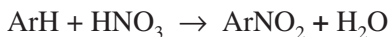


NITRATION

Nitration is the insertion of a nitro group ($-\text{NO}_2$) into an organic compound, usually through the agency of the reaction of a hydrocarbon with nitric acid. Concentrated sulfuric acid may be used as a catalyst.



More than one hydrogen atom may be replaced, but replacement of each succeeding hydrogen atom represents a more difficult substitution.

The nitrogen-bearing reactant may be:

1. Strong nitric acid
2. Mixed nitric and sulfuric acid
3. A nitrate plus sulfuric acid
4. Nitrogen pentoxide (N_2O_5)
5. A nitrate plus acetic acid

Both straight chain and ring-type carbon compounds can be nitrated; alkanes yield nitroparaffins.

The process for the production of nitrobenzene from benzene involves the use of mixed acid (Fig. 1), but there are other useful nitrating agents, e.g., inorganic nitrates, oxides of nitrogen, nitric acid plus acetic anhydride, and nitric acid plus phosphoric acid. In fact, the presence of sulfuric acid in quantity is vital to the success of the nitration because it increases the solubility of the hydrocarbon in the reaction mix, thus speeding up the reaction, and promotes the ionization of the nitric acid to give the nitronium ion (NO_2^+), which is the nitrating species. Absorption of water by sulfuric acid favors the nitration reaction and shifts the reaction equilibrium to the product.

Nitration offers a method of making unreactive paraffins into reactive substances without cracking. Because nitric acid and nitrogen oxides are strong oxidizing agents, oxidation always accompanies nitration. Aromatic nitration reactions have been important particularly for the manufacture of explosives. Nitrobenzene is probably the most important nitration product.

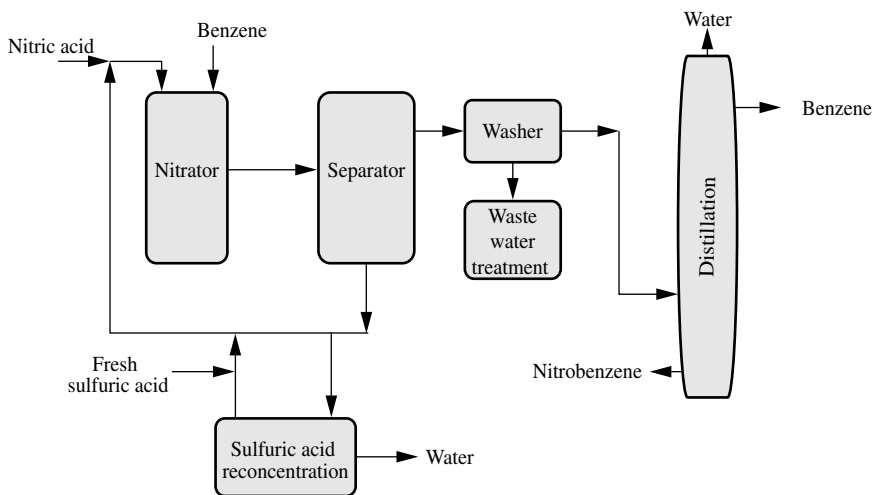


FIGURE 1 Production of nitrobenzene from benzene.

Certain esters of nitric acid (cellulose nitrate, glyceryl trinitrate) are often referred to as nitro compounds (nitrocellulose, nitroglycerin), but this terminology should be avoided.

Vapor-phase nitration of paraffin hydrocarbons, particularly propane, can be brought about by uncatalyzed contact between a large excess of hydrocarbon and nitric acid vapor at around 400°C, followed by quenching. A multiplicity of nitrated and oxidized products results from nitrating propane; nitromethane, nitroethane, nitropropanes, and carbon dioxide all appear, but yields of useful products are fair. Materials of construction must be very oxidation-resistant and are usually of ceramic-lined steel. The nitroparaffins have found limited use as fuels for race cars, submarines, and model airplanes. Their reduction products, the amines, and other hydroxyl compounds resulting from aldol condensations have made a great many new aliphatic syntheses possible because of their ready reactivity.

Nitration reactions are carried out in closed vessels that are provided with an agitating mechanism and means for controlling the reaction temperature. The nitration vessels are usually constructed of cast iron and steel, but often acid-resistant alloys, particularly chrome-nickel steel alloys, are used.

Plants may have large (several hundred gallon capacity) nitration vessels operating in a batch mode or small continuous units. The temperature is held at about 50°C, governed by the rate of feed of benzene. Reaction is rapid in well-stirred and continuous nitration vessels. The reaction products are

decanted from the spent acid and are washed with dilute alkali. The spent acid is sent to some type of recovery system and yields of 98 percent can be anticipated.

Considerable heat evolution accompanies the nitration reaction, oxidation increases it, and the heat of dilution of the sulfuric acid increases it still further. Increased temperature favors dinitration and oxidation, so the reaction must be cooled to keep it under control. Good heat transfer can be assured by the use of jackets, coils, and good agitation in the nitration vessel. Nitration vessels are usually made of stainless steel, although cast iron stands up well against mixed acid.

When temperature regulation is dependent solely on external jackets, a disproportional increase in nitration vessel capacity as compared with jacket surface occurs when the size of the machine is enlarged. Thus, if the volume is increased from 400 to 800 gallons, the heat-exchange area increases as the square and the volume as the cube of the expanded unit. To overcome this fault, internal cooling coils or tubes are introduced, which have proved satisfactory when installed on the basis of sound calculations that include the several thermal factors entering into this unit process.

A way of providing an efficient agitation inside the nitration vessel is essential if local overheating is to be mitigated. Furthermore, the smoothness of the reaction depends on the dispersion of the reacting material as it comes in contact with the charge in the nitration vessel so that a fairly uniform temperature is maintained throughout the vessel.

Nitration vessels are usually equipped with one of three general types of agitating mechanism: (1) single or double impeller, (2) propeller or turbine, with cooling sleeve, and (3) outside tunnel circulation.

The *single-impeller* agitator consists of one vertical shaft containing horizontal arms. The shaft may be placed off center in order to create rapid circulation past, or local turbulence at, the point of contact between the nitrating acid and the organic compound.

The *double-impeller* agitator consists of two vertical shafts rotating in opposite directions, and each shaft has a series of horizontal arms attached. The lower blades have an upward thrust, whereas the upper ones repel the liquid downward. This conformation provides a reaction mix that is essentially homogeneous.

The term *sleeve-and-propeller* agitation is usually applied when the nitration vessel is equipped with a vertical sleeve through which the charge is circulated by the action of a marine propeller or turbine. The sleeve is

usually made of a solid bank of acid-resisting cooling coils through which cold water or brine is circulated at a calculated rate. In order to obtain the maximum efficiency with this type of nitration vessel, it is essential to maintain a rapid circulation of liquid upward or downward in the sleeves and past the coils.

OXIDATION

Oxidation is the addition of oxygen to an organic compound or, conversely, the removal of hydrogen.

Reaction control is the major issue during oxidation reactions. Only partial oxidation is required for conversion of one organic compound into another or complete oxidation to carbon dioxide and water will ensue.

The most common oxidation agent is air, but oxygen is frequently used. Chemical oxidizing agents (nitric acid, dichromates, permanganates, chromic anhydride, chlorates, and hydrogen peroxide) are also often used.

As examples of oxidation processes, two processes are available for the manufacture of phenol, and both involve oxidation. The major process involves oxidation of cumene to cumene hydroperoxide, followed by decomposition to phenol and acetone. A small amount of phenol is also made by the oxidation of toluene to benzoic acid, followed by decomposition of the benzoic acid to phenol.

Benzoic acid is synthesized by liquid-phase toluene oxidation over a cobalt naphthenate catalyst with air as the oxidizing agent. An older process involving halogenation of toluene to benzotrichloride and its decomposition into benzoic acid is still used available.

Maleic acid and anhydride are recovered as by-products of the oxidation of xylenes and naphthalenes to form phthalic acids, and are also made specifically by the partial oxidation of benzene over a vanadium pentoxide (V_2O_5) catalyst. This is a highly exothermic reaction, and several modifications of the basic process exist, including one using butylenes as the starting materials.

Formic acid is made by the oxidation of formamide or by the liquid-phase oxidation of *n*-butane to acetic acid. The by-product source is expected to dry up in the future, and the most promising route to replace it is through carbonylation of methanol.

Caprolactam, adipic acid, and hexamethylenediamine (HMDA) are all made from cyclohexane. Almost all high-purity cyclohexane is obtained by hydrogenating benzene, although some for solvent use is obtained by careful distillation of selected petroleum fractions.

Several oxidative routes are available to change cyclohexane to cyclohexanone, cyclohexanol, and ultimately to adipic acid or caprolactam. If phenol is hydrogenated, cyclohexanone can be obtained directly; this will react with hydroxylamine to give cyclohexanone oxime that converts to caprolactam on acid rearrangement. Cyclohexane can also be converted to adipic acid, then adiponitrile, which can be converted to hexamethylenediamine. Adipic acid and hexamethylenediamine are used to form nylon 6,6. This route to hexamethylenediamine is competitive with alternative routes through butene.

Acetaldehyde is manufactured by one of several possible processes: (1) the hydration of acetylene, no longer a significant process. (2) the Wacker process, in which ethylene is oxidized directly with air or 99% oxygen (Fig. 1) in the presence of a catalyst such as palladium chloride with a copper chloride promoter. The ethylene gas is bubbled, at atmospheric pressure, through the solution at its boiling point. The heat of reaction is removed by boiling of the water. Unreacted gas is recycled following condensation of the aldehyde and water, which are then separated by distillation, (3) passing ethyl alcohol over a copper or silver gauze catalyst gives a 25 percent conversion to acetaldehyde, with recirculation making a 90 to 95 percent yield possible, and (4) a process in which lower molecular weight paraffin hydrocarbons are oxidized noncatalytically to produce mixed compounds, among them acetaldehyde and acetic acid.

Liquid-phase reactions in which oxidation is secured by the use of oxidizing compounds need no special apparatus in the sense of elaborate means for temperature control and heat removal. There is usually provided a kettle form of apparatus, closed to prevent the loss of volatile materials and fitted with a reflux condenser to return vaporized materials to the reac-

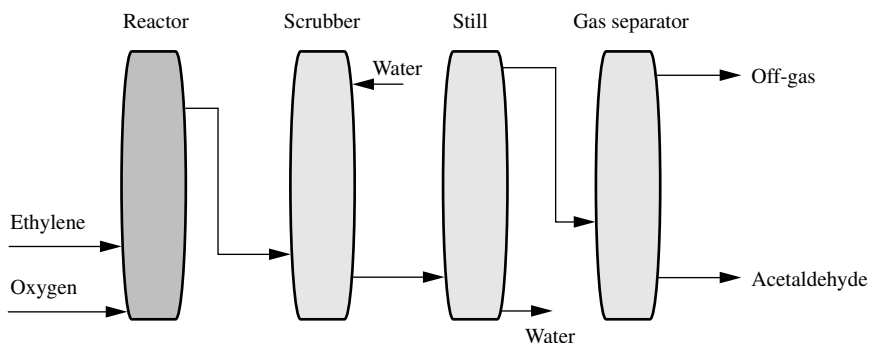


FIGURE 1 Production of acetaldehyde by the oxidation of ethylene.

tion zone, with suitable means for adding reactants rapidly or slowly as may be required and for removing the product, and provided with adequate jackets or coils through which heating or cooling means may be circulated as required.

In the case of liquid-phase reactions in which oxidation is secured by means of atmospheric oxygen—for example, the oxidation of liquid hydrocarbons to fatty acids—special means must be provided to secure adequate mixing and contact of the two immiscible phases of gaseous oxidizing agent and the liquid being oxidized. Although temperature must be controlled and heat removed, the requirements are not severe, since the temperatures are generally low and the rate of heat generation controllable by regulation of the rate of air admission.

Heat may be removed and temperature controlled by circulation of either the liquid being oxidized or a special cooling fluid through the reaction zone and then through an external heat exchanger. Mixing may be obtained by the use of special distributor inlets for the air, designed to spread the air throughout the liquid and constructed of materials capable of withstanding temperatures that may be considerably higher at these inlet ports than in the main body of the liquid. With materials that are sensitive to overoxidation and under conditions where good contact must be used partly to offset the retarding effect of necessarily low temperatures, thorough mixing may be provided by the use of mechanical stirring or frothing of the liquid.

By their very nature, the vapor-phase oxidation processes result in the concentration of reaction heat in the catalyst zone, from which it must be removed in large quantities at high-temperature levels. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material, and maintenance of temperature at the proper level is necessary to ensure the correct rate and degree of oxidation. With plant-scale operation and with reactions involving deep-seated oxidation, removal of heat constitutes a major problem. With limited oxidation, however, it may become necessary to supply heat even to oxidations conducted on a plant scale.

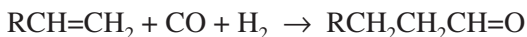
In the case of vapor-phase oxidation of aliphatic substances such as methanol and the lower molecular weight aliphatic hydrocarbons, the ratio of reacting oxygen is generally lower than in the case of the aromatic hydrocarbons for the formation of the desired products, and for this reason heat removal is simpler. Furthermore, in the case of the hydrocarbons, the proportion of oxygen in the reaction mixture is generally low, resulting in low per-pass conversions and, in some instances, necessitating preliminary heating of the reactants to reaction temperature.

Equipment for the oxidation of the aromatic hydrocarbons requires that the reactor design permit the maintenance of elevated temperatures, allow the removal of large quantities of heat at these elevated temperatures, and provide adequate catalyst surface to promote the reactions.

OXO REACTION

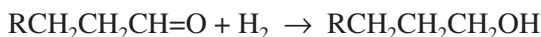
The *oxo reaction* is the general or generic name for a process in which an unsaturated hydrocarbon is reacted with carbon monoxide and hydrogen to form oxygen function compounds, such as aldehydes and alcohols.

In a typical process for the production of oxo alcohols, the feedstock comprises an olefin stream, carbon monoxide, and hydrogen. In a first step, the olefin reacts with CO and H₂ in the presence of a catalyst (often cobalt) to produce an aldehyde that has one more carbon atom than the originating olefin:



This step is exothermic and requires an ancillary cooling operation.

The raw aldehyde exiting from the oxo reactor then is subjected to a higher temperature to convert the catalyst to a form for easy separation from the reaction products. The subsequent treatment also decomposes unwanted by-products. The raw aldehyde then is hydrogenated in the presence of a catalyst (usually nickel) to form the desired alcohol:



The raw alcohol then is purified in a fractionating column. In addition to the purified alcohol, by-products include a light hydrocarbon stream and a heavy oil. The hydrogenation step takes place at about 150°C under a pressure of about 1470 psi (10.13 MPa). The olefin conversion usually is about 95 percent.

Among important products manufactured in this manner are substituted propionaldehyde from corresponding substituted ethylene, normal and *iso*-butyraldehyde from propylene, *iso*-octyl alcohol from heptene, and trimethylhexyl alcohol from di-*isobutylene*.

See Hydroformylation.