



## Study of Thermal and Detonation Reactivities of the Mixtures Containing 1,3,5-Trinitroso-1,3,5-triazinane (TMTA)\*)

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**Abstract:** Thermal reactivities of 1,3,5-trinitroso-1,3,5-triazinane (TMTA), 1,3,5-trinitro-1,3,5-triazinane (RDX), 2,4,6-trinitrotoluene (TNT), TNT/TMTA and RDX/TMTA mixtures and mixtures of 1,3,5-trinitrobenzene (TNB) with TMTA and TMTA/RDX were specified by means of differential thermal analysis with outputs evaluation by the Kissinger method. The reactivities, expressed as  $E_a R^{-1}$  slopes of Kissinger relationship, correlate with squares of detonation velocities of the corresponding explosive samples in the sense of modified Evans-Polanyi-Semenov equation. Taking this fact it is stated that initiation of detonation of the mixtures with TMTA content proceeds through primarily fission of the TMTA molecule. If an ionic mechanism dominantly participates on thermal decomposition of some studied mixtures then resulting  $E_a R^{-1}$  values do not correlate in the sense of the equation. This is the case of the TNT/TMTA mixtures where TNT has acidic character toward TMTA. Also in TNB/TMTA/RDX mixture might react amine intermediates of TMTA thermal decomposition with RDX by ionic mechanism.

**Keywords:** 1,3,5-trinitrobenzene, 1,3,5-trinitroso-1,3,5-triazinane, 1,3,5-trinitro-1,3,5-triazinane, 2,4,6-trinitrotoluene, Detonation, DTA, Explosives, Initiation, Thermal reactivity, TMTA

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## Introduction

The homolytic character and the identity of the primary fission in both the low-temperature thermal decomposition and the detonation of energetic materials [1-8] were a motive for Zeman *et al.* to use the Evans-Polanyi-Semenov equation (E-P-S) [9, 10] in the study of the chemical micro-mechanism governing the initiation of detonation of energetic materials [2-5, 8, 11]. The original E-P-S equation describes a relationship between the activation energies,  $E$ , of most substitution reactions of free radicals and the corresponding heats of reaction,  $\Delta H$ , [9, 10]:

$$E = B \pm \alpha' \Delta H \quad (1)$$

where  $B$  is the constant for the given homological series,  $\alpha'$  being a non-dimensional gradient [9, 10]. It is valid for narrow sets of substance structures and documents that the strength of bond being split is a decisive factor in the given reaction [9, 10]. Substitution of  $\Delta H$  by heat of explosion  $Q$  and  $E$  by activation energy,  $E_a$ , of the low-temperature thermal decomposition has led to the first version of the modified E-P-S eqn.[2-5] in the general form:

$$E_a = C \pm \alpha \cdot Q \quad (2)$$

where  $E_a$  and  $C$  are in  $\text{kJ mol}^{-1}$  and  $\alpha$  (the difference between eqn. (1)) is in  $\text{g mol}^{-1}$  [2-5]. Eqn. (2) is applicable to the detonation transformation of energetic materials [2-5, 8, 11].

The heat of explosion in this relationship can be substituted by the square of the detonation rate,  $D^2$ , because exists definiendum [12, 13]:

$$Q = D^2 \{2 (\gamma^2 - 1)\}^{-1} \quad (3)$$

where  $\gamma$  is the polytropy coefficient which value for high explosives ranges from 2.79 to 3.48 [12].

For exploring relationships of the type of Eq. (2) we can use the results of differential thermal analysis (DTA) [2, 8, 11]. In the case of plastic and commercial (oxidizing system on the basis of ammonium nitrate) explosives [8, 11], the differential thermal analysis (DTA) with evaluation according to Kissinger method [14] proved useful. The method plots  $\ln (\varphi/T_{max}^2)$  against reciprocal peak temperature,  $T_{max}$ , for a series of experiments at different heating

rates,  $\varphi$  (see also Figure 2 in the present paper). Using the slope in the Kissinger relationship, i. e.  $E_a R^{-1}$ , and taking into account Eq. (3), Eq. (2) was modified into the following form [8, 11]:

$$E_a R^{-1} = b \pm a \cdot D^2 \quad (4)$$

where the  $D$  is the experimentally determined values of the rate of detonation. On the basis of this approach it was stated [8] that initiation of the detonation of explosives based on mixtures of a fuel and /or high explosive with an ammonium nitrate oxidizing system proceeds primarily through decomposition of this system (this statement was also verified by results from a study of interactions of the nitros- and nitramines with ammonium nitrate [15]). In the present paper, the above-mentioned method and Eq. (4) have been used to study the detonation reactivity of explosive mixtures with content of 1,3,5-trinitroso-1,3,5-triazinane (R-salt, TMTA). In this respect, the present paper can be considered as a continuation of the previous paper [8]. Presented topic is, at the same time, an adjacent ascent of the forensic analysis study of the post-explosion TMTA products [16].

## Experimental

### Substances

The 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5-trinitrobenzene (TNB), all the military grade, and pure 1,3,5-trinitroso-1,3,5-triazinane (TMTA or R-salt) were used. TMTA is a solid substance crystallizing in the form of drab yellow needles with the melting point of 105-107 °C [17]; it was prepared by nitrosolysis of hexamethylenetetramine according to the published method [21]. The TMTA is sensitive to the trace of acidity [17-20] and in the molten state it may react with such metals as iron, copper and aluminium [17, 20].

### Explosive mixtures

Explosive mixtures were prepared by using the casting technology from the used individual explosives (TNT, TNB, TMTA and RDX). A survey of the tested explosives, their rates of detonation and characteristics of thermal reactivities are shown in Table 1.

The procedure of casting was taken from paper [22]: a preparation of casting

mixture of 73% wt. RDX, 1% wt. anthracene (AnT) and 1% wt. diphenylamine (DPA) was carried out by incorporating dry RDX into melted casting matrix (i. e. TMTA + AnT + DPA). The matrix was melted in a boiling water bath with continuous stirring. Analogous incorporating of TMTA into melted TNT was used in the case of the TNT/TMTA (50 : 50) mixture preparing which DTA record is presented in Figure 1.

Casting mixture TMTA with TNB was prepared by synchronous bringing of the two components into stirred TNB/TMTA melt on the water bath (75-80 °C); the melt was prepared by evaporation of a solvent from solution of the mixture TNB with TMTA in acetone. The TNB/TMTA melt had a smell of amines and formaldehyde during its preparation. Onset of its melting is 66.3 °C and corresponding peak lies at 78.4 °C. Density of the mixture was 1.03 g cm<sup>-3</sup>.

Mixture TNB/TMTA/RDX was obtained by mechanical mixing of powdered casting mixture TNB/TMTA with RDX.

### Measurement of detonation velocity

The time (discontinuous) method was used to measure the detonation velocity of casting military TNT, casting TMTA and explosive mixtures TNT/TMTA and RDX/TMTA. This method is based on the registration of passing shock wave given by the length part of the charge [23]. The measured values of detonation velocities for tested explosives are given in Table 1. The detonation velocities of pure TMTA [19] and RDX [24] were taken from literature.

For all the samples studied the detonation velocities were also calculated by means of the well know Kamlet & Jacobs method [25] for maximum theoretical density (TMD) of the given explosive. Corresponding results are summarized in Table 1, too.

### Non-isothermal differential thermal analysis (DTA)

We used a DTA 550 Ex apparatus [15, 26] 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 was being in direct contact with the air atmosphere.

The tested sample (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<sup>-1</sup>. The results of these measurements were evaluated by means of the software delivered with the DTA apparatus [26]. Examples of the corresponding DTA records are presented in Figure 1. The results obtained were treated using

the Kissinger method [14]; the treatment for pure substances is graphically presented in Figure 2.

**Table 1.** Composition of studied explosives, their detonation velocities and thermal stabilities ( $E_a R^{-1}$ )

Sample name	Code design.	Kissinger slope $E_a/R$ [K]	Detonation velocity [km s <sup>-1</sup> ]	
			experimental	calculated
2,4,6-Trinitrotoluene	TNT	15724	6.47	7.20
1,3,5-Trinitro-1,3,5-triazinane	RDX	32211	8.70 <sup>a</sup>	8.85
1,3,5-Trinitroso-1,3,5-triazinane cryst.	TMTA <sub>pure</sub>	15572	7.50-7.80 <sup>b</sup>	7.67
1,3,5-Trinitroso-1,3,5-triazinane casting	TMTA <sub>cast.</sub>	12456	7.30	7.67
Casting mixture of 75% RDX + 23% TMTA + 1% Anthracene + 1 % Diphenylamine	RDX/TMTA	20850	8.00	8.22
Casting mixture of 58% TNT + 42 %TMTA	TNT/TMTA	15363	6.95	7.30
Casting mixture of 50% TNB + 50 %TMTA	TNB/TMTA	13243	-	7.45
Casting mixture of 33.33%TNB + 33,3 %TMTA + 33.33% RDX	TNB/TMTA/RDX	33403	5.85 <sup>c</sup>	7.88

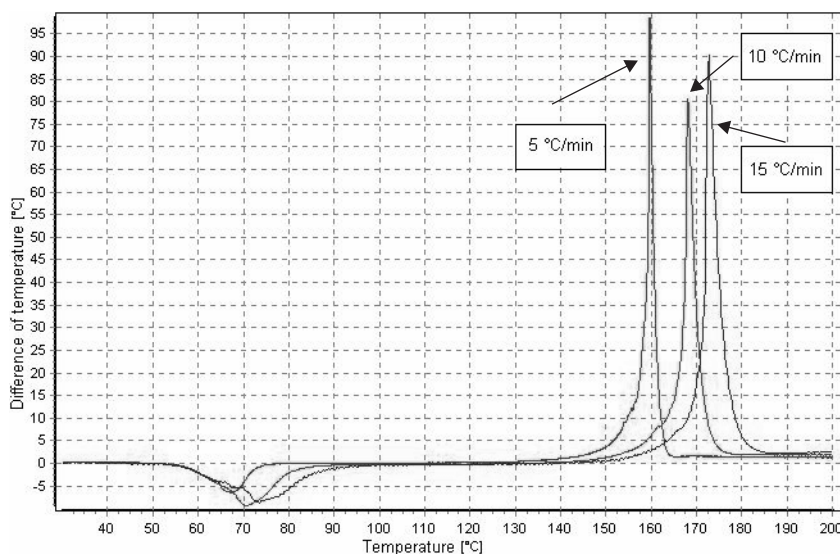
Notes to Table 1: a) data taken from [19, 24],  
 b) data taken from [17],  
 c) for density  $\rho = 1.16 \text{ g cm}^{-3}$ .

The values  $E_a R^{-1}$  thus obtained (see in Table 1) were then plotted against the squares of the experimental values of detonation velocities of the substances and studied mixtures (see Figure 3).

## Results and Discussion

On the basis of mixture RDX with TMTA it is possible, without bigger problems, to prepare a castable explosive with RDX content up to 75% wt. [22]. The explosive is very powerful, detonation parameters and performance superior

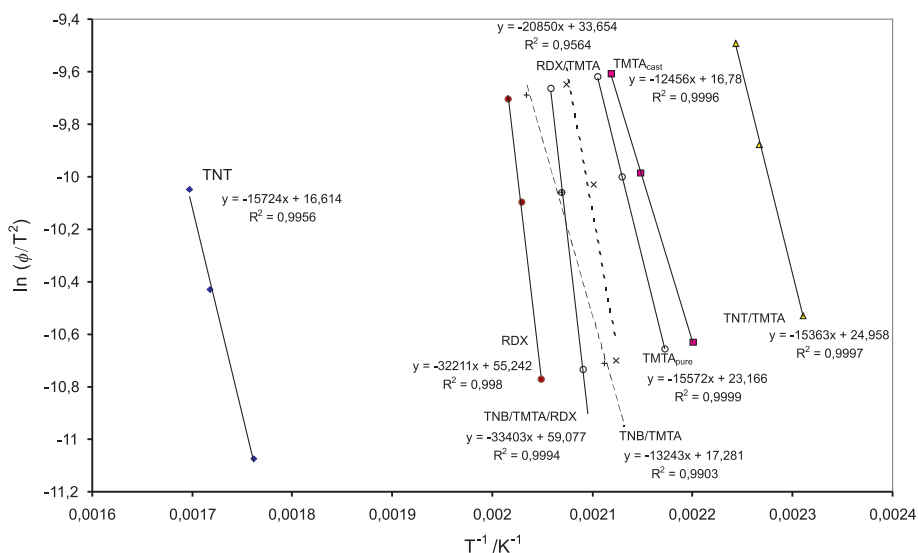
to mixture RDX/TNT 75/25 [22]. Its impact sensitivity is lower than in the case of TNT [22]. Figure 2 shows that the thermal stability of the RDX/TMTA mixture is higher than the stability of TMTA; stabilising effect of diphenylamine in this mixture has a positive influence on this stabilisation. On the other hand, the same Figure 2 documents reversed influence of thermal stress of TMTA on its thermal reactivity (melting TMTA<sub>cast</sub> is more reactive - corresponding line in the Figure 2 lies starboard to line of the pure substance). This stress should be expressed also in the change of detonation velocity of TMTA (see Table 1 and Figure 3). The said change, of course, can lie also in density decreasing ( $\rho = 1.37 \text{ g cm}^{-3}$ ) of the final TMTA charge due to its aeration by gaseous products of TMTA decomposition.



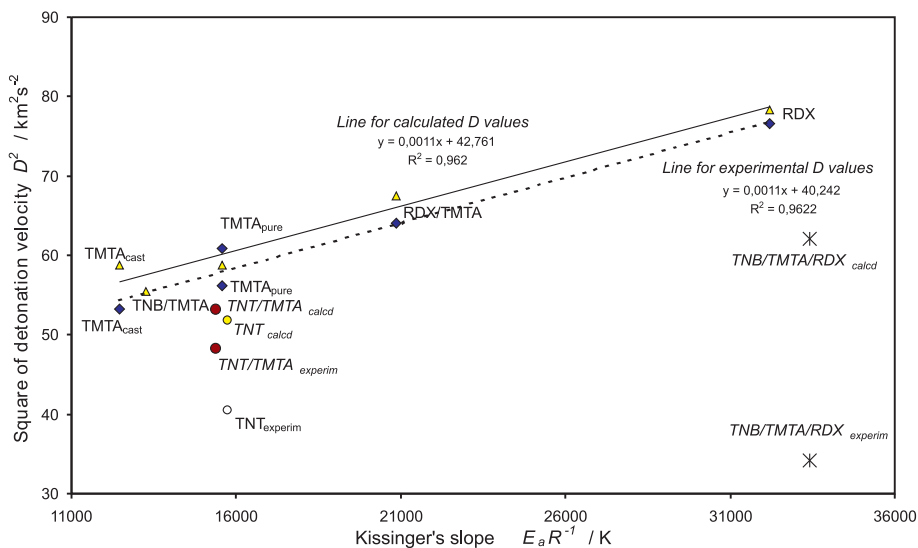
**Figure 1.** DTA records of the explosive mixture of TNT/TMTA at the heating rates 5, 10 and 15 °C min<sup>-1</sup> and samples mass of 0.05 g.

Figure 3 documents the initiation of the detonation of explosives based on mixtures with TMTA content proceeds primarily through decomposition of this polynitrosamine.

As well as in nitramines thermal decomposition (see Ref. [1] and references herein, namely Ref. [33]) the published values of Arrhenius parameters for this decomposition of nitrosamines in the condensed state correspond to the primary homolysis of N–N bond in their molecules [27-30]. Figure 3 also shows correlation on the basis of *D* values calculated for maximum theoretical crystal density (TMD) by means of well known Kamlet & Jacobs method [25].



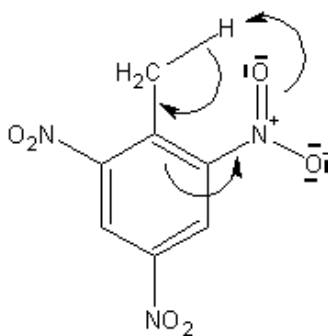
**Figure 2.** DTA results treated using the Kissinger method [14], here  $\phi$  is the rate of temperature increase and  $T$  is the peak temperature.



**Figure 3.** Modified Evans-Polanyi-Semenov equation for the studied samples.

It is logical that this calculation could not regard chemical changes in TMTA sample, which was submitted to thermal stress (see difference between the TMTA<sub>pure</sub> and TMTA<sub>cast</sub> data in Table 1 and Figure 3). The indicated relationship in Figure 3 fully corresponds to findings obtained by analogous study of mixtures on the basis of ammonium nitrate [8].

It follows also from Figure 2 that mixture of TNT with TMTA (TNT/TMTA) is the most reactive from all the studied samples. It might be caused by acidic character of TNT due to electronic transfer (see Figure 4) [31-33]:



**Figure 4.** Acidic character of TNT due to hydrogen atom of methyl group migration.

TNT behaves toward TMTA as acid although the existence of the *aci*-form of TNT should be not favored [34]. This fact is in a good accordance with already mentioned sensitivity of TMTA to the trace of acidity [17-19]. A melt of the TNT and TMTA mixture slowly decomposes already in the temperature region near its melting point: blowholes sporadically escape from the melt as early as at 55 °C without exothermal effect (see Figure 1) and without smell. The melt mixture, step by step, gets brown. This effect has to manifest oneself in outputs from DTA of the mixture – it might be a reason of nonexistent correlation of the corresponding  $E_a R^{-1}$  value in the sense of modified E-P-S equation (see Figure 3).

The TNT data don't correlate in the sense of E-P-S equation in Figure 3. Primary fission of the TNT molecule in its initiation processes should lie namely in N–OH bond homolysis in molecule of its *aci*-form (so called “trinitrotoluene mechanism”) [31-33].

Analogous to TNT also TNB has a negative influence on TMTA stability. Preparation of TNB/TMTA melt was connected with an obvious escape of formaldehyde and amines from the melt mixture. In the case of TNT this escape wasn't registered because methyl group of this polynitro arene is able



to participate in aldol and subsequently in N-Mannich condensations [35]. As the reactions are not radical, corresponding  $E_a R^{-1}$  value cannot correlate in the sense of E-P-S equation (see Figure 3).

Amines formation in the TNB/TMTA melt can be the reason of higher thermal reactivity of TNB/TMTA/RDX mixture compared to expectation; RDX has no use for alkaline media in which decomposition is labile [36, 37]. Mechanism of the decomposition is ionic [36]. It means that in the thermal decomposition of TNB/TMTA/RDX mixture should dominate the ionic mechanisms and, therefore, characteristic of this decomposition (i. e. slope  $E_a R^{-1}$ ) cannot correlate with the E-P-S equation (see Figure 3).

## Conclusion

The initiation of detonation of the explosives based on mixtures of 1,3,5-trinitroso-1,3,5-triazinane (TMTA) with 1,3,5-trinitro-1,3,5-triazinane (RDX) and/or 2,4,6-trinitrotoluene (TNT) or 1,3,5-trinitrobenzene (TNB) proceeds primarily through decomposition of the TMTA. Modification of the Evans-Polanyi-Semenov equation, in which the activation energy is substituted by a slope  $E_a R^{-1}$  of Kissinger's relationship and at the same time the heat of reaction by square of detonation velocity,  $D^2$  is applicable to study the mechanism of these explosive mixtures detonation.

However, thermal decomposition characteristics of TMTA mixtures do not correlate with the equation if ionic mechanisms dominate in this decomposition. This is the case of TNT/TMTA mixture where the TNT behaves toward TMTA as acid. Corresponding mixtures slowly decompose already in the temperature region up to 55 °C. Mixture of TNB/TMTA/RDX is another example, in which amine intermediates of TMTA decomposition might react with RDX by ionic reactions.

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