Research paper

Selective Nitration of Toluene using Nitrogen(V) Oxide in Dichloromethane and Catalysts

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Abstract: A series of toluene nitration reactions was carried out using a nitrogen(V) oxide (N_2O_5) solution in dichloromethane (CH_2Cl_2), with and without the addition of solid catalysts. N_2O_5 in CH_2Cl_2 was found to be a more active and selective mixture compared to 100% nitric acid and a mixture of nitric acid(V) in CH_2Cl_2. Temperature has a significant effect on the composition of the products of nitration of toluene with N_2O_5 in CH_2Cl_2; as the reaction temperature was decreased, the amount of *meta*-nitrotoluene decreased to approx. 1-1.2%, at a nitration temperature below –40 °C. The use of molecular sieves with toluene adsorption resulted in a quite powerful *para* effect, demonstrated by a significant increase in the amount of the *para* isomer, while reducing the *ortho-* and *meta*-isomers. The most pertinent effect was obtained when using 13X molecular sieves. In addition to improving the selectivity, the use of molecular sieves also leads to a higher degree of nitration of toluene (toluene/N_2O_5 = 1:1) due to the resulting nitric acid being absorbed by the pores of the molecular sieve.

Keywords: nitration, nitrogen(V) oxide, toluene, nitrotoluenes

1   Introduction

Nitrotoluenes (NTs) are intermediate products in trinitrotoluene (TNT) synthesis. The direct nitration of toluene with a nitrating mixture (nitric(V) acid/sulphuric(VI) acid) results in the production of the three NT isomers, namely *ortho-*, *para-* and *meta*-NT. The presence of the *meta*-isomer in the toluene nitration product results in the formation of asymmetric higher nitro derivatives of toluene in the subsequent stages of nitration. The presence of these derivatives in the final product (TNT) is undesirable, as they are characterized by low persistence and stability and should therefore be eliminated. At present, they are eliminated by the sulphating process, which produces toxic and non-degradable wastewater, called red water due to its characteristic colour [1, 2]. Currently, the methods proposed for purification of red water have proven to be insufficient or not cost-effective [3]. The development of TNT manufacturing methods bypassing the production of red water could be a solution, for instance by nitrating toluene with a more selective nitrating mixture instead of the traditional mixture, which affords 4.5% of the *meta*-NT isomer. Many nitrating agents of this type are reported in the literature. Examples of such reagents are N_2O_5 in dichloromethane [4], nitric(V) acid/acetic anhydride [5] or nitric(V) acid with zeolites[6], where 1.5-2% of the *meta*-isomer is produced.

N_2O_5 is a nitrating agent that generates increasing interest due to the selectivity of the nitration reactions and their potential for environmentally friendly processes involved in the production of high-energy materials. N_2O_5 in dichloromethane was proposed for nitration of toluene [4, 7]. The nitration of toluene with N_2O_5 takes place in high yield (95%) and has a weak, and thus easily controllable exothermic effect. Furthermore, the reaction is not accompanied by side oxidation reactions, caused by a covalent, non-dissociated form of N_2O_5 in organic solvents. During nitration with N_2O_5, a cyclic transition state is involved, which is dipolar and solvated by the inert solvent. Consequently, the nitrating mixture of N_2O_5/organic solvent constitutes a mild, though quite selective nitration mixture [8].

Millar *et al.* [4] conducted a study of the nitration of toluene with N_2O_5 in CH_2Cl_2 in both batch and continuous processes. They demonstrated that a reduced share of *meta* substituted NT, of about 1.3-1.5% (1.4-1.5% in a flow system), is possible when using N_2O_5 in CH_2Cl_2 at a temperature below –35 °C. Lower proportions of *meta*-NT may allow the production of TNT according to military type I specifications, with no need for additional TNT purification with sodium sulphite.

The selectivity of toluene nitration can be improved by the addition of a catalyst. A catalyst can control the reaction in such a way as to yield the

minimum amount of the *meta*-isomer, and at the same time increase the activity of the nitrating agent. Most often, the catalysts used involve solid acids. Solid acid catalysts particularly favour the *para* positon by forcing the toluene molecule into an appropriate orientation in the catalyst pores. [9]. Seven phases of the activity of solid catalysts can be distinguished, such as substrate diffusion through a laminar layer, diffusion into the pores, adsorption onto active centres, chemical reaction, desorption from the surface and diffusion of the product into the reaction medium [10].

A number of papers have been devoted to the catalytic ability of zeolites in electrophilic reactions [11, 12], in particular nitration reactions using nitric acid, usually in dehydrating media, such as acetic anhydride or others [13-16]. According to the report [17], no *meta*-NT is formed when toluene is nitrated with nitrogen(V) acid and added ZSM-5 zeolite.

There are remarkably few reports on the use of N_2O_5 in this reaction type; a study with the use of N_2O_5 and zeolite involved the application of excess substrate (toluene) as the solvent and was carried out at elevated temperature [18]. By contrast, in the report [19] it was found that H-faujasite-720 zeolite demonstrated the highest regioselectivity during the dinitration step with N_2O_5, and the achieved ratio of 2,4-dinitrotoluene (2,4-DNT) to 2,6-dinitrotoluene (2,6-DNT) was 4.3:1 (at 0 °C, reaction time 3 min, 94% yield). In the first step, the ratio of 4-NT to 2-NT was 0.8 to 0.9; compared to approx. 0.5 when an acid mixture was used. These effects were explained in terms of the size of the pores in the zeolite, comparable to the molecular size of the benzene ring, which would not favour the formation of the bulky *ortho*-nitro products.

Furthermore, the paper [20] describes the process of nitration with N_2O_5 adsorbed on montmorillonite K-10. This system is able to nitrate benzene to dinitrobenzene and can be used for nitration in non-toxic solvents such as hexane. In addition, nitration with N_2O_5 with ZSM-5 zeolite is described. According to the authors of this paper, the catalysts reduce the amount of acidic waste and allow certain types of nitration to be carried out at low temperature. In turn, paper [21] describes nitration with N_2O_5 with silica-supported molybdenum(VI) oxide.

The use of a selective nitrating agent such as N_2O_5 in CH_2Cl_2 and low-cost, eco-friendly catalysts, in the selective nitration of toluene can potentially prevent the formation of undesirable isomers that ultimately lead to the production of red water during the TNT purification step.

The aim of the present study was to investigate the effect of various factors, including the addition of low-cost, commercially available and easily modifiable catalysts, on the nitration of toluene with N_2O_5 in dichloromethane, whilst paying particular attention to minimizing the formation of the *meta*-NT isomer.

2   Experimental

The following reagents were used in the study: toluene p.d.a. (Chempur), CH_2Cl_2 p.d.a. (Chempur), sodium bicarbonate p.d.a. (POCh), magnesium sulphate p.d.a. (Chempur), calcium hydride p.d.a. 93% (Acros Organics), nitrogen (IV) oxide synthesized in the laboratory from sodium (III) nitrate and 65% nitrogen(V) acid, molecular sieves 3A, 4A, 13X (Chempur), bentonite (CERTECH), clinoptilolite (Zeocem), amberlyst-15 (Sigma-Aldrich), silica gel 60 (Roth). MCM-41 was synthesized as described in the paper [22].

The CH_2Cl_2 used in the reaction was dried with calcium hydride and distilled in an argon atmosphere. The dried CH_2Cl_2 was stored in a flask over molecular sieves. The catalysts were dried at 120 °C overnight before use.

2.1 Synthesis of N_2O_5

N_2O_5 was obtained by the reaction of nitrogen dioxide with ozone. For this purpose, a round-bottom spherical flask filled with liquid nitrogen dioxide was placed in an acetone/dry ice cooling bath at –10 °C and an ozone/oxygen mixture was passed in. The resulting N_2O_5 crystallized in the form of white crystals in the receiver, a round-bottom flask immersed in an acetone/dry ice bath and equipped with a cold trap. After the reaction was completed, the cold trap with N_2O_5 was weighed and dissolved in dichloromethane cooled to –30 °C. The resulting solution was poured into a dark glass bottle with a Teflon cap. The bottle was stored in a polystyrene box with dry ice.

2.2 Analysis of the concentration of N_2O_5 in CH_2Cl_2

The resulting solution of N_2O_5 in dichloromethane was analyzed. 5 mL of the solution was weighed in a weighing dish on an analytical balance to the accuracy of 0.001 g. Subsequently, the sample was extracted three times with 50 mL of distilled water. The extract obtained was poured into a 250 mL volumetric flask and filled up up to the mark with water. The solution was titrated against 0.1 M NaOH solution in presence of phenolphthalein indicator.

2.3 Nitration of toluene with N_2O_5 in CH_2Cl_2

ortho-Toluene (1 g) and dichloromethane (10.5 g) were added to a 100 mL round-bottomed, three-necked flask equipped with a pressure-equalized funnel, thermometer and mechanical stirring bar, placed in a dry ice/acetone cooling bath. A pre-cooled 8.8% solution of N_2O_5 in CH_2Cl_2 was added to the toluene solution cooled to –20 °C. After the addition was complete, the reaction mixture was stirred for an hour at the temperature of –20 °C. Subsequently, the liquid

in the flask was poured into a beaker of distilled water, the organic layer was separated from the acids and washed with 0.5% sodium bicarbonate solution to obtain pH = 7. Finally, the organic solution was washed with distilled water, separated and dried with a small amount of magnesium sulphate. The CH_2Cl_2 was evaporated on an evaporator at a bath temperature of 40 °C. CH_2Cl_2 was added to the residue (4 g per gram of product) and then analyzed by GC-MS.

The nitration reaction with a catalyst was performed in a correspond manner. The catalyst was added to the flask containing toluene and CH_2Cl_2 (0.68 g per 1 g of toluene), followed by the addition of the solution of N_2O_5. Upon completion, the catalyst was filtered off on a Schott funnel, washed with CH_2Cl_2 (20 mL) and subsequently the filtrates were combined. The procedure was then continued as in the case of nitration without the catalyst.

2.4 Nitration of toluene absorbed in molecular sieves with N_2O_5 in CH_2Cl_2

The molecular sieves were dried at 250 °C overnight. After cooling, the sieves were placed in a vacuum desiccator over phosphorus(V) oxide and additionally dried overnight at 2 mbar pressure, at room temperature. The dried sieves were weighed, immersed in excess toluene and stored for 24 h in a flask closed with a glass stopper. The sieves were then drained on a Schott type funnel. The amount of toluene absorbed was determined from the sieve weight gain. The weight of the sieves, which was equivalent to 2 g of toluene, was calculated. For 3A sieves the weight was 9.82 g, for 4A sieves it was 10.76 g, and for 13X sieves it was 7.32 g.

An 8.8% solution of N_2O_5 in CH_2Cl_2 (19.5 mL) was added to a 100 mL three-necked flask with a mechanical stirring bar, which was placed in a dry ice/acetone cooling bath. The mixture was then stirred and cooled to –20 °C. After cooling, a preset amount of sieves was added to maintain the temperature at –20 °C. After the addition, the resulting mixture was stirred for another 1 h at the temperature of –20 °C. Subsequently, the sieves were drained and washed thoroughly three times on the filter with CH_2Cl_2 (3×20 mL). The combined filtrates were washed with distilled water, followed by 0.5% sodium bicarbonate solution, and again with water, to obtain pH = 7. The washed solution was dried with a small amount of magnesium sulphate. The CH_2Cl_2 was evaporated on an evaporator at a bath temperature of 40 °C. CH_2Cl_2 was added to the residue (4 g per gram of product) and analyzed by GC-MS.

2.5 Analysis of products

The resulting products were analyzed using a GC/MS system equipped with a GC 7890A gas chromatograph and a VL MSD 5975C detector by Agilent

Technologies. The analysis was performed with a 30 m × 250 µm × 0.25 µm HP-1701 column, the temperature programme was in the range 40-250 °C with a helium flow rate of 1 mL/min. The total analysis was set for 30 min. An injection volume of 1 µL was applied, using the programmable temperature of the injection chamber and solvent elimination, the so-called PTV technique. The mass detector operated in the mass range of 10-700 m/z. The identification of the substances in the sample was performed using the MS NIST 2.0f spectral library.

3   Results and Discussion

The selective nitrating agent, namely N_2O_5 in CH_2Cl_2, and commercially available, low-cost, easily modifiable, eco-friendly catalysts were used in the investigation of the selective nitration of toluene. The aim of the study was to obtain the minimum amount of the *meta*-isomer in the resulting mononitrotoluene.

Initially, a series of nitration reactions were carried out for toluene with a solution of N_2O_5 in CH_2Cl_2 with no catalyst. The studies were aimed at process optimization and examination of the selectivity of this nitration mixture. The effects of such parameters as reactant molar ratio, temperature and reaction time were investigated. The reaction products were analyzed by GC/MS as described in Section 2.5. The reaction was carried out twice for each specific reaction condition. The results in the Tables represent the arithmetic mean of the analytical results.

Firstly, the effect of the N_2O_5/toluene ratio on the composition of the nitration products was investigated. The reactions were carried out for the following toluene:N_2O_5 molar ratios: 1:1, 1:2, 1:3, at a temperature of –20 °C. The reaction products were compared with those from the nitration reaction of toluene with 100% nitric acid and a solution of nitric acid in CH_2Cl_2 under similar conditions. The results obtained are shown in Table 1.

Table 1.   Composition of the products of nitration of toluene with N_2O_5/CH_2Cl_2, 100% nitric acid and a mixture of nitric acid in CH_2Cl_2 as a function of reactant ratio

Reactant conc. [% mass]				N_2O_5: toluene ratio [mol/mol]	Composition of toluene nitration product [%]					
Toluene in CH_2Cl_2	N_2O_5 in CH_2Cl_2	HNO_3	HNO_3 in CH_2Cl_2		Toluene	o-NT	m-NT	p-NT	2,6-DNT	2,4-DNT
8.7	8.8	–	–	1:1	0	59.4	1.6	39.0	0	0
8.7	8.8	–	–	2:1	0	0	0	0	17.5	82.5
8.7	8.8	–	–	3:1	0	0	0	0	15.8	84.2
100	–	100	–	3:1	13.9	46.9	2.6	36.6	0	0
100	–	–	20	3:1	31.6	33.2	1.8	33.4	0	0

The data presented in Table 1 served to demonstrate that the stoichiometry of the reactants has a significant effect on the composition of the toluene nitration product. The mono-nitration reaction of toluene at a temperature of –20 °C is already completed at a N_2O_5/toluene molar ratio of 1:1, where the post-reaction mixture does not contain toluene and results in *ortho*-NT (59.4%) as the main product. For a N_2O_5/toluene molar ratio greater than or equal to 2:1, the nitration mixture (N_2O_5/CH_2Cl_2) has the ability to nitrate toluene quantitatively to DNTs. Asymmetric DNT is also produced, however its amount in the mixture is close to the limit of the measurement error. The investigated nitrating mixture is not sufficiently strong to nitrate DNT to TNT under these conditions.

When comparing the results of nitration of toluene (under similar conditions) using N_2O_5/CH_2Cl_2 with 100% nitric acid and the nitric acid/CH_2Cl_2 mixture, the nitrating mixtures based on 100% nitric acid clearly appear to have poorer nitrating capabilities than the N_2O_5/CH_2Cl_2 mixture, and therefore a higher excess must be used than in the case of N_2O_5/CH_2Cl_2. Despite the use of an excess ratio of nitric acid to toluene of 3:1, unreacted toluene is still observed when using 100% nitric acid, *i.e.* 13.9% unreacted toluene remains in the reaction products, and 31.6% when using a 20% solution of nitric acid in CH_2Cl_2. No DNT was produced in either case.

The amount of the *meta*-isomer in the nitration products also depends on the nitrating agent used, the smallest quantity of *meta*-NT is produced by the reaction of toluene with N_2O_5/CH_2Cl_2 and amounts to 1.6%. The highest quantity of *meta*-NT is produced by the nitration of toluene with 100% nitric acid and amounts to 3% of pure NT. This leads to the conclusion that N_2O_5 in CH_2Cl_2 represents a more vigorous and selective nitration mixture compared to 100% nitric acid and the nitric acid in CH_2Cl_2 mixture.

The effect of temperature on the selectivity of the nitration of toluene with N_2O_5 in CH_2Cl_2 was also investigated. The reactions were carried out in the temperature range of –60 to +25 °C at a toluene to N_2O_5 molar ratio of 1:1. The results are listed in Table 2, and Figure 1 shows the effect of temperature of toluene nitration on the amount of the *meta*-isomer.

Table 2.   Composition of the products of nitration of toluene with N_2O_5/CH_2Cl_2 as a function of temperature

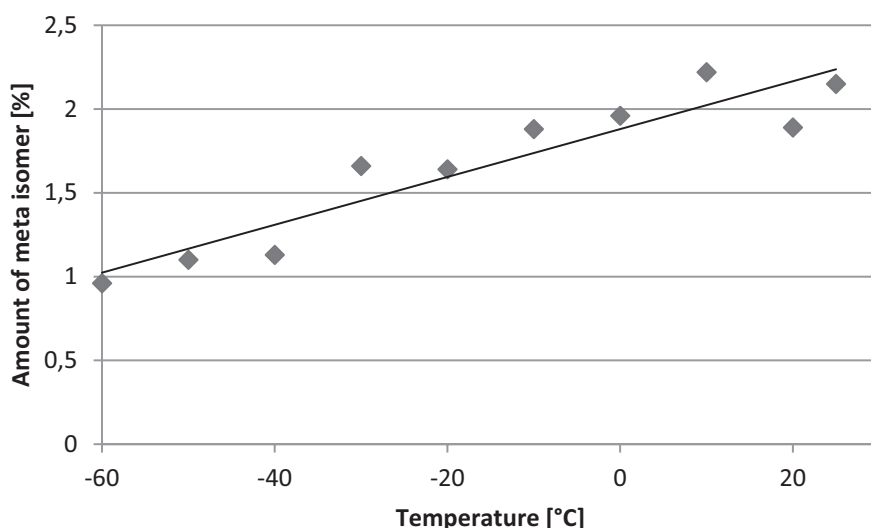| Reactant conc. [wt.%]		Tempe-rature [°C]	Composition of toluene nitration product [%]					
N_2O_5 in CH_2Cl_2	Toluene in CH_2Cl_2		Toluene	*o*-NT	*m*-NT	*p*-NT	2,6-DNT	2,4-DNT
8.8	8.7	–60	0	62.5	1.0	36.5	0	0
		–50		62.8	1.1	36.1		
		–40		61.6	1.2	37.2		
		–30		59.4	1.6	39.0		
		–20		59.4	1.6	39.0		
		–10		59.6	1.8	38.6		
		0		59.3	2.0	38.7		
		10		57.4	2.2	40.4		
8.24		20		58.0	1.9	40.1		
8.8		25		561	2.2	41.7		

Figure 1.   Effect of the temperature of toluene nitration with N_2O_5 in CH_2Cl_2 on the amount of *meta*-NT in the product

The analytical results indicated that temperature has a significant effect on the composition of the product of toluene nitration with N_2O_5 in CH_2Cl_2. The results in Table 2 can be used to conclude that with decreasing temperature, the amount of the *meta*-isomer decreased to the level of about 1-1.2% at nitration temperatures below –40 °C. At the same time, the amount of the *para*-isomer decreased and the amount of the *ortho*-isomer increased. This is caused by differences in the energy of activation in the reactions leading to the production of the different NT isomers. The results obtained are in agreement with previous work [4]. In the reaction carried out at room temperature, the amount of the *meta*-isomer was 2.2%, which is remarkably low compared to the nitration of toluene with the conventional HNO_3/H_2SO_4 nitrating mixture used in industry, where the amount of the *meta*-isomer in the product is about 4.5% [4].

Subsequently, the kinetics of the reaction of toluene nitration to mononitrotoluenes with N_2O_5 in CH_2Cl_2 was investigated. After the addition of N_2O_5 in CH_2Cl_2 to the flask with toluene was completed, an amount of approx. 10 mL of the reaction mixture was pipetted into a flask with toluene at various intervals and then poured into water (50 mL). The reaction workup proceeded as described in Section 2.3. The reactions were carried out at –40, –20 and 0 °C (Table 3).

Table 3. Kinetics of toluene nitration with N_2O_5 in CH_2Cl_2 to mononitrotoluenes at different temperatures

Reaction parameters: N_2O_5/toluene [mol/mol] ratio = 1:1, conc. N_2O_5/DCM = 8.8%, toluene conc./DCM = 8.7%			
Collection time after addition [min]	Amount of toluene [%] at the temperature [°C] of		
	–40[b)	–20[c)	0[d)
0[a)	10.8	6.0	0
5	6.7	4.8	
10	4.5	1.8	
15	1.7	0	
20	0		
30			
40			
50			
60			

[a) immediately after addition
[b) Addition time was 22 min 30 s
[c) Addition time was 12 min 10 s
[d) Addition time was 12 min 32 s

As demonstrated in Table 3, the nitration of toluene with N_2O_5 occurs rapidly. The reaction is complete in 20 min after injection at the temperature of –40 °C, and in 15 min after injection at –20 °C, whereas at of 0 °C, the nitration is complete almost immediately.

During the following stages of the study, the effect of the addition of solid catalysts on the selectivity of toluene nitration with N_2O_5 in CH_2Cl_2 was investigated. The reactions were carried out at –20 °C with a toluene/N_2O_5 molar ratio of 1:1 as described in Section 2.3. The results obtained are listed in Table 4.

Table 4.   Composition of the reaction products of toluene nitration with N_2O_5/CH_2Cl_2 system*) in the presence of solid catalysts at –20 °C

Catalyst	Composition of reaction product [%]			o/p ratio	Yield [%]
	o-NT	m-NT	p-NT		
No catalyst	59.4	1.6	39.0	1.52	84.9
Bentonite	59.1	1.5	39.4	1.50	85.2
3A sieves	58.6	1.6	39.8	1.47	77.5
4A sieves	58.9	1.6	39.5	1.49	92.3
13X sieves	59.0	1.6	39.4	1.50	86.1
Amberlyst	59.7	1.6	38.7	1.54	68.0
Silica SiO_2	59.6	1.6	38.8	1.54	73.2
Clinoptilolite	59.0	1.7	39.3	1.50	73.2
MCM-41	58.7	1.6	39.7	1.48	89.1

* toluene/N_2O_5 ratio of 1:1; temperature –20 °C, 8.8% N_2O_5 in CH_2Cl_2; ratio toluene/cat. 1/0.68 w/w

The results in Table 4 demonstrate that the added catalysts had no effect on the selectivity of the reaction. The individual results obtained are comparable within experimental error, which can be due to the chosen method of performing the reaction. The catalyst was added to 8.7% solution of toluene in CH_2Cl_2, followed by the addition of the 8.8% solution of N_2O_5 in CH_2Cl_2 within 5 min. Under these conditions, the toluene was not absorbed into the pores of the catalyst, so the nitration reaction did not take place within the pores of the catalyst, but occurred in the solvent, outside the catalyst. As demonstrated above, the reaction between toluene and N_2O_5 occurred swiftly and therefore no increased selectivity of this reaction was observed. This was due to the fact that the catalysts could not take advantage of the shape effect, whereby the presence of catalyst pores of the size matching the size of the toluene molecule forces the toluene molecule into the pores of the catalyst in an appropriate orientation, thus favouring the *para*-position.

It was therefore decided to carry out the nitration reaction differently, namely by nitrating the toluene pre-absorbed in the molecular sieves. The reactions were conducted using 3A, 4A and 13X sieves, as described in Section 2.4. The results of these analyses are listed in Table 5.

Table 5.   Nitration of toluene pre-adsorbed on molecular sieves with 8.8% N_2O_5 solution in CH_2Cl_2

Sieve	Composition of reaction products [%]					o/p ratio	Yield [%]
	o-NT	m-NT	p-NT	2,6-DNT	2,4-DNT		
No sieve	59.4	1.6	39.0	–	–	1.52	85
3A	29.3	1.0 (1.48)*	37.1	6.4	26.2	0.79	62
4A	20.7	0.8 (1.41)*	35.1	9.0	34.4	0.59	58
13X	12.4	0.4 (1.1)*	23.7	10.3	53.2	0.52	60

* values in brackets correspond to the amount of meta-NT, as expressed in composition of NT alone

The results obtained demonstrated that molecular sieves provide a quite strong *para*-effect, as shown by the significant increase in the amount of the *para*-isomer to the detriment of the *ortho*- and *meta*-isomers. The reactions are also favourable from the point of view of the amount of *meta*-isomer, as the quantity of the *meta*-isomer did not exceed 1.5% of the mononitrotoluenes in any of the reactions. When comparing the nitration reaction of toluene pre-absorbed on molecular sieves with the nitration reaction of toluene in the presence of molecular sieves as catalysts, some significant differences in the composition of the post-reaction mixtures can be observed. The former reaction is characterized by a remarkably improved selectivity due to the fact that toluene has been absorbed into the pores of the sieves, and therefore the reaction occurs within the sieves for most of the time. By contrast, if the sieves are added to the toluene in dichloromethane solution, the reaction occurs in the pores only partially, whilst it occurs in the solvent for most of the time.

The most pertinent effect was obtained using 13X molecular sieves, as the pore dimensions of this catalyst (average pore size is 10 Å) are closest to those of the toluene molecule (the critical diameter of toluene is 6.7 Å), allowing the nitronium cation to attack mainly the *para*-position of toluene.

Furthermore, this reaction resulted in a relatively high amount of DNT (toluene/ N_2O_5 ratio = 1:1). It may be argued that this manner of running the reaction, in addition to increasing the selectivity, also results in an increased degree of nitration of toluene. It can be assumed that the nitric acid resulting from the reaction of toluene with N_2O_5 is absorbed in the pores of the molecular sieves, resulting in a high local concentration of this acid. A relatively high concentration

of nitric(V) acid yields a nitrating mixture capable of nitrating MNT. Under the same reaction conditions, however with nitric(V) acid instead of N_2O_5, the nitration reaction of toluene does not proceed. The yield of the reaction carried out with molecular sieves is slightly lower than in the absence of sieves, due to the difficulty in extracting the absorbed NT in the catalyst pores.

4   Conclusions

♦   A series of toluene nitration reactions were carried out using an 8.8% solution of N_2O_5 in CH_2Cl_2, both without and with the addition of various catalysts. The results obtained serves to demonstrate that N_2O_5 in CH_2Cl_2 is a more active and selective mixture than 100% nitric(V) acid and nitric(V) acid in CH_2Cl_2.

♦   The mononitration reaction of toluene at –20 °C occurs readily at a N_2O_5/toluene molar ratio of 1:1. For N_2O_5/toluene molar ratios higher than or equal to 2:1, the nitrating mixture (N_2O_5/CH_2Cl_2) is able to nitrate toluene quantitatively to DNT under these conditions. The temperature has a significant effect on the composition of the product of the nitration of toluene with N_2O_5 in CH_2Cl_2; as the reaction temperature is decreased, the amount of the *meta*-isomer is decreased to about 1-1.2% at nitration temperatures below –40 °C. The nitration reaction of toluene with N_2O_5 is swift. It is complete within 15 min at –20 °C, and occurs almost immediately at 0 °C.

♦   The use of molecular sieves for the reaction with adsorbed toluene provides a very strong *para*-effect, as shown by a significant increase in the amount of the *para*-isomer to the detriment of the *ortho*- and *meta*-isomers. The most significant effect was obtained using 13X molecular sieves, as the pore dimensions of this catalyst (average pore size is 10 Å) are closest to those of the toluene molecule (the critical diameter of toluene is 6.7 Å) allowing the nitronium cation to attack mainly the *para*-position of toluene.

♦   The use of 13X molecular sieves reduces the amount of the *meta*-isomer in the mononitration products to 1.1%, compared with 1.6% in the reaction not catalyzed with molecular sieves, under the same reaction conditions.

♦   In the additions to improve the selectivity, the use of molecular sieves also contributes to a higher degree of nitration of toluene at a toluene/N_2O_5 ratio of 1:1. The nitric acid formed in the reaction of toluene with N_2O_5 is absorbed by the pores of the molecular sieves and nitrates MNT to DNT. Under identical conditions for this process run with nitric(V) acid instead of N_2O_5, no further nitration of the toluene occurs.

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