Chemical of the Week

ACETIC ACID & ACETIC ANHYDRIDE

Acetic acid is the chemical compound responsible for the characteristic odor and sour taste of vinegar. Typically, vinegar is about 4 to 8% acetic acid. As the defining ingredient of vinegar, acetic acid has been produced and used by humans since before the dawn of recorded history. In fact, its name comes from the Latin for vinegar, *acetum*. Vinegar is formed from dilute solutions of alcohol, such as wine, by the action of certain bacteria in the presence of oxygen. These bacteria require oxygen, and the overall chemical change is the reaction of ethanol with oxygen to form acetic acid and water.

$$CH_3CH_2OH + O_2 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}OH + H_2O$$

The name, vinegar, comes from the French, *vin aigre*, which means "sour wine." Nevertheless, vinegar may also be obtained from other fermented beverages such as malt or cider.

Because vinegar is acidic, it has a variety of properties useful around the house. Mineral deposits left when hard water evaporates, such as those formed on plumbing fixtures and in tea kettles, dissolve in acids, so vinegar can be used to remove them. Because it is acidic, vinegar also inhibits the growth of bacteria, so vinegar is used as a preservative in foods, such as pickled vegetables, and as a mild disinfectant in cleaning. Of course, its sour taste, which is also a result of its acidity, makes it popular as a flavoring in cooking and in salad dressings.

Pure acetic acid was first isolated about 1700 by the distillation of vinegar. When pure, acetic acid is a clear, colorless liquid with a sharp, irritating odor of vinegar. In poorly heated laboratories, the acid was oftentimes found frozen inside its container because its freezing point is only slightly below room temperature at 16.7°C. The term glacial (ice-like) came to be applied to the pure acid in either its solid or liquid state. Glacial acetic acid boils at 118°C, and has a density of 1.049 g/mL at 25°C. It is flammable with a flash point of 39°C. Through hydrogen-bonding interactions, acetic acid is miscible (mixable) in all proportions with water, ethyl alcohol, and diethyl ether. Pure or concentrated solutions of acetic acid are very corrosive and can cause painful burns. Aqueous solutions of acetic acid freeze at temperatures below the freezing point of water.

For many years, the bulk of commercial acetic acid was produced by the oxidation of ethanol. Today, most industrial production of acetic acid is by the Monsanto process, in which carbon monoxide reacts with methanol under the influence of a rhodium complex catalyst at 180°C and pressures of 30–40 atm.

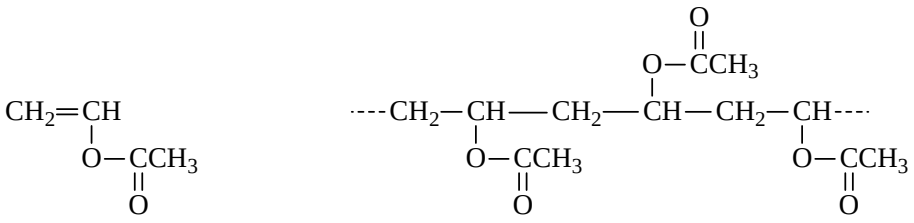
$$CO + CH_3OH \xrightarrow{[Rh(CO)_2I_2]^-} CH_3\overset{\overset{O}{\|}}{C}OH$$

Acetic acid is classified as a weak acid, because it does not completely dissociate into its component ions when dissolved in aqueous solution. At a concentration of 0.1 M, only about 1% of the molecules are ionized. In solution, there is a dynamic equilibrium between the neutral molecules and the acetate and hydronium ions.

$$CH_3\overset{\overset{O}{\|}}{C}OH + H_2O \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}O^- + H_3O^+$$

The acid dissociation constant (K_a value) for acetic acid is 1.8×10^{-5} at 25°C.

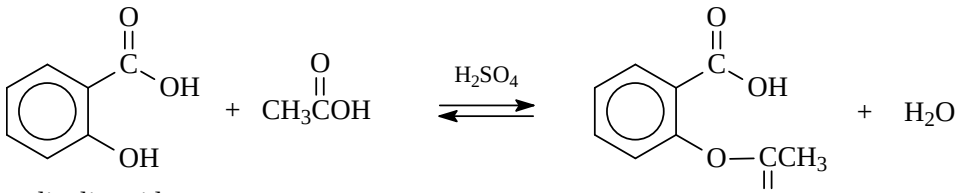
Acetic acid is an important industrial chemical. About 3.2×10^9 kilograms of acetic acid were produced in the United States in 1999. The primary use of this chemical is in the manufacture of assorted acetate esters. These are substances formed by reacting acetic acid with a substance containing a hydroxyl (–OH) group. Cellulose, found in cotton and wood, is a polymeric material containing multiple hydroxyl groups. It reacts with acetic acid to yield cellulose acetate, which is used to make films and textiles. Some photographic films are made of cellulose acetate, and rayon is made from cellulose acetate fibers. Vinyl acetate, another ester of acetic acid, polymerizes to form poly(vinyl acetate), which is used in water-based latex paints and in glues for paper and wood.



vinyl acetate poly(vinyl acetate)

Acetic acid is also used as a fungicide and as a solvent for many organic compounds.

Acetic acid is also used in the preparation of pharmaceuticals. Aspirin (acetylsalicylic acid) is formed by the reaction between acetic acid and salicylic acid.



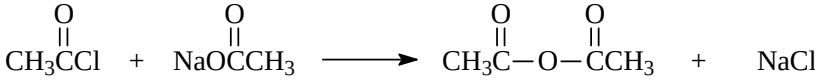
salicylic acid aspirin

This esterification reaction is reversible, however, and the presence of water can lead to hydrolysis of the aspirin. Thus, an *anhydrous* ("without water") reagent could lead to better yields of product. This reagent is acetic anhydride.

Acetic anhydride is a clear, colorless, mobile (free-flowing) liquid with a sharp odor similar to that of acetic acid. It hydrolyzes in water to yield acetic acid. In its liquid or vapor state, acetic anhydride can irritate body tissues, possibly leading to the death of such tissue. Acetic anhydride melts at –73°C, boils at 139°C, and has a density of 1.080 g/mL at 15°C. It is flammable with a flash point of 54°C. This compound is readily combustible and represents a fire hazard.

As the name indicates, an acid anhydride is a compound that is related to an acid by the loss of water. Acetic anhydride can by prepared by the dehydration of acetic acid at 800°C.

Alternatively, the reaction between the acid chloride and a salt of acetic acid (e.g. sodium acetate) yields acetic anhydride and a salt.



As with acetic acid, the primary use of acetic anhydride is used in the manufacture of cellulose acetate for films and plastic goods; about 75 percent of the acetic anhydride produced annually in the United States is used for this purpose. Approximately 1.5 percent of the annual acetic anhydride production is used in the synthesis of aspirin. Other uses include the manufacture of industrial chemicals, pharmaceuticals, perfumes, plastics, synthetic fibers, explosives, and weed killers. Because acetic anhydride reacts with water, it is sometimes used as a dehydrating agent in reaction mixtures where removal of water is necessary.