Thermal reactivity of some nitro- and nitroso-compounds derived from 1,3,5,7-tetraazabicyclo[3.3.1]nonane at contamination by ammonium nitrate

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Abstract

Thermal reactivity of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT), 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DNPT), 1,3,5-trinitroso-1,3,5-triazinane (TMTA or *R*-salt), 1,3,5-trinitro-1,3,5-triazinane (hexogen or RDX), 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocane (DADN), α-modification of the 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (octogen or HMX) and of their mixtures with 2 wt.% of ammonium nitrate (AN) has been examined by means of non-isothermal differential thermal analysis. The resulting data were analyzed according to the Kissinger method. The reactivity was expressed as the E_aR^{-1} slopes of the Kissinger relationship. A relatively high reactivity has been found with mixtures of DPT and DNPT with AN. Electronic charges q^N at nitrogen atoms in molecules of the compounds studied were calculated by means of ab initio DFT B3LYP/6-31G** method. The relationships were confirmed between the slopes E_aR^{-1} and the q^N values for the nitrogen atoms primarily undergoing reaction. On the basis of these relationships it is stated that the destabilizing effect of AN is due to acidolytic attack of nitric acid (resulting from dissociation of ammonium nitrate) at the nitrogen atoms with the most negative q^N values in the molecules of the compounds studied.
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Keywords: Ab initio DFT B3LYP/6-31G**; Ammonium nitrate; 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane; 3,7-Dinitroso-1,3,5,7-tetraazabicyclo [3.3.1]nonane; 1,3,5-Trinitroso-1,3,5-triazinane; 1,3,5-Trinitro-1,3,5-triazinane; 1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetrazocane; 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane; DTA; Thermal decomposition; Thermal reactivity

1. Introduction

Ammonium nitrate (AN) is used as oxidising component in explosive mixtures [1–3]. It also represents one of the side products in the synthesis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT) by the Hale method [4,5] and it can be one of raw materials in the production of technologically attractive nitramines 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (octogen or HMX) and 1,3,5-trinitro-1,3,5-triazinane (hexogen or RDX) [5,6]. In Ref. [7] it

was pointed out that, from the standpoint of technological-safety risks, AN represents and undesirable impurity in DPT and its dinitroso analogue, i.e. 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DNPT); the last one was used as an active component of the blowing agents for rubber and polymers [8,9]. The 1,3,5,7-tetraazabicyclo[3.3.1]nonane (HMTA) is a starting material in production of these reactive energetic Mannich *N*-bases [4–6,9,10].

It was shown [7] that exothermic reaction of DNPT and DPT with AN primarily takes place in solid phase at relatively low temperatures. With regard to the importance of DPT for synthesis of HMX [4–6] the present paper is focused on the primary step of splitting in the given reaction. For a

more detailed specification of this step, the study also covers further important compounds synthesized from HMTA, namely 1,3,5-trinitroso-1,3,5-triazinane (TMTA or *R*-salt), 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocane (DADN), RDX and α-modification of HMX. Some of these compounds can act as fuel or fortifying components of energetic materials containing AN. Also for this reason, the thermal reactivity of their mixtures with AN is dealt with in the present paper, which directly links this paper to Ref. [7] and is connected with the topic dealt with in Ref. [3].

2. Experimental

2.1. Substances

For the investigation of stability parameters, the studied samples were prepared in the quality grade "pure": DNPT was a product of the HMTA nitrosolysis [7,10] with subsequent stabilization by washing with 2% ammonia solution [11], DPT resulted from HMTA nitrolysis [12] with subsequent recrystallization from dimethyl sulfoxide, TMTA was prepared according to a known procedure [13] and recrystallized from pentanol, DADN was a product of the 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane nitrolysis [14] with subsequent crystallization from dimethylformamide, and α-HMX resulted from the nitrolysis of DADN [15]. RDX was a commercial product of HMTA nitrolysis by nitric acid in the Special Production Plant of the Slovak Company Chemza Strážske (a member of CHEMKO holding). Ammonium nitrate was used in quality "pro analysis"; the onset of its exothermic decomposition at the heating rate of 5 °C min^{-1} was at 216 °C and the peak was at 279 °C.

2.2. Differential thermal analysis

We used a DTA 550 Ex apparatus [3,7,16] specially developed at the Department of Theory and Technology of Explosives for thermal analyses of explosives. The measurements were carried out at atmospheric pressure, the tested sample being in direct contact with the air atmosphere. The sample tested (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm in length. The reference standard was 0.05 g aluminum oxide. We used linear rates of temperature increase, viz. 5, 10, and 15 °C min^{-1}. The results of these measurements were treated by means of the software delivered with the DTA apparatus [14]. The measurements were realized with pure substances and with their mixtures with 2 wt.% of AN. Examples of the corresponding DTA records are presented in Figs. 1–7. The results obtained were treated using the Kissinger method [17]; the treatment for pure substances is graphically presented in Fig. 8. The values E_aR^{-1} thus obtained (see in Table 1 where r is a correlation coefficient) were then plotted against the results of the calculation of electronic charges, q^N, at nitrogen atoms (Figs. 9–11).

Table 1
Survey of the substances studied, their code designation, charges q^N at nitrogen atoms, and slopes E_aR^{-1} of the Kissinger's relationship for their exothermic decomposition (where r is a correlation coefficient); designation pure corresponds to the exothermic decomposition of pure substance, AN1st to the first and AN2nd to the second exothermic peaks of its mixture with AN
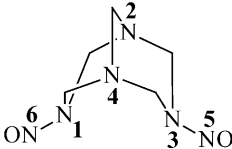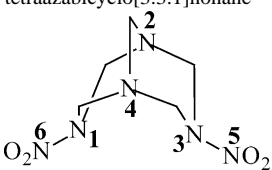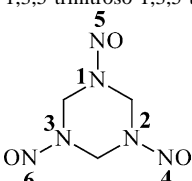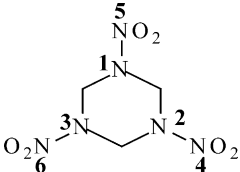
N	q^N (electron)
DNPT: 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane[a]	

1	−0.2683
2	−0.3914
3	−0.2685
4	−0.3901
5	0.1639
6	0.1635

| DPT: 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane[b] | |

1	−0.3330
2	−0.4103
3	−0.3328
4	−0.4103
5	0.6610
6	0.6610

| TMTA: 1,3,5-trinitroso-1,3,5-triazinane[c] | |

1	−0.2717
2	−0.2746
3	−0.2775
4	0.1867
5	0.1903
6	0.1868

| RDX: 1,3,5-trinitro-1,3,5-triazinane[d] | |

1	−0.3435
2	−0.3435
3	−0.3435
4	0.6771
5	0.6771
6	0.6771

Table 1 (*Continued*)

N	q^N (electron)
DADN: 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocane[e]	

1	−0.3138
2	−0.4936
3	−0.3264
4	−0.4651
5	0.6374
6	0.6720

| HMX: 1,3,5,7-tetranitro-1,3,5,7-tetrazocane[f] | |

1	−0.3022
2	−0.3015
3	−0.3022
4	−0.3015
5	0.6850
6	0.6829
7	0.6850
8	0.6829

[a] $E_aR^{-1} = 28314$ K, $r^2 = 0.9507$ (pure); $E_aR^{-1} = 32990$ K, $r^2 = 0.8116$ (AN1st); $E_aR^{-1} = 48456$ K, $r^2 = 0.9880$ (AN2nd).

[b] $E_aR^{-1} = 27434$ K, $r^2 = 0.9977$ (pure); $E_aR^{-1} = 24748$ K, $r^2 = 0.8857$ (AN1st); $E_aR^{-1} = 14430$ K, $r^2 = 0.9880$ (AN2nd).

[c] $E_aR^{-1} = 15572$ K, $r^2 = 0.9379$ (pure); $E_aR^{-1} = 14346$ K, $r^2 = 0.9253$ (AN1st); $E_aR^{-1} = 16661$ K, $r^2 = 0.9828$ (AN2nd).

[d] $E_aR^{-1} = 32211$ K, $r^2 = 0.9980$ (pure); $E_aR^{-1} = 35190$ K, $r^2 = 0.8596$ (AN1st and AN2nd).

[e] $E_aR^{-1} = 28085$ K, $r^2 = 0.9975$ (pure); $E_aR^{-1} = 22079$ K, $r^2 = 0.9977$ (AN1st); $E_aR^{-1} = 30114$ K, $r^2 = 0.9949$ (AN2nd).

[f] $E_aR^{-1} = 36766$ K, $r^2 = 0.9955$ (pure); $E_aR^{-1} = 20703$ K, $r^2 = 1.0000$ (AN1st); $E_aR^{-1} = 50017$ K, $r^2 = 0.9724$ (AN2nd).

In the cases of DPT, DNPT and TMTA we also used isothermal DTA and three temperatures for each sample. The results were treated in the sense of relation [18]:

$$\ln \tau = E(RT)^{-1} + C \tag{1}$$

where τ is the induction period of thermal explosion of sample in seconds, and E the activation energy of this process. The isothermal DTA results are presented in Table 2.

### 2.3. Electronic charges at nitrogen atoms

The calculation of electronic charges q^N at nitrogen atoms of the compounds investigated was carried out by means of the Mulliken population analysis of electron densities obtained at ab initio level by DFT B3LYP/6-31G** method [19]. The calculation provided by total optimization the equilibrium geometry of an isolated molecule in the gas phase at 0 K. A survey of the compounds studied, their codes and the results obtained are presented in Table 1.

3. Results and discussion

As shown in the study [7], an addition of 2 wt.% AN to DPT results in a stability decrease of the final mixture (Fig. 2). Also the DNPT sample with the same additive exhibits a very lowered thermal stability (see Fig. 3), which was already observed earlier [9] with a sample containing only 0.17 wt.% AN. It was pointed out [7] that the explosion of DNPT occurred in the region of III-II polymorphous transition of AN (above 84.2 °C, see also Ref. [9]), while the onset of DPT decomposition is situated in the region of II–I polymorphous transition of AN (125.2 °C). The reactivity of DNPT is higher (as in the case of DPT and for the same reason) as in the case of their hydrolysis (acidolysis) [7]. From the point of view of molecular structure, both substances are Mannich *N*-bases, which is reflected in their reactivity, too [7]. The DTA records in Figs. 2 and 3 show that after the present amount of AN has reacted (the first peak of exothermic decomposition), the decomposition of sample is interrupted (as it is the case with DNPT) or considerably suppressed (DPT).

Acidolysis of DPT and DNPT with nitric acid can be a potential cause of decomposition in the temperature region of the first exothermic peak of these compounds (DNPT is explosively decomposed on contact with mineral acid [7,9]). In solid state, ammonium nitrate is dissociated according to the following equilibrium [1,2,20–23]:

$$NH_4NO_3 \rightleftharpoons NH_{3(g)} + HNO_{3(l,g)} \tag{2}$$
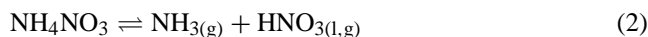
The temperature dependence of the dissociation constant was described [21] over the temperature range in which crystalline phase IV of AN is stable (−17–32 °C). A real sample of crystalline AN always contains moisture, which cannot be removed [22]. Besides that, it always also contains its eutectic mixture with its dissociation products [22]. Thus, the primary step in decomposition of DNPT or DPT should consist in interaction of tertiary aza atoms No. 2 in their molecules (see Table 1) with nitric acid as generally expressed by Scheme 1: with consecutive splitting of the ammonium cation (in this case R can be CH_2, ON, CH_3CO or O_2N). The splitting in both following compounds should start by replacement of nitrosonium cation from TMTA molecule by the proton of nitric acid and by the protonation of acetamido grouping in the DAND molecule (i.e. protonation of 2-nitrogen; see Table 1); this stands in accordance with the first exothermic peaks in Figs. 4 and 6. The above-said facts are confirmed by the relationship between the charges of the nitrogen (aza) atoms primarily attacked and the slopes of the Kissinger relation-

Table 2
Results of isothermal DTA (processing according to the Eq. (1))

Mixture	Isothermal exposition		Note
	Temperature (°C)	Induction period (s)	
DNPT + AN	60	309.9	Thermal explosion with activation energy $E = 72.7\,kJ\,mol^{-1}$
	65	264.3	
	80	74.0	
DPT + AN	120	32.1	Relatively slow and incomplete decomposition—processing according to Eq. (1) is impossible
	125	29.7	
	130	30.0	
TMTA + AN	90	666.9	Faster decomposition with activation energy $E = 106.9\,kJ\,mol^{-1}$
	100	114.3	
	120	38.5	
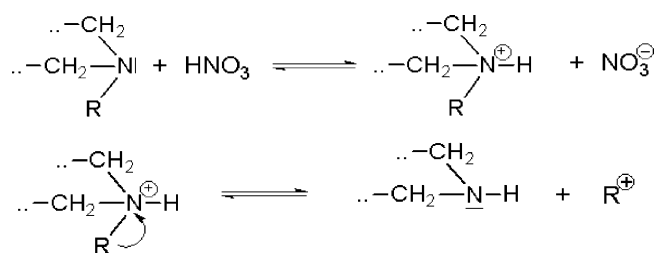
Scheme 1. Primary attack of the nitrogen (aza) atoms by nitric acid produced from dissociation of ammonium nitrate according to equilibrium (2).

ship, E_aR^{-1}, for the peak of their first exothermic decomposition. This relationship is documented in Fig. 9. There, the data of DNPT and DPT correspond to the reactions with AN in solid phase, and the data of DADN correspond with the reaction of the solid substance with the melt of AN. The primary attack of proton upon these molecules takes place at the nitrogen (aza) atom having the most negative value of charge q^N (nitrogen atoms No. 2 in Table 1), which does not carry a nitroso or a nitro group. Also the data of RDX correlate with the set mentioned, this substance reacting with AN melt in the temperature region at the beginning of its melting; the peak of the first exothermic decomposition of RDX is only
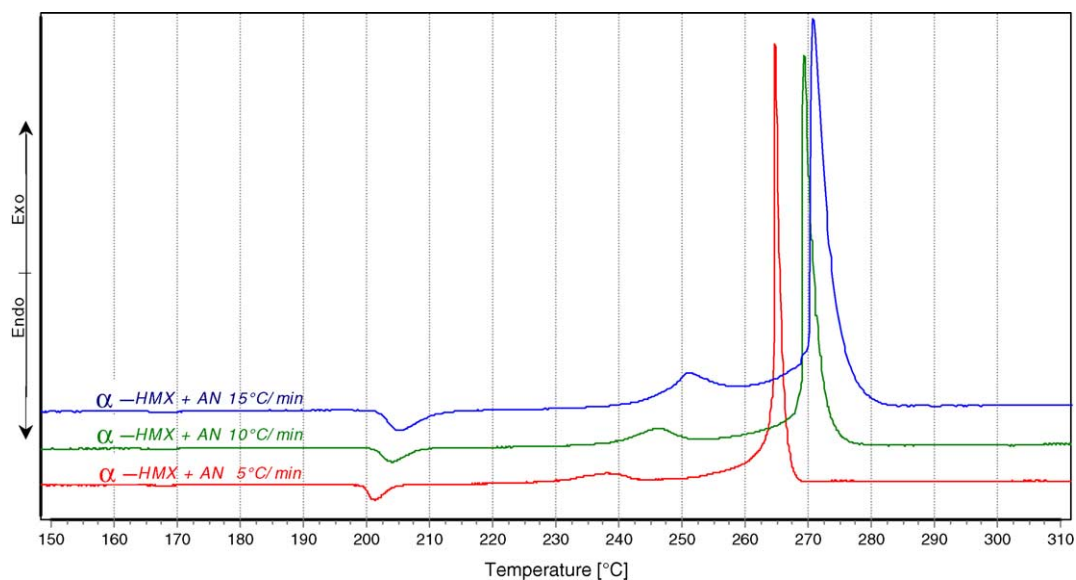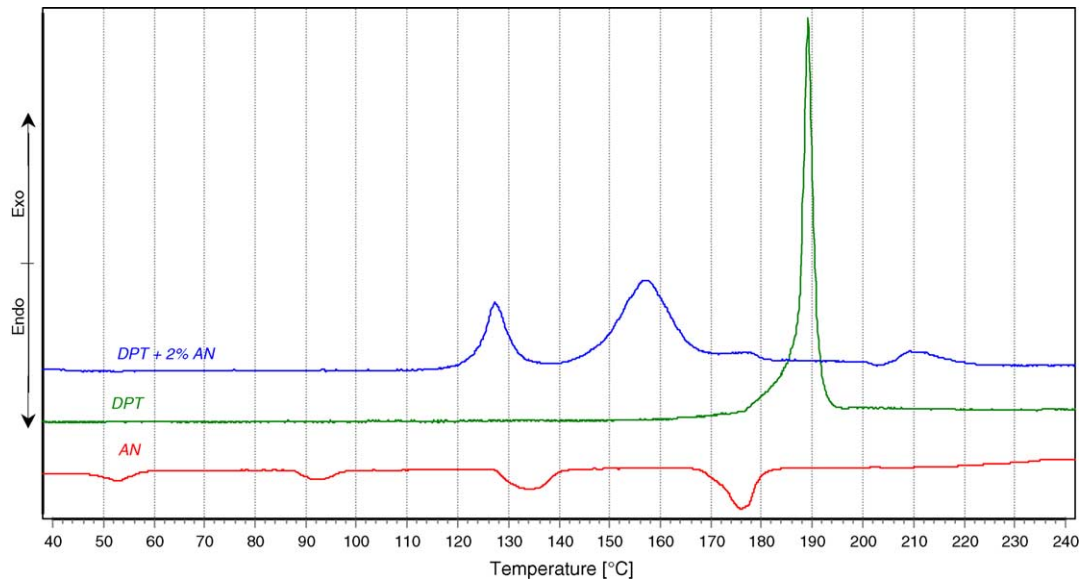

Fig. 1. DTA-records of α-HMX.

Fig. 2. Mutual comparison of the DTA-records of ammonium nitrate (AN), pure 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT) and mixture of DPT with 2 wt.% of AN for linear rate of temperature increase $5\,^{\circ}\text{C}\,\text{min}^{-1}$.

slightly indicated—see Fig. 5. What has been said indicates that in the initiation of thermal decomposition of the mixture of RDX and AN, the acidolysis of the mentioned nitramine plays a significant role. The less distinct peak of acidolysis-oxidation reaction of AN with HMX (Figs. 1 and 7) can be due to the prevailing decomposition of AN into nitrogen (I) oxide and water [1,2,20–23] at temperatures above $216\,^{\circ}\text{C}$; this is supported by the position of the curve of the prominent exothermic decomposition of AN, e.g. in Figs. 6 and 7. A similar interaction of RDX and HMX with another ammonium

salt of strong acid, namely with ammonium perchlorate, is mentioned in Ref. [24]. From of all substances studied, only TMTA reacts with solid AN in melt from the very beginning (Fig. 4). The primary reaction of TMTA, HMX and RDX with AN should begin by replacement of nitroso and/or nitro groups by the hydrogen atom of nitric acid; that is why the data of these substances form a single set in Fig. 9.

The DTA records (Figs. 1–7) show that, except for RDX, this primary acidolysis-oxidation reaction is not transformed into a spontaneous decomposition of the whole sample. The
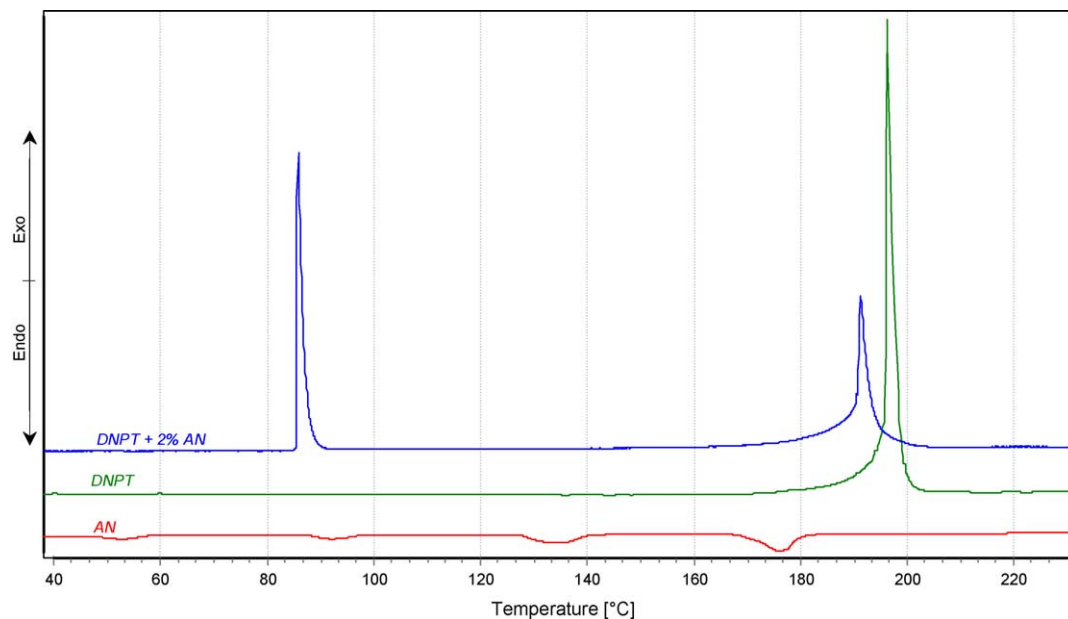

Fig. 3. Mutual comparison of the DTA-records of ammonium nitrate (AN), pure 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DNPT) and mixture of DNPT with 2 wt.% of AN for linear rate of temperature increase $5\,^{\circ}\text{C}\,\text{min}^{-1}$.
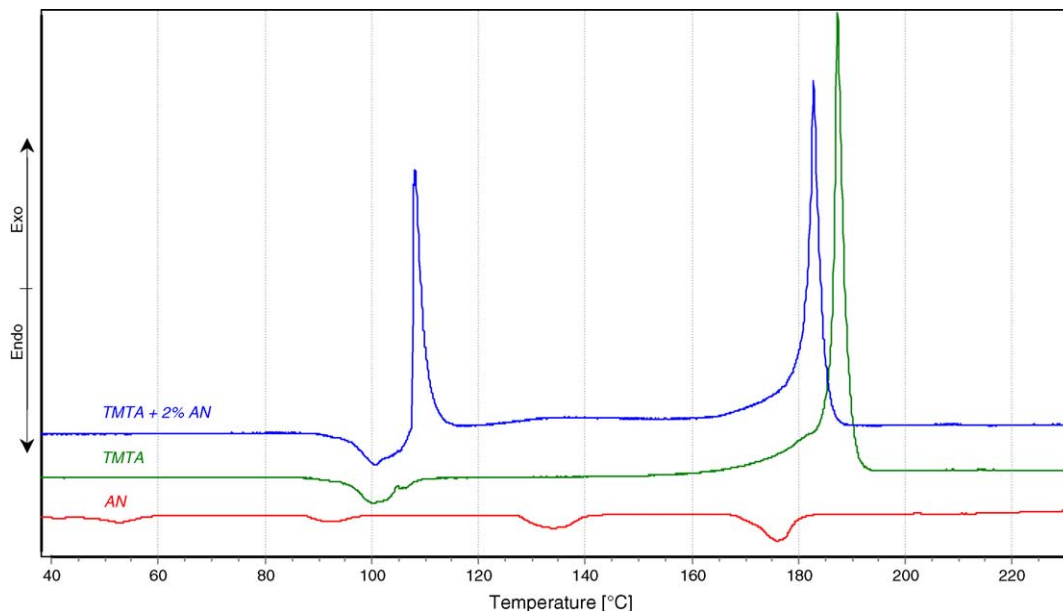
Fig. 4. Mutual comparison of the DTA-records of ammonium nitrate (AN), pure 1,3,5-trinitroso-1,3,5-triazinane (TMTA), and mixture of TMTA with 2 wt.% of AN for linear rate of temperature increase 5 °C min^{-1}.

risks of this reaction were verified for the most reactive substances, i.e. DPT, DNPT and TMTA by means of the method of thermal explosion [18] using isothermal DTA (see Table 2). According to results of this method, the temperature region of occurrence of acidolysis-oxidation reaction is a limiting factor of stability of all these samples contaminated with ammonium nitrate. However, in the case of the mixture of DPT with AN, the decomposition in the given temperature region is relatively slow and incomplete. The E value, obtained here

for DNPT in the sense of Eq. (1), i.e. 72.7 kJ mol^{-1}, lies between the values for pure (i.e. 80.1 kJ mol^{-1} [37]) an technical product (68 kJ mol^{-1} [38]) determined in the conditions of the corresponding blowing agents production but in temperature range 180–210 °C. Nevertheless, DTA onsets of this DNPT thermal decomposition under the conditions were 130–145 °C [37].

The thermal decomposition of the substances studied (in their pure state) starts with homolysis of N–N bond
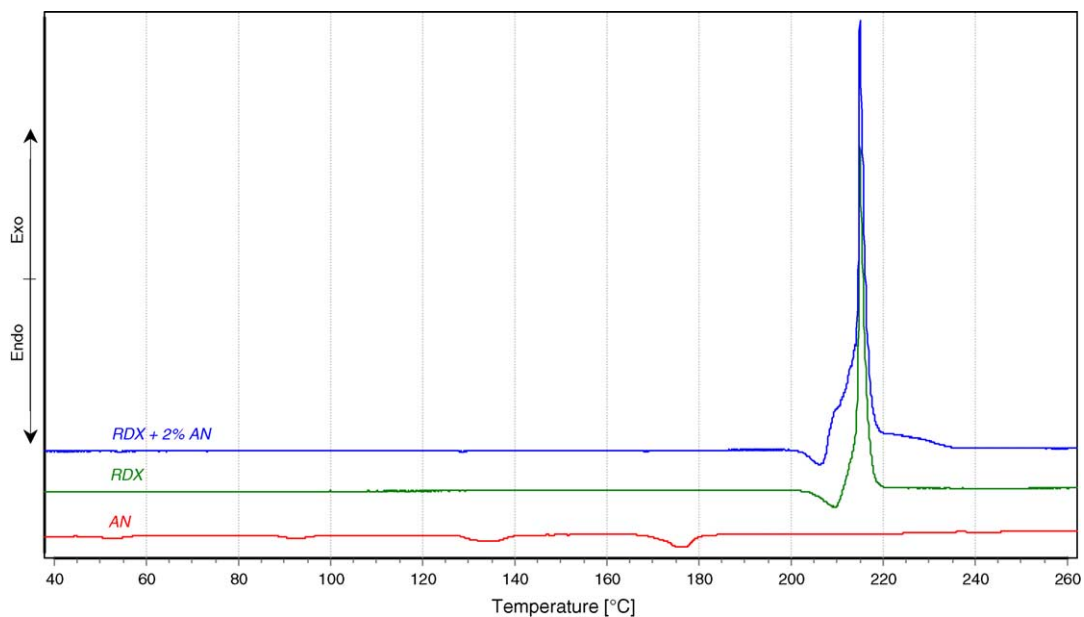

Fig. 5. Mutual comparison of the DTA-records of ammonium nitrate (AN), pure 1,3,5-trinitro-1,3,5-triazinane (RDX), and mixture of RDX with 2 wt.% of AN for linear rate of temperature increase 5 °C min^{-1}.
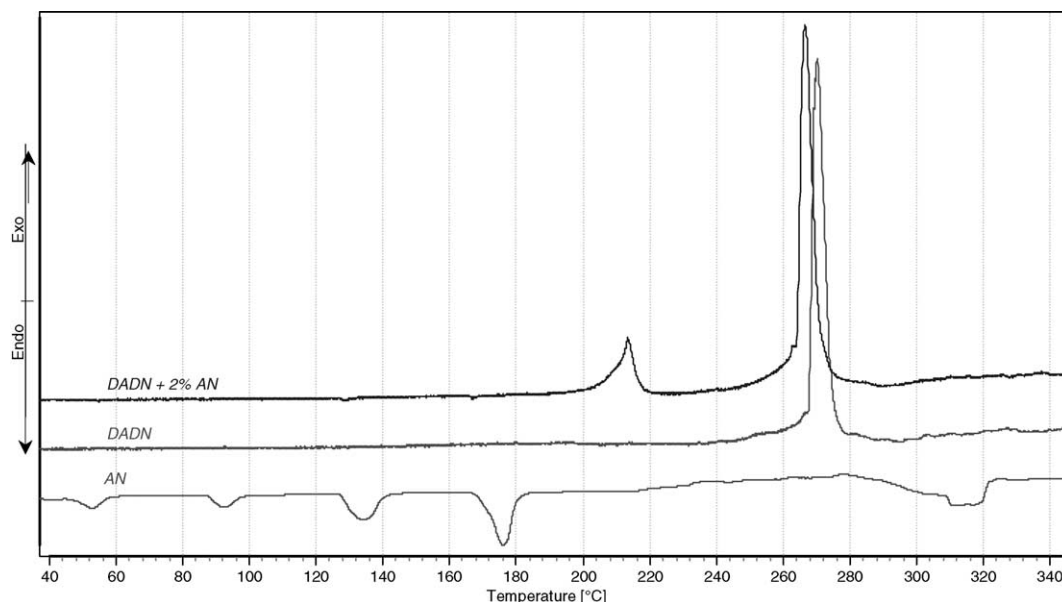
Fig. 6. Mutual comparison of the DTA-records of ammonium nitrate (AN), pure 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocane (DADN), and mixture of DADN with 2 wt.% of AN for linear rate of temperature increase $5\,^{\circ}C\,min^{-1}$; published melting point of pure DADN is $265\,^{\circ}C$ [14].

[22,25–28]. In the case of nitramines, a relationship was found between the E_aR^{-1} values and charges at nitrogen atoms of the leaving nitro groups [28]. However, the primarily leaving groups (nitroso and nitro groups with the most positive q^N values) in the molecules of the compounds studied are chemically heterogeneous. Therefore, the present paper adopts, for deriving an analogous relationship, the charges at nitrogen (aza) atoms—"carriers" of the primarily leaving groups (for those of the pure substances, see Fig. 10). These aza atoms are parts of molecular skeletons, and the values of charges located at them are thus also distinctly affected by the conformation of molecule. Mutually similar conformations of molecules of DPT [29] and DNPT [30] differ from those of RDX [31], DADN [32], TMTA and δ polymorph of HMX [33] (a demonstrable thermolysis of the HMX polymorphs takes place in the temperature region of formation of
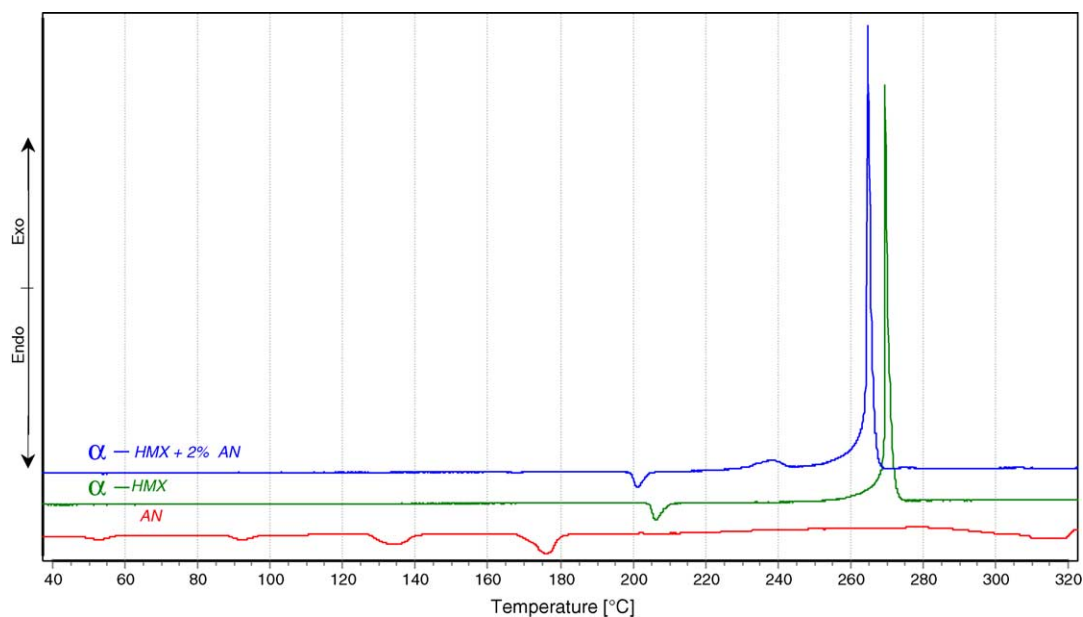

Fig. 7. Mutual comparison of the DTA-records of ammonium nitrate (AN), pure α-modification of the 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), and mixture of HMX with 2 wt.% of AN for linear rate of temperature increase $5\,^{\circ}C\,min^{-1}$.
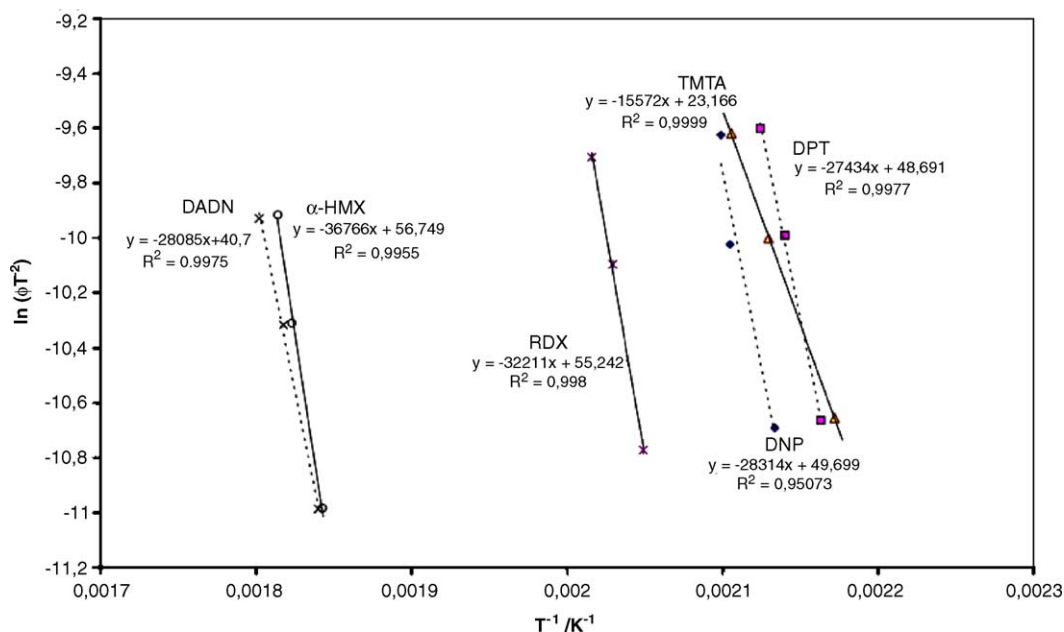
Fig. 8. DTA results treated using the Kissinger method [17] for pure substances, here Ø is the rate of temperature increase and *T* is the peak temperature.

its δ polymorph because the liquid phase of HMX is unstable [34–36]). However, as follows from Fig. 10, it is possible to find mutual similarities of conformations in the reaction centers of molecules of TMTA, DADN and RDX, and furthermore, molecules of DPT, DADN and δ-HMX. These facts are reflected in the indicated dependences in this figure. After the AN present has been consumed in the first acidolysis-

oxidation reaction, the decomposition in the non-reacted portions of the substance should again begin (continue) by homolyses of N−N bonds. This is documented in Fig. 11, where the dependence for TMTA, DADN and RDX has practically the same shape as that in Fig. 10. The thermal decompositions of TMTA, DADN and RDX take place in liquid phase (the melting point of DADN, i.e. 265 °C [14], in the DTA
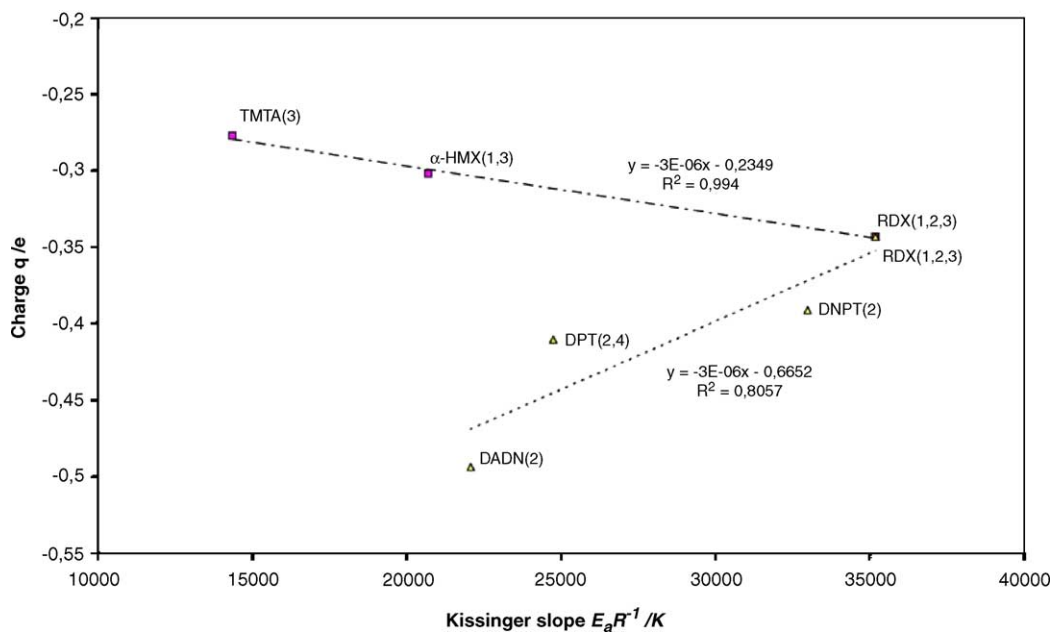

Fig. 9. Relationship between electronic charges q^N at aza atoms, primary attacked by proton from nitric acid, and slopes $E_a R^{-1}$ of the Kissinger's relationship for the first exothermic reaction of the substances contaminated by AN – numbers in parenthesis correspond to the nitrogen atoms in molecule according to Table 1.
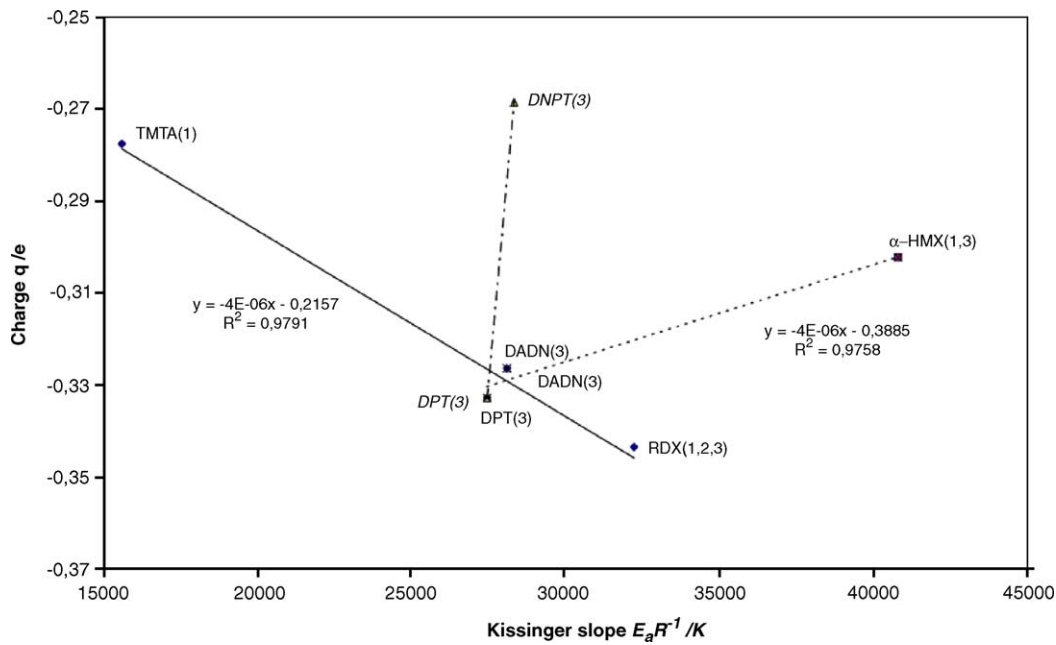
Fig. 10. Relationship between electronic charges q^N at aza atoms, bearers of the first outgoing nitroso or nitro groups, and slopes E_aR^{-1} of the Kissinger's relationship for exothermic decomposition of the pure substances – numbers in parenthesis correspond to the nitrogen atoms in molecule according to Table 1.

Fig. 11. Relationship between electronic charges, q^N, at aza-nitrogen atoms, "carriers" of the first outgoing nitroso or nitro groups, and slopes E_aR^{-1} of the Kissinger's relationship for the second exothermic reaction of the substances contaminated by AN – numbers in parenthesis correspond to the nitrogen atoms in molecule according to Table 1.
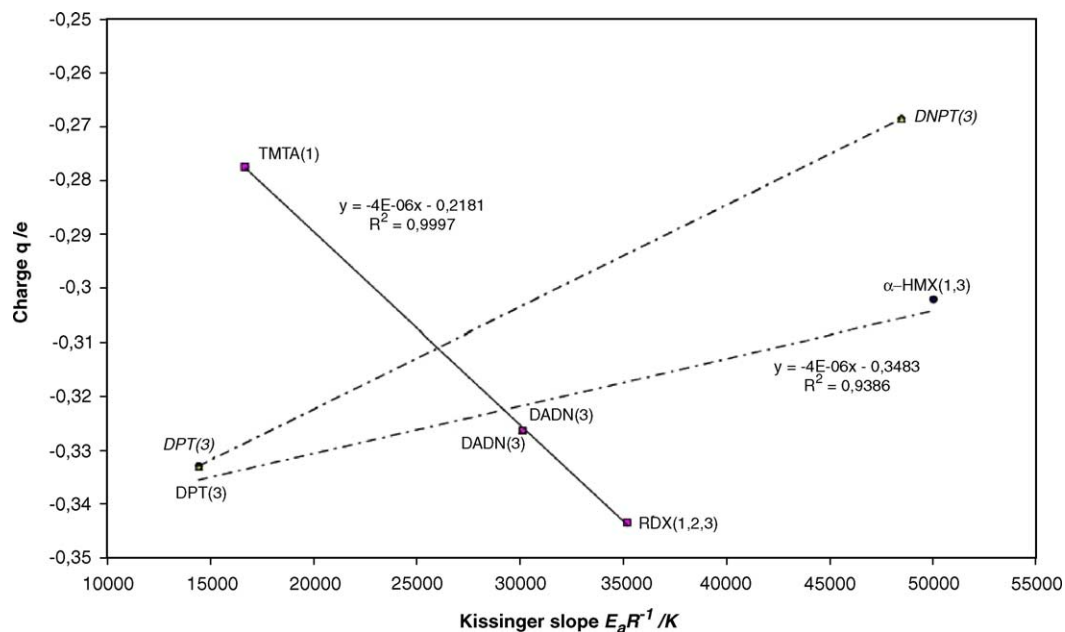
record is overlapped by its exothermic decomposition—see Fig. 6), which can be the reason of the facts mentioned; in these cases the effect of state of aggregation of the samples on the E_aR^{-1} values makes itself felt. The condensed products of acidolysis-oxidation reaction cause a lowering of the values of onsets of the peaks of the second exothermic decomposition of the substances studied in contrast to the onsets of pure substances (see Figs. 2–7).

4. Conclusion

DPT, DNPT, TMTA, RDX, DADN, and HMX are technologically and otherwise interesting substances synthesized from 1,3,5,7-tetraazabicyclo[3.3.1]nonane (HMTA). In the syntheses of some of them, their processing and application, it is possible that they come into contact with ammonium nitrate (AN), or they are directly mixed with this oxidizer. The

resulting mixtures exhibit increased thermal reactivity compared with the pure compounds. Such an increase is prominent with the mixtures of AN with energetic Mannich *N*-bases DPT and DNPT. The reason lies in the acidolytic attack of nitrogen (aza) atoms of the substances studied by the nitric acid resulting from dissociation of ammonium nitrate. With the low AN content used in the mixture and with non-isothermal regime of differential thermal analysis (DTA), it is possible to separately record the peak of exothermic reaction of the substance with AN and subsequently its exothermic decomposition; an exception is the mixture of AN with RDX, in which both the reactions start almost simultaneously. The technological-safety risk is limited by the temperature region of occurrence of the acidolytic reaction also in the cases of the DPT, DNPT and TMTA contaminated with AN. The position of reaction centers of acidolytic attack in the molecules of the substances studied can be specified on the basis of mutual comparison of slope values $E_a R^{-1}$ of the Kissinger relationship (from non-isothermal DTA) and electronic charges q^N at aza atoms of the compounds investigated. Logically, this attack takes place at the nitrogen atoms having the most negative values of q^N in the molecules of these compounds.

Acknowledgements

References

[1] J.C. Oxley, S.M. Kaushink, N.S. Gilson, Thermal decomposition of ammonium nitrate-based composites, Thermochim. Acta 153 (1989) 269.

[2] R. Turcotte, P.D. Lightfoot, R. Fouchard, D.E.G. Jones, Thermal hazard assessment of AN and AN-based explosives, J. Hazard. Mater. A 101 (2003) 1.

[3] S. Zeman, P. Kohlíček, A. Maranda, A study of chemical micromechanism governing detonation initiation of condensed explosive mixtures by means of differential thermal analysis, Thermochim. Acta 398 (2003) 185.

[4] W.J. Chute, D.C. Downing, A.F. McKay, G.S. Meyers, G.F. Eright, The nitrolysis of hexamethylenetetramine. I. The significance of 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetrazacyclooctane, Can. J. Res. 27B (1949) 218.

[5] E.Yu. Orlova, N.A. Orlova, V.F. Zhilin, G.M. Shutov, L.I. Vitkovskaya, Oktogen – termostoykoe vzryvchatoe veschestvo (Octogen – A Thermostable Explosive), Izdat. Nedra, Moscow, 1975.

[6] W.E. Bachmann, W.J. Horton, E.L. Yeuner, N.W. McNaughton, L.B. Scott, Cyclic and linear nitramines formed by nitrolysis of hexamine, J. Am. Chem. Soc. 73 (1951) 2769.

[7] J. Vágenknecht, S. Zeman, Some characteristics of 3,7-dinitro-3,7-dinitroso- and dinitrate compounds derived from 1,3,5,7-tetraazabicyclo[3.3.1]nonane, J. Hazard. Mater. doi:10.1016/j.jhazmat.2004.10.026.

[8] S. Quinn, Chemical blowing agents: providing production, economic and physical improvements to a wide range of polymers, plastics, Addit. Compd. 3 (2001) 16.

[9] S. Zeman, Some Problems of Dinitrosopentamethylenetetramine (DNPT) Production, Res. Report 7503863, ÚVTEI-STK Prague, 1975 (in Czech).

[10] E. Kubínyiová, B. Procházka, S. Zeman, A method of the 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane preparation, Czech. Patent 182625 (December 1977, in Czech).

[11] S. Zeman, P. Kurajda, J. Růžička, F. Chaloupka, F. Fridrich, B. Procházka, A method of stabilization of the 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane, CS Patent 210824 (October 1981 in Czech).

[12] S. Zeman, M. Dimun, A method of production of the 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane, CS Patent 206382 (December 1980 in Slovak).

[13] A. Le Roux, Sur la triméthyléne trinitrosamine, Mém. Poudres 33 (1951) 237.

[14] V.I. Siele, M. Warman, J. Leccacorvi, R.W. Hutchinson, R. Motto, E.E. Gilbert, T.M. Benzinger, M.D. Coburn, R.K. Rohwer, R.K. Davey, Alternative Procedures for Preparing HMX, Propellants Explos. 6 (1981) 67.

[15] S. Zeman, M. Dimun, A method of production of the 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, CS Patent 227913 (June 1982 in Slovak).

[16] M. Krupka, Devices and equipment for testing of energetic materials, in: J. Vágenknecht (Ed.), Proceedings of the Fourth Seminar on "New Trends in Research of Energetic Materials", University Pardubice, April 2001, p. 222.

[17] H.E. Kissinger, Reaction kinetics in differential thermal analysis, Anal. Chem. 29 (1957) 1702.

[18] H. Henkin, R. McGill, Rates of explosive decomposition of explosives. Experimental and theoretical kinetic study as a function of temperature, Ind. Eng. Chem. 44 (1952) 1391.

[19] TITAN v.1.0.8. [CPU Intel P4/3.2 GHz (800 MHz) 512 kB L2, 1 GB RAM, 36 GB SCISI HD]. Wavefunction, Schrödinger Inc., USA, 2001.

[20] A. Kolaczkowski, A. Biskupski, J. Schroeder, Effect of ammonia on the thermal decomposition of ammonium nitrate, J. Chem. Technol. Biotechnol. 31 (1981) 327.

[21] M. Mozurkewich, The dissociation constant of ammonium nitrate and its dependence on temperature, relative humidity and particle size, Atmos. Environ. Part A: Gen. Top. 27 (1993) 261.

[22] G.B. Manelis, G.M. Nazin, Yu.M. Rubtsov, V.A. Strunin, Thermal Decomposition and Combustion of Explosives and Gunpowders (in Russian), Izdat. Nauka, Moscow, 1996, p. 116.

[23] S. Vyazovkin, J.S. Clawson, C.A. Wight, Thermal dissociation kinetics of solid and liquid ammonium nitrate, Chem. Mater. 13 (2001) 960.

[24] Z. Liu, C. Yin, Y. Kong, F. Zhao, Y. Luo, H. Zhou, Interaction of ammonium perchlorate with HMX and RDX during decomposition, Tuijin Jishu 21 (2000) 70;
Z. Liu, C. Yin, Y. Kong, F. Zhao, Y. Luo, H. Zhou, Interaction of ammonium perchlorate with HMX and RDX during decomposition, Chem. Abstr. 134 (2001) 149664.

[25] Y. Shu, B.L. Korsounskii, G.M. Nazin, Mechanism of thermal decomposition of secondary nitramines, Usp. Khim. 73 (2004) 320 (in Russian).

[26] S. Zeman, Modified Evans–Polanyi–Semenov relationship in the study of chemical micromechanism governing detonation initiation of individual energetic materials, Thermochim. Acta 384 (2002) 137.

[27] S. Zeman, A Study of chemical micromechanism of the organic polynitro compounds initiation, in: P. Politzer, J. Murray (Eds.), Energetic Materials, Part II, Elsevier Sci. BV, 2003, p. 25 (Chapter 2).

[28] S. Zeman, Z. Friedl, Relationship between electronic charges at nitrogen atoms of nitro groups and thermal reactivity of nitramines, J. Thermal Anal. Calorim. 77 (2004) 217.

[29] C.S. Choi, S. Bulusu, The crystal structure of dinitropentamethylenetetramine (DPT), Acta Cryst. B 30 (1974) 1576.

[30] C.J. Brown, J.L. Craft, *N,N′*-dinitrosopentamethylenetetramine, $C_5H_{10}N_6O_2$, Acta Cryst. C 39 (1983) 1132.

[31] C.S. Choi, E. Prince, Crystal structure of cyclotrimethylen-etrinitramine, Acta Cryst. B 28 (1972) 2857.

[32] A. Santorio, C.S. Choi, J.E. Abel, 1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN), Acta Cryst. B 31 (1975) 2126.

[33] R.E. Cobbledick, R.W.H. Small, The crystal structure of δ-form of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (δ-HMX), Acta Cryst. B 30 (1974) 1918.

[34] J.N. Maycock, V.R. Pai Verneker, Thermal decomposition of δ-HMX (cyclotetramethylenetetranitramine), Explosivstoffe 17 (1969) 5.

[35] S. Zeman, Some predictions in the field of the physical thermal stability of nitramines, Thermochim. Acta 302 (1997) 11.

[36] S. Zemam, Analysis and prediction of the arrhenius parameters of low-temperature thermolysis of nitramines by means of the ^{15}N NMR spectroscopy, Thermochim. Acta 333 (1999) 121.

[37] S. Zeman, Survey on Quality and Technical Safety Data of the DNPT-Blowing Agents, Chemko Co., Strážske, Slovak Report, July 1987 (in Russian).

[38] S. Zeman, Z. Tokár, Blowing agents on the basis of DNPT produced by the Chemko Co., Prospectus in Russian, Chemko Co., Strážske, Slovak Report, 1990.