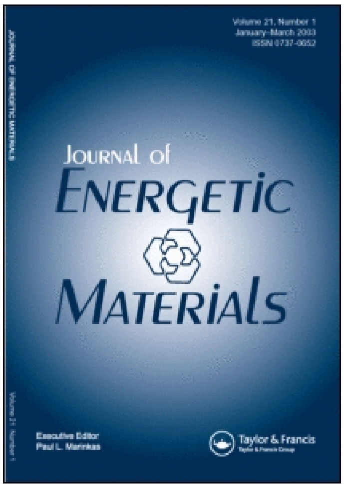

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# 1,3,3-trinitroazetidine (TNAZ). Study of thermal behaviour. Part II

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# 1,3,3-TRINITROAZETIDINE (TNAZ).
# STUDY OF THERMAL BEHAVIOUR. PART II.

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## ABSTRACT

Thermal behavior of TNAZ (1,3,3 – trinitroazetidine) was studied by using differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetryc analysis (TGA).

It was found out that TNAZ is thermally more stable than RDX, but less stable than HMX and TNT. The reaction of intensive thermal decomposition starts at 183–230 °C, depending on heating rate, while the first exothermic reaction was observed at 178 °C at the heating rate of 1 °C/min.

By applying multiple heating rate DSC measurements and Ozawa's method the activation energy of 161.3 kJ/mol and pre-exponential factor of $8.27 \cdot 10^{13}$ 1/s were calculated from DSC peak maximum temperature-heating rate relationship. By the same method the activation energy of 157.5 kJ/mol and pre-exponential factor of $4.55 \cdot 10^{13}$ 1/s were calculated from DTA peak maximum temperature.

By applying Flynn-Wall isoconversional method it was calculated from DSC measurements that the activation energy equals between 140 and 155.6 kJ/mol at degrees of conversion ranging between 0.3 and 0.7, while pre-exponential factor ranges between $7.8 \cdot 10^{12}$ and $1.92 \cdot 10^{13}$ 1/s.

## INTRODUCTION

The study of thermal behavior is a very important starting point for the selection and exploitation of an energetic material in military systems, and also in civilian applications. In the case of 1,3,3-trinitroazetidine (TNAZ), a new steam-castable and superior performing explosive[1-7], research activities in this field have been started only recently[5,7,8-18]. There are several reports on the TNAZ thermal characterization, its initial dissociation mechanism, and a rapid decomposition process[4,5,11,15,17]. The values of the thermodynamic parameters of the melting process and the kinetic parameters of the exothermic decomposition reaction of TNAZ have been reported in several papers[5,11,13,17,18].

It has been concluded on the basis of DSC measurements that TNAZ should be thermally more stable than 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), but more reactive than 1,3,5,7-tetranitro-1,3,5,7- tetrazacycloctane (HMX)[5,11]. DSC thermograms, obtained at 10 °C/min heating rates, and using TNAZ samples closed in sealed sample pans, have shown that the exothermic decomposition of TNAZ takes place at temperatures ranging between 244 and 250 °C[5,7,11].

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Measurements by means of accelerating rate calorimeter (ARC) have shown a remarkable adiabatic self-heating only above 180 °C[7]. Nearly the same degree of stability, as was detected for HNIW, was indicated for TNAZ by means of the ARC technique[7]. When heating 0.25 g of TNAZ for 22 hours at 120 °C in the helium atmosphere at the pressure of 0.1 MPa (Chemical Reactivity Test), 0.045–0.049 $cm^3$ gaseous products are set free[5]. In the vacuum stability test of TNAZ at 110 °C for 20 hours, 0.01 $cm^3/g$ gaseous products were obtained (for TNT it was 0.01, for HMX 0.06 and for ε–HNIW 0.02 $cm^3/g$)[19].

Several papers deal with the study of kinetics and mechanism of thermal decomposition of TNAZ in a gas phase[8-10], liquid phase[11-13], in 0.01–1.0 % solutions in benzene, water, acetone, methanol[12,13], and by means of SCF-MO-AMI calculations[14] The homolysis of the $N\text{-}NO_2$ bond was proved as a primary step of thermolysis of the secondary nitramines in a condensed state[20-23]. However, TNAZ contains also two $C\text{-}NO_2$ bonds in its molecule. Authors of the papers[12,13] prefer here the $N–NO_2$ bond homolysis (the theoretical value of its dissociation energy is 186.6 kJ/mol)[13] to the $C–NO_2$ bond homolysis (the theoretical value of its dissociation energy is 194.8 kJ/mol)[13]. On the other hand, the primary homolytic fission of $C–NO_2$ bond is indicated by the AM1 study[14] of thermolysis of TNAZ molecule.

Some authors have identified 1-nitroso-3,3-dinitroazetidine (NDNAZ) as the stable intermediate of thermal decomposition of TNAZ in condensed state[13,15]. The same intermediate was also recorded in a laser-induced decomposition of TNAZ. According to the authors of the paper cited, the laser-induced pyrolysis starts with both a monomolecular nitro-nitrite rearrangement followed by the loss of NO and a bimolecular reaction producing NDNAZ[16]. In contrast to the conclusions of the above-cited papers[10,12,13,14], the authors of the study[17] do not consider the splitting off of $NO_2$ to be the primary step of the laser-induced pyrolysis of TNAZ.

During the pyrolysis of TNAZ vapors highly diluted with argon in a single-pulse shock tube within the temperature interval of 477–827 °C, the primary product to be split off was $NO_2$[10]. The following parameters were determined for this monomolecular decomposition: the activation energy of 199 kJ/mol and pre-exponential factor of $9.1 \cdot 10^{13}$ 1/s (this log*A* value corresponds to the activation entropy of 4.6 J/mol·K). The value of the activation energy might signalize homolytic fission of $N\text{-}NO_2$ bond as primary step of the pyrolysis.

The kinetic study of TNAZ thermolysis by means of DSC on samples weighing 0.5 mg, loaded in closed steel sample cells, gave the value of the activation energy of 133 kJ/mol and pre-exponential factor $6.31 \cdot 10^9$ 1/s. With regard to the fact that this log*A* value corresponds to a negative value of the activation entropy ($\Delta S^{\ne} = -70.15$ J/mol·K), the above-mentioned Arrhenius parameters cannot be connected with the homolyses of $C–NO_2$ or $N–NO_2$ bonds.

From the above mentioned follows that there is some discrepancy in principles and physical conditions of methods applied. Consequently, there is also a discrepancy in the results obtained and in the opinions derived. It also follows that the application of differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetric analysis (TGA) to more detailed study of TNAZ thermal behavior is missing in open literature.

# EXPERIMENTAL

## TNAZ Synthesis

Synthesis of TNAZ was started from *tris*(methylol)-nitromethane, formaldehyde and *tert*-butylamine and was conducted according to the route[24]. The product was purified by the crystallization from 55 % ethanol. TNAZ purity was higher than 99%, controlled by IR and HPLC techniques. The melting point of TNAZ, determined by DSC, was 100.59 ± 0.21 °C.

## Thermal Analysis

DSC measurements were conducted using *TA Instruments* apparatus, model DSC 2910. TGA and DTA measurements were carried out simultaneously using *TA Instruments* simultaneous TGA-DTA apparatus, model SDT 2960. DSC, DTA and TGA experiments were carried out under nitrogen purging with 100 ml/min at several heating rates ranging from 1 to 20 °C/min. TNAZ samples weighing from 0.5 to 3 mg, loaded in an aluminum sample pan, were used.

DTA measurements were also performed by using DTA apparatus, model DTA 550-Ex, manufactured by *LEX*, Czech Republic[25,26] . The measurements were carried out under static air atmosphere conditions at several heating rates ranging from 5 to 20 °C/min. $Al_2O_3$ was used as a reference material. Samples weighing about 50 mg, loaded in open glass tubes measuring 5.2 mm in outer diameter and 48 mm in length, were used.

# RESULTS AND DISCUSSION

## Thermal characterisation of TNAZ

DSC curve of TNAZ, along with those for several commonly used high explosives, is given in Figure 1. The sharp endothermic peak visible on TNAZ curve around 100 °C corresponds to the melting, while the exothermic peak visible at temperatures between 215 °C and 260 °C corresponds to the thermal decomposition.

The first deviation of DSC curve of TNAZ from the base line, i.e. the first exothermic reaction is observable at about 190 °C. However, an intensive thermal decomposition of TNAZ begins at about 217 °C, with exothermic peak onset temperature at 239.3 °C. The exothermic peak onset temperature for RDX under the same experimental conditions is about 208 °C, that suggests that TNAZ is thermally more stable than RDX.

Some authors have noted in their reports that the shape of TNAZ DSC thermogram depends dramatically on testing conditions[17]. It was confirmed in this paper – the shape of TNAZ DSC curves depends on sample weight, heating rate, the method of sample loading in a sample pan (sealed or open), etc. (Figures 2 and 3).

From the results given in Figures 2 and 3 it is clear that the shape of DSC curve, at the same heating rate, is influenced by the method of sample loading into a sample pan, as well as by the sample weight.

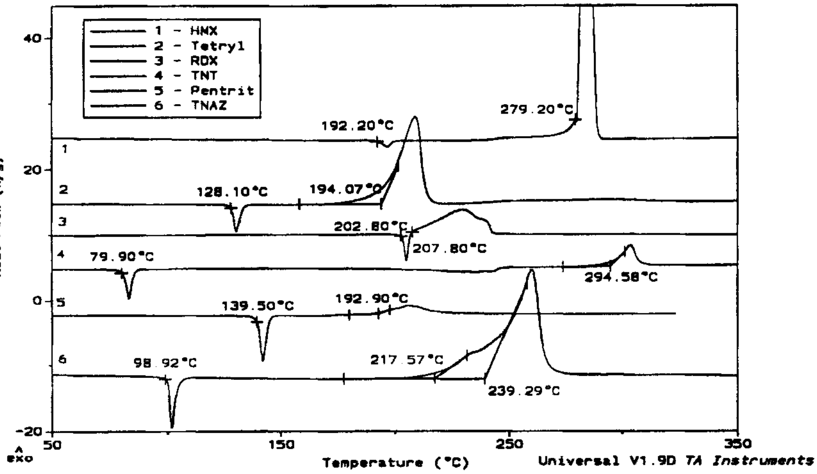

FIGURE 1. DSC curves of TNAZ and several commonly used high explosives (heating rate 10 °C/min, nitrogen atmosphere, sample mass 0.5–3 mg)

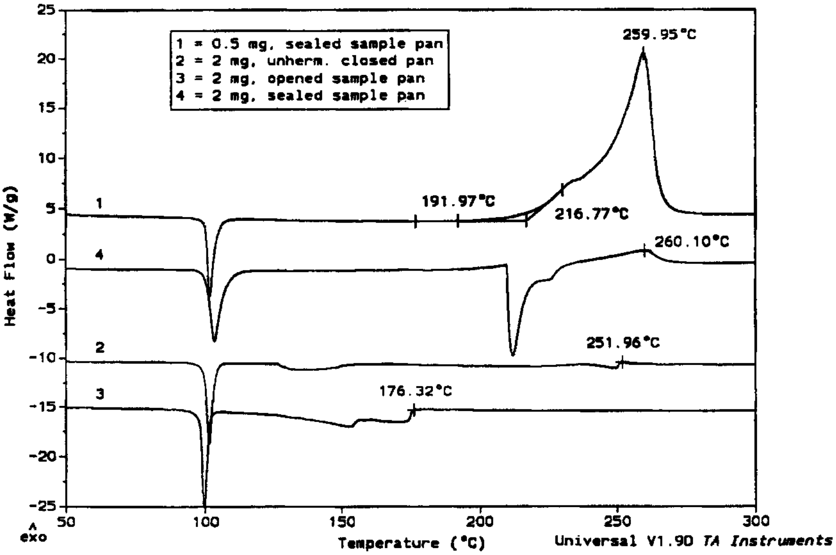

FIGURE 2. DSC curves of TNAZ obtained under different testing conditions (heating rate 10 °C/min, sample mass 0.5–3 mg, nitrogen atmosphere)

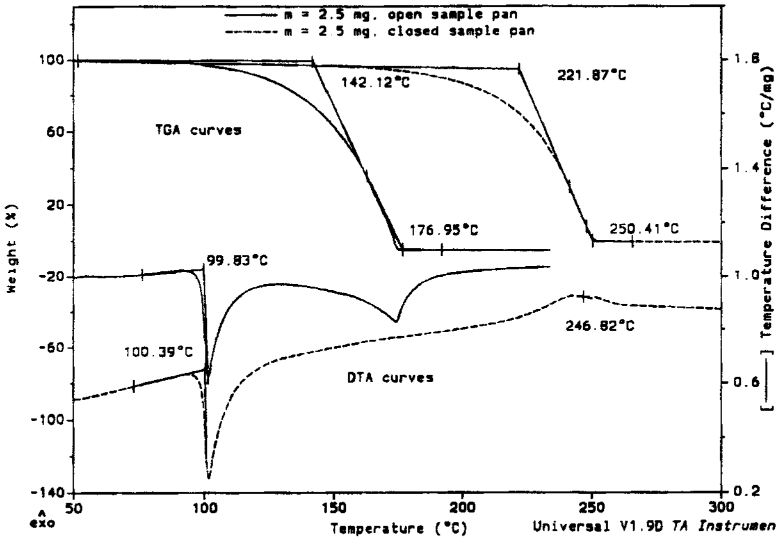

FIGURE 3. TGA and DTA curves of TNAZ obtained under different testing conditions (heating rate 10 °C/min, sample mass 2.5 mg, and nitrogen atmosphere)

As mentioned earlier, endothermic peak visible at about 100 °C on DSC and DTA curves corresponds to TNAZ melting process. On the basis of several measurements it was found out that the melting temperature of TNAZ equals 100.59 ± 0.21 °C, while the melting enthalpy equals 153.3 ± 1.6 J/g. These results are in good agreement with the results reported in literature (Table 1).

The influence of TNAZ sample mass and the method of sample loading into the sample pan on the shape of DSC, TGA and DTA curves is clearly visible from Figures 1–3. For example, if very small samples (~0.5 mg), loaded in an open sample pan, are used then the molten sample evaporates completely before the rapid decomposition begins (Figure 2, curve 3). This explains why there is no exothermic peak corresponding to TNAZ decomposition. The returning of DSC curve to the base line at 176.3 °C is due to the change of the heat capacity after TNAZ sample evaporates completely.

The same conclusion follows from TGA and DTA curves given in Figure 3, obtained under identical experimental conditions. The rapid loss of sample mass in temperature range 140–177 °C is the consequence of liquid TNAZ evaporation. The sample evaporates completely up to 177 °C.

However, when TNAZ samples (50 mg) were loaded into an open glass tube and heated at the same rate as the 0.5 mg samples, the material does not evaporate completely before the rapid decomposition begins. This is visible from DTA curve obtained by using DTA 550-Ex apparatus, from which an exothermic peak corresponding to the thermal decomposition is visible in the range 212-260 °C (Figure 4).

TABLE 1. Melting temperatures, melting enthalpies, and temperatures of exothermal decomposition

| Author | Melting temperature (°C) | Melting enthalpy (J/g) | Temperature of exothermal decomposition (onset) (°C) | Ref. |
|---|---|---|---|---|
| J. X. Zhang et al. | 99.00 ± 0.1 | 157.8 ± 1.56 | 221 | 11 |
| R. L. Simpson et al. | 96.83–99.45 | | 245 | 5 |
| R. L. McKenny et al. | 99.3–101.1 | 139.6 | 244–256 | 18 |
| S. Konrad and K. Doris | 101 | 147.1–149.2 | > 240 | 17 |
| J. Oxley et al. | 101 | 133.9 | 258 | 13 |
| This work | 100.59 ± 0.21 | 153.3 ± 1.6 | Onset of main peak at 220–251 °C, depending on heating rate* | |

* The main exothermic peak onset temperature was 220–251 °C, while main peak's shoulder onset temperature was 183-230 °C, depending on heating rate. The temperature of the first deviation of DSC curve from the base line, i.e. the temperature of the beginning of exothermal reaction was 178–195 °C, depending on heating rate.

In order to suppress TNAZ sample sublimation and evaporation we have used two methods of sample pan closing – unhermetically closed (i.e. covered but not sealed) aluminum sample pans and a sealed aluminum sample pan. When TNAZ sample was tested in unhermetically closed sample pan it was possible to detect small exothermic peak corresponding to the thermal decomposition, even in the case when small sample mass had been used. It is visible from DSC curve 2 in Figure 2, and from DTA curve given in Figure 3: small exothermic peak with maximum at about 250 °C corresponds to the exothermic decomposition of a small non-evaporated part of TNAZ sample. Very intensive sample mass loss in the range 222–250 °C, visible from TGA curve given in Figure 3 corresponds to the exothermic decomposition followed by the sample evaporation.

When TNAZ samples were tested in sealed aluminum sample pans then the sublimation and evaporation could be suppressed almost completely. This is visible from DSC curves 1 and 4, Figure 2, on which a large exothermic peak corresponding to the exothermal decomposition is clearly visible in the range 216–265 °C. It is found out from DSC results obtained under such experimental conditions that the slow thermal decomposition begins at 178–195 °C, while the rapid decomposition begins at 183–230 °C, depending on the heating rate.

An unexpected endothermic peak visible at about 205 °C on DSC curve 4 (Figure 2) is the consequence of the heat loss at the moment of a sample pan covering disrupture under the action of pressure of evaporated TNAZ and evolved gaseous decomposition products inside the sealed sample pan. It can be avoided using TNAZ samples weighing less than 0.5 mg (since the pressure inside the sealed sample pan will be then insufficient to disrupt sample pan).

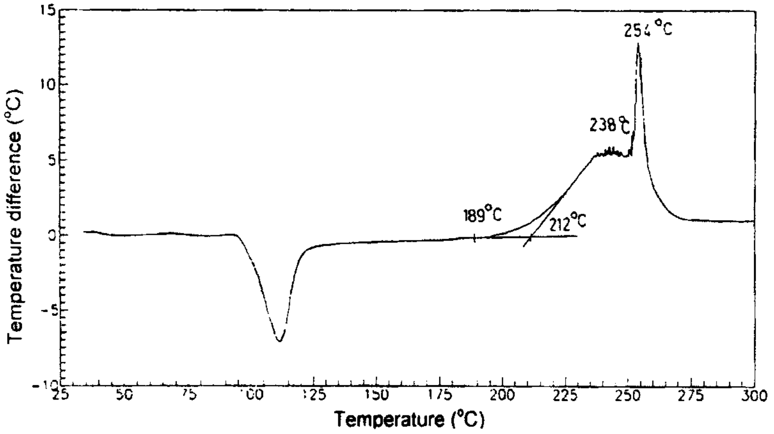

FIGURE 4. DTA curves of TNAZ obtained with 10 °C/min heating rate (sample mass 50 mg, static air atmosphere)

It is important to note that the main exothermic DSC and DTA peaks are asymmetric and that they have a shoulder. It is visible from DSC curve 1 (Figure 2) and DTA curve (Figure 4): The main exothermic peak, which has a maximum at 254–260 °C, has a shoulder in the range 215–240 °C. Such shape of the main exothermic peak is connected with the processes taking place inside the sealed aluminum sample pan, where a part of evaporated TNAZ and evolved gaseous decomposition products are present. The shape of peak indicates that the rate of decomposition increases moderately in the initial stage and then exhibits autocatalytic increase at the end of the decomposition.

According to K. Anderson et al.[15] the key decomposition intermediate of TNAZ is 1-nitroso-3,3-dinitroazetidine (NDNAZ). The key feature of NDNAZ decomposition is the autocatalysis after the initial induction period, and the formation of polymeric residue. It is possible that the residue catalyses decomposition of TNAZ and its intermediate product NDNAZ. The shape of DSC and DTA exothermic peaks suggests that the decomposition has the initial stage in which the rate of decomposition increases moderately up to about 240 °C, after which a rapid, autocatalytic, decomposition takes place. It is possible that the first decomposition stage, i.e. peak shoulder, is due to TNAZ decomposition and formation of NDNAZ, while the second stage corresponds to the autocatalytic decomposition of TNAZ and its intermediate NDNAZ.

However, there is one more process at the peak temperatures that probably influences the shape of the peak and the processes taking place. According to B. Wang et al.[27] it is a boiling point which occurs at 252 °C. The local minimum at about 240–245 °C on the DTA curve (Figure 4) may be due to the TNAZ boiling.

## TNAZ sublimation and evaporation

It is known that TNAZ sublimes considerably. TGA measurements carried out using an open sample pan (Figure 3) proved that. TNAZ sample mass loss before the melting temperature is due to the sublimation, while a rapid sample mass loss after the melting temperature, in the range 140–176 °C, is due to the evaporation (since the thermal decomposition of TNAZ begins above 180 °C). From Figure 5, it is seen that at a heating rate of 1 °C about 14 % of the sample sublimes, while at a heating rate of 20 °C/min only about 2.5 % sublimes.

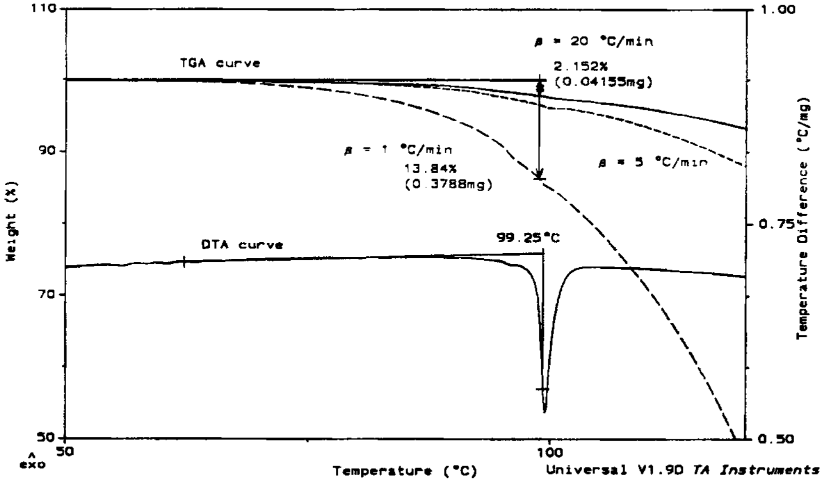

FIGURE 5. TGA curves of TNAZ obtained at different heating rates (sample mass 2.5 mg, open sample pan, nitrogen atmosphere)

These data, and data given in Figure 6 and obtained under isothermal conditions, show that the rates of TNAZ sublimation and evaporation are considerable. For example, the rate of TNAZ sublimation at a temperature of 75 °C in the initial stage is almost constant and equals 0.134 %/min, while the rate of sublimation at 85 °C is 0.276 %/min, i.e. about two times higher. At temperature 75 °C sample completely sublimes after approximately 750 min, and after about 400 min at 85 °C.

The rate of evaporation is higher and equals 1.88 %/min at 105 °C. This means that the sample will evaporate completely after approximately 50 min. It should be mentioned that the rates of sublimation and evaporation are dependent on sample surface, which means that these results are valid only for given experimental conditions. Anyway, they suggest that the rates of these processes are considerably high.

## DSC and DTA non-isothermal decomposition kinetics of TNAZ

The kinetic parameters of TNAZ decomposition were determined on the basis of multiple heating rate DSC and DTA experiments, applying non-isothermal isoconversional Flynn-Wall and Ozawa's methods[28,29]. Non-isothermal DSC experiments were carried out using 0.5 and 2.5 mg sample weights. The experiments were run in sealed aluminum sample pans. Several commonly used high explosives were also tested in order to determine relative thermal stability of TNAZ. The results of DSC measurements are summarized in Table 2.

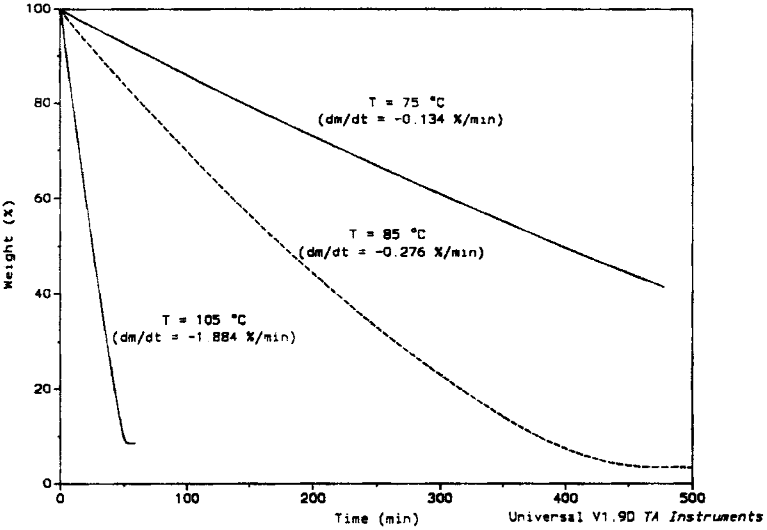

FIGURE 6. Isothermal TGA curves obtained at several temperatures (sample mass 2.5 mg, open sample pan, nitrogen atmosphere)

TABLE 2. Summary of DSC results obtained at different heating rates and different TNAZ sample size

| TNAZ sample mass ≈ 0.5 mg | | | | TNAZ sample mass ≈ 2.5 mg* | | |
|---|---|---|---|---|---|---|
| Heating rate (°C/min) | Peak maximum (°C) | Peak range (°C) | Heat of reaction (J/g) | Heating rate (°C/min) | Peak maximum (°C) | Peak range (°C) |
| 1.0 | 229.81 | 170-244 | 3250 | - | - | - |
| 2.0 | 239.21 | 180-258 | 2213 | 2.0 | 237.80 | 201-250 |
| - | - | - | - | 3.51 | 240.46 | 207-252 |
| 5.02 | 251.44 | 180-280 | 2230 | 5.05 | 251.64 | 209-272 |
| 10.10 | 260.08 | 180-287 | 1842 | 10.04 | 254.45 | 225-272 |
| 15.18 | 253.28 | 186-290 | – | 15.14 | 363.51 | 222-280 |
| 20.39 | 270.63 | 190-301 | 1758 | 20.52 | 266.87 | 238-287 |

* Since there was a considerable heat loss at the moment of the sample pan covering disrupture, values of the heat of reaction are not reliable.

By applying Ozawa's method the activation energy and pre-exponential factor for TNAZ, RDX, HMX, and TNT were calculated from the logarithm of heating rate-peak maximum temperature relationship (Figure 7). The results of calculation are given in Table 3.

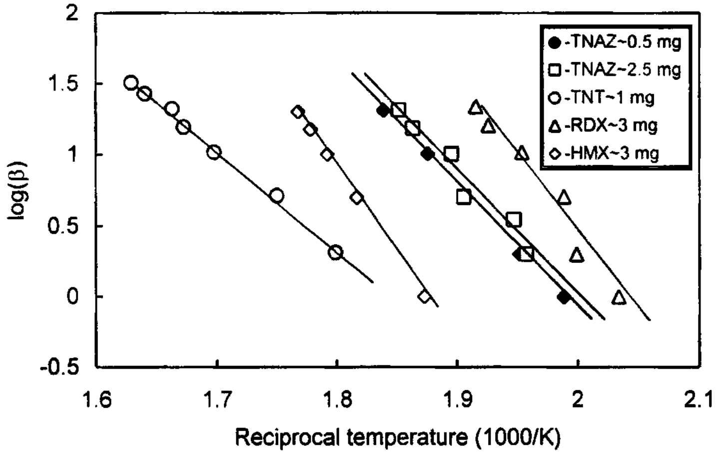

FIGURE 7. Logarithm of heating rate *vs.* reciprocal peak maximum temperature

TABLE 3. Values of thermal decomposition kinetic parameters for TNAZ, RDX, HMX, and TNT, determined from DSC measurements by isoconversional Ozawa's method

| Explosive | Activation energy (kJ/mol) | Pre-exponential factor (1/s) |
|---|---|---|
| TNAZ (0,5 mg) | 160.7 | 6.07 $10^{13}$ |
| TNAZ(2.5 mg) | 161.9 | 1.05 $10^{14}$ |
| TNT | 123.5 | 6.63 $10^{8}$ |
| HMX | 226.9 | 2.58 $10^{19}$ |
| RDX | 207.9 | 3.32 $10^{19}$ |

The mean value of the activation energy from these two measurements is 161.3 kJ/mol, and the mean value of pre-exponential factor is 8.27 $10^{13}$ 1/s.

The kinetic parameters of TNAZ thermal decomposition were determined also from DTA measurement, which were conducted on samples weighing 50 mg, and under static air conditions. The measurements were performed at three different heating rates: 5, 10 and 15 °C/min. The results of measurements are given in Table 4.

TABLE 4. Summary of DTA results

| Heating rate (°C/min) | Peak maximum temperature (°C) |
|---|---|
| 5 | 244.72 |
| 10 | 254.11 |
| 15 | 259.90 |

From data given in Table 4 the activation energy of 157.5 kJ/mol and pre-exponential factor 4.55·1013 1/s were calculated according to Ozawa's method.

In order to compare thermal stability of TNAZ and those for several commonly used high explosives the rate constants for these explosives were calculated using the values of kinetic parameters given in Table 3. The Arrhenius plots of these rate constants are shown in Figure 8.

The thermal stability of TNAZ at temperatures 200–300 °C is better than that of RDX, but worse than that of HMX and TNT. The same conclusion regarding TNAZ thermal stability was reported by J. Oxley et al.[13]. At temperatures between 100 and 200 °C RDX, TNT and TNAZ have comparable thermal stability, while HMX has considerably better stability than TNAZ and other explosives.

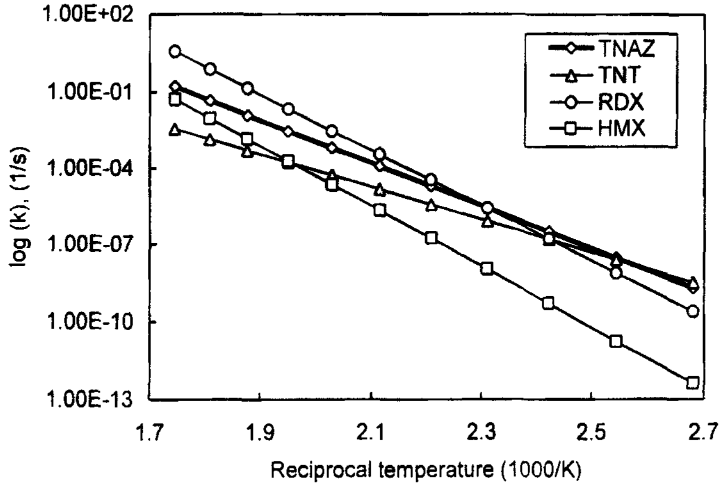

FIGURE 8. Arrhenius kinetic plots of TNAZ and some commonly used high explosives

The kinetic parameters were calculated also from the same DSC results applying the Flynn-Wall isoconversional method. The calculation was performed in the following way. The experiments were carried out at several heating rates ($\beta_j$). Then the degree of conversions ($\alpha_k$) was calculated from the total peak area ($A$) and area ($A_{k,j}$) at temperature $T_{k,j}$, at which degree of conversion $\alpha_k$ was reached at heating rate ($\beta_j$):

$$a_k = \frac{A_{k,j}}{A} \quad (1)$$

A plot of $\log(\beta_j)-1/T_{k,j}$ for each of $k$ degrees of conversion $\alpha_k$ yielded $k$ isoconversional lines from whose slopes the activation energies at each degree of conversion were calculated according to the method described by Flynn[27]. The results of calculation for several degrees of conversions are given in Table 5.

As follows from Table 5 the activation energy changes with the degree of conversion. Such behavior is characteristic for the complex reaction mechanisms, consisting of a number of separate processes, rates of which change with the degree of conversion, i.e. with temperature.

The extrapolated value of the activation energy to zero conversion equals about 110 kJ/mol, while its maximum value corresponding to the conversion 0.4, equals 155.6 kJ/mol. This value is close to values obtained from DSC and DTA peak maximum temperature according to the Ozawa's method (161.3 and 157.5 kJ/mol respectively).

TABLE 5. Activation energies and pre-exponential factors at different degree of conversions

| Degree of conversion | Activation energy (kJ/mol) | Pre-exponential factor (1/s) |
|---|---|---|
| 0.05 | 118.0 | $2.63 \cdot 10^{8}$ |
| 0.10 | 128.4 | $1.83 \cdot 10^{10}$ |
| 0.20 | 143.9 | $1.00 \cdot 10^{12}$ |
| 0.30 | 152.0 | $7.80 \cdot 10^{12}$ |
| 0.40 | 155.6 | $1.92 \cdot 10^{13}$ |
| 0.50 | 154.0 | $1.42 \cdot 10^{13}$ |
| 0.60 | 152.0 | $8.75 \cdot 10^{12}$ |
| 0.70 | 148.6 | $5.03 \cdot 10^{12}$ |
| 0.80 | 145.1 | $2.63 \cdot 10^{12}$ |
| 0.90 | 138.1 | $6.33 \cdot 10^{11}$ |

It was found out that degrees of conversion corresponding to DSC peak maximum temperature change from 0.83 at heating rate of 1 °C/min, to 0.72 at heating rate of 20 °C/min. This means that the main precondition for the applicability of Ozawa's method, which says that the degree of conversion at peak maximum temperature does not depend on heating rate and is not fulfilled entirely. For this reason activation energies calculated according to the Flyn-Wall method seem to be more reliable.

## CONCLUSIONS

On the basis of DSC, DTA, and TGA measurements the following can be concluded:

1. Thermal behavior, i.e. DSC, DTA and TGA thermogram's shape and position depend strongly on testing condition, mainly on sample mass and the way of TNAZ sample loading into the sample pan (in an open or sealed sample pan).
2. The melting temperature of TNAZ is 100.59 ± 0.21 °C, while the heat of fusion equals 153.3 ± 1.6 kJ/g.
3. The rate of TNAZ sublimation is high even at low temperatures.
4. Under non-isothermal conditions TNAZ tested in an open sample pan evaporates before the decomposition reaction takes place.
5. Under non-isothermal condition the thermal decomposition reaction of TNAZ was observed at 178 °C at heating rate of 1 °C/min, and at 195 °C at 20 °C/min heating rate.
6. The activation energy and pre-exponential factor of the exothermic decomposition of TNAZ determined by Ozawa's method are 161.6 kJ/mol and $8.27 \cdot 10^{13}$ 1/s respectively, calculated from DSC peak maximum temperature, and 157.6 kJ/mol and $4.55 \cdot 10^{13}$ 1/s, calculated from DTA peak maximum temperature. The activation energy calculated by Flynn-Wall method on the basis of DSC results lies between 130 and 155.6 kJ/mol for degrees of conversion ranging between 0.3 and 0.7.
7. TNAZ is thermally more stable than RDX but less stable than HMX and TNT.

## REFERENCES

1. Z. Jalový, S. Zeman, P. Vávra, M. Sućeska, K. Dudek and M. Rajić, J. Energ. Mater. 19 (2001) - in press
2. Army SBIR Award (Phase I) No. A96-013, U. S. Army Res. Office, Res. Triangle Park, NC (1996); http://www.aro.ncren.net/ AROWASH/RT/A9620031.htm.
3. S. Borman, Chem. Eng. News **72,** 18 (1994).
4. G. A. Olah, and D. R. Squire, "Chemistry of Energetic Materials", Acad. Press, Inc., San Diego, 1991.
5. R. I. Simpson, R. G. Garza, M. F. Foltz, D. I. Ornellas, and P. A. Utriev, "Characterisation of TNAZ", Rep. UCRL-ID-119572, Lawrence Livermore Lab., 1994.
6. A. Sanderson, "The Characterisation and Development of New Energetic Materials", Proc. 27th Int. Annual Conf. ICT, Karlsruhe, June 1996, p. 18/1.
7. K. Schmid and D. Kaschmieder, "Synthesis and Properties of TNAZ", Proc. 31st Int. Annual Conf. ICT, Karlsruhe, June 2000, p. 10/1.
8. S. H. Bauer and Yi-Xue Zhang, J. Energ. Mater. **17**, 161 (1999).
9. Y.-X. Zhang and S. H. Bauer, Int. J. Chem. Kinet. **31**, 655 (1999).
10. Y.-X. Zhang and S. H. Bauer, J. Phys. Chem. **A 102,** 5846 (1998).
11. J. Zhang, R. Hu, Ch. Zhu, G. Feng and Q. Long, Thermochim. Acta **298,** 31 (1997).
12. J. C. Oxley, A. B. Kooh, R. Szekeres and W. Zheng, J. Phys. Chem. **98,** 7004 (1994).
13. J. C. Oxley, J. Smith, W. Zheng, E. Rogers and M. Coburn, J. Phys. Chem. **A 101,** 4375 (1997).

14. J. Zhang, Ch. Zhu, X. Gong and H. Xiao, Wuli Huaxue Xuebao **13**, 612 (1997).
15. K. Anderson, J. Homsy, R. Behrens and S. Bulusu, "Mechanistic and Kinetic Studies of the Thermal decomposition of TNAZ and NDNAZ", CPIA Publ. **657**, 37 (1997).
16. N. R. Garland and H. H. Nelson, J. Phys. Chem. **B 102**, 2663 (1998).
17. S. Konrad and K. Doris, "Synthesis and Properties of TBAZ", 31st Annual Conf. ICT, Karlsruhe, 2000, p.10/1.
18. R. L. McKenney, T. G. Floyd, W. E. Stevens, T. G. Archibald, A. P. Marchand, G. V. M. Sharma, S. G. Bott, J. Energ. Mater. **16**, 1 (1998).
19. K. Dudek, P. Mareček and P. Vávra, "Laboratory Testing of HNIW Mixtures", Proc. 31st Int. Annual Conf. ICT, Karlsruhe, 2000, p. 110/1.
20. M. D. Cook, J. Energ. Mater. **5,** 257 (1987).
21. V. P. Stepanov, A. A. Fedotov, A. N. Pavlov and G. M. Nazin, "Mass Spetrometric Study of Elementary Stages of Thermal Decomposition of Cyclic Polynitramines", in B. V. Novozhilov (Ed.), Proc. 9th All-Union Symp. Combust. Explos., Acad. Sci. USSR, Chernogolovka, 1989, p. 100.
22. C. A. Wight and T. R. Botcher, J. Am. Chem. Soc. **114**, 8303 (1992).
23. S. Zeman, Thermochim. Acta **333**, 121 (1999).
24. M. D. Coburn, M. A. Hiskey, J. C. Oxley, J. L. Smith, W. Zheng and E. Rogers, J. Energ. Mater. **16**, 73 (1998).
25. O. Němčák and M. Hanus, "Compatibility of TNT, RDX and PETN with the Corrosion Products of Common Metals", Proc. 10th Symp. Chem. Pbrobl. Connected Stab. Explos., Margretetrop, 1995, p. 187.
26. M. Krupka and M. Hanus, "Using of the DTA in Criminalistic Expertises of Explosives", Int. Symp. on Ecolog. Liquidation, Detection & Ident. of Explosives Before and After Explosion. Hotel Labe, Pardubice, Sept. 1996, p. 59.
27. B. Wang, C. Zhu, Q. Longi, HanHeng CaiLiao **3,** 7 (1995).
28. J. H. Flynn, J. Therm. Analys. **27**, 95 (1983).
29. T. Ozawa, J. Therm. Analys. **2**, 301 (1970).