name
$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	propanoic acid
$\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	2-chloropropanoic acid
$\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	3-methylbutanoic acid
$\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{O} \\ \quad \quad \parallel \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{Cl} \end{array}$	2,2,3-trichloropropanoic acid

R-2. Carboxylic Acids React with Alcohols to Produce Esters

Carboxylic acids react with alcohols in the presence of an acid catalyst to produce esters. The equation for the reaction is

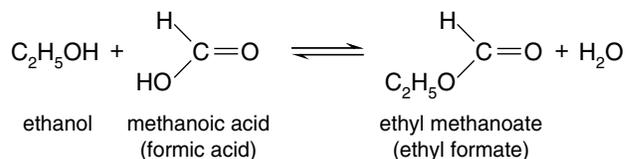


where R and R' represent possibly different alkyl groups. As the carboxylic acid–alcohol reaction equation indicates, the general formula for an **ester** is

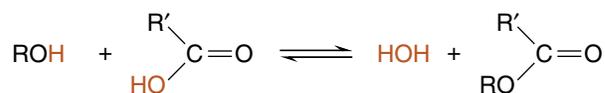


where the R group comes from the alcohol. The pleasant odors of flowers and fruits are due to esters. Table R.2 lists some naturally occurring esters and

their odors. Esters are named by first naming the alkyl group from the alcohol and then designating the acid, with its *-oic* ending changed to *-oate*. For example,



Such reactions are called **esterification reactions**. Let's look at an esterification reaction equation more closely. We write the equation as



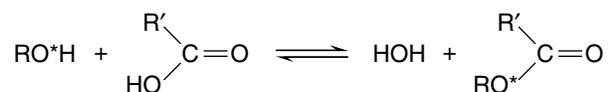
The coloring used in this equation emphasizes that the water is formed from the –OH group of the acid and the hydrogen atom of the alcohol. This reaction

TABLE R.2 Various esters and their odors

Structure	Name	Odor
$ \text{C}_2\text{H}_5\text{—O—}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{—H} $	ethyl methanoate (ethyl formate)	rum
$ \text{C}_5\text{H}_{11}\text{—O—}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{—CH}_3 $	pentyl ethanoate (amyl acetate)	bananas
$ \text{C}_8\text{H}_{17}\text{—O—}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{—CH}_3 $	octyl ethanoate (octyl acetate)	oranges
$ \text{CH}_3\text{—O—}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{—C}_3\text{H}_7 $	methyl butanoate (methyl butyrate)	apples
$ \text{C}_2\text{H}_5\text{—O—}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{—C}_3\text{H}_7 $	ethyl butanoate (ethyl butyrate)	pineapples
$ \text{C}_5\text{H}_{11}\text{—O—}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{—C}_3\text{H}_7 $	pentyl butanoate (amyl butyrate)	apricots, pears

is quite unlike an acid-base neutralization reaction, in which the water is formed by the reaction between a hydroxide ion from the base and a hydronium ion from the acid. Alcohols do not react like bases. The similarity in their chemical formulas, for example, $\text{CH}_3\text{OH}(l)$ versus $\text{NaOH}(s)$, is superficial.

We can verify this result experimentally by synthesizing the alcohol with oxygen-18, which we write as RO^*H , where we use an asterisk to denote the oxygen-18 atom. When we carry out the esterification reaction, we find that the oxygen-18 ends up in the ester and not in the water. We can illustrate this result schematically by writing

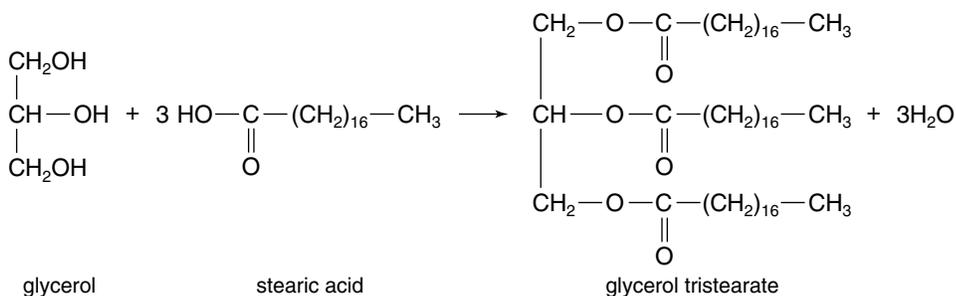


It's easy to detect the incorporation of oxygen-18 in the ester by using mass spectrometry.

We have written all the above esterification equations with double arrows to emphasize that esterification reactions are reversible. The equilibrium constants for esterification reactions are usually not large, so appreciable quantities of both reactants and products are present at equilibrium. You will learn more efficient methods of preparing carboxylic acids and esters if you take a course in organic chemistry.

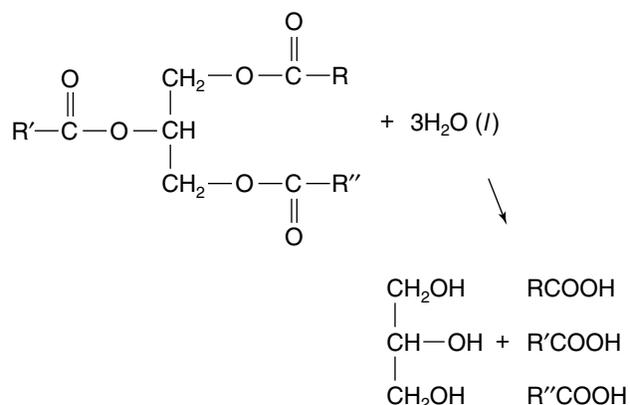
R-3. Fats and Oils Are Esters

Fats and oils are called **triglycerides**, which are triesters of the trialcohol glycerol with long hydrocarbon-chain carboxylic acids, such as octadecanoic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}(s)$ (generally referred to by its common name stearic acid). We write the equation describing the reaction between glycerol and stearic acid as shown below:



The product of this reaction is a triester because it contains three ester groups. Triesters are comprised of glycerol and long-hydrocarbon-chain carboxylic acids, called **fatty acids**. Because the fatty acids have long hydrocarbon chains, they are insoluble in water but soluble in organic solvents such as diethyl ether, chloroform, and acetone.

Complete hydrolysis of a fat or an oil yields three fatty acid molecules for every molecule of glycerol:



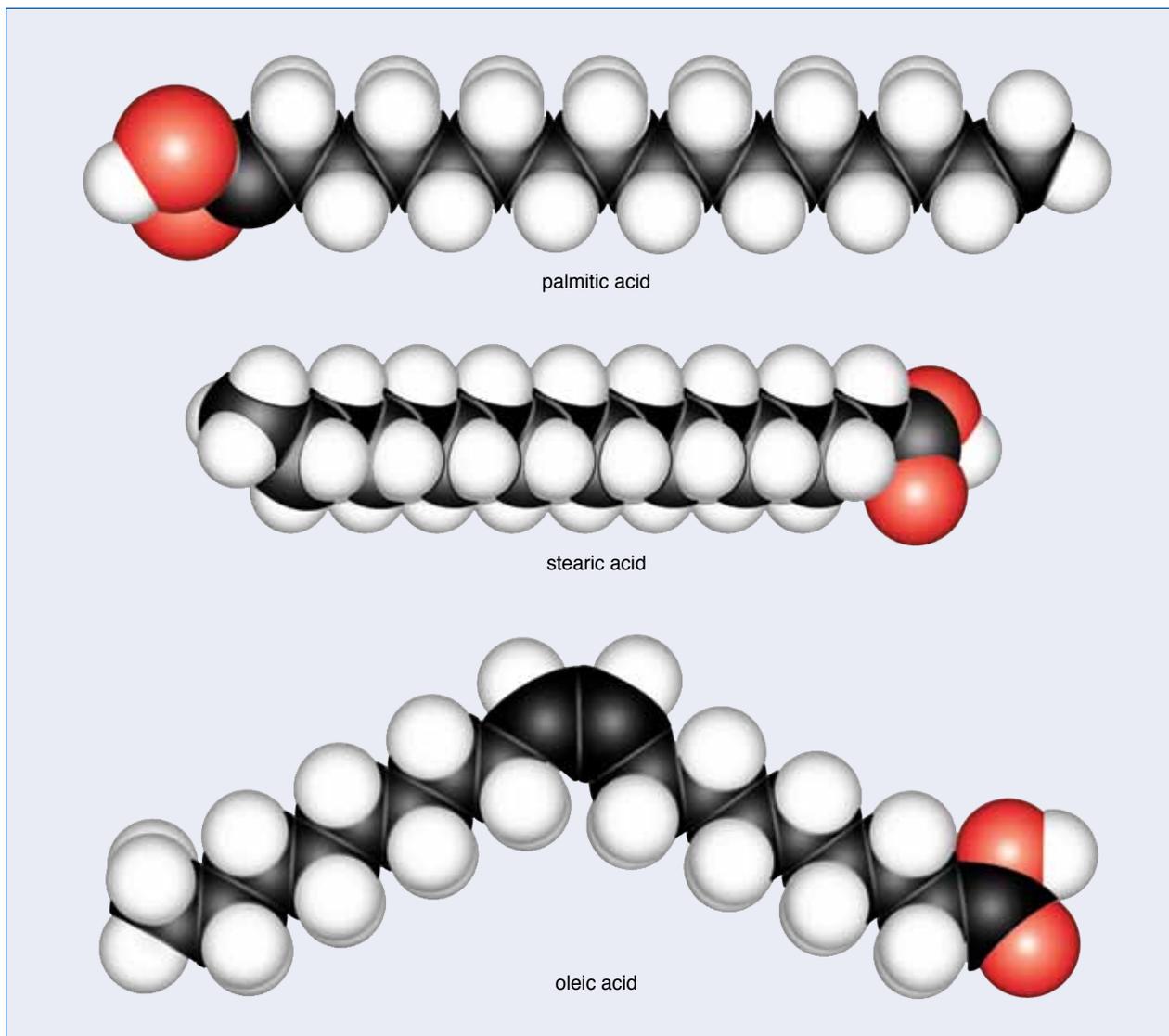
where R, R', and R'' are hydrocarbon chains. Of the 50 or more fatty acids that have been obtained from fats and oils, the three most abundant are

$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
hexadecanoic acid (palmitic acid)

$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
octadecanoic acid (stearic acid)

$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
cis-9-octadecanoic acid (oleic acid)

These three fatty acids are generally referred to by their common names; there is no need to memorize the formulas or names of these acids.



Note that palmitic acid and stearic acid have saturated hydrocarbon chains, whereas oleic acid has an unsaturated hydrocarbon chain. Triglycerides rich in saturated fatty acids are generally solids at room temperature and are called **fats**. Beef tallow is about 45% by mass saturated fatty acids. Triglycerides rich in unsaturated fatty acids are generally liquids at room temperature and are called **oils**. Vegetable oils such as corn oil, soybean oil, and olive oil are all over 85% by mass unsaturated fatty acids.

For reasons of convenience and dietary preference, oils often are converted to fats by hydrogenating some of the double bonds in the unsaturated triglyceride. The products are sold as shortening (Crisco), margarine, and other food products. Saturated fats

are alleged to be a dietary factor in atherosclerosis; therefore, for health reasons, vegetable oils have become increasingly popular.

TERMS YOU SHOULD KNOW

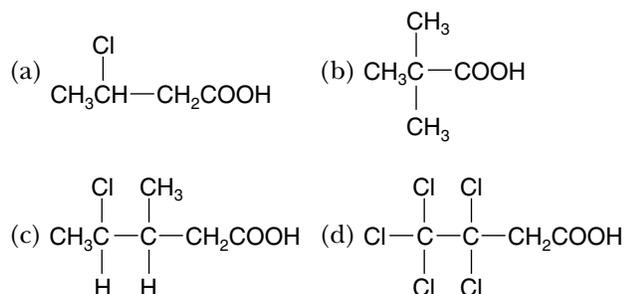
carboxylic acid	R1
carboxyl group	R2
ester	R4
esterification reaction	R4
triglyceride	R5
fatty acid	R5
fat	R6
oil	R6

QUESTIONS

R-1. Write the structural formula for each of the following carboxylic acids:

- propanoic acid
- 2-methylpropanoic acid
- 3,3-dimethylbutanoic acid
- 3-methylpentanoic acid

R-2. Give the IUPAC name of the following compounds:



R-3. Complete and balance the following equations:

- $\text{HCOOH}(aq) + \text{NaOH}(aq) \rightarrow$
- $\text{HCOOH}(aq) + \text{CH}_3\text{OH}(aq) \xrightarrow{\text{H}^+(aq)}$
- $\text{HCOOH}(aq) + \text{Ca}(\text{OH})_2(aq) \rightarrow$

R-4. Complete and balance the following equations:

- $\text{CH}_3\text{CH}_2\text{COOH}(aq) + \text{NH}_3(aq) \rightarrow$
- $\text{CH}_3\text{CH}_2\text{COOH}(aq) + \text{CH}_3\text{OH}(aq) \xrightarrow{\text{H}^+(aq)}$
- $\text{CH}_3\text{CH}_2\text{COOH}(aq) + \text{CH}_3\text{CH}_2\text{OH}(aq) \xrightarrow{\text{H}^+(aq)}$

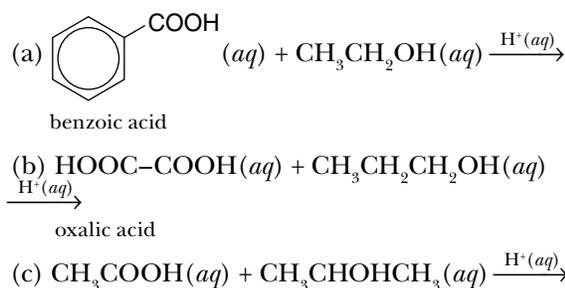
R-5. Complete and balance the following acid-base equations and name the salt formed in each case:

- $\text{CH}_3\text{CH}_2\text{COOH}(aq) + \text{KOH}(aq) \rightarrow$
- $\begin{array}{c} \text{CH}_3\text{CH}-\text{COOH} \\ | \\ \text{CH}_3 \end{array} (aq) + \text{KOH}(aq) \rightarrow$
- $\text{Cl}_2\text{CHCOOH}(aq) + \text{Ca}(\text{OH})_2(aq) \rightarrow$

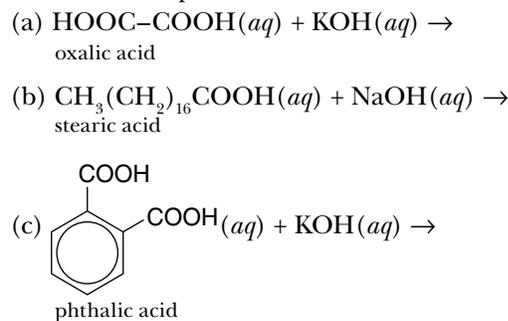
R-6. Write the structural formula for each of the following salts:

- sodium 2-chloropropanoate
- rubidium methanoate
- strontium 2,2-dimethylpropanoate
- lanthanum ethanoate

R-7. Complete and balance the following equations and name the products:



R-8. Complete and balance the following equations and name the products:



R-9. Animal fats and vegetable oils are triesters of glycerol with long-chain acids called fatty acids. These esters are generally called glycerides. Write a Lewis formula for the glyceride product in the following reaction:

