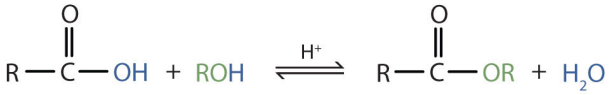
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation

Learning Objectives

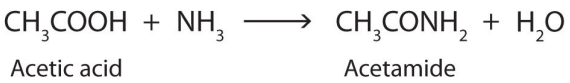
- To identify and describe the substances from which most esters are prepared.
- To identify and describe the substances from which most amides are prepared.

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

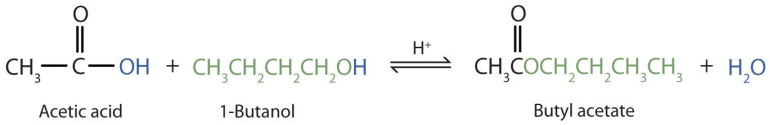


Amide formation



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:

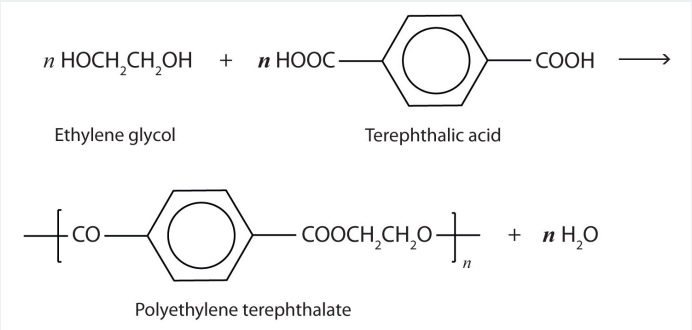


The reaction is reversible and will reach equilibrium with approximately equivalent amounts of reactants and products. Using excess amounts of alcohol and continuously removing a product, can drive the reaction towards the product side as per LeChatelier's principle.

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:



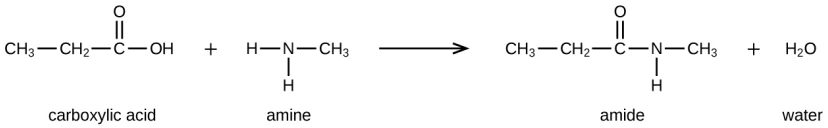
Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called 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 (NH_3) a *primary amide* is formed:

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

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.

$$\underset{\text{1,6-Hexanediamine}}{n\,H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2} + \underset{\text{Adipic acid}}{n\,HOOCCH_2CH_2CH_2CH_2COOH} \longrightarrow$$

$$\underset{\text{Nylon 66 (a polyamide)}}{-HN[COCH_2CH_2CH_2CH_2CONHCH_2CH_2CH_2CH_2CH_2CH_2NH]_nCO-} + 2n\,H_2O$$

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.
