NITROBENZENE AND NITROTOLUENES

1. Introduction

Nitrobenzene [98-95-3] (oil of mirbane), $C_6H_5NO_2$, is a toxic pale yellow liquid with an odor that resembles bitter almonds; aqueous solutions are tasting sweet. Depending on the purity, its color varies from pale yellow to yellowish brown.

Nitrobenzene was first synthesized in 1834 by treating benzene with fuming nitric acid (1), and first produced commercially in England in 1856 (2). The relative ease of aromatic nitration has contributed significantly to the large and varied industrial applications of nitrobenzene, other aromatic nitro compounds, and their derivatives. Nitrobenzene is nowadays an important chemical intermediate its major use lying in the conversion to aniline mainly used in the polyurethane industry.

1.1. Physical Properties. Nitrobenzene is readily soluble in most organic solvents and is completely miscible with diethyl ether, benzene, and also miscible with alcohol. Nitrobenzene is only slightly soluble in water with a solubility of 0.19% at 20°C and 0.8% at 80°C and is steam volatile. Nitrobenzene is a good organic solvent especially known the be used in Friedel-Crafts reactions because of the good solubitility for the aluminum trichloride catalyst. The physical properties of nitrobenzene are summarized in Table 1.

Nitrobenzene forms binary azeotropes (3), for example, with acetamide (bp at 101 kPa: 202°C; 76% nitrobenzene), benzotrichloride (210.7; 98,5%), benzyl alcohol (204.2°C; 38%), 4-chlorophenol (219.9°C, 92%), *N,N*- diethylaniline (210,7°C, 97%), ethylene glycol (185.9°C, 41%), and propionamide (205.4°C, 76%).

1.2. Chemical Properties. Nitrobenzene reactions involve substitution on the aromatic ring and reactions involving the nitro group. Under the more common electrophilic conditions, the substitution occurs at a slower rate than for benzene, due to the electron-withdrawing properties of the nitro goup, which at the same time promotes substitution in the meta position. Nitrobenzene can undergo halogenation, sulfonation, and nitration, but it does not undergo Friedel-Crafts reactions. Under nucleophilic conditions, the nitro group promotes ortho and para substitution.

The reduction of the nitro group to yield aniline is the most commercially important reaction of nitrobenzene. Usually, the reaction is carried out by the catalytic hydrogenation of nitrobenzene, either in the gas or in the liquid phase with or without solvent, or by using iron borings and dilute hydrochloric acid (the Bechamp process), which represents the oldest known procedure to produce aniline.

Depending on the conditions, the reduction of nitrobenzene can lead to a variety of other products. The series of possible reduction products and intermediates is shown in Fig. 1 (see AMINES BY REDUCTION). Nitrosobenzene, *N*-phenylhydroxylamine, and aniline are primary reduction products. Azoxybenzene is formed by the condensation of nitrosobenzene and *N*-phenylhydroxylamine in alkaline solutions, and azoxybenzene can be reduced to form azobenzene and hydrazobenzene. The reduction products of nitrobenzene under various conditions are given in Table 2. Intermediate stages like nitrosobenzene are quite unstable and usually not isolable.

1.3. Manufacturing and Processing.

Nitrobenzene is manufactured commercially by the direct nitration of benzene using a mixture of nitric and sulfuric acids, which commonly is referred to as mixed or nitrating acid. Because two phases are formed in the reaction mixture and the reactants are distributed between them, the rate of nitration is controlled by mass transfer between the phases as well as by chemical kinetics (7), the reaction regime depending on several parameters, eg, sulfuric acid concentration, mixing energy (droplet size), temperature, and degree of conversion.

The reaction vessels are generally acid-resistant, glass-lined steel vessels or tubes equipped with efficient agitators or mixing devices. By vigorous agitation, the interfacial area of the heterogeneous reaction mixture is maintained as high as possible, thereby enhancing the mass transfer of reactants.

Nitrobenzene can be produced by either a batch or a continuous process. With a typical batch process, the reactor vessel is charged with benzene, then the nitrating acid (56–60 wt% H_2SO_4, 27–32 wt% HNO_3, and 8–17 wt% H_2O) is added slowly below the surface of the benzene. The temperature of the mixture is maintained at 50–55°C by adjusting the feed rate of the mixed acid and the amount of cooling. The temperature can be raised to ~90°C toward the end of the reaction to promote completion of reaction. The reactors contain internal cooling coils which control the temperature of the highly exothermic reaction (see EXPLOSIVES AND PROPELLANTS; NITRATION). In addition, batch reactors can be equipped with circulating external heat-exchange loops. This allows for efficient temperature control during the beginning of the reaction, when the reactor is not full enough to touch the internal cooling coils.

The reaction mixture is fed into a separator where the spent acid settles to the bottom and is drawn off to be refortified. The crude nitrobenzene is drawn from the top of the separator and washed in several steps with a dilute base, eg, sodium carbonate, sodium hydroxide, magnesium hydroxide, and then water. Depending on the desired purity of the nitrobenzene, the product can be distilled. Usually, a slight excess of benzene is used to ensure that little or no nitric acid remains in the spent acid. The batch reaction time generally is 2–4 h, and typical yields are 95–98 wt% based on benzene charged.

Because a continuous nitration process generally offers lower capital costs and more efficient labor usage than a batch process, most if not all of the nitrobenzene producers use continuous processes. The most common continuous process variants for the production of nitrobenzene are the isothermal on and the adiabatic nitration. Whereas the isothermal nitration used to be the most common nitration method in the past, nowadays state of the art is represented by the adiabtic nitration process.

A scheme of a typical continous isothermal nitration process is given in Fig. 2. Benzene and the nitrating acid (56–65 wt% H_2SO_4, 20–26 wt% HNO_3, and 15–18 wt% water) are fed into the nitrator, which can be a stirred cylindrical reactor with internal cooling coils and external heat exchangers or a cascade of such reactors. The nitrator also can be designed as a tubular reactor, eg, a tube-and-shell heat exchanger with appropriate cooling, involving turbulent flow (8). Generally, with a tubular reactor, the reaction mixture is pumped through the reactor in a recycle loop and a portion of the mixture is withdrawn and fed into the separator. A slight excess of benzene usually is fed into the nitrator to ensure that the nitric acid in the nitrating acid is consumed to the maximum possible extent and to minimize the formation of dinitrobenzene. The temperature of the nitrator is maintained at 50–100°C by varying the amount of cooling. Reaction times of 10–30 min are typical, and theoretical yields are 96–99%. The reaction mixture flows from the nitrator into a separator or centrifuge where it is separated into two phases. The aqueous phase or spent acid is drawn from the bottom and concentrated in a sulfuric acid reconcentration step or is recycled to the nitrator where it is mixed with nitric and fresh sulfuric acid immediately prior to being fed into the nitrator.

In the continous isothermal process, the spent sulfuric acid is generally reconcentrated in order to restore its nitration activity and to avoid waste streams of sulfuric acid by replacing spent acid by fresh acid. The reconcentration process (SAC = sulfuric acid concentration) is performed in a vacuum distillation using tantalum evaporators. Here H_2SO_4 concentrations of 75–92% are achieved (9). If the process is carried out at 130–195°C, these medium concentration ranges are sufficient to restore a suitable nitration activity and to destroy traces of organic by-products, thus preventing any loss in the efficiency or capacity of the nitration process. Compared to the isothermal nitration most commonly used today, adiabatic nitration processes (10) exhibits many advantages due to the fact that the heat of the reaction is not removed. First of all, exessive cooling of the reaction mixture, and thus involved costs in energy and investment, can be avoided. Furthermore, by working on an appropriate temperature level, the excess heat can be efficiently used for the sulfuric acid reconcentration step. This also allows the use of azeotropic 68% nitric acid instead of much more expensive and more dangerous highly concentrated 98% nitric acid. Thus, the heat of the nitration reaction (−117 kJ/mol) can be used so effectively that the process involving nitration and sulfuric acid concentration can be operated nearly authothermally, ie, only minor amounts of energy have to be introduced into the system. An additional advantage of this method is the reduction in reaction times to 0.5–7.5 min, leading to further savings in investment costs.

In a typical adiabatic nitration process, benzene and nitric acid are fed into a large recycle stream of sulfuric acid at temperatures of 80–110°C. The results in mixed-acid compositions of 4–8% HNO_3, 62–64% H_2SO_4 and 24–34% H_2O. The reaction mixture is led through a pipe reactor with static mixing devices or a casade of stirred tank reactors. By the nitration reaction, the reaction mixture is heated up to temperatures of 120–140°C. In order to suppress the unwanted dinitration reaction, benzene is used in excess of ~8–12 mol% with respect to nitric acid, leading to a complete consumption of nitric acid. After phase separation, the organic phase is removed for further processing, the acid phase is fed into a vacuum sulfuric acid reconcentration step, in which the inherent heat of the reaction is used to evaporate the excess water thereby cooling down the sulfuric acid to the required cycle acid temperature. The reconcentrated sulfuric acid is then fed back into the reaction. Benzene contained in the off gas and from nitrobenzene distillation is condensated and recycled back into reaction. Typical yield of a modern adiabatic nitration process is 99.3–99.8%. Most prominent by-products are mono- and dinitrophenols, as well as picric acid and small amounts of dinitrobenzene. Today, with this highly developed technique plant scales of 300–400 T/a are achieved.

Other options have been developed to eliminate the need for sulfuric acid concentration processes. In the azeotropic nitration of benzene (11,12) the nitration step is carried out at higher than usual temperatures (120–160°C). Because excess benzene is used, the higher temperature allows water to be removed as a water–benzene azeotrope. The water is separated and the benzene phase, containing ~8% nitrobenzene, is recycled back into the reactor. The dry sulfuric acid is then reused continuously.

Another concentration method involves passing an inert gas, eg, N_2 or CO_2, through the reaction medium (13). As the gas passes through, it becomes humidified and carries captured water with it. Most of the energy required for the gas humidification comes from the heat of reaction. An advantage is that expensive drying equipment is not needed. Also, the sulfuric acid mist formed in typical concentrators is minimized. Du Pont uses a similar process in its nitrobenzene production facility.

Because the highest possible interfacial area is desired for the heterogeneous reaction mixture, advances have also been made in the techniques used for mixing the two reaction phases. Several jet impingement reactors have been developed that are especially suited for nitration reactions (14). Reaction rates and yields are boosted in this method. It is also claimed that the formation of by-products, eg, mono-, di-, and trinitrophenol, is reduced by 50%. Another technique is to atomize the reactant layers by pressure injection through an orifice nozzle into a reaction chamber (15). This technique uses pressures of typically 0.21–0.93 MPa (30–135 psi) and consistently produces droplets <1 μm in size. The process is economical to build and operate, is safe, and leads to a substantially pure product. One drawback using these mixing devices, however, is the high dynamic pressure loss limiting the thoughput of the reactors due to the limited pumping power of the cycle acid pumps.

In all processes, the work-up of the crude nitrobenzene is very similar. In general, the crude nitrobenzene flows through a series of washer–separators where at first residual acid is removed by washing with water (acidic washing), then phenolic by-products and other organic acids are removed by a washing step with dilute base, followed by final washing steps with pure water. The product then is distilled to remove water and benzene, and if required, the nitrobenzene can be refined by vacuum distillation. The nitration process is unavoidably associated with the disposal of wastewater from the washing steps and from reconcentration of sulfuric acid. This water can contain nitrobenzene, mono- and polynitrated phenolics, carboxylic acids, other organic by-products, residual base, and inorganic salts from the neutralized spent acid that was present in the product. Treatment of this wastewater represents a significant expense for the producer. In some process, variants wastewater is extracted with benzene to remove the nitrobenzene, and benzene that is dissolved in the water is stripped from the water prior to the final waste treatment. In other process, variants nitrobenzene and benzene are removed by a stripping process alone.

Due to increasingly strict environmental regulations, effort has been put into reducing the amount of contaminants in the waste stream of the nitration process. For example, residual nitrobenzene can be removed from wastewater with a multistage extraction process in which the organic and aqueous phases are run countercurrent to each other (16). In the first step, the organic phase comes into contact with a countercurrent stream of alkali water that neutralizes residual acid. In the second step, the organic phase is extracted with water to remove residual alkali. Finally, the combined water layers are extracted with a stream of 0.5 parts of benzene per 1 part water. The benzene extracts only nitrobenzene, leaving any nitrophenols or picric acids in the water. This method can extract up to 99.44% of nitrobenzene from the wastewater.

A highly efficient process for removal of the highly bacterial toxic nitrophenols and picric acid in the wastewater stream coming from alkaline washing is the so-called thermal pressure decomposition, where the wastewater after stripping of residual nitrobenzene and benzene is heated up to 300°C at a pressure of 100 bars. The concentration of nitrophenolic compounds in the wastewater can be reduced to <5 ppm without adding any addtional oxidant before applying the final biological treatment (17).

The need for neutralization of the organic phase with alkali can be reduced by extracting the acidic contaminants using molten salts, preferably a mixture of zinc nitrate and magnesium nitrate, at 55–70°C (18). Since the two phases are not miscible, the organic layer can be removed, leaving behind the acidic contaminants in the molten salt. The salts are then regenerated by flashing off nitric acid. If necessary, the organic phase can undergo a polishing neutralization.

The acidic contaminants can also be removed by employing a system that utilizes extractions, precipitation, distillation, and other treatments for rendering the waste stream acceptable for current disposal standards (19–21). First Chemical Corporation uses such a system. Residual nitric acid can be removed by a multistage countercurrent liquid–liquid extraction. The nitric acid (~25%) is then reconcentrated by distillation for further use.

Environmental aspects, as well as the requirement of efficient mixing in the mixed-acid process, have led to the development of single-phase nitrations. These can be divided into liquid- and vapor-phase nitrations. One liquid-phase technique involves the use of 98% by weight nitric acid, with temperatures of 20–60°C and atmospheric pressure (22). The molar ratios of nitric acid/benzene are 2 : 1 to 4 : 1. After the reaction is complete, excess nitric acid is vacuum distilled and recycled. An analogous process is used to simultaneously produce a nitrobenzene and dinitrotoluene mixture (23). A conversion of 100% is obtained without the formation of nitrophenols or nitrocresols. The nitrobenzene and dinitrotoluene are separated by distillation.

The use of vapor-phase nitrations has been one of the most active areas in research for aromatic nitration chemistry since the 1970s. Although several approaches have been reported, most of the patents issued have one technique in common: the use of solid nitration catalysts (qv). The nitric acid–benzene mixture flows through the solid catalyst in a continuous process using the appropriate molar ratios, temperatures, and pressures. Obviously, this technique eliminates the need for neutralizing or washing the product to remove acidic contaminants. The catalysts range from silica–alumina types to transitional-metal catalysts. The percent conversion varies depending on the catalyst used. Table 3 summarizes some of the reported results.

The drawback in most of the described approaches is a lack of long-term stability of the catalyst. Todate, vapor-phase nitration of benzene has been operated on an industrial scale. Generally, one can say that because of the development of the high energy integrated low investment adiabatic nitration it will be difficult for research to find an efficient and economic alternative process. The major goal that remains to be achieved is a by-product free nitration process, since the majority of investment and operating costs are presently linked to processing procedures for product and waste water.

1.4. Economic Aspects. Two main areas affecting the economic aspects for nitrobenzene production are process related costs, including raw material costs, energy requirements, waste treatment, etc, and the United States and world demand for products made from nitrobenzene. The most significant costs related to the production process are raw material costs. These typically are at least 85% of the production costs for nitrobenzene.

Annual statistics for the U.S. nitrobenzene market from 1960 to 1994 are shown in Table 4 (30,31). More recently, U.S. demand has increased to 2.9 million lb in 2004 and is expected to grow to 3.5 million in 2008. The U.S. production in 2005 is planned to be 3.01 million lb. Prices between 1999 and 2004 vary between a low of 0.35 ¢/lb and a current high of 0.65 ¢/lb (32). As of mid-2005, the principal U.S. producers of nitrobenzene were Rubicon Inc., First Chemical Corporation, Du Pont and BASF Corporation.

1.5. Specifications and Test Methods. Specifications for double-distilled nitrobenzene are listed in Table 5.

Several qualitative spot tests are applicable to nitrobenzene and depend on a characteristic color developed by its reaction with certain reagents (32). However, these tests are not specific to nitrobenzene because other aromatic nitro compounds yield colored products that are similar or only slightly different in color. One example of such a test is the heating or fusing of nitrobenzene with diphenylamine, which yields a reddish-yellow color. In general, calorimetric methods also are subject to interferences from aromatic nitro compounds. Certain colorimetric methods are based on the nitration of nitrobenzene to *m*-nitrobenzene and subsequent determination by the generation of a red-violet color with acetone and alkali. A general titrimetric method for the determination of aromatic nitro compounds is based on reduction with titanium(III) sulfate or chloride in acidic solution followed by back-titration of excess titanium(III) ions with a standard ferric alum solution (33). Although the freezing and distillation ranges of nitrobenzene are commonly used indicators of purity, most modern techniques use instrumental methods, eg, gas chromatography and high pressure liquid chromatography (hplc). A further tested parameter is electrical conductivity in order to control the efficiency of the washing process.

1.6. Health and Safety Factors. Nitrobenzene is a very toxic substance; the maximum allowable concentration for nitrobenzene is 1 ppm or 5 mg/m^3 (6). It is readily absorbed by contact with skin and by inhalation of vapor. If a worker was exposed for 8 h to 1 ppm nitrobenzene in the working atmosphere, ~25 mg of nitrobenzene would be absorbed, of which about one-third would be by skin absorption and the remainder by inhalation. The primary effect of nitrobenzene is the conversion of hemoglobin to methemoglobin; thus the conversion eliminates hemoglobin from the oxygen-transport cycle. Exposure to nitrobenzene may irritate the skin and eyes. Nitrobenzene affects the central nervous system and produces fatigue, headache, vertigo, vomiting, general weakness, and in some cases unconsciousness and coma. There generally is a latent period of 1–4 h before signs or symptoms appear. Nitrobenzene is a powerful methemoglobin former, and cyanosis appears when the methemoglobin level reaches 15%. Chronic exposure can lead to spleen and liver damage, jaundice, and anemia. Alcohol ingestion tends to increase the toxic effects of nitrobenzene; thus alcohol in any form should not be ingested by the victim of nitrobenzene poisoning for several days after the nitrobenzene poisoning or exposure. Impervious protective clothing should be worn in areas where risk of splash exists. Ordinary work clothes that have been splashed should be removed immediately, and the skin washed thoroughly with soap and warm water. In areas of high vapor concentrations (>1 ppm), full face masks with organic-vapor canisters or air-supplied respirators should be used. Clean work clothing should be worn daily, and showering after each shift should be mandatory.

With respect to the hazards of fire and explosion, nitrobenzene is classified as a moderate hazard when exposed to heat or flame. Nitrobenzene is classified by the ICC as a Class-B poisonous liquid.

1.7. Uses. The largest end use for nitrobenzene is in the production of aniline (see ANILINE AND ITS DERIVATIVES). Approximately 98% of nitrobenzene is converted to aniline; the demand for nitrobenzene fluctuates with the demand for aniline. The remaining 2% of nitrobenzene capacity is used to produce a variety of other products, such as *para*-aminophenol [123-30-8] (PAP) and nigrosine dyes. The U.S. producers of PAP are Mallinckrodt, Inc., Rhône-Poulenc, and Hoechst Celanese. Mallinckrodt is the largest producer having increased the capacity steadily from 30 million lb in 1991 to 70 million lb in 2005 (32). The PAP product is used primarily as an intermediate for acetaminophen [103-90-2].

A smaller volume use of PAP is the production of dyestuffs and resins. Nigrosine dyes are widely used as black colorants in plastics, inks (qv), textiles, and shoe polishes.

1.8. Derivatives. *Mononitrochlorobenzenes. Properties.* The physical properties of the ortho, meta, and para isomers of nitrochlorobenzene are summarized in Table 6.

o-Nitrochlorobenzene crystallizes in light yellow, monoclinic needles. It is insoluble in water and very soluble in benzene, diethyl ether, and hot ethanol. *o*-Nitrochlorobenzene reactions involve the nitro group, chlorine atom, and aromatic ring. The nitro group can be partially reduced to the corresponding intermediate or fully to the amino group. The aromatic ring can be nitrated, leading to the formation of 2,4-dinitrochlorobenzene [97-00-7] and 2,6-dinitrochlorobenzene [606-21-3], or it can be sulfonated, yielding 3-nitro-4-chlorobenzenesulfonic acid [121-18-6]. The chlorine atom can be replaced easily by OH, OCH_3, OC_6H_5, NH_2, etc, by nucleophilic attack. Treatment of *o*-nitrochlorobenzene with aqueous sodium hydroxide at 130°C results in the formation of *o*-nitrophenol [88-75-5], and with aqueous methanolic potassium hydroxide at high temperature and pressure, *o*-nitroanisole [91-23-6] is formed. When *o*-nitrochlorobenzene is treated with aqueous ammonia under high temperature and pressure, *o*-nitroaniline [88-74-4] is formed. *o*-Nitrochlorobenzene condenses with aniline to form 2-nitrodiphenylamine [119-75-5].

m-Nitrochlorobenzene is a pale yellow crystalline solid that can exist as a stable or labile form in the solid state. It is insoluble in water, very soluble in benzene and diethyl ether, and soluble in acetone, chloroform, and hot ethanol. Unlike the ortho and para isomers, the chlorine atom of *m*-nitrochlorobenzene is not activated for nucleophilic substitution.

p-Nitrochlorobenzene crystallizes in light yellow monoclinic prisms. It is insoluble in water and very soluble in benzene, diethyl ether, and hot ethanol. *p*-Nitrochlorobenzene undergoes the same reactions described for the ortho isomer to yield the analogous para derivatives. Tin(II) chloride and hydrochloric acid convert *p*-nitrochlorobenzene to *p*-chloroaniline. The aromatic ring of the para isomer can undergo additional substitution by nitration to yield 2,4-dinitrochlorobenzene, by chlorination to yield 3,4-dichloronitrobenzene [99-54-7], or by sulfonation to yield 2-chloro-5-nitrobenzenesulfonic acid [96-73-1]. The chlorine atom is activated and, as with the ortho isomer, can be easily displaced by nucleophilic attack. Treatment with aqueous ammonia at elevated temperature and pressure results in the formation of *p*-nitroaniline [100-01-6]. Treatment with aqueous sodium hydroxide under pressure gives *p*-nitrophenol [100-02-7]. *p*-Nitrochlorobenzene reacts with sodium disulfide to form 4,4′-dinitrodiphenyl disulfide [100-32-3], which is an intermediate in the preparation of sulfanilamide derivatives.

Manufacturing and Processing. Chlorobenzene can be nitrated at 40–70°C with a nitrating acid consisting of 52.5 wt% H_2SO_4, 35.5 wt% HNO_3, and 12 wt% H_2O. The technique and equipment are similar to that described for the nitration of benzene. The resulting product is a mixture of isomers containing ~ 34 wt% *o*-nitrochlorobenzene, 65 wt% *p*-nitrochlorobenzene, and 1 wt% *m*-nitrochlorobenzene. The mixture is cooled to a temperature slightly above its freezing point (~15°C) and a large portion of the para isomer slowly crystallizes and is separated from the mother liquor. The liquid mixture of isomers is separated by a combination of fractional distillation and crystallization. Other methods of preparing the mononitrochlorobenzenes are chlorination of nitrobenzene, the diazotization of nitroanilines and replacement by chlorine (Sandmeyer reaction), and the reaction of phosphorus pentachloride with the nitrophenols. These reactions are used on a laboratory scale, but are not of commercial interest.

Several patents have been issued that offer improvements in chloronitrobenzene production. Most are vapor-phase nitrations using solid catalysts. Table 7 lists some of these results.

Economic Aspects. U.S. production of chloronitrobenzenes in 1993 was 54,431 metric tons/year of which 19,099 metric tons were the ortho isomer and 35,332 metric tons the para isomer. The meta isomer is not isolated in U.S. production. The bulk fob prices of *o*- and *p*-chloronitrobenzene were $1.72/kg and $2.01/kg, respectively. Chloronitrobenzenes are manufactured by Du Pont and Monsanto Co. In 2003, global capacity for *p*-nitrochlorobenzene had grown to 430,000 metric tons, of which 58% are produced in China. Market perspectives, however, are critical due to falling demand and environmental legislation (34).

Health and Safety Factors. The mononitrochlorobenzenes are toxic substances that may be absorbed through the skin and lungs giving rise to methemoglobin. Their toxicity is about the same as or greater than that of nitrobenzene. The para isomer is less toxic than the ortho isomer, and the maximum allowable concentration that has been adopted for *p*-nitrochlorobenzene is 1 mg/m^3 (0.1 ppm) (6). The mononitrochlorobenzenes are moderate fire hazards when exposed to heat or flame. They are classified by the ICC as Class-B poisons. The same handling precautions should be used for these compounds as are used for nitrobenzene.

Uses. *o*-Nitrochlorobenzene is used in the synthesis of azo dye intermediates, eg, *o*-chloroaniline (Fast Yellow G Base), *o*-nitroaniline (Fast Orange GR Base), *o*-anisidine (Fast Red BB Base), *o*-phenetidine, and *o*-aminophenol (see DYES, AZO). It also is used in corrosion inhibitors, pigments, and agriculture chemicals. *p*-Nitrochlorobenzene is used principally in the production of intermediates for azo and sulfur dyes. Other uses include pharmaceuticals (qv), photochemicals, rubber chemicals (qv), and insecticides (see INSECTICIDES). Typical intermediates manufactured from the para isomer are *p*-nitroaniline (Fast Red GC Base), *p*-anisidine, *p*-aminophenol, *p*-nitrophenol, *p*-phenylenediamine, 2-chloro-*p*-anisidine (Fast Red R Base), 2,4-dinitrochlorobenzene, and 1,2-dichloro-4-nitrobenzene.

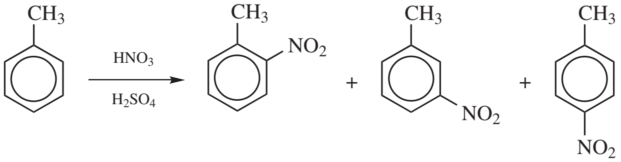
Other Nitrochlorobenzenes. *2,4-Dinitrochlorobenzene.* This compound is a yellow solid that can exist in three forms: one stable and two labile. The stable α-form crystallizes in yellow rhombic crystals from diethyl ether; mp α is 53.4°C, β 43°C, and 27°C; bp at 101 kpa (= 1atm) 315°C with slight decomposition; d_4^{22} α 1.697 g/cm^3, d_4^{20} β 1.680 g/cm^3; flash point (closed cup) 194°C; vapor density (air = 1) 6.98 (05,06). 2,4-Dinitrochlorobenzene [97-00-7] is insoluble in water and soluble in benzene, hot ethanol, diethyl ether, and carbon disulfide.

3,4-Dichloronitrobenzene. This compound crystallizes in needles from ethanol and has both a stable and labile form. The stable α-form has a melting point of 42–43°C, and the β-form is a liquid that changes to the α-form at 15°C (6); bp at 101 kpa (1 atm) 225–256°C; d_4^{75} 1.4558 g/cm^3; vapor density (air = 1), 6.6 (3,5,6). It is insoluble in water and soluble in diethyl ether, hot ethanol, and benzene. It can be prepared by the chlorination of *p*-nitrochlorobenzene or by the nitration of *o*-dichlorobenzene. The isomers are separated by fractional distillation and crystallization. 3,4-dichloronitrobenzene [99-54-7] is produced by Du Pont.

2,5-Dichloronitrobenzene. 2,5-Dichloronitrobenzene [89-61-2] crystallizes in prisms or plates from ethanol; mp 56°C; bp at 101 kpa (1 atm) 267°C; d_4^{75} 1.4390 g/cm^3; vapor density (air = 1), 6.6 (3,6). It is insoluble in water and soluble in hot ethanol, diethyl either, and benzene. It is prepared by the nitration of *p*-dichlorobenzene and is used extensively in the manufacture of dyestuff intermediates. 2,5-dichloronitrobenzene is produced by Du Pont.

2. Nitrotoluenes

2.1. Mononitrotoluenes. The mononitration of toluene results in the formation of a mixture of the ortho, meta, and para isomers of nitrotoluene. The presence of the methyl group on the aromatic ring facilitates the nitration, but it also increases the ease of oxidation as a side reaction.



Physical and Chemical Properties. *o*-Nitrotoluene [88-72-2] is a clear yellow liquid. The solid is dimorphous and the melting points of the α- and β-forms are −9.55 and −3.85°C, respectively. *o*-Nitrotoluene is infinitely soluble in benzene, diethyl ether, and ethanol. It is soluble in most organic solvents and only slightly soluble in water (0.065 g in 100 g of water at 30°C). The physical properties of *o*-nitrotoluene are listed in Table 8.

The strong electron−acceptor action of the nitro group in *o*-nitrotoluene confers increased reactivity on the methyl group; thus the methyl group is easily oxidized. Oxidation with potassium permanganate or potassium dichromate causes the formation of *o*-nitrobenzoic acid [552-16-9]. When boiled with a sodium hydroxide solution, *o*-nitrotoluene exhibits the phenomena of autoxidation and reduction and yields anthranilic acid. When the oxidation is carried out with manganese dioxide and sulfuric acid, *o*-nitrobenzoic acid or *o*-nitrobenzaldehyde [552-89-6] is formed, depending on the reaction conditions. One method of reducing *o*-nitrotoluene to *o*-toluidine is by iron powder and hydrochloric acid. Alkaline reduction with iron or zinc leads in a stepwise fashion to azoxy, azo, and hydrazo compounds, depending on the reaction conditions. Nitration of *o*-nitrotoluene gives 2,5-dinitrotoluene [121-14-2] and 2,6-dinitrotoluene [606-20-2]. Chlorination of *o*-nitrotoluene in the absence of iron yields *o*-nitrobenzyl chloride [612-23-7], *o*-chlorotoluene, or *o*-chlorobenzyl chloride, depending on the reaction conditions. In the presence of iron, chlorination results in the formation of 2-nitro-6-chlorotoluene [83-42-1] and 2-nitro-4-chlorotoluene [89-59-8].

m-Nitrotoluene [99-08-1] is a clear yellow liquid that freezes at 16.1°C. It is soluble in most organic solvents, eg, ethanol, benzene, and diethyl ether, and is only sparingly soluble in water, 0.05 g/100 g of water at 30°C. The physical properties of *m*-nitrotoluene are given in Table 9.

m-Nitrotoluene does not have an active methyl group as do the ortho and para isomers. It is oxidized readily to *m*-nitrobenzoic acid [121-92-6] by chromic acid and more slowly by potassium hexacyanoferrate(III) in alkaline solution. *m*-Nitrobenzaldehyde [99-61-6] is the chief product of the electrolytic oxidation of *m*-nitrotoluene. Acid, neutral, or catalytic reduction of *m*-nitrotoluene yields *m*-toluidine. Nitration of *m*-nitrotoluene yields primarily 3,4-dinitrotoluene [610-39-9] and small amounts of 2,3-dinitrotoluene [602-01-7] and 2,5-dinitrotoluene [619-15-8].

p-Nitrotoluene [99-99-0] crystallizes in colorless rhombic crystals. It is only slightly soluble in water, 0.044 g/100 g of water at 30°C; moderately soluble in methanol and ethanol; and readily soluble in acetone, diethyl ether, and benzene. The physical properties of *p*-nitrotoluene are listed in Table 10.

The methyl group of *p*-nitrotoluene is activated by the para nitro group. *p*-Nitrotoluene is oxidized to *p*-nitrobenzoic acid [62-23-7] by potassium hexacyanoferrate(III) in alkaline solution, potassium permanganate, or potassium dichromate. *p*-Nitrotoluene is converted to *p*-nitrobenzaldehyde [555-16-8] by electrolytic oxidation in an acetic acid–sulfuric acid mixture or by treatment with lead(IV) oxide in concentrated sulfuric acid. *p*-Nitrotoluene is reduced by iron and hydrochloric acid to *p*-toluidine.

Alkaline reduction with iron leads to the formation of a mixture of azoxy, azo, and hydrazo compounds, depending on the reaction conditions. Nitration of *p*-nitrotoluene gives 2,4-dinitrotoluene. Chlorination can occur on either the aromatic ring or the methyl group, and the resulting product depends on the catalyst and reaction conditions used. Under free-radical reaction conditions, *p*-nitrobenzyl chloride [100-14-1] is formed, and in the presence of iron or antimony(III) chloride, 4-nitro-2-chlorotoluene [121-86-8] is obtained. *p*-Nitrotoluene undergoes sulfonation, yielding 2-methyl-5-nitrobenzenesulfonic acid [32784-87-5]. Heating *p*-nitrotoluene with an alcoholic potassium hydroxide solution results in the formation of 4,4′-dinitrostilbene [2501-02-2].

Manufacture and Processing. Mononitrotoluenes are produced by the nitration of toluene in a manner similar to that described for nitrobenzene. The presence of the methyl group on the aromatic ring facilitates the nitration of toluene, as compared to that of benzene, and increases the ease of oxidation that results in undesirable by-products. Thus the nitration of toluene generally is carried out at lower temperatures than the nitration of benzene to minimize oxidative side reactions. Because toluene nitrates at a faster rate than benzene, the milder conditions also reduce the formation of dinitrotoluenes. Toluene is less soluble than benzene in the acid phase, thus vigorous agitation of the reaction mixture is necessary to maximize the interfacial area of the two phases and the mass transfer of the reactants. The rate of a typical industrial nitration can be modeled in terms of a fast reaction taking place in a zone in the aqueous phase adjacent to the interface where the reaction is diffusion controlled.

Mononitrotoluenes can be produced by either a batch or continuous process. With a typical batch process, the toluene is fed into the nitrator and cooled to ∼25°C. The nitrating acid (52–56 wt% H_2SO_4, 28–32 wt% HNO_3, and 12–20 wt% H_2O) is added slowly below the surface of the toluene and the temperature of the reaction mixture is maintained at 25°C by adjusting the feed rate of the nitrating acid and the amount of cooling. After all of the acid is added, the temperature is raised slowly to 35–40°C. After completion of the reaction, the reaction mixture is put into a separator where the spent acid is withdrawn from the bottom and is reconcentrated. The crude product is washed in several steps with dilute caustic and then water. The product is steam distilled to remove excess toluene and then dried by distilling the remaining traces of water. The resulting product contains 55–60 wt% *o*-nitrotoluene, 3–4 wt% *m*-nitrotoluene, and 35–40 wt% *p*-nitrotoluene. The yield of mononitrotoluenes is ∼96%.

Although several patents pertain to the production of nitrotoluene, most of these processes report yields of only 50% or lower (r15,r24–r26,r28,r29). The main thrust for these patents has been the nitration of benzene, with toluene being included to strengthen the patent estate. A few higher yield processes, however, have been reported. Toluene reacts with nitronium salts, eg, NO_2BF_4, in the presence of catalytic amounts of crown ethers or polyethers to give nitrotoluene in 70% yield (37). The reaction occurs at room temperature and gives lower yields of *m*-nitrotoluene, which is desirable. Another process reacts toluene with nitric acid (qv) in the presence of solid silica–alumina catalysts in the gas phase to form nitrotoluene in 95% yield (27). Both of these methods have the advantage of eliminating the use of sulfuric acid.

The separation of the isomers is carried out by a combination of fractional distillation and crystallization. In a fractional vacuum distillation step, the distillate, obtained at a head temperature of 96–97°C at 1.6 kpa (12 mmHg), is fairly pure *o*-nitrotoluene and can be purified further by crystallization. The meta isomer is distilled from a mixture of *m*- and *p*-nitrotoluene and can be purified further by additional distillation and crystallization steps. The bottoms product from the distillation steps is cooled in a crystallizer to obtain *p*-nitrotoluene.

Effort has focused on increasing the amount of the para isomer formed in the mononitration of toluene, because it generally is in the greatest demand of the three isomers. In a typical nitration with mixed nitric and sulfuric acids, the ratio of *p*-nitrotoluene: *o*-nitrotoluene (para/ortho) usually is 0.6. Nitration of toluene with nitric acid in the presence of phosphoric acid leads to an increase in formation of the para isomer with a para/ortho ratio of 1.11 (7,38,39). Nitration with nitric acid in the presence of various aromatic sulfonic acids either in solution or on a support, eg, diatomaceous earth, results in increased selectivity toward para substitution with para/ortho ratios of 0.8–1.5 (40–42). Normally with this technique, a large excess of toluene and a relatively large amount of catalyst must be used with highly concentrated nitric acid. Another approach to increase the selectivity for para nitration has been the addition of anhydrous calcium sulfate, where the amount added is based on moles of water formed in the nitration reaction; para/ortho ratios of 1.20–1.35 are obtained (43). Gas-phase nitration of toluene with nitric acid in the presence of a carrier substance, based on SiO_2 and/or Al_2O_3 and impregnated with a high boiling inorganic acid, has been described (44). This technique is carried out with a large excess of toluene at 0.7–6.7 kpa (5.3–50.3 mmHg) and 100–140°C; para/ortho ratios of 1.2–2.0 are obtained. The effect of the different catalysts on the isomer distribution of the mononitrotoluenes is summarized in Table 11.

If pure isomers are required, the ortho and meta compounds can be prepared by indirect methods. *o*-Nitrotoluene can be obtained by treating 2,4-dinitrotoluene with ammonium sulfide followed by diazotization and boiling with ethanol. *m*-Nitrotoluene can be prepared from *p*-toluidine by acetylation, nitration deacetylation, diazotization, and boiling with ethanol. A fairly pure *p*-nitrotoluene, which has been isolated from the isomeric mixture, can be purified further by repeated crystallization.

Economic Aspects. Annual 1993 U.S. production of the mononitrotoluenes is 26,000 metric tons, with ~16,120 metric tons of the ortho isomer, 780 metric tons of the meta isomer, and 9100 metric tons of the para isomer. The prices of *o*-, *m*-, and *p*-nitrotoluene in bulk fob are \$1.15/kg, \$2.54/kg, and \$3.64/kg, respectively. The mononitrotoluenes are manufactured by Du Pont and First Chemical Corp.

Specifications and Test Methods. *o*-Nitrotoluene can be analyzed for purity and isomer content by infrared (ir) spectroscopy with an accuracy of ~1%. *p*-Nitrotoluene content can be estimated by the decomposition of the isomeric toluene diazonium chlorides because the ortho and meta isomers decompose more readily than the para isomer. A colorimetric method for determining the content of the various isomers is based on the color which forms when the mononitrotoluenes are dissolved in sulfuric acid (47). From the absorption of the sulfuric acid solution at 436 and 305 nm, the ortho and para isomer content can be determined, and the meta isomer can be obtained by difference. However, this and other colorimetric methods are subject to possible interferences from other aromatic nitro compounds. A titrimetric method, based on the reduction of the nitro group with titanium(III) sulfate or chloride, can be used to determine mononitrotoluenes (33). Chromatographic methods, eg, gas chromatography or hplc, are well suited for the determination of mononitrotoluenes as well as its individual isomers. Freezing points are used commonly as indicators of purity of the various isomers.

Health and Safety Factors. The toxic effects of the mononitrotoluenes are similar to, but less pronounced than, those described for nitrobenzene. The maximum allowable concentration for the mononitrotoluenes is 2 ppm (11 mg/m^3) (6). Mononitrotoluenes are low grade methemoglobin formers (4) and may be absorbed through the skin and respiratory tract. The toxicity of alkyl nitrobenzenes decreases with an increasing number of alkyl groups and increases with an increasing number of nitro groups. The mononitrotoluenes represent moderate fire hazards when exposed to heat or flame. The same precautions used in handling nitrobenzene should be used for these compounds.

Uses. *o*-Nitrotoluene is used in the synthesis of intermediates for azo dyes, sulfur dyes, rubber chemicals, and agriculture chemicals. Typical intermediates are *o*-toluidine, *o*-nitrobenzaldehyde, 2-nitro-4-chlorotoluene, 2-nitro-6-chlorotoluene, 2-amino-4-chlorotoluene (Fast Scarlet TR Base), and 2-amino-6-chlorotoluene (Fast Red KB Base). *p*-Nitrotoluene is used principally in the production of intermediates for azo and sulfur dyes. Typical intermediates are *p*-toluidine, *p*-nitrobenzaldehyde, and 4-nitro-2-chlorotoluene.

2.2. Dinitrotoluenes. Dinitration of toluene results in the formation of a number of isomeric products, and with a typical sulfuric–nitric acid nitrating mixture the following mixture of isomers is obtained: 75 wt% 2,4-dinitrotoluene [121-14-2], 19 wt% 2,6-dinitrotoluene [606-20-2], 2.5 wt% 3,4-dinitrotoluene [610-39-9], 1 wt% 2,3-dinitrotoluene [602-01-7], and 0.5 wt% 2,5-dinitrotoluene [619-15-8]. The dinitrotoluenes are carcinogenic, a moderate fire and explosion hazard when exposed to heat or flame, however, they are sensitive to impact and have detonation propagating properties especially at higher temperatures. The maximum allowable concentration in air is 1.5 mg/m^3 (0.2 ppm). Dinitrotoluenes are used as intermediates for the production of toluene diisocyanate and dyestuffs. They also are used as explosives.

Dinitrotoluene as an isomeric mixture is manufactured in large scale continuous plants with annual capacities of 200.000–300.000 metric tons. Most commonly a two-stage isothermal nitration with azeotropic nitric acid as nitrating agent and sulfuric acid (75–96%) as nitration catalyst is applied. Reaction apparatus, loop or stirred tank reactors, are very similar to those used in continuous isothermal nitration of benzene (see above). Spent sulfuric acid is reconcentrated in large sulfuric acid concentration units (SAC) by multistage vacuum distillation. After washing the DNT isomeric mixture (mp 55°C) is in most cases directly converted to toluylene diamine (TDA) by hydrogenation.

2,4-Dinitrotoluene crystallizes in yellow needles from carbon disulfide and is soluble in a number of organic solvents. It is only slightly soluble in water, 0.03 g/100 g of water at 22°C. Its physical properties are listed in Table 12.

2,4-Dinitrotoluene can be prepared by the nitration of *p*-nitrotoluene with yields of ∼ 96% or it can be obtained from the direct nitration of toluene. 2,4-Dinitrotoluene is oxidized to 2,4-dinitrobenzoic acid [610-30-0] by potassium permanganate or chromic acid, and is reduced to 2,4-diaminotoluene by iron and acetic acid. It is reduced partially by zinc chloride and hydrochloric acid to 2-amino-4-nitrotoluene [99-55-8] and by ammonium sulfide to 4-amino-2-nitrotoluene [119-32-4].

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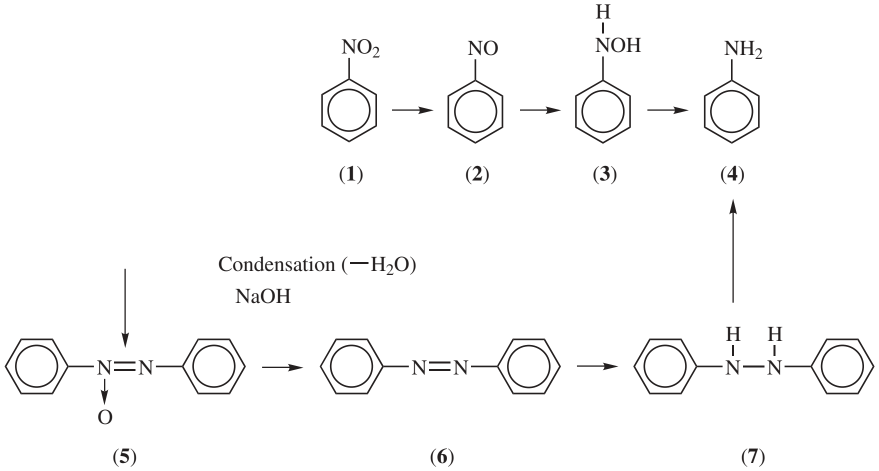

Fig. 1. Reduction Products of Nitrobenzene (**1**): nitrosobenzene [98-95-3] (**2**); *N*-phenylhydroxylamine [100-65-2] (**3**); aniline [62-53-3] (**4**); azoxybenzene [495-48-7] (**5**); azobenzene [103-33-3] (**6**); and hydrazobenzene [122-66-7] (**7**).

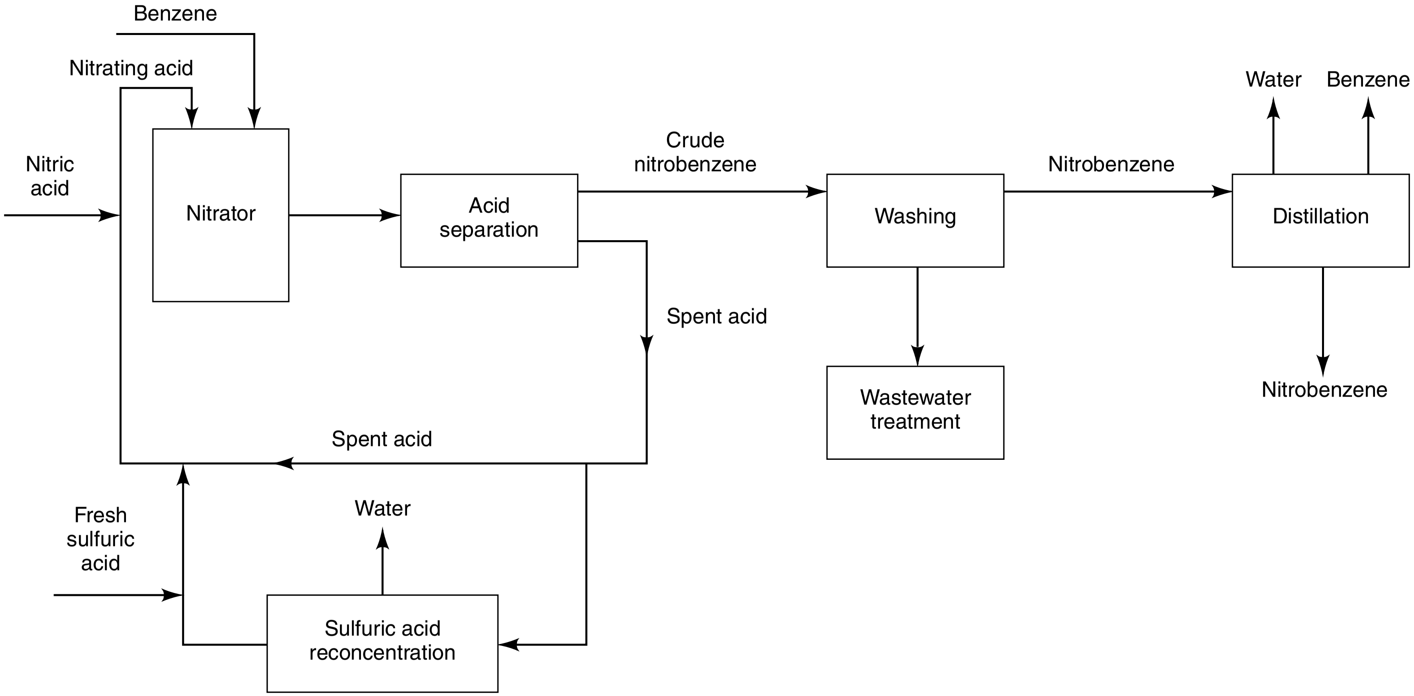

Fig. 2. Typical continuous nitrobenzene process.

Table 1. **Physical Properties of Nitrobenzene**

Property	Value	Reference
mp, °C	5.85	3
bp, °C		3
at 101 kPa[a]	210.9	
13 kPa[a]	139.9	
0.13 kPa[a]	53.1	
density, g/cm^3		
d_4^{0b}	1.223	3
d_4^{10}	1.213	3
d_4^{25}	1.199	4
refractive index, $n_D{}^{20}$	1.55296	3
viscosity at 15°C, mPa(= cP)	2.17	5
surface tension at 20°C, mN/m(= dyn/cm)	46.34	5
dielectric constant at 25°C	34.82	5
specific heat at 30°C, J/g[c]	1.509	5
latent heat of vaporization, J/g[c]	331	5
latent heat of fusion, J/g[c]	94.2	5
heat of combustion at constant volume, MJ/mol	3.074	3
flash point (closed cup),°C	88	4
autoignition temperature,°C	482	6
explosive limit at 93°C, vol % in air	1.8	6
vapor density (air = 1)	4.1	4

[a] To convert kPa to mmHg, multiply by 7.5.

[b] Supercooled liquid.

[c] To convert J to cal, divide by 4.184.

Table 2. **Reduction Products of Nitrobenzene**

Reagent	Product
Fe, Zn, or Sn + HCl	aniline
H_2 + metal catalyst + heat (gas phase or solution)	aniline
$SnCl_2$ + acetic acid	aniline
Zn + NaOH	hydrazobenzene, azobenzene
Zn + H_2O	*N*-phenylhydroxylamine
Na_3AsO_3	azoxybenzene
$LiAlH_4$	azobenzene
$Na_2S_2O_3 + Na_3PO_4$	sodium phenylsulfamate, $C_6H_5NHSO_3Na$

Table 3. **Vapor-Phase Nitration of Benzene**

Catalyst	Conversion,%	Reference
alumina–silica–metal oxide	99	23
acidic sheet clay, acidic composite oxides	91	24
solid supported sulfuric catalysts	96	25
silica–alumina zeolites	95	26
molecular sieves, $\geq 5 \times 10^{-4}$ μm	92	27
nitrate salts (KNO_3, $NaNO_3$, $LiNO_3$)	40	28

Table 4. **U.S. Production, Sales, and Prices of Nitrobenzene**[a]

Year	Production, t	Sales, t	Price,[b] $/kg
1960	73,600	2,800	0.24
1962	90,500	4,100	0.24
1964	108,500	4,300	0.21
1966	148,300	6,200	0.21
1968	180,500	5,200	0.19
1970	248,400	7,600	0.19
1972	250,000	5,700	0.19
1974	229,800	8,800	0.21
1976	185,500	8,800	0.51
1978	378,750	9,163	0.51
1980	412,770	na[c]	na[c]
1982	351,444	8,482	0.73
1984	464,933	12,746	0.73
1986	434,497	na[c]	0.73
1988	557,919	na[c]	0.73
1990	532,972	na[c]	0.73
1992	612,350	na[c]	0.73
1994	739,356	na[c]	0.73

[a] Ref. 29.
[b] Ref. 30.
[c] Not available = na.

Table 5. **Specifications of Double-Distilled Nitrobenzene**[a]

Property	Value
purity,%	≥99.8
color	clear, light yellow to brown
freezing point,°C	≥5.13
distillation range (first drop),[a] °C	≥207
dry point,[b] °C	212
moisture,%	<0.1
acidity as HNO_3,%	<0.001

[a] Boiling at 207–210°C is 95%.

[b] Temperature at which no liquid remains.

Table 6. **Physical Properties of Mononitrochlorobenzenes**

Property	*o*-Nitrochlorobenzene	*m*-Nitrochlorobenzene	*p*-Nitrochlorobenzene
CAS Registry Number	[88-73-3]	[121-73-3]	[100-00-5]
melting point, °C	32.5[a]	46 (stable)[b]	83[c]
		24 (labile)[b]	
boiling point, °C$^{d}_{\mathrm{kPa}}$	246^{a}_{100}	236^{a}_{101}	242^{a}_{101}
	$119^{b}_{1.1}$		$113^{b}_{1.1}$
density,[e] g/mL	1.368	1.534	1.520
flash point,[c] closed cup, °C	123	103	110

[a] Ref. 5.

[b] Ref. 3.

[c] Ref. 6.

[d] To convert kPa to mmHg, multiply by 7.5.

[e] d_4^{22}.

Table 7. **Vapor-Phase Nitration of Chlorobenzene**

Catalysts	Conversion,%	Reference
alumina–silica–metal oxide	100	23
group 4b–3b mixed oxide	80	33
acidic sheet clay, acidic composite oxides	90	24
solid-supported sulfuric catalysts	93	25
HNO_3/phosphoric acid mixture (anhydrous)	100	34

Table 8. **Physical Properties of *o*-Nitrotoluene**

Property	Value	Reference
melting point, °C		
α	−9.55	3
β (stable form)	−3.85	3
boiling point, °C		
at 101 kPa[a]	221.7	35
0.13 kPa[a]	50.0	6
density, g/mL		
d_{15}^{19}	1.1622	6
d_4^{20}	1.163	4
d_4^{60}	1.124	5
refractive index, n_D^{20}	1.5474	3
surface tension at 20°C, mN/m (= dyn/cm)	44.1	5
viscosity at 20°C, mPa (= cP)	2.37	5
heat of combustion at constant volume, MJ/mol[b]	3.75	5
vapor density (air = 1)	4.72	6
flash point (closed cup), °C	106	6

[a] To convert kPa to mmHg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

Table 9. **Physical Properties of *m*-Nitrotoluene**

Property	Value	Reference
melting point, °C	16.1	5
boiling point, °C		
at 101 kPa[a]	231.9	5
13.3 kPa[a]	156.9	35
0.13 kPa[a]	50.2	35
density, g/mL, d_4^{20}	1.1581	5
refractive index, $n_D{}^{20}$	1.5470	3
surface tension at 25°C, mN/m(= dyn/cm)	43.5	5
viscosity at 20°C, mPa(= cP)	2.33	5
heat of combustion at constant volume, MJ/mol[b]	3.732	36
vapor density (air = 1)	4.72	6
flash point (closed cup),°C	106	6

[a] To convert kPa to mmHg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

Table 10. **Physical Properties of *p*-Nitrotoluene**

Property	Value	Reference
melting point, °C	53.5	5
boiling point, °C		
at 101 kPa[a]	238.5	5
1.2 kPa[a]	104.5	3
0.13 kPa[a]	53.7	6
density, g/mL		
d_4^{20}	1.286	35
d_4^{73}	1.1038	3
refractive index, $n_D^{62.6}$	1.5346	4
surface tension at 60°C, mN/m(= dyn/cm)	42.3	5
viscosity at 60°C, mPa(= cP)	1.2	5
heat of combustion at constant volume, MJ/mol[b]	3.718	5
vapor density (air = 1)	4.72	6
flash point (closed cup), °C	106	6

[a] To convert kPa to mmHg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

Table 11. **Isomer Ratio of Mononitrotoluenes with Different Catalysts**

Catalyst	Para, wt%	Ortho, wt%	Meta, wt%	p/o ratio	Conversion,%	Reference
normal mixed acid	38	58	4	0.6	98	
H_3PO_4	50.2	45.1	4.3	1.11	99.6	38
m-benzenedisulfonic acid (BDA)	43.6	53.8	2.9	0.81	92.8	37
BDA on Celite 545				1.53	92	45
anhydrous $CaSO_4$	54.4	43.2	2.3	1.26	89	40
5% H_2SO_4 on Al_2O_3	62.5	34.0	3.5	1.84	61.1	41
NO_2BF_4/polyether				0.91	70	46
silica–alumina zeolite	55	40	5	1.4	95	26
alumina–silica–metal oxide	52	48	0	1.09	48.7	23

Table 12. **Physical Properties of 2,4-Dinitrotoluene**

Property	Value	Reference
melting point,°C	64–66	5
boiling point at 101 kPa (= 1 atm),°C	300[a]	5
density, g/mL		
d_4^{15}	1.521	6
d_4^{71}	1.321	5
vapor density (air = 1)	6.27	6
heat of combustion, MJ/mol[b]	3.568	5
flash point,°C	207	6

[a] Slight decomposition.

[b] To convert J to cal, divide by 4.184.