NITRATION

1. Introduction

Nitration is defined in this article as the reaction between a nitration agent and an organic compound that results in one or more nitro ($-NO_2$) groups becoming chemically bonded to an atom in this compound. Nitric acid is used as the nitrating agent to represent C-, O-, and N-nitrations. O-nitrations result in esters. N-nitrations result in nitramines.

$$\mathrm{C{-}H + HNO_3 \longrightarrow C{-}NO_2 + H_2O}$$
$$\mathrm{C{-}OH + HNO_3 \longrightarrow C{-}O{-}NO_2 + H_2O}$$
$$\mathrm{N{-}H + HNO_3 \longrightarrow N{-}NO_2 + H_2O}$$

In the examples, a nitro group is substituted for a hydrogen atom, and water is a by-product. Nitro groups may, however, be substituted for other atoms or groups of atoms. In Victor Meyer reactions which use silver nitrite, the nitro group replaces a halide atom, eg, I or Br. In a modification of this method, sodium nitrite dissolved in dimethyl formamide or other suitable solvent is used instead of silver nitrite (1). Nitro compounds can also be produced by addition reactions, eg, the reaction of nitric acid or nitrogen dioxide with unsaturated compounds such as olefins or acetylenes.

Nitrations are highly exothermic, ie, ca 126 kJ/mol (30 kcal/mol). However, the heat of reaction varies with the hydrocarbon that is nitrated. The mechanism of a nitration depends on the reactants and the operating conditions. The reactions usually are either ionic or free-radical. Ionic nitrations are commonly used for aromatics; many heterocyclics; hydroxyl compounds, eg, simple alcohols, glycols, glycerol, and cellulose; and amines. Nitration of paraffins, cycloparaffins, and olefins frequently involves a free-radical reaction. Aromatic compounds and other hydrocarbons sometimes can be nitrated by free-radical reactions, but generally such reactions are less successful.

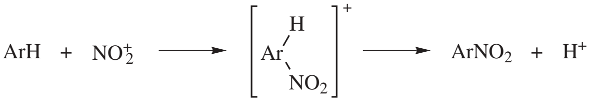
2. Ionic Nitration Reactions

Acid mixtures containing nitric acid and a strong acid, eg, sulfuric acid, perchloric acid, selenic acid, hydrofluoric acid, boron trifluoride, or an ion-exchange resin containing sulfonic acid groups, can be used as the nitrating feedstock for ionic nitrations. These strong acids are catalysts that result in the formation of nitronium ions, NO_2^+. Sulfuric acid is almost always used industrially since it is both effective and relatively inexpensive.

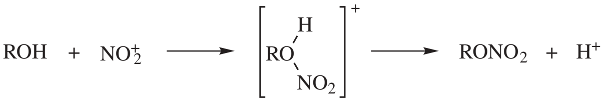
Most ionic nitrations are performed at 0–120°C. For nitrations of most aromatics, there are two liquid phases: an organic and an acid phase. Sufficient pressure, usually slightly above atmospheric, is provided to maintain the liquid phases. A large interfacial area between the two phases is needed to expedite transfer of the reactants to the interface and of the products from the interface. The site of the main reactions is often at or close to the interface (2). To provide large interfacial areas, a mechanical agitator is frequently used.

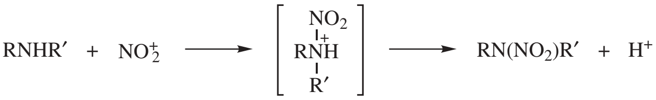
2.1. Mechanism.

The NO_2^+ mechanism has been accepted since about 1950 for the nitration of most aromatic hydrocarbons, glycerol, glycols, and numerous other hydrocarbons in which mixed acids or highly concentrated nitric acid are used. The mechanism has been discussed in detail and critically analyzed (1). NO_2^+ attacks an aromatic compound (ArH) as follows:



For an alcohol, glycol, or glycerol, or for amines, the reaction may be represented:





When sulfuric acid is present in the mixed acids, the following ionization reactions occur. These ionic reactions are rapid, and equilibrium concentrations of NO_2^+ are likely to be present at all times in the acid phase. NO_2^+ concentrations depend mainly on the composition of the mixed acids but decrease to some extent as the temperature increases (3).

$$H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O \tag{1}$$

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+ \tag{2}$$

$$2\,HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \tag{3}$$

$$HNO_3 + H_2O \rightleftharpoons NO_3^+ + H_3O^+ \tag{4}$$

Figure 1 indicates how the NO_2^+ concentrations vary at 20°C as a function of the molar composition of the acid mixture; these results were determined using Raman spectra readings.

To model previously researched NO_2^+ data (3), equilibrium constants were first calculated for equations 1–3. At 20°C, $K_1 = 0.0622$, $K_2 = 211.7$, and $K_3 = 154 \times 10^{-6}$. The experimental data are predicted in general within the bounds of experimental accuracy. Because equation 4 is not an independent equation in this set, K_4 can be calculated at 20°C as 0.524.

Benzene, toluene, and other aromatics that are easily nitrated can sometimes be nitrated using acids having zero NO_2^+ concentrations (see Fig. 1). Two explanations for this are (*1*) NO_2^+ is actually present but in concentrations too low to be measured by Raman spectra, and (*2*) NO_2^+ is hydrated to form $H_2NO_3^+$, which is also a nitrating agent.

A considerable body of experimental results have been reported when N_2O_5–HNO_3 and N_2O_5–solvent mixtures were used as nitrating agents (4,5). NO_2^+ is produced in such mixtures as follows:

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$$

The overall nitration reaction between an aromatic and N_2O_5 mixtures is as follows:

$$ArH + N_2O_5 \longrightarrow ArNO_2 + HNO_3$$

Mixtures of HNO_3, H_2SO_4, and SO_3 also result in high concentrations of NO_2^+, and toluene can be readily nitrated at −40 to −10°C as a result (6). At these low temperatures, the formation of the meta-isomer of mononitrotoluene (MNT) is greatly reduced. Such a reduction is highly desired in the production both of dinitrotoluenes (DNTs) employed to produce intermediates for polyurethane production and of trinitrotoluene (TNT), which is a high explosive. *m*-MNT results in the production of undesired DNT and TNT isomers (see NITROBENZENE AND NITROTOLUENES).

Substituted aromatics, eg, alkylbenzenes, sometimes experience attack at the substituent position by NO_2^+ (7). A cyclohexadienyl cation is formed; it is unstable and the nitro group migrates on the ring to a carbon atom that is attached to a hydrogen. Loss of the proton results in a stable nitroaromatic.

In addition to the conventional mixed acids commonly used to produce DNT, a mixture of NO_2 and H_2SO_4 (8), a mixture of NO_2 and oxygen (9), and just HNO_3 (10) can also be used. Terephthalic acid and certain substituted aromatics are more amenable to nitrations using HNO_3, as compared to those using mixed acids. For compounds that are easily nitratable, acetic acid and acetic anhydride are sometimes added to nitric acid (qv). Acetyl nitrate, which is a nitrating agent, is produced as an intermediate as follows:

$$(CH_3CO)_2O + HNO_3 \longrightarrow CH_3CONO_3 + CH_3COOH$$

Acetic anhydride and acetic acid increase the solubility of the two phases in each other, and they are employed for the commercial N-nitration of hexamethylenetetramine [100-97-0] (11) to form cyclotrimethylenetrinitramine [121-82-4] (RDX), $(CH_2)_3(NNO_2)_3$. Renewed consideration has been given to replacing H_2SO_4 with an improved solid catalyst to reduce the environmental problems of disposal or reconcentration of the waste acid and to increase production of desired nitrated isomers. For example, a catalyst with suitable pore size might increase the production of 4-MNT and reduce that of 3-MNT when toluene is nitrated.

The nitronium-ion mechanism predicts reasonably well most aspects of aromatic nitrations including isomer distribution, kinetics, and relative rates in mixtures (1). Isomer distribution, eg, for mononitration of toluene, is predicted well. However, the distribution is difficult to explain when the mixed acids contain $\geq$90 wt% H_2SO_4. In general, the rates of nitration are essentially proportional to the NO_2^+ concentrations (see Fig. 1). The relative rates of nitration when mixtures of aromatics are used are in accord with substituents on the aromatic ring affecting the reactivity of the compound because of polar and steric factors. Aromatics with attached alkyl groups, eg, toluene, ethylbenzene, or cumene, are more reactive than benzene. An alkyl group increases the electron density of the ring at the ortho and para positions. As a result, NO_2^+ reacts predominately at these positions of the ring. Mass-transfer effects, and hence agitation, however, affect the relative importance of isomers produced (12). Aromatics with attached nitro groups, eg, mononitrobenzene (MNT), are always nitrated with considerably more difficulty than the unnitrated aromatics. Attached nitro groups reduce the electron density of the ring and are meta-directing. Generally, an aromatic compound is almost completely mononitrated before being di- or trinitrated, since more stringent conditions are required for the subsequent nitration steps than for the initial one.

Nitrous acid or nitrite salts may be used to catalyze the nitration of easily nitratable aromatic hydrocarbons, eg, phenol or phenolic ethers. It has been suggested that a nitrosonium ion (NO^+) attacks the aromatic, resulting initially in the formation of a nitrosoaromatic compound (13). Oxidation of the nitrosoaromatic then occurs:

$$\mathrm{ArNO} + \mathrm{HNO_3} \longrightarrow \mathrm{ArNO_2} + \mathrm{HNO_2}$$

The nitrosonium ion is produced from nitrous acid and nitric acid.

$$\mathrm{HNO_2} + \mathrm{HNO_3} \rightleftharpoons \mathrm{NO^+} + \mathrm{NO_3^-} + \mathrm{H_2O}$$

Some investigators, however, believe NO_2^+ is the nitrating agent for these easily nitrated aromatics.

Numerous by-products have been detected during aromatic nitrations (14,15). Two types of oxidations involving HNO_3 occur during toluene nitrations: (*1*) oxidation of the methyl group and (*2*) ring oxidations or decompositions yielding gaseous by-products. Ring decompositions are reported (16) to occur primarily in the acid phase and are the principal method of oxidation during the manufacture of TNTs. However, numerous oxidations also occur in the hydrocarbon phase owing to the solubility of HNO_3 in nitroaromatics. HNO_3 solubility in general increases as the amounts of DNTs and especially TNTs increase in the organic phase, and as the concentrations of HNO_3 increase in the acid phase. H_2SO_4 and water are, however, much less soluble in the organic phase. Dissolved HNO_3, which is essentially anhydrous, is an effective oxidizing agent especially at higher temperatures. Oxidation-type by-products include benzaldehyde, nitrobenzaldehydes, nitrophenols, nitrocresols, nitrobenzoic acid, tetranitromethane, nitrous acid, NO_x, and water. Condensation by-products are also often produced in significant quantities. The white compound produced in TNT processes is a solid and is an example of condensation.

Zeolites have recently been employed as solid catalysts for the vapor-phase nitration of aromatics with nitric acid. Additional research is required to improve yields and to minimize loss of catalytic activity as the nitration progresses (see MOLECULAR SIEVES).

2.2. Kinetics of Aromatic Nitrations. The kinetics of aromatic nitrations are functions of temperature, which affects the kinetic rate constant, and of the compositions of both the acid and hydrocarbon phases. In addition, a larger interfacial area between the two phases increases the rates of nitration since the main reactions occur at or near the interface. Larger interfacial areas are obtained by increased agitation and by the proper choice of the volumetric % acid in the liquid–liquid dispersion. At high % acid, the dispersions are acid-continuous, but at low % acid, they are hydrocarbon-continuous. Unfortunately no quantitative evidence is available on how the interfacial area varies as the % acid in the dispersion changes. Research indicates, however, that at least for some dispersions, a maximum interfacial area occurs in both the acid-continuous and the hydrocarbon-continuous regions, but not at the boundary between the two (17). The viscosities and densities of the two phases and the interfacial tension between the phases are important physical properties affecting the interfacial area. Such properties are, of course, dependent on both temperature and the respective compositions of the phases. Temperature also changes the solubilities of various compounds in either the acid or hydrocarbon phase (18,19). Such dissolved compounds often result in by-product formation.

Rates of nitration determined over a range of temperatures in two-phase dispersions have been used to calculate energies of activation from 59–75 kJ/mol (14–18 kcal/mol). Such energies of activation must be considered as only apparent, since the true kinetic rate constants, NO_2^+ concentrations, and interfacial area all change as temperature is increased.

Increased agitation of a given acid–hydrocarbon dispersion results in an increase in interfacial areas owing to a decrease in the average diameter of the dispersed droplets. In addition, the diameters of the droplets also decrease to relatively low and nearly constant values as the volume % acid in the dispersions approaches either 0 or 100%. As the droplets decrease in size, the ease of separation of the two phases, following completion of nitration, also decreases.

2.3. Industrial Applications. Significant process changes have occurred in many nitration plants. Batch nitrations were used almost exclusively in the 1940s, but continuous-flow units are widely used in the 1990s, especially in plants having relatively large production capacities. A well-designed continuous-flow plant often offers all of the following advantages, per unit weight of product, as compared to batch units: increased safety, decreased energy requirements, reduced amounts of undesired by-products, fewer environmental problems, reduced labor requirements, and lower operating expenses.

Many nitrated products are explosives, including DNT, TNT, and nitroglycerine (NG). At least some mononitroaromatics can also be exploded under certain conditions (20). Because of the high heats of nitration, runaway reactions followed by severe explosions have occurred in industrial batch nitrators. To minimize these potential hazards, the compositions of the feed acids and reaction conditions are currently better controlled than formerly. The objective is to so operate that most of the HNO_3 reacts within the reactor, and the resulting used acid is mainly a mixture of H_2SO_4 and water. In some processes, 99% or more of the feed HNO_3 reacts. Dispersions (or mixtures) of such a waste acid and the nitration product are relatively safe to handle.

Considerable effort has been made to minimize energy requirements in the nitration plants. For example, both Chemetics, Inc. (21) and Josef Meissner GmbH and Co. (22) have developed adiabatic processes for the production of nitrobenzene (NB). The heat of nitration is used to provide energy for preheating the feed streams and for flashing of the used acid phase. In the Chemetics process, mixed acids and a 10% excess of benzene are fed to the bottom of a series of well-agitated reactors. The temperature increases to a considerable extent because of the nitration. Over 99.5% of the nitric acid reacts, and about 90% of the benzene is converted to NB. The two phases are separated, and the hydrocarbon phase is distilled to separate NB and benzene. The hot acid phase containing mainly H_2SO_4 and water is flashed at subatmospheric pressure to obtain an acid containing up to 70% H_2SO_4. Only a small amount of heat needs to be added to reconcentrate the acid. The reconcentrated acid is combined with feed HNO_3 and is then recycled. Six such plants have been built, including the world's largest NB plant. In Meissner units, benzene and mixed acids (a mixture of 98% HNO_3 and 98% H_2SO_4) are contacted in a special mixing device and the dispersion then flows to a separation device. The nitration in this unit is apparently completed within, at most, several seconds.

Centrifugal separators are used in many modern processes to rapidly separate the hydrocarbon and used acid phases. Rapid separation greatly reduces the amounts of nitrated materials in the plant at any given time. After an explosion in a TNT plant (16), decanters (or gravity separators) were replaced with centrifugal separators. In addition, rapid separation allows the hydrocarbon phase to be quickly processed for removal of the dissolved nitric acid, NO_x, etc. These dissolved materials lead to undesired side reactions. The organic phase generally contains some unreacted hydrocarbons in addition to the nitrated product.

A significant concern in all nitration plants using mixed acids centers on the disposal method or use for the waste acids. They are sometimes employed for production of superphosphate fertilizers. Processes have also been developed to reconcentrate and recycle the acid. The waste acid is frequently first stripped with steam to remove unreacted HNO_3 and NO_x. Water is then removed by low pressure evaporization or vacuum distillation. The resulting acid can often be concentrated to 93–96% H_2SO_4 at the nitration plant. When the waste acid contains large amounts of dissolved organics, as occurs in a few nitration plants, the acid is then often converted at high temperatures, in the presence of air, to mainly SO_2 plus carbon oxides. The SO_2 is then oxidized to SO_3 and converted back to concentrated H_2SO_4.

DNT processes have been developed by Meissner (22), Chematur Engineering (23), and Biazzi (24). In all of the processes, one reactor (or a series of reactors) is used for the production of MNT and another for DNT production. In each process, highly concentrated H_2SO_4 and HNO_3 are used to prepare the mixed acids for the nitration of MNT, to produce DNTs. The acid mixture present after the dinitration step contains mainly H_2SO_4 and water. It is mixed with concentrated HNO_3, and the resulting mixed acids are used for the nitration of toluene to produce MNTs. The used acid mixture after the mononitration step generally contains 70–72% H_2SO_4, 0.1–0.5% HNO_3, and NO_x; small amounts of dissolved organics, including MNTs and DNTs; and the remainder water. In the Meissner process, a single mixing device with low residence time is used for the mononitration reactor, and a second one for the dinitration reactions. In the Chematur process, a single pump reactor is used for each nitrating step. This reactor provides intense mixing of the two phases so that the nitrations are completed in less than one second. Chematur claims that its pump reactor provides much better mixing of the two phases, compared to an agitated autoclave reactor. In the Biazzi process, continuous-flow agitated reactors are provided, and heat-transfer surfaces are used to remove the heats of nitration. More than one reactor in series is employed by Biazzi for each nitration step.

Nitroglycerin (NG) processes of Meissner (22) and Chematur (23,25) employ an injection nozzle for the intimate mixing and hence rapid nitration of the glycerol and mixed acids. In its NG process, Biazzi (24) uses a reactor of similar design to that used in its DNT process. All three companies, however, employ just one reactor for the nitration of glycerol. The feed acids employed for these NG processes contain at most only a small amount of water. The used acids produced contain typically 70–72% H_2SO_4, 8–12% HNO_3, 0.5–3.0% NG, small amounts of NO_x, and 12–18% water. In these processes, as well as the DNT processes, the amount of explosive materials in the reactor is low, especially in those reactors which require only a small residence time to complete the nitrations. These processes are highly automated, which reduces labor costs and also serves to minimize the dangers to plant operators.

Flow processes are also available (11,22,23,26) for the production of cellulose nitrates (see CELLULOSE ESTERS, INORGANIC). The cellulose repeating unit ($C_6H_{10}O_5$) contains three hydroxyl groups, all of which can be nitrated. The number of groups which are nitrated (or esterified) determines whether the product is used as a plastic, as lacquer, or as gunpowder. Operating conditions are selected that reduce the molecular weight of the cellulose to only a limited extent during nitration. When the cellulose linters (or fibers) are contacted with concentrated mixed acids, diffusion of the acids into the fibers and of water out of the fibers occurs. NO_2^+ concentrations expectably vary as a function of residence time and radial position in the fibrous material.

2.4. Nitrations Using N_2O_5. Considerable worldwide interest has occurred in the late 1980s and the early and mid-1990s for nitrations using N_2O_5, which itself is generated by two processes. First, an electrolysis process is used with a solution of HNO_3 and N_2O_4 to produce a solution of HNO_3 and N_2O_5 (27–29). Second, a solution of an inert organic solvent such as CH_2Cl_2 and N_2O_4 is contacted with ozone to produce a solution containing N_2O_5 (5). A large pilot plant has been used to investigate nitrations using N_2O_5–HNO_3 solutions. Production of nitramines (or N-nitrations) is particularly promising, since these compounds are more stable in the presence of N_2O_5–HNO_3 solutions as compared to mixed acids containing H_2SO_4 (5). Good results have been obtained for the production of the high explosives, cyclotetramethylenetetranitramine [2691-41-0] or (HMX) (30) and DADN. Another high explosive, polynitrofluorene, has been produced via C-nitrations, for the first time. The overall exothermicities of the reactions are less when N_2O_5 is used, as compared to mixed acids (5). When N_2O_5 is employed, part of N_2O_5 is generally converted to HNO_3. With mixed acids, the water produced is dissolved with high exothermicity in H_2SO_4.

Solutions of CH_2Cl_2 and N_2O_5 have only mild nitrating power. Yet some nitrations are rapid: the N_2O_5 reacts on an almost stoichiometric basis, and only minimal residual acid is present upon completion of the nitration. Some nitrations having unique characteristics can be accomplished (5). For example, organic compounds with three- or four-atom rings which contain either oxygen or nitrogen heteroatoms nitrate readily. The rings are opened, and a nitrate or nitramine group is formed at each end of the resulting molecules. Essentially no water is produced as a by-product. For ethylene oxide, $NO_2OCH_2CH_2ONO_2$ is formed. Certain plasticizers and melt-castable explosives have also been produced, some for the first time.

3. Free-Radical Nitrations of Paraffins

Both vapor-phase and liquid-phase processes are employed to nitrate paraffins, using either HNO_3 or NO_2. The nitrations occur by means of free-radical steps, and sufficiently high temperatures are required to produce free radicals to initiate the reaction steps. For liquid-phase nitrations, temperatures of about 150–200°C are usually required, whereas gas-phase nitrations fall in the 200–440°C range. Sufficient pressures are needed for the liquid-phase processes to maintain the reactants and products as liquids. Residence times of several minutes are commonly required to obtain acceptable conversions. Gas-phase nitrations occur at atmospheric pressure, but pressures of 0.8–1.2 MPa (8–12 atm) are frequently employed in industrial units. The higher pressures expedite the condensation and recovery of the nitroparaffin products when cooling water is employed to cool the product gas stream leaving the reactor (see NITROPARAFFINS).

3.1. Chemistry.

Free-radical nitrations consist of rather complicated nitration and oxidation reactions (31). When nitric acid is used in vapor-phase nitrations, the reaction of equation 5 is the main initiating step where NO_2 is a free radical, either $\cdot NO_2$ or $\cdot ONO_2$. Temperatures of >ca 350° are required to obtain a significant amount of initiation, and equation 5 is the rate-controlling step for the overall reaction. Reactions 6 and 7 are chain-propagating steps.

$$HNO_3 \longrightarrow \cdot OH + NO_2 \tag{5}$$

$$RH + \cdot OH \longrightarrow R + H_2O \tag{6}$$

$$R + HNO_3 \longrightarrow RNO_2 + \cdot OH \tag{7}$$

When nitrogen dioxide is used, the main reaction steps are as in equations 8 and 9.

$$RH + NO_2 \longrightarrow R + HNO_2 \longrightarrow R + OH + NO \tag{8}$$

$$R + NO_2 \longrightarrow RNO_2 \tag{9}$$

These reactions occur as low as 200°C. The exact temperature depends on the specific hydrocarbon that is nitrated, and reaction 8 is presumably the rate-controlling step. Reaction 9 is of minor importance in nitration with nitric acid, as indicated by kinetic information (32).

An important side reaction in all free-radical nitrations is reaction 10, in which unstable alkyl nitrites are formed (eq. 10). They decompose to form nitric oxide and alkoxy radicals (eq. 11) which form oxygenated compounds and low molecular weight alkyl radicals which can form low molecular weight nitroparaffins by reactions 7 or 9. The oxygenated hydrocarbons often react further to produce even lighter oxygenated products, carbon oxides, and water.

$$R + ONO \longrightarrow RONO \tag{10}$$

$$RONO \longrightarrow NO + RO\cdot \tag{11}$$

Reactions 8 and 9 are important steps for the liquid-phase nitration of paraffins. The nitric oxide which is produced is oxidized with nitric acid to reform nitrogen dioxide, which continues the reaction. The process is complicated by the presence of two liquid phases; consequently, the nitrogen oxides must transfer from one phase to another. A large interfacial area is needed between the two phases.

Dinitroparaffins, such as 2,2-dinitropropane, can be produced during liquid-phase nitrations which are at relatively low temperatures. Dinitroparaffins have apparently never been produced, however, with gas-phase nitrations which are at higher temperatures.

Nitroparaffins are produced that contain either the same or fewer number of C atoms as compared to the feed *n*-paraffin. When propane is nitrated, 1-nitropropane, 2-nitropropane, nitroethane, and nitromethane are all produced, in addition to a significant amount of oxygenated hydrocarbons (containing one or two carbon atoms) and carbon oxides. When nitric acid is the nitrating agent at 410–420°C, the nitroparaffin mixture contains approximately 25,40,10, and 25 wt%, respectively, of these four nitroparaffins (33). For nitrations of propane with NO_2 at 280°C, the relative amounts are about 14,52,9, and 25 wt%, respectively (34). When *n*-butane is nitrated, both 1-nitro- and 2-nitrobutane are produced, in addition to the above four nitroparaffins. When the nitrating temperature is lowered, the average molecular weight of the nitroparaffin mixture increases, ie, fewer C–C bonds are broken. Side reactions which occur in the reactor, but have not been shown in equations 5–11, include the attack by free radicals and subsequent reaction of nitroparaffins initially produced. At lower temperatures such as those used for NO_2 nitrations, some higher molecular weight nitroparaffins are converted to lower molecular weight ones. At higher temperatures as used for HNO_3 nitrations, the side reactions lead mainly to the destruction of nitroparaffins.

Only 20–40% of the HNO_3 is converted in the reactor to nitroparaffins. The remaining HNO_3 produces mainly nitrogen oxides (and mainly NO) and acts primarily as an oxidizing agent. Conversions of HNO_3 to nitroparaffins are up to about 20% when methane is nitrated. Conversions are, however, often in the 36–40% range for nitrations of propane and *n*-butane. These differences in HNO_3 conversions are explained by the types of C–H bonds in the paraffins. Only primary C–H bonds exist in methane and ethane. In propane and *n*-butane, both primary and secondary C–H bonds exist. Secondary C–H bonds are considerably weaker than primary C–H bonds. The kinetics of reaction 6 (a desired reaction for production of nitroparaffins) are hence considerably higher for both propane and *n*-butane as compared to methane and ethane. Experimental results also indicate for propane nitration that more 2-nitropropane [79-46-9] is produced than 1-nitropropane [108-03-2]. Obviously the hydroxyl radical attacks the secondary bonds preferentially even though there are more primary bonds than secondary bonds.

Conversions per pass of NO_2 to nitroparaffins tend to be significantly less than when HNO_3 is used. When propane is nitrated with NO_2, conversions are as high as 27%, but they are much less for nitrations of methane and ethane. The remaining NO_2 reacts mainly to produce NO, and a considerable number of oxidation steps occur. The theoretically maximum conversion of NO_2 to nitroparaffins is 66.7%.

$$2\ \mathrm{RH} + 3\ \mathrm{NO_2} \longrightarrow 2\ \mathrm{RNO_2} + \mathrm{H_2O} + \mathrm{NO}$$

HNO_3 conversions to nitroparaffins pass through a maximum at paraffin:HNO_3 molar ratios of approximately 4:1 to 6:1 (32). At higher ratios, a high fraction of the HNO_3 reacts to form alkyl free radicals. At lower ratios, a large fraction of HNO_3 decomposes, as in reaction 5.

Attempts have been made to increase the conversions of both HNO_3 and NO_2 to nitroparaffins by adding oxygen, ozone, or halogens such as chlorine or bromine to the feed mixture (35–38). Significantly higher conversions, often in the 50–70% range, have been obtained. Such additives promote the formation of free radicals, but increase the production of oxygenated or halogenated compounds. These additives have apparently never been employed commercially.

When cyclohexane is nitrated to produce nitrocyclohexane [1122-60-7], the following techniques minimize undesired C–C breakage in the ring: low temperature nitrations with NO_2 (31), careful control of the reactor temperatures, and use of halogen additives. Oxygen increases the level of C–C bond breakage.

3.2. Processes for Paraffin Nitrations. Propane is thought to be the only paraffin that is commercially nitrated by vapor-phase processes. Temperature control is a primary factor in designing the reactor, and several approaches have been investigated (32). Excess amounts of propane are used to help provide a heat sink and help moderate the temperature. As already indicated, excess but controlled amounts of propane also increase the HNO_3 conversions to nitroparaffins. A significant amount of steam is also present in the reactor as a heat sink whenever HNO_3 is used as the nitrating agent. Between 60–70% HNO_3 (and the remainder water) is commonly used as the feed acid. Reactors in laboratory units have often been designed for good heat transfer. Relatively small-diameter tubular reactors, fluidized-bed reactors, and molten salt reactors have all been successfully used.

In a commercial unit, a spray nitrator (39) is operated adiabatically. The liquid HNO_3 feed is sprayed directly into the hot and preheated propane feed. The heat of nitration provides the heat to vaporize the HNO_3 and to preheat it to the desired temperature for nitration. At one time, several spray nitrators were operated in series, with additional HNO_3 being sprayed into each nitrator (32). In such an arrangement, the optimum propane:HNO_3 ratios did not occur, and considerable amounts of nitroparaffins degraded.

For vapor-phase processes, the product stream from the nitrator must be separated. The nitroparaffins, excess propane, and NO plus NO_2 (which are converted back to HNO_3), are recovered. The oxygenated products are removed, but there are generally insufficient amounts for economic recovery.

The vapor-phase process of Société Chemique de la Grande Paroisse for production of nitroparaffins employs propane, nitrogen dioxide, and air as feedstocks (34). The yields of nitroparaffins based on both propane and nitrogen dioxide are relatively high. Nitric oxide produced during nitration is oxidized to nitrogen dioxide, which is adsorbed in nitric acid. Next, the nitric dioxide is stripped from the acid and recirculated.

Nitromethane [75-52-5] is produced in China. Presumably a modified Victor Meyer method is being employed. Nitromethane is transported in drums or smaller containers. Two tank cars of nitromethane exploded in separate incidents in the 1950s. Both explosions occurred in the switching yard of a railroad station. In both cases, essentially adiabatic vapor compression of the nitromethane–air mixture in the gas space of the tank car resulted in the detonation of the liquid nitromethane. Other nitroparaffins do not, however, detonate in this manner.

4. Health and Safety Factors

The danger of an explosion of a nitrated product generally increases as the degree of nitration increases, eg, trinitroaromatics are more hazardous as compared to dinitroaromatics or especially mononitroaromatics. Nitroaromatics and some polynitrated paraffins are highly toxic when inhaled or when contacted with the skin. All nitrated compounds tend to be highly flammable.

BIBLIOGRAPHY

“Nitration” in *ECT* 1st ed., Vol. 9, pp. 314–330, by Willard deC. Crater, Hercules Powder Co.; in *ECT* 2nd ed., Vol. 12, pp. 784–796, by Lyle F. Albright, Purdue University; in *ECT* 3rd ed., Vol. 15, pp. 841–853, by Lyle F. Albright, Purdue University.

CITED PUBLICATIONS

1. G. S. Olah, R. Malhotra, and S. C. Narang, *Nitration: Methods and Mechanism*, VCH Publishers, New York, 1989.
2. C. Hanson and H. A. M. Ismail, *Chem. Eng. Sci.* **32**, 775 (1977).
3. M. B. Zaman, *Nitronium Ions in Nitrating Acid Mixtures*, Ph.D. dissertation University of Bradford, U.K., 1972.
4. J. F. Fischer, in H. Feuer and A. T. Nielsen, eds., *Nitro Compounds: Recent Advances in Synthesis and Chemistry*, VCH Publishers, New York, 1990, “Chapt. 3”.
5. G. E. Bagg, personal communication, Defense Research Agency, Fort Halstead, Kent, U.K., 1993.
6. M. E. Hill and co-workers, in *ACS Symposium Series No. 22*, American Chemical Society, Washington, D.C., 1976, “Chapt. 17”, 253–271.
7. P. C. Myhre, in Ref. 6, Chapt. 4, 87–94.
8. U.S. Pat. 4,123,466 (Oct. 31, 1978), C. Y. Lin, F. A. Stuber, and H. Ulrich (to the Upjohn Co.).
9. U.S. Pat. 4,028,425 (June 7, 1977), E. Gilbert (to United States of America).
10. U.S. Pat. 4,918,250 (Apr. 17, 1990) and 5,001,272 (Mar. 19, 1991), R. W. Mason, P. C. Imm, and K. J. Bordelon (to Olin Corp.).

11. T. Urbanski, *Chemistry and Technology of Explosives*, Vols. **1–3**, The Macmillan Co., New York, 1964, 1965; Vol. 4, Permagon Press, Elmsford, N.Y., 1983.
12. B. Milligan, *IEC Fundamentals* **25**, 83 (1986).
13. C. A. Bunton and co-workers, *J. Chem. Soc.*, 2628 (1950).
14. L. F. Albright, D. F. Schiefferle, and C. Hanson, *J. Appl. Chem. Biotechnol.* **26**, 522 (1976).
15. H. Suzuki, *Synthesis*, 217 (Apr. 1977).
16. E. Gilbert, in S. M. Kaye, ed., *Encyclopedia of Explosives and Related Items*, Vol. **9**, U.S. Army Armament Research and Development Command, Dover, N.J., 1980, T235–286.
17. D. J. am Ende, Ph.D. dissertation, Purdue University, Ind., 1993.
18. C. Hanson and H. A. M. Ismail, *J. Appl. Chem. Biotechnol.* **25**, 319 (1975).
19. D. F. Schiefferle, C. Hanson, and L. F. Albright, in Ref. 6, Chapt. 11, 176–189.
20. R. C. Dartnell and T. A. Ventrone, *Chem. Eng. Prog.* **67**(6), 58 (1971).
21. A. Tisan, personal communication, Chemetics International Co. Ltd., Vancouver, B.C., Canada, 1993.
22. G. Pelster and G. Langecker, personal communication, Josef Meissner GmbH and Co., Köln, Germany, 1993.
23. D. G. Klima, personal communication, Chematur Engineering, Karlskoga, Sweden, 1993.
24. Technical data, Biazzi, SA, Chailly/Montreux, Switzerland, 1993.
25. B. Brunnberg, in Ref. 6, Chapt. 24, 341–343.
26. Ref. 16, N62–68.
27. U.S. Pat. 4,443,308 (Apr. 17, 1984), C. C. Coon, J. E. Harrar, R. K. Pearson, and R. R. McGuire (to United States of America).
28. U.S. Pat. 5,120,408 (June 9, 1992), J. R. Marshall, D. J. Schriffin, F. C. Walsh, and G. E. Bagg (to United Kingdom).
29. U.S. Pat. 5,181,996 (Jan. 26, 1993), G. E. Bagg (to United Kingdom).
30. U.S. Pat. 4,432,902 (Feb. 21, 1984), R. R. McGuire, C. C. Coon, J. E. Harrar, and R. K. Pearson (to United States of America).
31. R. Lee and L. F. Albright, *Ind. Eng. Chem. Proc. Des. Dev.* **4**, 411 (1965).
32. L. F. Albright, *Chem. Eng.* **73**(12), 149 (1966).
33. G. B. Bachman, L. M. Addison, J. V. Hewett, L. Kohn, and A. Millikan, *J. Org. Chem.* **17**, 906 (1952).
34. U.S. Pat. 3,780,115 (Dec. 18, 1973), P. L'Honore, G. Cohen, and J. Jacquinot (to Société Chemique de la Grande Paroisse).
35. G. G. Bachman, H. B. Hass, and L. M. Addison, *J. Org. Chem.* **17**, 914 (1952).
36. G. B. Bachman, H. B. Hass, and J. V. Hewett, *J. Org. Chem.* **17**, 928 (1952).
37. G. B. Bachman, J. V. Hewett, and A. Millikan, *J. Org. Chem.* **17**, 935 (1952).
38. G. B. Bachman and L. Kohn, *J. Org. Chem.* **17**, 942 (1952).
39. U.S. Pat. 2,418,241 (Apr. 1947), L. A. Stengel and R. G. Egly (to Commercial Solvents Corp.).

LYLE F. ALBRIGHT
Purdue University

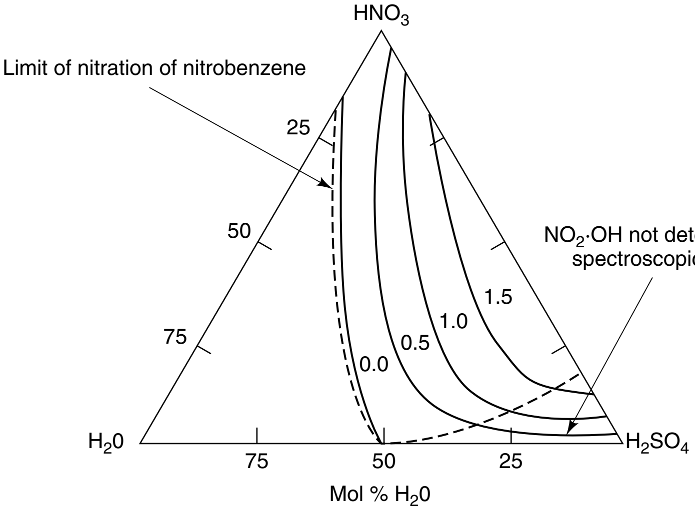


Fig. 1. Concentration of NO_2^+ in mol/1000 g solution. NO_2^+ concentrations increase with decreased amounts of water. The highest NO_2^+ concentrations occur at approximately 2:1 molar ratios of H_2SO_4 to HNO_3. At high concentrations of H_2SO_4, almost all of the HNO_3 is ionized to form NO_2^+. About 3% of pure HNO_3 ionizes to produce NO_2^+.