Review

Review of the Methods for Selective Nitration of Toluene

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Abstract: A solution to the problems encountered with the treatment of wastewater during the industrial production of TNT could be the use of the mixture of nitrotoluenes (NTs) with no or a smaller amount of the *meta*-NT compared to the mixture resulting from conventional mononitration. This can be achieved by selective nitration of toluene with a nitration mixture which is more selective than conventional nitrating mixtures. This paper presents a review of the literature related to the methods for selective nitration of toluene using the following nitrating agents: nitric(V) acid, acetyl nitrate(V), nitrogen(V) oxide and others.

Keywords: toluene, nitration, selective nitration of toluene

1 Introduction

2,4,6-Trinitrotoluene (TNT) is one of the most frequently produced explosives in the world. Nitro-Chem in Bydgoszcz (Poland) produces 10000 tons of TNT per year – the highest in Europe [1]. Due to its physical and chemical properties and low production costs, TNT has been widely used in civil as well as military technological applications [2]. It is obtained as a result of the three-step nitration

of toluene. In addition to TNT, unsymmetrical trinitrotoluene isomers are also formed in the reaction. The formation of these isomers is connected to the nitration of *meta*-nitrotoluene (*meta*-NT) produced in the first step. The presence of unsymmetrical trinitrotoluenes is undesirable as it decreases the melting point of TNT, causing failure to meet the applicable standards [3]. Currently, in order to eliminate unsymmetrical trinitrotoluenes, the process of sulphiting is used, thus leading to the formation of toxic and difficult to neutralize wastewater called "red waters" [4, 5].

In [6], the authors found that red waters undergo slow degradation and their neutralization is both problematic and expensive. Furthermore, no successful method for their disposal has been found. One of the ways to overcome this problem is the development of a method of TNT production avoiding the formation of unsymmetrical trinitrotoluenes or minimizing their formation. A process that would prevent the formation of red waters could be conducted by:

(i)   starting the synthesis of TNT with *ortho*- or *para*-nitrotoluene (*ortho*-NT or *para*-NT, respectively) instead of toluene,

(ii) separation of the mononitrotoluenes and removal of the *meta*-NT, or

(iii) developing another synthesis route for TNT.

The development of a different method for TNT synthesis as proposed in the patent [7] would probably entail greater cost, relying on rather expensive and not readily available raw materials. An interesting route for obtaining high-purity TNT without sulfitation is to start the synthesis with *ortho*- or *para*-NT [8, 9], however access to significant amounts of these compounds is difficult.

A pertinent way to solve this problem is to obtain a mixture of NTs with no *meta*-NT formed or one where the *meta*-NT appears in lower quantities than in the mixture resulting from a conventional mononitration method. This can be achieved by the selective nitration of toluene by means of a more selective nitration mixture compared to the conventional nitrating mixture.

The main producers of NT in the world include: Aaarti Industries Limited, LANXESS, Panoli Intermediates India Private Limited, EMCO Dyestuff, R.K. Synthesis Limited, Shree Chemopharma Ankleshwar Pvt Ltd..

2   Selective Methods for the Nitration of Toluene

2.1 Selective nitration of toluene with nitrating agents based on nitric(V) acid (HNO₃)

HNO_3 is a weaker acid than sulfuric(VI) acid (H_2SO_4). It is encountered in the form of the acid and the pseudo-acid, which has esterifying and nitrating effects.

The addition of water increases the amount of the acid form, whereas H_2SO_4 shifts the equilibrium towards the pseudo-acid [10]. At –40 °C, only 3.5% of HNO_3 undergoes autoionization to form the nitronium cation [11]. Hence, 100% HNO_3 is a milder nitrating agent compared to a HNO_3/H_2SO_4 mixture, the nitronium ion being the active nitrating agent.

According to [4], nitration with 94% HNO_3 results in the formation of 2.5% *meta*-NT. By contrast, in [10] the authors note that nitration of toluene with 100% HNO_3 at 25 °C yields 4.6% of the *meta*-NT. In reference [12], Topchiev, in turn, states that at 0 °C 3.1% *meta*-NT is formed, whereas 2.7% *meta*-NT is formed at –20 °C.

Nitration with HNO_3 can be more selective if the reaction is conducted in an organic solvent, ionic liquid or in presence of a catalyst, which will be discussed further in the following sections.

2.1.1 Selective nitration of toluene by means of HNO_3 in presence of catalysts

The selectivity of nitration with HNO_3 can be increased by the addition of a catalyst. This can lead to reaction in such a way as to minimize the formation of the *meta*-NT, and at the same time increase the nitrating activity of HNO_3. The most common catalysts are solid acids, *i.e.* various types of solids or compounds deposited on silica, which are Lewis acids and behave similarly to H_2SO_4. Hence, these catalysts launch and accelerate nitration reactions even when the HNO_3 is diluted. These catalysts particularly favour the *para* position by forcing the appropriate position of the toluene molecule into the pores of the catalyst [13]. The operating mechanism of solid catalysts consists of six stages [14]:
–   diffusion of the substrate through the laminar layer,
–   diffusion into the pores,
–   adsorption on active sites,
–   chemical reaction,
–   desorption from the surface, and
–   the diffusion of product away from the surface into the reaction medium.

An example of nitration by means of sodium nitrate(V) with the addition of H_2SO_4 adsorbed on silica has been reported in [15]. As a result of this process, HNO_3 is formed *in situ*. The main product of nitration at 25 °C is *para*-NT, in a yield of 85%. On the other hand, in [16] the nitration of toluene with HNO_3 by means of Claycop was described. This process led to 86% 2,4-dinitrotoluene (2,4-DNT) and 13% 2,6-dinitrotoluene (2,6-DNT).

Furthermore, in the patent [17] toluene was nitrated with 90% HNO_3 in the presence of H-ZSM-5 zeolite. The reaction was run at about 100 °C and the

content of the *meta*-NT ranged from trace amounts up to 1.6%. The content of the *para*-NT was significantly high. In [18] a number of examples of nitration with HNO₃ by means of zeolites were reported. These catalysts exhibit a strong *para* effect. The strongest effect was observed with the use of H⁺Beta zeolite, where the *para*/*ortho* ratio was 2.23. The above paper [18] also described the nitration of toluene with HNO₃ vapour in the presence of H-Beta zeolite and H₃PO₄/ZSM-5-surf-170. This process results in the formation of 77% and 97.9% of *para*-NT, respectively.

In addition to zeolites, other catalysts can be used in nitration reactions with HNO₃, such as zirconium, zirconium cerium, or their sulfate variants. The amount of the *meta*-NT ranged from 2% to 3%. These reactions were run at temperatures between 60 and 90 °C. A sulfate version of the catalyst demonstrated a finer selectivity (lower amount of the *meta*-NT). These catalysts did not demonstrate *para*-selectivity [19]. In [20], a similar catalyst was used where molybdenum(VI) oxide was adsorbed on zirconium(IV) oxide doped silica. Nitration was carried out with HNO₃ in 1,2-dichloroethane at its boiling temperature. The most favorable results were obtained for the catalyst heated at 500 °C. No *meta*-NT was detected in the reaction products, the *para*/*ortho* ratio was to 1.2, and 90% yield was obtained. Molybdenum compounds as nitration catalysts were also used in [21]. In this study, phosphoromolybdic acid on silica was applied. The most suitable result was achieved when 5.7% of tetraoxophosphoric(V) acid (H₃PO₄) was added, which resulted in the formation of 1.3% of the *meta*-NT and an *ortho*/*para* ratio of 0.77. Unfortunately, after the reaction had been completed the catalyst was not suitable for further use.

Mechanochemical nitration with the molybdenum oxide and sodium nitrate(V) is an interesting example of nitration with molybdenum(VI) oxide deposited on silica. The reaction takes place in a planetary mill and no additional solvent is required. The *para*/*ortho* ratio ranges from 1.14 to 1.47. As the temperature is increased, the degree of toluene conversion increased along with the amount of oxidation by-products. The disadvantage of the process lies in the need for extraction and consumption of the catalyst, which hinders its application in continuous processes [22].

The literature data leads to the conclusion that a catalyst and HNO₃ based system is more selective than a conventional nitrating mixture. Smaller amounts of the *meta*-NT appear in the reaction products, whereas the proportion of the *para*-NT sometimes increases. Furthermore, the presence of catalyst increases the nitrating activity of the acid. The consumption of the catalyst and the need for its replacement are obstacles to running continuous processes.

2.1.2 Selective nitration of toluene with HNO₃ in organic solvents

Urbański [4, 23] claims that no 1050 and 1040 cm^{-1} lines can be found in the infrared absorption when a solution of HNO₃ in organic solvents is used. Therefore, nitrogen(V) oxide (N₂O₅) cannot be formed. HNO₃ becomes less associated than in H₂SO₄. HNO₃-solvent bonds are formed, which was confirmed by the measurements of solvent vapour pressure and Raman spectra [4, 10] for ether and dioxane solutions. In the case of chloroform and carbon tetrachloride, no nitrate(V) and nitronium ions were detected in the Raman spectra. Their spectra are similar to HNO₃ vapour. Therefore, HNO₃ exhibits less nitrating activity due to the reduced polar environment. The nitration reactions of benzene homologues with such systems constitute zero-order reactions [10, 23].

HNO₃/dichloromethane can serve as an example of such a system. In [24] the nitration with HNO₃ in dichloromethane with the addition of salts of transition metals complexes, such as tetramine copper(II) sulphate, chloropentamine cobalt(II) chloride, and manganese(III) acetylacetonate, was described. The addition of these salts was expected to increase the nitration selectivity. In the course of this examination, *para*-NT was obtained in a yield of 85%. According to [25], when toluene is nitrated with HNO₃ in dichloromethane, 3.1% of the *meta*-NT is formed at 20 °C, whereas 3.8% is formed at 30 °C.

In [26], toluene was nitrated with a 20% solution of HNO₃ in dichloromethane at an HNO₃/toluene molar ratio of 5:1 and at a temperature of −20 °C, and 2.56% of the *meta*-NT was formed. Another example of such a system is HNO₃ in chloroform. According to the patent [27], nitration of toluene with 100% HNO₃ in chloroform at room temperature yields 2.1% of the *meta*-NT.

HNO₃ in carbon tetrachloride is another example of this system. According to Olah *et al.* [28], 3% of the *meta*-NT is formed when the reaction is conducted at 25 °C. In [29], it was reported that the content of the *meta*-NT was 3.7% when nitrated at 35 °C. Adamiak [30], in turn, noted that when toluene is nitrated with 100% HNO₃ in carbon tetrachloride with the addition of silica deposited molybdenum(VI) oxide, 0.8% of the *meta*-NT is formed at room temperature.

Another nitrating system of this type is HNO₃/hexane, which is a two-phase system. According to [31], the nitration of toluene with 95% HNO₃ in hexane at the boiling temperature yields 4.1% of *meta*-NT.

In [32], toluene was nitrated with HNO₃ in hexane at a concentration of 36%, HNO₃/toluene molar ratio of 1.8:1, at room temperature. The reaction was conducted for 45 min. Consequently, 5% of the *meta*-NT was obtained with 57% conversion. Furthermore, the authors described the nitration of this mixture using a variety of zeolites. The lowest level of the *meta*-NT was obtained when NaY zeolite was added, with 70% conversion. In the remaining cases, this conversion ranged from 3 to 5% and a larger amount of the *para*-NT was observed.

By contrast, in the patent [33] the nitration of toluene with 90% HNO_3 in acetonitrile was proposed. This gave a high proportion of the *ortho*-NT in the reaction products. When the reaction was carried out at 40 °C, the *ortho/para* ratio was 5.6.

Table 1 presents the results of nitration with HNO_3 in various solvents with the addition of silica deposited molybdenum(VI) oxide [30]. These data serve to indicate that the less polar the solvent is, the lower is the content of the *meta*-NT.

Table 1.   Content of the products of nitration of toluene by means of HNO_3 with the addition of silica-deposited molybdenum(VI) oxide in different solvents [30]

Solvent	Composition of reaction products [% mass]		
	ortho-NT	*meta*-NT	*para*-NT
Nitromethane	59.1	3.3	37.6
Nitroethane	58.5	2.6	38.9
Toluene	46.7	2.3	51.0
Carbon tetrachloride	46.8	0.8	52.4
1,1,2,2-Tetrachloroethane	45.2	1.5	53.3
Dichloromethane	45.3	2.2	52.5
1,2-Dichloroethane	45.6	2.2	52.2

As can be observed, the nitration with HNO_3 with the addition of a solvent is more selective than the conventional nitration method. This method can also be used in continuous processes. In the case of nitration in an organic solvent with a catalyst, the selectivity of the reaction is increased. The *para* position is then particularly favoured. It should be noted however, that the catalyst is being used up, which poses a problem in the possible application of this nitration method in continuous processes.

Another example of a selective method is the nitration with HNO_3 in polyfluorocarbons [34]. According to the authors of this paper, no unsymmetrical derivatives are formed during the nitration. This method of nitration was reported as environmentally friendly, since polyfluorocarbons do not affect the ozone layer and H_2SO_4 is not used. However, the reaction products need to be extracted from polyfluorocarbons by means of dichloromethane. This method is selective, however the high costs of polyfluorocarbons pose certain difficulties [34].

Another interesting nitrating agent is a mixture of HNO_3 and trifluoromethanesulfonic acid in organochlorine solvents [35]. In this system, an ion pair with the nitronium cation is formed by the following reaction:

$$2CF_3SO_3H + HNO_3 \rightarrow NO_2^+CF_3SO_3^- + H_3O^+ + CF_3SO_3^-$$
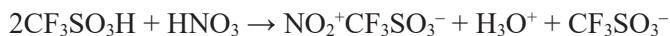
According to the patent [35], the reaction should be conducted in an inert gas atmosphere, with an excess of the nitrating agent at a temperature below −60 °C. The reaction was run in dichloromethane and trichlorofluoromethane. The amount of the *meta*-NT did not exceed 0.53%. At higher temperatures, DNTs were formed and the content of the asymmetric derivatives did not exceed 1.72%. Nitration of toluene with a mixture of HNO_3 and trifluoromethanesulfonic acid is a selective method, however the harmful effect of trifluoromethanesulfonic acid on the environment and the separation of the product for the further nitration stages are detrimental factors.

### 2.1.3 Nitration of toluene with HNO₃ in ionic liquids

Ionic liquids are substances characterized by their ionic structure in the liquid state. Because of this property, they exhibit fine electrical conductivity. Low melting point organic salts are currently used as ionic liquids in technological applications.

In [36] the use of nitration of toluene in an ionic liquid has been reported. In this study, toluene was nitrated with 65% HNO_3 in *N,N*-diethylethanaminium-2-(sulfooxy)ethyl sulfate. The reaction was conducted at 80 °C. When the reaction was completed, the mixture was extracted with diethyl ether and then separated on a silica gel column. The authors reported that 85% of *para*-NT, 14% of *ortho*-NT and 1% of DNT were formed.

Nitration of toluene with HNO_3 in ionic liquids is a more selective method compared to conventional nitration. The problem however, lies in the high boiling points of ionic liquids, entailing the need to extract the product with a solvent, which is not feasible in industrial applications. Furthermore, the costs of ionic liquids are quite high. The authors of the paper did not investigate the possibility of reusing the ionic liquid or the costs associated with the additional reagent supply or replacement.

2.2. Nitration of toluene by means of nitrating agents based on acetyl nitrate(V)

Acetyl nitrate(V) is formed as a result of the reaction of HNO_3 with acetic anhydride, which is described by the following equation [37]:

$$Ac_2O + HNO_3 \rightarrow AcOH + AcONO_2$$
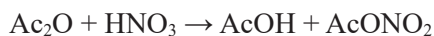
In addition to the above method, it can also be formed by the reaction of acetic anhydride with N_2O_5 [23, 37, 38], or *via* the reaction of silver nitrate(V) with acetyl chloride [38], as described by the following equations, respectively:

$$(CH_3CO)_2O + N_2O_5 \rightarrow 2CH_3COONO_2$$

$$CH_3COCl + AgNO_3 \rightarrow CH_3COONO_2 + AgCl$$
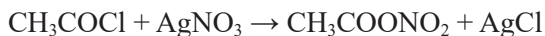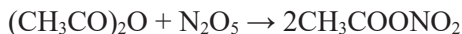
Acetyl nitrate(V) is characterized by its explosive properties and explodes when heated above 60 °C [37, 38]. Acetyl nitrate can undergo distillation under reduced pressure (22°C/70 mmHg) [38]. Following [23], Gillespie and Millen (1948), the compound exhibits poorer nitrating properties than the nitronium cation. As reported in [23], the following substances behave as nitrating agents in the mixture of HNO_3 and acetic anhydride: HNO_3, $H_2NO_3^+$, $AcONO_2$, $AcONO_2H^+$, NO_2^+, N_2O_5.

Numerous examples of using nitrating systems consisting of HNO_3 and acetic anhydride for the nitration of toluene have been reported in the literature. In [39], nitration of toluene with acetyl nitrate(V) with addition of *β*-zeolite yields *para*-NT as the main product. On the other hand, in [37] the results of nitration with acetyl nitrate(V) with the addition of various zeolites have been reported. The highest value of the *para*/*ortho* ratio (2.8) was obtained for H-PB5. Furthermore, the above-mentioned study reports on the possibility of nitrating toluene to DNT with acetyl nitrate(V) in the presence of zeolites [37].

In the case of nitration of toluene with a mixture of HNO_3 and acetic anhydride with the addition of HBEA-500 zeolite at room temperature, 2.6% of the *meta*-NT was obtained at 99.5% conversion [40]. By contrast, the paper [41] describes the nitration of toluene with acetic anhydride and HNO_3 with the addition of trifluoroacetic anhydride and H*β* zeolite. As a result of nitration, DNTs are formed with 2,4-DNT as the main product.

In addition to nitration with acetyl nitrate(V) in presence of zeolites or other catalysts, other sources provide information on nitration with the pure HNO_3/acetic anhydride system, with no additional catalysts. According to [28], the *meta*-NT content in the nitration of toluene with this mixture was: 2% at 0 °C, 2-3% at 25 °C, 5% at 30 °C, whereas the *ortho*/*para* ratio was 1.76 for nitration at 40 °C. On the other hand, reference [10] reports that the amount of *meta*-NT formed during nitration by means of the HNO_3/acetic anhydride mixture at 25 °C was 2.8%. This has also been confirmed in [25].

The nitration of toluene with acetyl nitrate(V) in various solvents has also been reported in the literature. According to [42] the nitration with acetyl nitrate(V) in dichloromethane yields 1.55% of the *meta*-NT. By contrast, according to [43], 2.8% of the *meta*-NT is formed in the reaction of toluene with acetyl nitrate(V) in nitromethane at 25 °C.

The nitration of toluene with acetyl nitrate(V) in carbon tetrachloride in the presence of various catalysts has been described in the literature. In [44], montmorillonite K-10 was used as a catalyst, and the reaction was carried out at the boiling temperature of the solvent. A mixture of NTs containing 2% of the *meta*-NT was obtained in a yield of 75-98%. In [45], Claycop, *i.e.* montmorillonite impregnated with anhydrous copper(II) nitrate(V), was added. A mixture of DNTs was obtained in a yield of 95% and 1% of unsymmetrical isomers.

Acetyl nitrate(V) is a more selective nitrating agent compared to conventional nitrating mixtures. During the nitration of toluene with this reagent, 2-3% of the *meta*-NT is formed. The addition of solid catalysts does not significantly contribute to an increased content. On the contrary, the content of the *para*-NT is increased. The selectivity of nitration with acetyl nitrate(V) can be enhanced by conducting the process in low-polarity organic solvents.

The problem of using acetyl nitrate(V) in industrial applications is associated with its explosive properties. When using nitration methods in the presence of a catalyst, a difficulty is associated with the consumption of the catalyst and the need for its replacement, which is an obstacle in running continuous processes.

2.3 Selective nitrating agents based on N_2O_5

N_2O_5 appears in the form of a white crystalline solid and as such, it exhibits an ionic structure. By contrast, in the gaseous state it demonstrates a covalent structure. In the ionic form, it has the following structure $[NO_2^+][NO_3^-]$ [11].

Two types of nitrating mixtures based on N_2O_5 can be distinguished. The first type includes mixtures where N_2O_5 appears in its ionic form. Such properties are shared amongst solutions of N_2O_5 in strong mineral acids such as HNO_3 and H_2SO_4. The mechanism of nitration is initiated by the attack of the nitronium cation on the aromatic ring. The second type includes nitrating mixtures where N_2O_5 is present in its covalent form. Solutions of N_2O_5 in organic solvents exhibit this property [10]. It has been reported [10] that molecular N_2O_5 acting as the electrophile performs the function of the nitrating agent in N_2O_5/organic solvent mixtures. According to this theory, a neutral, dipole, cyclic transition state is formed as a result of the aromatic ring with N_2O_5 combination. This reaction occurs in a single step. The mechanism was verified by the fact that changing the solvent from carbon tetrachloride to nitromethane gave a six-fold increase in the reaction rate.

The advantages of nitration by means of N_2O_5 are as follows [48]: much faster, less exothermic, easily controllable reactions resulting in less oxidation by-products, higher yields, effortless product isolation, no waste acids. Moreover, all nitration reactions that normally use typical nitrating agents can be carried

out more effectively. There is also the possibility of synthesizing high-energy materials that cannot be obtained via the use of conventional nitrating mixtures.

N_2O_5 in dichloromethane is an example of a highly selective system where N_2O_5 occurs in its covalent form. It was used in [3] in a semi-technical application. The content of the *meta*-NT ranged from 1.4% to 1.9%. The reactions were carried out at (–40) to (–20) °C.

In [28], the authors reported that when toluene is nitrated with N_2O_5 in acetonitrile at a temperature of 0 °C, 3% of the *meta*-NT is formed. On the other hand, nitration with N_2O_5 in liquid sulfur dioxide at –30 °C yields 5% of *meta*-NT. When nitration was in supercritical carbon monoxide(IV) at 22 °C, 2% of *meta*-NT was formed [49]. In [34], the authors used N_2O_5 for nitration in octadecafluorodecalin to obtain 2,4- and 2,6-DNT.

Additionally, nitration with N_2O_5 in ionic liquids was conducted [50]. Nitration with N_2O_5 in an ionic liquid is slightly more selective as compared to nitration without this reagent. No increase in selectivity was observed with additional use of ionic liquid.

N_2O_5 can be used for nitration in a manner similar to the use of HNO_3 in the presence of solid catalysts. In [51], toluene was nitrated with N_2O_5 in dichloromethane in the presence of H-ZSM-5 zeolite. A mixture of *ortho*- and *para*-NT with a molar ratio of 6:94 was obtained. In the patent [52], the nitration with N_2O_5 in dichloromethane and chloroform in the presence of H-ZSM-5 zeolite was investigated. The amount of the *meta*-NT ranged from 0 to 1%.

In turn, in [53] the nitration with N_2O_5 in dichloromethane with the addition of iron(III) 2,4-pentanedioate at a temperature of –100 °C was described. The reaction yielded 4- and 2-NT in a ratio of 65:31. This reaction proceeded faster than the corresponding reaction with no catalyst at 0 °C. The selectivity of nitration with N_2O_5 in the presence of catalysts is slightly increased. Moreover, as in the case of nitration with N_2O_5 without added catalyst, the content of the *para*-NT is increased.

Kyodai nitration involves mixing the substance to be nitrated with nitrogen(IV) oxide (NO_2), followed by streaming ozone through the resulting solution. The name of the process refers to the colloquial name of Kyoto University where it was first developed in 1991. The reaction can also be conducted in solvents [54]. In [55], the Kyodai nitration of toluene in 10-times the amount of dichloromethane at –10 °C yielded 2% of the *meta*-NT in 3 h. A similar process was carried out with the use of catalysts in [55]. The main products were DNTs, with a pronounced excess of 2,4-DNT, which provides for *para* selectivity. Kyodai nitration is a selective reaction, however, the application of this method in continuous processes is problematic.

N_2O_5 is a selective nitrating agent. The problems, however, relate to the absence of an efficient production method in industrial processes and high costs. Another major disadvantage of N_2O_5 is its instability and tendency to degrade when exposed to temperature, light and moisture. Furthermore, anhydrous solvents must be used in the reaction.

2.4 Selective nitrations based on other reagents

In addition to the above mentioned reagents, the nitration of toluene with other nitrating agents has been described in the literature. Examples include urea nitrate(V), nitrourea, guanidine nitrate(V) and nitroguanidine with the addition of H_2SO_4. The results for toluene nitration by means of these nitrating agents are listed in Table 3 [56]. These reactions were carried out at room temperature.

Table 3. Nitration of toluene by means of other nitrating agents [56]

Nitrating agent	Nitrating agent:toluene ratio [mol/mol]	Reaction products [%]					
		ortho-NT	*meta*-NT	*para*-NT	2,6-DNT	2,4-DNT	2,3-DNT
Guanidine nitrate(V)	1:1	42	2	38	0	0	0
	2:1	0	0	0	10	89	1
Nitroguanidine	1:1	4	0	2	86	7	0
	2:1	0	0	0	13	87	2
Urea nitrate(V)	1:1	3	0	1	11	86	0
	2:1	0	0	0	17	82	1
Nitrourea	1:1	59	0	41	0	0	0
	2:1	0	0	0	9	91	0

It can be observed that these types of nitration are selective. An excess of the nitrating agent contributes to the formation of DNTs. The problems in the application of these reagents in continuous processes is associated with the solid physical state of the nitrating agents.

3 Summary

♦ Numerous nitrating mixtures that are more selective than the conventional nitration mixtures have been reported in the literature. In [16, 17], despite the use of a traditional nitrating mixture, less asymmetric DNTs were

obtained than with the use of the conventional nitration method, however, the proportion continues to be high.

♦   Fuming HNO_3 is a more selective nitrating mixture than the conventional mixture, however the level of undesirable reaction products is still too high to obtain TNT of fine quality.

♦ HNO_3/organic solvent systems are more selective than traditional nitrating mixtures. This is due to the formation of HNO_3-organic solvent bonds. Furthermore, the organic solvent environment reduces the activity of the nitronium cation, giving a lower heat of reaction and more straightforward control of the reaction than in the case of a conventional nitrating mixture. These systems can be used in continuous processes and their advantages in the nitration of toluene are multifold. The reaction runs smoothly and is characterized by a slight increase in temperature of only a few degrees. Other favorable factors include the absence of H_2SO_4, which, as production waste poses a serious problem for the natural environment, effortless concentration of HNO_3 and its potential reuse, the possibility of multiple use and recycling of the solvent, or higher tolerance margins for operating at low temperatures. When temporarily cooled to –40 °C, HNO_3 does not solidify rapidly and hence the risk of the reaction getting out of control is reduced. Unlike the nitration with 100% HNO_3, these mixtures are characterized by a much lower viscosity at low temperatures, which makes the process easily controllable. Difficulty is related to the need to use an excess of the nitrating agent and a high level of solvent consumption [6]. In addition, some organic solvents, such as carbon tetrachloride, are not environmentally friendly.

♦   Nitration with HNO_3 in polyfluorocarbons is a selective nitration method. Difficulties are associated with the high cost of polyfluorocarbons and their detrimental environmental effects.

♦   Nitration by means of HNO_3 in ionic liquids is a selective nitration method, however the high costs of ionic liquids and the need for product extraction poses a problem.

♦ HNO_3 with the addition of a catalyst is a more selective agent than 100% HNO_3. The reaction products contain less *meta*-NT, while the proportion of *para*-NT is sometimes increased. In addition, the catalyst stimulates the nitrating activity of the acid. The main problem is the consumption of the catalyst and the need to replace it, which hinders its application in a continuous process.

♦   Acetyl nitrate(V) is a mild and selective nitrating agent. It is not capable of nitrating toluene to DNTs [30]. During the nitration, less of the *meta*-NT is produced thus enhancing its application potential in continuous processes.

On the other hand, acetyl nitrate(V) has a number of disadvantages, such as the requirement for *in situ* production, its explosive properties, the toxicity of acetic anhydride, problems relating to the extraction of acetic acid and the regeneration of already used reagents. Solid catalysts slightly increase the selectivity of toluene nitration. As in the case of nitration by means of HNO_3, the proportion of the *para*-NT in the reaction products is increased. Catalysts are also able to activate acetyl nitrate(V) more extensively, so that DNTs are formed [41]. As in the case of HNO_3, difficulty is associated with the consumption of the catalyst and the need to replace it, which poses an obstacle in continuous processes. When nitrating with acetyl nitrate(V) in polar solvents, the selectivity of nitration remains practically unchanged, whereas it is increased slightly in non-polar solvents.

♦ N_2O_5 in organic solvents is an effective and selective nitrating agent (particularly in organochlorine solvents). Continuous nitration using N_2O_5 is possible. Regretfully, this reagent is not currently manufactured on an industrial scale and no inexpensive and efficient production method has been developed. The instability of N_2O_5 is a big disadvantage, as it becomes degraded under the influence of temperature, light and moisture, which requires the use of anhydrous solvents in the process. The addition of a solid catalyst or ionic liquid slightly increases the nitration selectivity. As in the case of HNO_3, during nitration in presence of solid catalyst, the proportion of the *para*-NT is increased and, likewise, one disadvantage is linked to the consumption of the catalyst, preventing its use in continuous processes.

♦ Kyodai nitration is a selective nitration method and can be carried out in the presence of solid catalysts. Difficulty is associated with the inability to use this method in continuous processes.

♦ Nitration by means of urea nitrate(V), nitrourea, guanidine nitrate(V) and nitroguanidine with the addition of H_2SO_4 is a selective method. Their use in continuous processes is problematic however, due to the solid physical state of the nitrating agents.

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