ESTERIFICATION

A variety of solvents, monomers, medicines, perfumes, and explosives are made from esters of nitric acid. Ethyl acetate, *n*-butyl acetate, *iso*-butyl acetate, glycerol trinitrate, pentaerythritol tetranitrate (PETN), glycol dinitrate, and cellulose nitrate are examples of such reactions.

Ester manufacture is a relatively simple process in which the alcohol and an acid are heated together in the presence of a sulfuric acid catalyst, and the reaction is driven to completion by removing the products as formed (usually by distillation) and employing an excess of one of the reagents. In the case of ethyl acetate, esterification takes place in a column that takes a ternary azeotrope. Alcohol can be added to the condensed overhead liquid to wash out the alcohol, which is then purified by distillation and returned to the column to react.

Amyl, butyl, and *iso*-propyl acetates are all made from acetic acid and the appropriate alcohols. All are useful lacquer solvents and their slow rate of evaporation (compared to acetone or ethyl acetate) prevents the surface of the drying lacquer from falling below the dew point, which would cause condensation on the film and a mottled surface appearance (*blushing*). Other esters of importance are used in perfumery and in plasticizers and include methyl salicylate, methyl anthranilate, diethyl-phthalate, dibutyl-phthalate, and di-2-ethylhexyl-phthalate.

Unsaturated vinyl esters for use in polymerization reactions are made by the esterification of olefins. The most important ones are vinyl esters: vinyl acetate, vinyl chloride, acrylonitrile, and vinyl fluoride. The addition reaction may be carried out in either the liquid, vapor, or mixed phases, depending on the properties of the acid. Care must be taken to reduce the polymerization of the vinyl ester produced.

Esters of allyl alcohol, e.g., diallyl phthalate, are used as bifunctional polymerization monomers and can be prepared by simple esterification of phthalic anhydride with allyl alcohol. Several acrylic esters, such as ethyl or methyl acrylates, are also widely used and can be made from acrylic acid and the appropriate alcohol. The esters are more volatile than the corresponding acids.

ETHYNYLATION

The *ethynylation* reaction involves the addition of acetylene to carbonyl compounds.

$$HC{\equiv}CH + R^1COR^2 \rightarrow HC{\equiv}CC(OH)R^1R^2$$

Heavy metal acetylides, particularly cuprous acetylide ($CuC{\equiv}CH$), catalyze the addition of acetylene ($HC{\equiv}CH$) to aldehydes ($RCH{=}O$).

FERMENTATION

Fermentation processes produce a wide range of chemicals that complement the various chemicals produced by nonfermentation routes. For example, alcohol, acetone, butyl alcohol, and acetic acid are produced by fermentation as well as by synthetic routes. Almost all the major antibiotics are obtained from fermentation processes.

Fermentation under controlled conditions involves chemical conversions, and some of the more important processes are:

1. O*xidation,* e.g., ethyl alcohol to acetic acid, sucrose to citric acid, and dextrose to gluconic acid
2. *Reduction,* e.g., aldehydes to alcohols (acetaldehyde to ethyl alcohol) and sulfur to hydrogen sulfide
3. *Hydrolysis,* e.g., starch to glucose and sucrose to glucose and fructose and on to alcohol
4. E*sterification,* e.g., hexose phosphate from hexose and phosphoric acid

FRIEDEL-CRAFTS REACTIONS

Several chemicals are manufactured by application of the Friedel-Crafts condensation reaction. Efficient operation of any such process depends on:

1. The preparation and handling of reactants
2. The design and construction of the apparatus
3. The control of the reaction so as to lead practically exclusively to the formation of the specific products desired
4. The storage of the catalyst (aluminum chloride)

Several of the starting reactants, such as acid anhydrides, acid chlorides, and alkyl halides, are susceptible to hydrolysis. The absorption of moisture by these chemicals results in the production of compounds that are less active, require more aluminum chloride for condensation, and generally lead to lower yields of desired product. Furthermore, the ingress of moisture into storage containers for these active components usually results in corrosion problems.

Anhydrous aluminum chloride needs to be stored in iron drums under conditions that ensure the absence of moisture. When, however, moisture contacts the aluminum chloride, hydrogen chloride is formed, the quantity of hydrogen chloride thus formed depends on the amount of water and the degree of agitation of the halide. If sufficient moisture is present, particularly in the free space in the container or reaction vessel or at the point of contact with the outside atmosphere, then hydrochloric acid is formed and leads to corrosion of the storage container.

In certain reactions, such as the isomerization of butane and the alkylation of isoparaffins, problems of handling hydrogen chloride and acidic sludge are encountered. The corrosive action of the aluminum chloride–hydrocarbon complex, particularly at 70 to 100°C, has long been recognized and various reactor liners have been found satisfactory.

The rate of reaction is a function of the efficiency of the contact between the reactants, i.e., stirring mechanism and mixing of the reactants. In fact, mixing efficiency has a vital influence on the yield and purity of the product. Insufficient or inefficient mixing may lead to uncondensed reactants or to excessive reaction on heated surfaces.