



Preparation of Low-melting Compositions Based on 1,3,3-Trinitroazetidine^{*)}

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Abstract: Investigations of TNAZ/AzDNAZ mixtures with different TNAZ contents revealed an eutectic composition TNAZ/AzDNAZ 35/65 with melting point of 61 °C. Combined introduction of nitro- and azido groups followed by nitration of tBuDNAZ/tBuAzNAZ mixtures in N₂O₅/CH₃CN and NH₄NO₃/(CH₃CO)₂O systems has been investigated. Possibility of synthesis TNAZ/AzDNAZ mixtures of various contents has been shown.

Keywords: TNAZ, nitration, eutectic mixture

Introduction

Recently intensive searches have been conducted of the new explosive materials possessing high energy of explosive transformation, density and stability. The most interesting compounds obtaining were hexanitrohexaazaisowurtzitane (CL-20), 1,3,3-trinitroazetidine (TNAZ), belonging to a class of cyclic nitroamines.

1,3,3-Trinitroazetidine has been synthesized in 1984 in the USA and represents four-membered heterocyclic nitroamine containing *gem*-dinitro group. Now works with TNAZ are carried on in the USA, France, Germany, South Korea and China.

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It is proposed to use TNAZ in artillery powder systems [1, 2], as a component of pyrotechnic mixtures [3, 4] and explosive compositions [5]. Also TNAZ may be used as a softener in mixtures with CL-20 and in gunpowders containing 4% of TNAZ [1].

One of advantages of TNAZ is rather low melting point (98-101 °C [6-9]) at sufficient power (approximately as RDX) and high density (1.84 g/cm³ [6, 8]), that makes it attractive to use in some special compositions.

TNAZ is capable of forming eutectic mixtures with high energetic substances, such as HMX, 2,4-dinitroimidazole, tetryl. TNAZ/tetryl eutectic composition with the melting point 81.5 °C (test DSC) [10].

Material and Methods

NMR spectra were obtained with a Bruker AM 300 and Unity INOVA-400 spectrophotometers. Chemical shifts are reported as δ values and are relative to internal HMDS. Melting points were run at 3 °C/min on a Boatus heating microtable. Infrared spectra were obtained on a Thermo Nicolet 360 FT IR spectrophotometer using KBr disks.

HPLC analysis was performed on "Milichrom-4" chromatograph, column UVM 3780/12, 2.0 x 60 mm, speed of submission of eluent 200 μ L/min. Acetonitrile/water 1/1, acetonitrile/water 35/65 as eluents was used. Thin-layer chromatography (TLC) was performed using DC-Alufohlen TLC plates from Merck.

Differential Scanning Calorimetry (DSC) experiments were performed on a Mettler Toledo DSC 822^e using aluminium sample pans. The instrument was calibrated daily using indium and aluminium standards. Traces were recorded at ramp rate of 10 °C/min between 25 to 200 °C under a flowing N₂ gas atmosphere (50 mL/min). The sample weight was 1.28 mg.

Synthesis of 3-azido-1-*tert*-butyl-3-nitroazetidide (tBuAzNAZ)

To a solution 2 g (8.9 mmol) (1-*tert*-butyl-3-nitroazetid-3-yl)methanol hydrochloride (**4**) in 4 mL of water, solution NaOH 2.49 g (62.3 mmol) in 6 ml of water was added at stirring. The white solid precipitated. After dissolution of a deposit the solution NaN₃ 2.89 g (44.5 mmol) in 6 mL of water was added. The mixture was maintained 10 min and added to solution K₃[Fe(CN)₆] 14.6 g (44.5 mmol) in 50 mL of water. The mixture is maintained at stirring within 4 hours. Reaction mixture was extracted with dichloromethane (4 x 30 mL). The extract was dried above MgSO₄ and the solvent was removed. Column

chromatography of the residue (silica gel, methylene chloride - carbon tetrachloride) gave 3-azido-1-*tert*-butyl-3-nitroazetidide (1.38 g, 78%). $^1\text{H NMR}$ (CDCl_3) δ , ppm: 3.93(d,2H J=10 Hz), 3.49(d,2H J=10 Hz), 1.01(s,9H), IR: 2969 (CH_3), 2128 (N_3), 1574 (NO_2), 1335 (NO_2) cm^{-1} .

Synthesis of 3-azido-1,3-dinitroazetidide (AzDNAZ)

To well stirred solution 1.3 g (6.5 mmol) 3-azido-1-*tert*-butyl-3-nitroazetidide in 10 mL (59 mmol) acetic anhydride, ammonium nitrate 0.8 g (9.8 mmol) was added. The mixture was heating up to 75 °C and stirring 1.5 hours. Then the reaction mixture was poured out in 15 mL of water. Then it is cooled to 0 °C. Result solution was extracted with ethyl acetate (3 x 15 mL). The extract is washed by 1% NaOH solution (40 mL) and the same volume of water. The extract was dried above MgSO_4 and removal of the solvent gave a white solid (0.59 g, 48%) melting point 77.5-80 °C. $^1\text{H NMR}$ (CDCl_3) δ , ppm: 5.06(d,2H, J=14 Hz), 4.63(d,2H, J=14 Hz), IR: 2136(N_3), 2135, 1576(N-NO_2), 1560(C-NO_2), 1342(C-NO_2), 1255(N-NO_2) cm^{-1} .

Synthesis of tBuDNAZ/tBuAzNAZ mixture

To a solution 2 g (8.9 mmol) (1-*tert*-butyl-3-nitroazetidide-3-yl)methanol hydrochloride (**4**) in 4 mL of water, solution NaOH 1.78 g (44.5 mmol) in 6 mL of water is added at stirring. The white solid precipitated. After dissolution of a deposit the solution NaN_3 1.7 g (26.7 mmol) in 4 mL of water is added. The mixture is maintained 10 min and added to solution $\text{K}_3[\text{Fe}(\text{CN})_6]$ 14.6 g (44.5 mmol) in 50 mL of water. The mixture is maintained at stirring within 2 hours. Then the solution of NaNO_2 1.2 g (17.8 mmol) is added and maintained for 2 hours. Reaction mixture is extracted with dichloromethane (4 x 30 mL). The extract is dried above MgSO_4 . Removal of the solvent gave tBuDNAZ/tBuAzNAZ (15/85) mixture as a yellow oil (1.4 g, 75%). IR: 2969 (CH_3), 2128 (N_3), 1574 (NO_2), 1335 (NO_2) cm^{-1} .

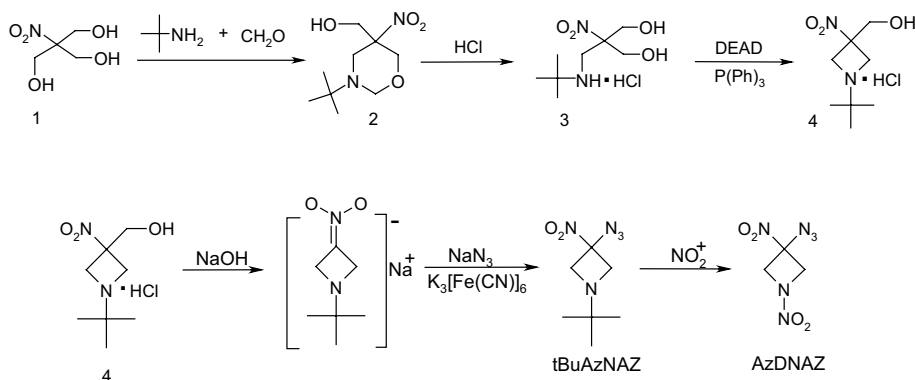
Synthesis of a TNAZ/AzDNAZ mixture

To well stirred solution tBuDNAZ/tBuAzNAZ (15/85, 1.3 g, 6.5 mmol) in acetic anhydride (10 mL, 59 mmol), ammonium nitrate (0.8 g, 9.8 mmol) was added. The mixture was heating up to 75 °C and stirring 1.5 hours. Then the reaction mixture was poured out in 15 mL of water. Then it was cooled to 0 °C. The white solid precipitated out and was filtered, washed with ice water (2 x 20 mL) and dried above P_2O_5 . The white solid is TNAZ/AzDNAZ mixture (8/92, 0.2 g, 19.4%) with m.p. 60-72 °C. Filtrate was extracted with ethyl acetate (3 x 15 mL). The extract was washed by 1% NaOH solution (40 mL) and the

same volume of water. The extract was dried above MgSO_4 and removal of the solvent gave TNAZ/AzDNAZ (37/63) as a yellow oil (0.4 g, 39%). IR: 2136 (N_3), 1604-1538 ($\text{C}-\text{NO}_2$) cm^{-1} .

Results and Discussion

Recently we synthesized a new energetic substance – 3-azido-1,3-dinitroazetidide (AzDNAZ). This substance has been obtained by nitration of 3-azido-1-tert-butyl-3-nitroazetidide (tBuAzNAZ). The oxidative substitution was carried out in the conditions similar to preparation of *gem*-dinitrocompound [11, 12]. Nitroisobutylglycerol has been chosen as the initial substance for synthesis of AzDNAZ (Scheme 1):



Scheme 1. Synthesis AzDNAZ [11].

Oxidizing azidation was carried out in the presence of big amounts of NaOH and one-electron oxidizer $\text{K}_3\text{Fe}(\text{CN})_6$. Reduction of amount of the NaOH or $\text{K}_3\text{Fe}(\text{CN})_6$ results in decrease of yield (Table 1). Partial replacement the $\text{K}_3\text{Fe}(\text{CN})_6$ on the $\text{Na}_2\text{S}_2\text{O}_8$ was lead to low selectivity of reaction.

Table 1.

NaOH, eq.	$\text{K}_3\text{Fe}(\text{CN})_6$, eq.	Yield of tBuAzNAZ, %
4	3	59
6	5	70
7	5	78

The reaction has been shown to lead to small amounts of 1-*tert*-butyl-3,3-dinitroazetidene (tBuDNAZ) as a by-product (10-15%).

Nitration was carried out in various nitrating systems. The yield AzDNAZ achieved 40-60% (Table 2), and the melting point was 77.5-80 °C [11].

Table 2.

Nitrating system (mol/mol)	Yield of AzDNAZ, %
HNO ₃ /Ac ₂ O 1/1	42
N ₂ O ₅ /CH ₃ CN	61
NH ₄ NO ₃ /Ac ₂ O 70°C	50

DSC analyses of various mixtures of α -nitroazide with TNAZ have shown that the compounds form an eutectic mixture with mass ratio TNAZ/AzDNAZ as 35/65 (Figure 1-4).

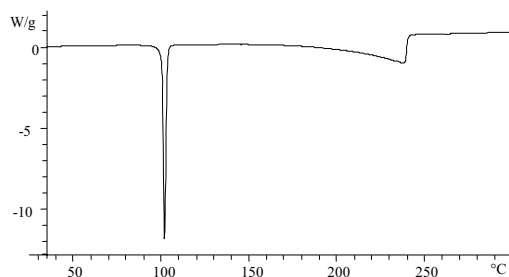


Figure 1. DSC analysis of TNAZ.

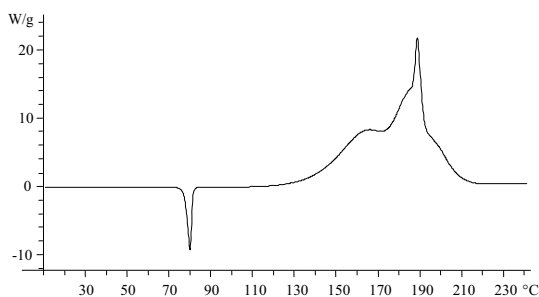


Figure 2. DSC analysis of AzDNAZ.

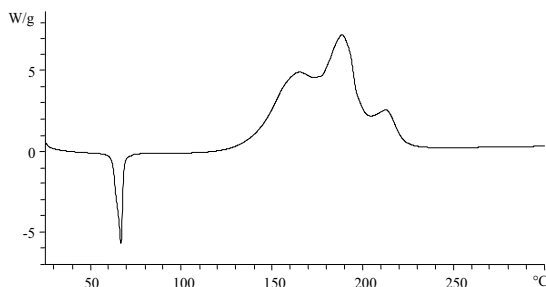


Figure 3. DSC analysis of mixture TNAZ/AzDNAZ 35/65.

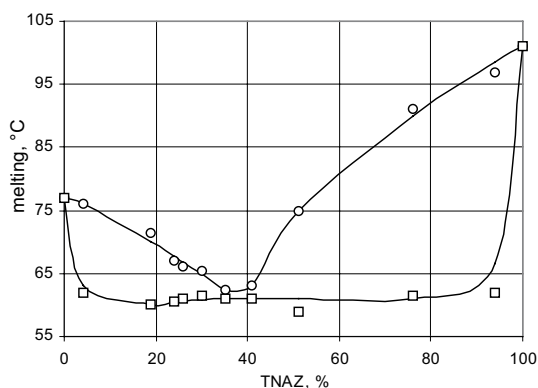
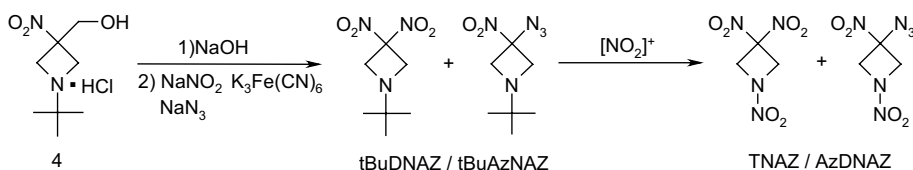


Figure 4. TNAZ/AzDNAZ melting-point diagram.

As oxidizing azidation and nitration take place in similar conditions there is an opportunity of preparation of mixture TNAZ/AzDNAZ simultaneously in one-pot (Scheme 2).



Scheme 2. Synthesis of TNAZ/AzDNAZ mixtures.

Research of kinetics of oxidizing nitration and azidation reactions, under optimum conditions resulted in (5 mol NaOH, 5 mol NaNO₂ or NaN₃, 5 mol K₃Fe(CN)₆) and has shown that nitration proceeds 3 times faster than azidation.

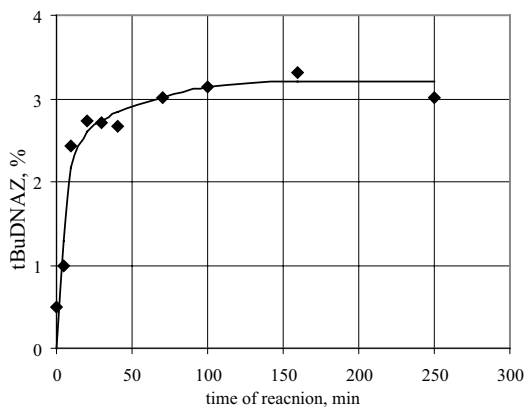


Figure 5. Kinetics of nitration.

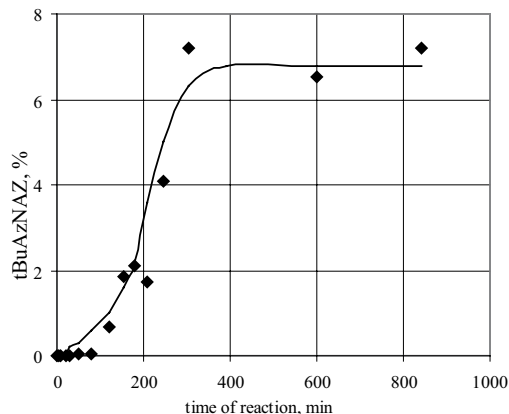


Figure 6. Kinetics of azidation.

Thus we made an assumption that various compositions of geminal nitro- and azidoazetidines can be obtained by not only changing the ratio NaN_3 and NaNO_2 , but also the way of their addition.

At a simultaneous addition of NaN_3 and NaNO_2 we obtained the mass ratio of the products as 80/20 (tBuDNAZ/tBuAzNAZ), with the total yield of the target product of 75%, which corresponds to the yield of oxidizing nitration.

No simultaneous addition of NaN_3 and NaNO_2 leads to increase in the content of azide in comparison with *gem*-dinitrocompound without increase in sodium azide (Figure 7).

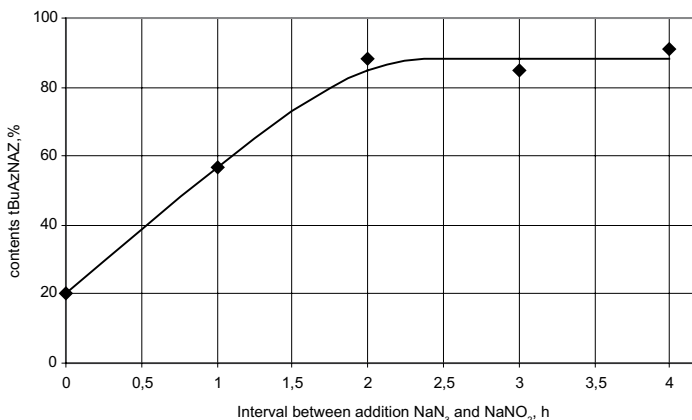


Figure 7. Dependence of tBuDNAZ/tBuAzNAZ mixture composition on the interval between addition of NaN_3 and NaNO_2 .

It has been shown that the 2-hours pause between addition of NaN_3 and NaNO_2 gives rise to formation of a mixture of 85% tBuAzNAZ and 15% tBuDNAZ. The composition of products was determined by HPLC method.

The earlier researches have shown that the most convenient systems for preparation TNAZ are: $\text{HNO}_3/\text{Ac}_2\text{O}$ 6/1, $\text{NH}_4\text{NO}_3/\text{Ac}_2\text{O}$, and also systems containing nitric anhydride. However, the maximum yield of TNAZ, 82%, was achieved in system $\text{NH}_4\text{NO}_3/\text{Ac}_2\text{O}$ (yields were 60-80% and by on different sources).

It has been shown that nitration of tBuAzNAZ occurs in this system with a smaller yield (40-60%) than tBuDNAZ (60-80%) that has been explained by lower stability of geminal nitroazide in acid medium. This behaviour of tBuAzNAZ can essentially change composition of the final mixture. Therefore, it has been carried out nitration of mixtures with high contents of tBuAzNAZ. As a result solid and liquid phases were obtained and analysed by HPLC. Results of the analysis have shown that the solid product represents a mixture with AzDNAZ content 92%, and the composition of the liquid phase is close to eutectic (TNAZ/AzDNAZ 37/67).

Conclusion

The new low-melting composition based on 1,3,3-trinitroazetidine has been proposed. The melting-point diagram of mixtures of TNAZ/AzDNAZ has been obtained.

The method of preparation of TNAZ/AzDNAZ mixtures by introduction of nitro- and azido- groups followed by nitration has been developed.

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