



Modelling of the Synthesis of 1,1-Diamino-2,2-dinitroethene (DADNE)

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Abstract: In this work the conditions and kinetics of nitration of 2-methylpyrimidine-4,6-dione (MPD), which leads to the formation of 1,1-diamino-2,2-dinitroethene (DADNE), are presented. An analysis of literature data enabled us to propose a model and a mathematical formulation of the synthesis of DADNE. The model was verified on the basis of literature data and our own experimental data. The influence of the addition time of nitric acid into a model reactor on temperature and composition of the reaction mixture was investigated. The proposed synthesis model could be useful in a study of the MPD nitration process on a large, laboratory scale.

Keywords: DADNE, modelling of the synthesis, kinetics

Introduction

1,1-Diamino-2,2-dinitroethene (DADNE, FOX-7) was obtained for the first time in 1998 [1, 2]. The detonation parameters of DADNE match those of RDX, whilst its sensitivity to various stimuli shows that it can be considered as a relatively safe explosive [3, 4]. Despite the passage of years since the first reports on the synthesis of DADNE, it is still intensively studied in many research centers. Current findings show clearly that DADNE is one of the leading candidates for use in modern insensitive munitions [5-10]. An excellent review article on DADNE is included in [11].

The kinetics of DADNE synthesis has been considered in few studies [12-14]. In paper [12], the kinetics of nitration of 2-methylpyrimidine-4,6-dione

(MPD) in a mixture of concentrated nitric acid (98%) and sulfuric acid (98%) was studied. MPD was added to the mixture of acids in the molar ratio of MPD : HNO₃ : H₂SO₄ 1:5.1:10.1, whilst maintaining a constant temperature in the reactor. A scheme for obtaining DADNE is shown in Figure 1. According to this scheme, 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione (tetranitroMPD, TNMPD) is a product of MPD nitration.

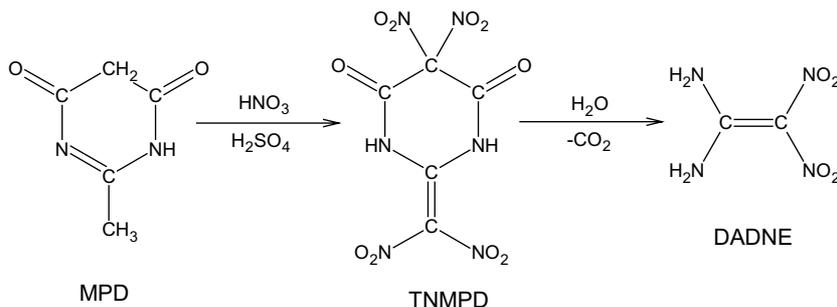


Figure 1. A scheme for DADNE synthesis [12].

An analysis of these results allowed the authors of work [12] to draw the following conclusions:

- (1) Nitration of MPD is a reaction of pseudo-second order (estimated value is 2.19).
- (2) The optimum reaction temperature for nitration is 15 °C.
- (3) The rate of heat generation during the reaction increases with temperature in an exponential manner.
- (4) The heating effect of the reaction (460 kJ/mol) is much larger than the activation energy (42 kJ/mol) estimated from the dependence of the reaction rate on temperature.
- (5) The exponential dependence of the rate of heat generation suggests that an efficient mixing and cooling system is essential for enlarging the scale of the process.
- (6) The relatively low activation energy suggests that the reaction is sensitive to temperature.
- (7) The pre-exponential factor in the equation for the reaction rate constant is 44.24×10^4 .

In other work [13] the kinetics and mechanism of two reactions resulting in DADNE as the product were analyzed. In one of them, MPD was a starting reactant. The nitration kinetics was studied using HPLC and UV spectrophotometry. A diagram of MPD nitration is shown in Figure 2.

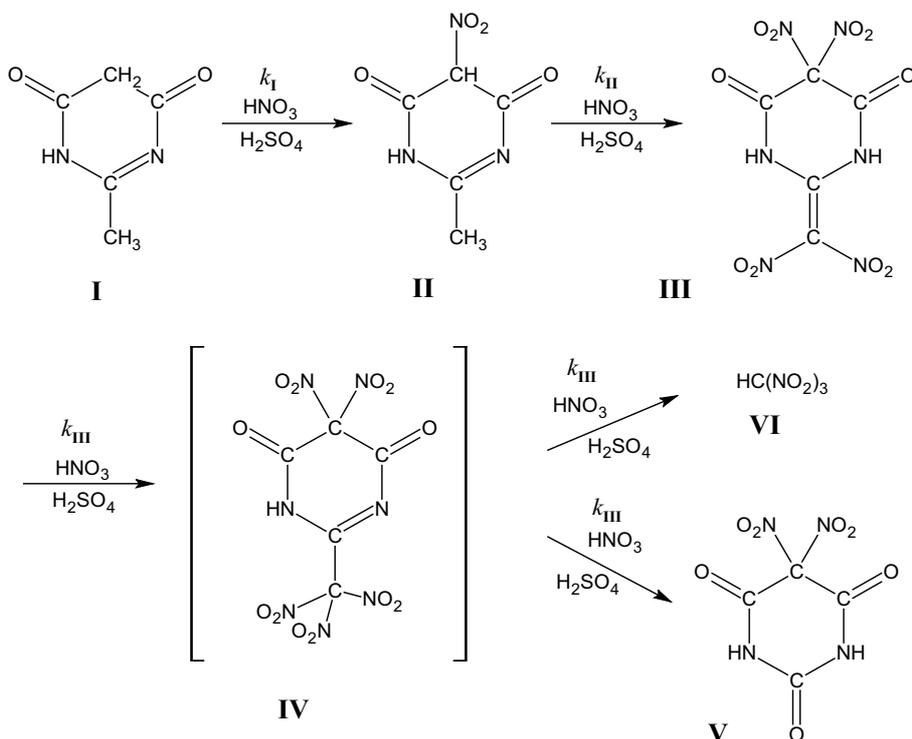


Figure 2. A scheme of MPD nitration [13].

According to this scheme, the product of nitration of **I** (MPD) is compound **II** (2-methyl-5-nitropyrimidine-4,6-dione – mononitroMPD, MNMPD), and compound **III** (tetranitroMPD, TNMPD) is a product of the nitration of **II**. Preliminary investigations of the MPD nitration reaction indicated that the process does not end with the synthesis of **III**. This latter compound is capable of relatively rapid change to give a mixture of further nitration products, of which one was identified as trinitromethane (**VI**). On the basis of the above observations and published data on the nitration of 2-methyl-1,3,5-triazine-4,6-dione and 5-alkyl-substituted derivatives of compound **I**, a conclusion was drawn in [12] that the nitration of **III** forms the structure **IV** (5,5-dinitro-2-(trinitromethyl) pyrimidine-4,6-dione – pentanitroMPD, PNMPD), which subsequently decomposes to a mixture of compounds of **V** (5,5-dinitrobarbituric acid) and **VI**.

The kinetics of the nitration of compound **I** was measured in [13] with a large excess of nitric acid. For an initial concentration of sulfuric acid within the limits of 78-98%, the data obtained are well described by equations concerning two or three consecutive first-order reactions.

If the initial concentration of the compounds nitrated in phase **I** and **II** is varied in the range $(0.3-0.9) \times 10^{-2} \text{ mol/dm}^3$, the rate constants remain the same, which indicates a first order reaction with respect to the compound being nitrated. The reaction orders with respect to nitric acid change between subsequent stages of the process. The observed data show that the reaction is first order for the first and third stages and approaches 2.5 for the second stage. Probably, the fractional order appears, because of the occurrence of three consecutive reactions as a single observed stage in the absence of a pronounced leading reaction [13].

The reaction rate constant k_I is approximately 10 times the rate constant k_{II} for the formation of compound **III** and constant k_{III} is one third that of k_{II} . The values of the activation energy and pre-exponential coefficient for the reactions I-III determined in [13] are summarized in Table 1.

Table 1. Activation energies and pre-exponential coefficients for the reactions I-III [13]

Parameter	k_I	k_{II}	k_{III}
E_a [kJ/mol]	91.8 ± 2.6	78.6 ± 5.7	65.5 ± 7.6
$\log A$	14.1 ± 0.5	11.9 ± 1.0	9.8 ± 1.3

The kinetics of MPD nitration at various temperatures (5, 10, 15 and 20 °C) was also studied in work [14]. The order of transformation of MPD into TNMPD was determined to be 1.65, which means that the MPD nitration is a reaction of pseudo-second order. The designated value of the activation energy (61.5 kJ/mol) is about 50% higher than the energy obtained in [12], but is slightly lower than the value of the activation energy for the reaction II as given in [13] (Table 1). The pre-exponential factor was estimated to be $\log A = 20.5$. For the conditions considered, the nitration time for 65% of MPD was also set out. Times of 411, 296, 141 and 113 minutes were obtained at 5, 10, 15 and 20 °C, respectively. Taking this into account and the exothermic nature of the nitration reaction of MPD, the reaction temperature of 15 °C is given as the optimal one.

Modelling of DADNE synthesis

We assumed that DADNE synthesis proceeds according to the scheme shown in Figure 2 ([13]). Three consecutive reactions can be carried out in a reactor with the corresponding rate constants k_I - k_{III} :



During the synthesis, concentrated nitric acid is added at a rate of s [dm^3/min] (n_s [mol/min]). This method of obtaining DADNE is used on a large laboratory scale [15]. Taking into account the results of the research carried out in [13], we can write the equations for the kinetics of changes in reactant concentrations in the following form:

$$\frac{dc_1}{dt} = -k_1 c_1 c_2 - c_1 \frac{1}{V} \frac{dV}{dt} \quad (4)$$

$$\frac{dc_2}{dt} = \frac{n_s}{V} - k_1 c_1 c_2 - 3k_{\text{II}} c_2^{2,5} c_3 - k_{\text{III}} c_2 c_4 - c_2 \frac{1}{V} \frac{dV}{dt} \quad (5)$$

$$\frac{dc_3}{dt} = k_1 c_1 c_2 - k_{\text{II}} c_2^{2,5} c_3 - c_3 \frac{1}{V} \frac{dV}{dt} \quad (6)$$

$$\frac{dc_4}{dt} = k_{\text{II}} c_2^{2,5} c_3 - k_{\text{III}} c_2 c_4 - c_4 \frac{1}{V} \frac{dV}{dt} \quad (7)$$

$$\frac{dc_5}{dt} = k_{\text{III}} c_2 c_4 - c_5 \frac{1}{V} \frac{dV}{dt} \quad (8)$$

where V is the volume of the reaction mixture, t – time, and c_1 , c_2 , c_3 , c_4 , and c_5 are the molar concentrations of MPD, HNO_3 , MNMPD, TNMPD and PNMPD, respectively.

The rate constants are described by the Arrhenius equation:

$$k_i = A_i \exp\left(\frac{E_{a,i}}{RT}\right), \quad i = \text{I, II, III} \quad (9)$$

We assumed that the volume of the reaction mixture changes only due to the flow of nitric acid:

$$\frac{dV}{dt} = s \quad (10)$$

We further assumed that the heat of the reactants is constant in the range of the temperatures tested. Then the heat balance in the reactor can be described by the equation:

$$\rho c_p V \frac{dT}{dt} = n_s \rho_s c_{ps} (T_0 - T) + r_Q V + U A (T_a - T) \quad (11)$$

where ρ and ρ_s are the densities of the reaction mixture and added nitric acid, respectively, c_p and c_{ps} – their specific heats, T and T_0 – the temperature of the mixture and the acid, r_Q – the rate of heat released during the synthesis, U – the coefficient of heat transfer to the cooling system, A – the area of the contact surface between the reactor and cooling system, T_a – the temperature at the surface.

We assumed that the density of the reaction mixture changes only due to the nitric acid supply:

$$\rho = \frac{m_p + \rho_p s t}{V_p + s t} \quad (12)$$

where m_p , V_p and ρ_p are the initial values of mass, volume and density of the reactants, respectively.

As at least three reactions involving HNO_3 operate during the synthesis process and the heating effect given in (12) refers to 1 mol of substrate (MPD), it was assumed that the heat of reaction can be associated with the loss of nitric acid in the reactor. Therefore, the reaction of one mole of HNO_3 leads to the release of $q = 115$ kJ in the reaction system, and the rate of heat output in 1 dm^3 of the reactants is described by the relationship:

$$r_Q = \left(-\frac{dc_2}{dt} + \frac{n_s}{V} \right) q \quad (13)$$

The solution of equations (4)-(13) allowed us to determine the changes in concentrations of individual reactants and in the reaction temperature. The system can be solved by the Runge-Kutta method of fourth order.

The results of modelling of DADNE synthesis

To verify the proposed model, the experimental results of DADNE synthesis presented in [12] and [14] were used. The authors of these papers studied the kinetics of synthesis at different temperatures by determining the resulting amount of DADNE at specified times from the start of the reaction. In paper [12], the kinetic parameters of MPD nitration were determined using a mixture of nitric acid (98%) and sulfuric acid (98%). The study was conducted on a small scale (about 70 ml of reaction mixture). MPD was added to the mixture of acids in such a way as to maintain a constant temperature in the nitration process. Further results were obtained by interrupting the process after a suitable time and determination of the resulting products, which enabled changes in concentration of the substrates to be identified indirectly. In a similar way, DADNE synthesis was studied in [14] where samples were taken in the course of the process on a larger scale (about 1 dm³ mixture), without interruption. Nitric acid (65%) was used for the synthesis instead of concentrated acid (98%). Crushed MPD was immediately introduced with vigorous stirring to a mixture of acid pre-cooled to a temperature of about 0 °C. The heat of MPD solution in the acids and the start of the exothermic process of nitration caused a rapid increase in temperature, which was stabilized at the desired level within 5 minutes.

To adapt the above theoretical model to the conditions of the experiments conducted in [12] and [14], we assumed that the temperature in the reaction mixture was kept constant. Since MPD was added to the mixture of acids very quickly, it was assumed that at time $t = 0$ all the substrates were located in the reactor and their total volume in the process remains constant ($s = 0$ and $dV/dt = 0$). With these assumptions, the MPD nitration is described by the system of equations (4)-(9) with the following initial conditions:

$$\begin{aligned}c_1(0) &= c_{10} \\c_2(0) &= c_{20} \\c_3(0) &= 0 \\c_4(0) &= 0 \\c_5(0) &= 0\end{aligned}\tag{14}$$

Based on the analysis of the results for the DADNE synthesis model, the value of the activation energy and the pre-exponential coefficients for the reactions I-III, given in Table 2, were used for the calculations. These values are within the limits of changes of the Arrhenius parameters presented in the paper [13] – Table 1.

Table 2. The values of the activation energy and the pre-exponential coefficient used in the calculations

Parameter	k_I	k_{II}	k_{III}
E_a [kJ/mol]	89.2	78.6	69.3
$\log A$	14.6	11.9	9.4

Analysis of the data contained in [12] enabled us to determine the initial molar concentrations of nitric acid and MPD in the reaction mixture: $c_{10} = 1.14 \text{ mol/dm}^3$, $c_{20} = 5.71 \text{ mol/dm}^3$. The results of the modelling of the MPD nitration process at various temperatures are shown in Figures 3-6. In the figures, the molar concentration of TNMPD is also shown, being defined on the basis of the amount of DADNE obtained in [12] at various times from the start of the synthesis.

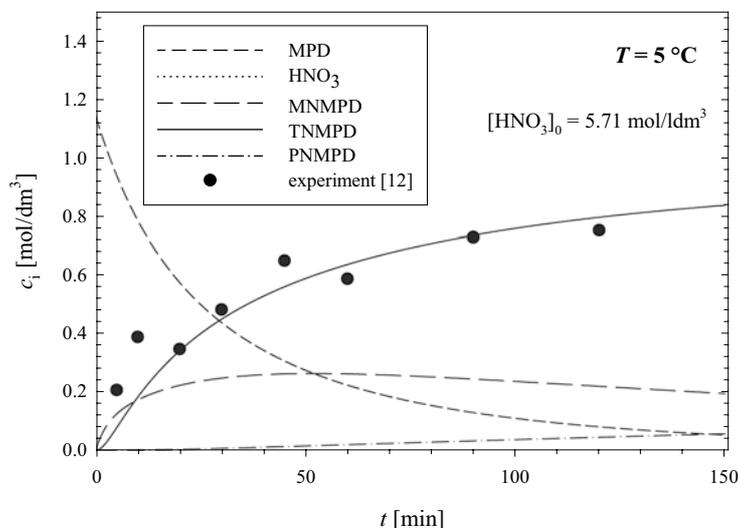


Figure 3. Variation of the reactant concentrations in the process of MPD nitration at 5 °C under the conditions given in [12].

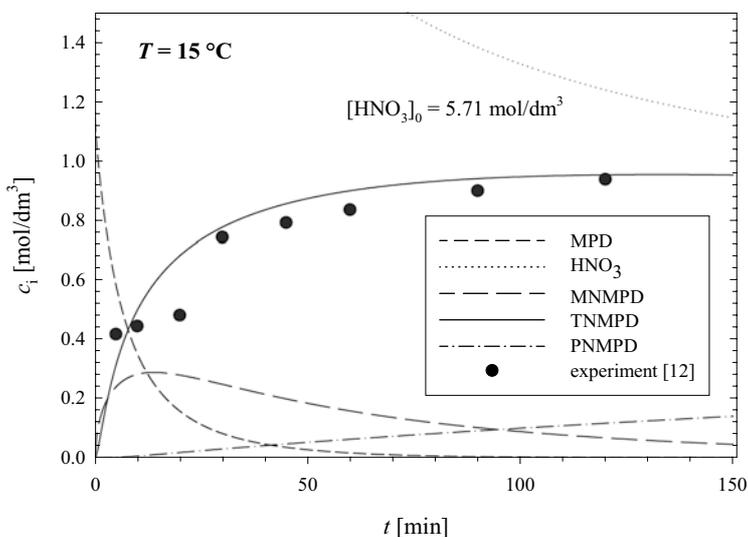


Figure 4. Variation of the reactant concentrations in the process of MPD nitration at 15 °C under the conditions given in [12].

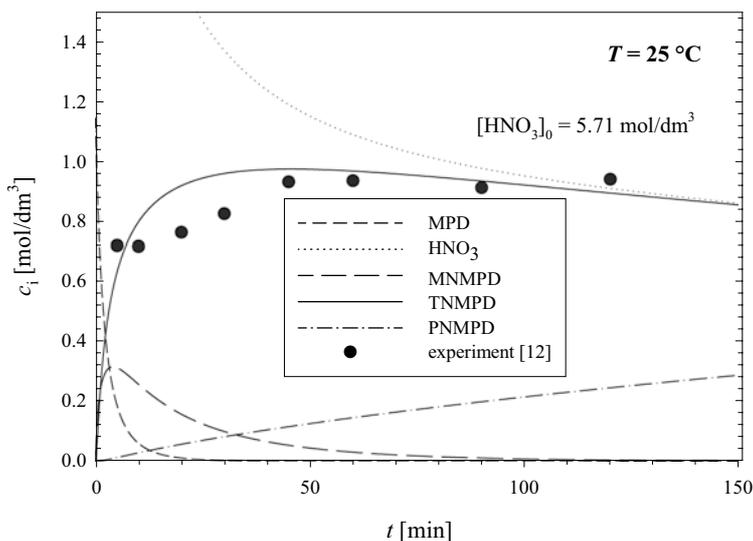


Figure 5. Variation of the reactant concentrations in the process of MPD nitration at 25 °C under the conditions given in [12].

For the conditions of DADNE synthesis conducted in [14], the initial concentrations of nitric acid and MPD are as follows: $c_{10} = 0.48 \text{ mol/dm}^3$,

$c_{20} = 2.24 \text{ mol/dm}^3$. The modelling results, together with the concentration of TMNPD determined experimentally, are shown in Figures 6-9.

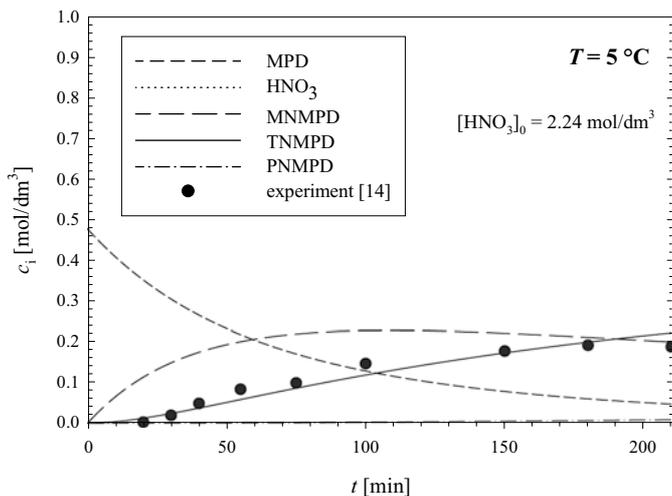


Figure 6. Variation of the reactant concentrations in the process of MPD nitration at 5 °C under the conditions given in [14].

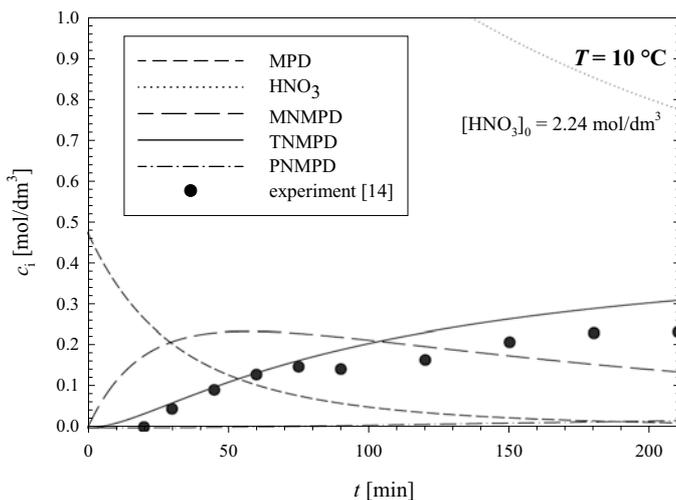


Figure 7. Variation of the reactant concentrations in the process of MPD nitration at 10 °C under the conditions given in [14].

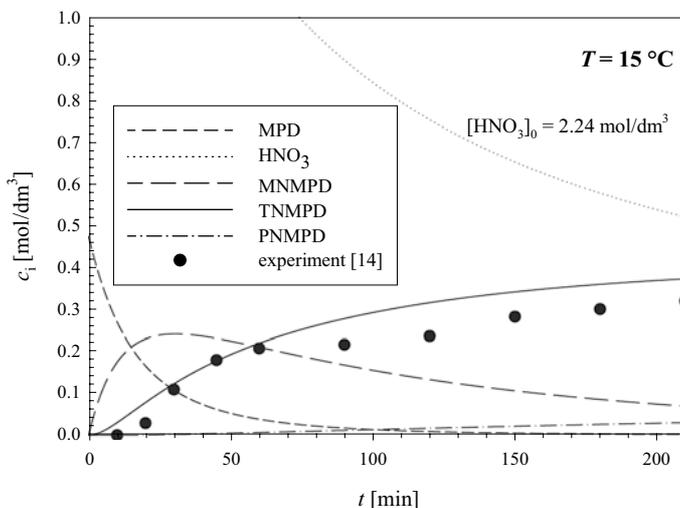


Figure 8. Variation of the reactant concentrations in the process of MPD nitration at 15 °C under the conditions given in [14].

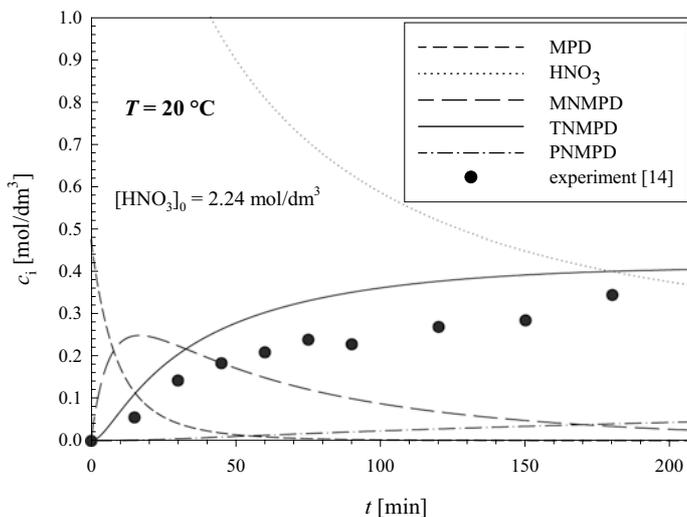


Figure 9. Variation of the reactant concentrations in the process of MPD nitration at 20 °C under the conditions given in [14].

A comparison of the calculated TNMPD concentration (solid line in Figures 3-9) with the concentration of the compound determined on the basis of experimental data shows a good quantitative agreement. The biggest differences

are observed for 25 °C (Figure 5) and 20 °C (Figure 9). In the case of DADNE synthesis at 25 °C under the conditions described in [12] a qualitative discrepancy is observed – the theoretical concentration of TNMPD falls in the second phase of synthesis, while the concentration estimated on the basis of the experimental data remains at the same level. It seems that the rate of reaction III adopted for the calculations requires further experimental verification.

Comparing the corresponding plots of Figures 3-9 for the same temperature we notice a difference in the speed of the process and changes in the composition of the reaction mixture during both analyzed experiments. These differences can be explained by a large divergence in the main initial concentrations of substrates (MPD and HNO₃) used in [12] and [14]. Although the molar ratio of reactants was comparable in both studies, they were diluted with varying amounts of sulfuric acid. Therefore, the changes in the composition of the reaction mixture containing a higher initial concentration of the major substrates (e.g., Figure 4) are, in the initial phase (approx. 30 min), more dynamic than those observed for a mixture of substrates with a lower initial concentration (Figure 8). After about 30 minutes the change in the composition in the two experiments proceeded at a similar rate, which was connected with the equilibration of the concentration of the main unreacted substrates.

A revised model for the synthesis of DADNE was used to investigate the influence of nitric acid addition time on changes in temperature and composition of the reaction mixture. It was assumed that the surface of a hypothetical batch reactor is 483 cm², the coefficient of heat transfer to the cooling system is 0.65 J/(min cm² K), and the contact surface temperature of the reactor and cooling system is 20 °C. The composition of the reaction mixture corresponded to that used in the tests in [14]. The total amount of nitric acid added to the reactor corresponded to a concentration of 2.24 mol/dm³, related to the final volume of the reaction mixture. It was assumed that nitric acid is added at a constant rate during 0, 30, 60 and 90 minutes. The solution of equations (4)-(13) allowed us to specify changes in the concentration of reactants and the reaction temperature. The calculation results are shown in Figures 10-14.

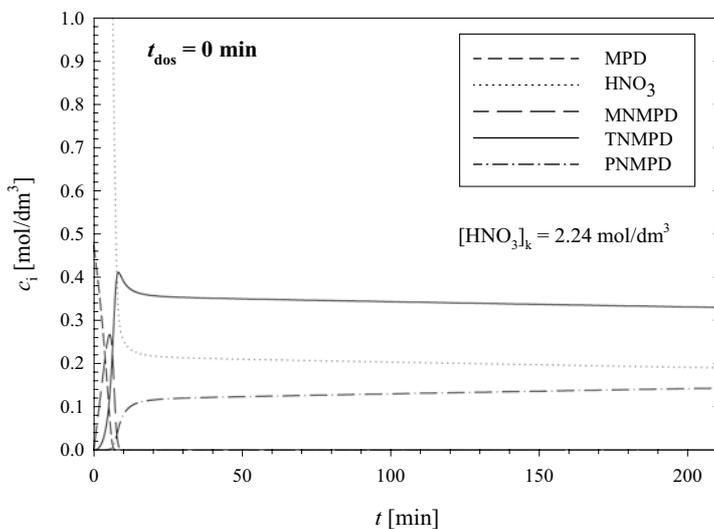


Figure 10. Variation of the reactant concentrations in the process of MPD nitration in the case of dosage of nitric acid at $t = 0$ min.

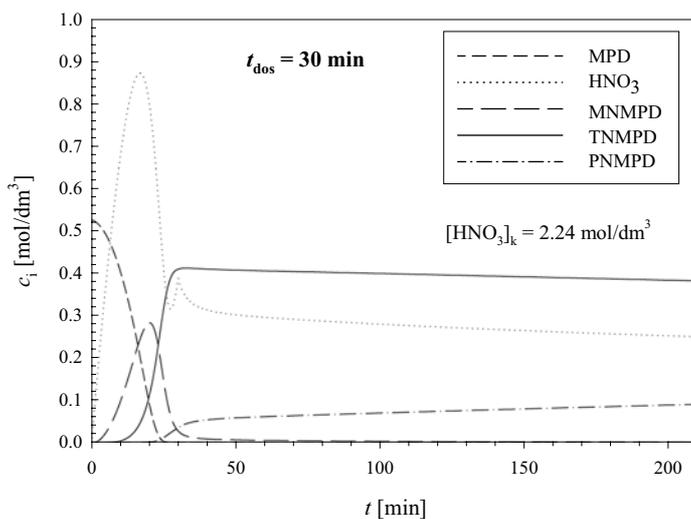


Figure 11. Variation of the reactant concentrations in the process of MPD nitration in the case of dosage of nitric acid during 30 min.

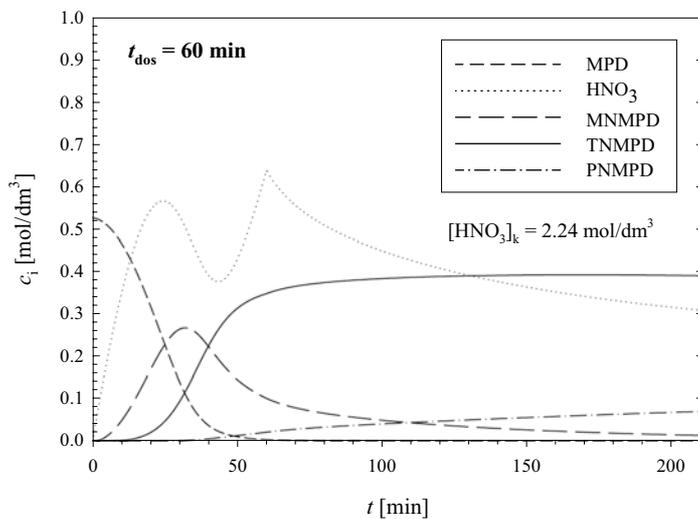


Figure 12. Variation of the reactant concentrations in the process of MPD nitration in the case of dosage of nitric acid during 60 min.

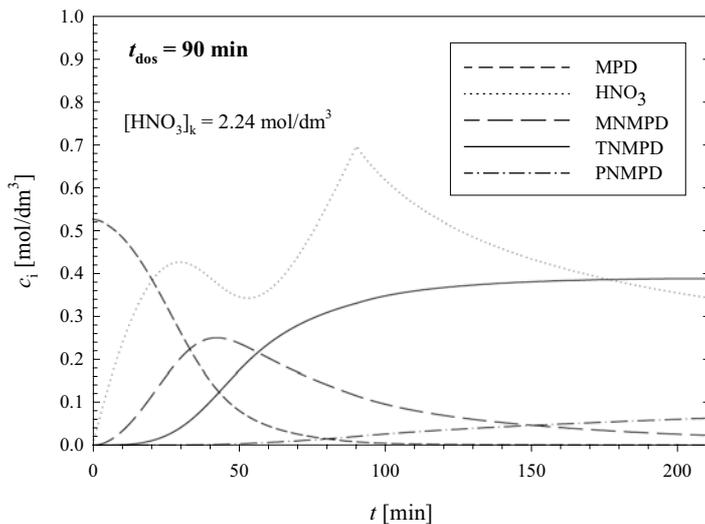


Figure 13. Variation of the reactant concentrations in the process of MPD nitration in the case of dosage of nitric acid during 90 min.

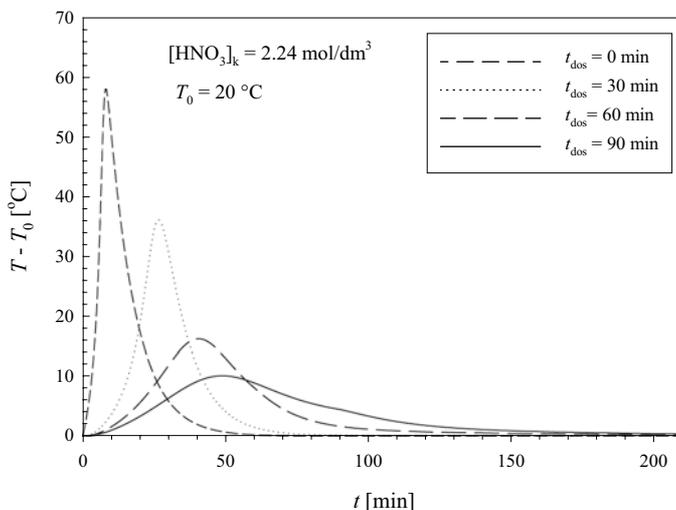


Figure 14. Variation of the temperature of the reactants in the process of nitration of MPD for various nitric acid addition times.

As would be expected, prolonged addition of nitric acid to the mixture of sulfuric acid and MPD significantly decreases the maximum temperature in the reactor. According to the authors of work [15], the process of MPD nitration should be discontinued if the temperature of the reactants increased above 35 $^{\circ}\text{C}$. The curves presented in Figure 14 show that the temperature for the assumed conditions of synthesis did not increase above 35 $^{\circ}\text{C}$, and the minimum time for the addition of nitric acid should be 60 min. Modelling of the MPD nitration for a specific reaction system requires the determination of accurate data on the cooling system and on the heat transfer through the walls of the reactor.

Summary

Safe DADNE synthesis requires close monitoring both of the reaction temperature and the speed of introduction of nitric acid into the reactor. The present work provides a theoretical model for the investigation of the influence of various factors on both the rise in temperature in the reactor, and the accumulation of nitric acid during the synthesis. To model the manufacturing process of DADNE synthesis on a laboratory scale, however, it is necessary to determine the actual characteristics of the reactor and its equipment, including the cooling system, and to examine carefully the reaction kinetics and the heat using, for example, a differential reaction calorimeter.

Acknowledgements

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