

Some properties of explosive mixtures containing peroxides Part II. Relationships between detonation parameters and thermal reactivity of the mixtures with triacetone triperoxide

Svatopluk Zeman*, Cécile Bartei

*Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice,
CZ-532 10 Pardubice, Czech Republic*

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Abstract

This study concerns mixtures of triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) and ammonium nitrate (AN) with added water (W), as the case may be, and two dry mixtures of TATP with urea nitrate (UN). Relative performances (RP) of the mixtures and their individual components, relative to TNT, were determined by means of ballistic mortar. Thermal reactivity of these mixtures was examined by means of differential thermal analysis and the data were analyzed according to the modified Kissinger method (the peak temperature was replaced by the temperature of decomposition onset in this case). The reactivity, expressed as the $E_a R^{-1}$ slopes of the Kissinger relationship, correlates with the squares of the calculated detonation velocities for the charge density of 1000 kg m^{-3} of the studied energetic materials. Similarly, the relationships between the $E_a R^{-1}$ values and RP have been found. While the first mentioned correlation (modified Evans–Polanyi–Semenov equation) is connected with the primary chemical micro-mechanism of the mixtures detonation, the relationships in the second case should be connected with the thermochemical aspects of this detonation.

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1. Introduction

Relative performance and detonation of mixtures with triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) were dealt with in Part 1 of this series [1]. In this present paper we are extending the earlier results by a study which starts from our previous findings about the chemical micro-mechanism initiation of condensed explosive mixtures [2–7]. An identity of the primary fragmentations in the low-temperature thermolysis and initiation reactions of energetic materials [2–7] is a base of approach to this problem (similarly as in Refs. [4,5]). Therefore, a relationship between thermal reactivity, determined by means of simple differential thermal analysis (DTA), and experimentally determined detonation velocities, or calculated heat of explosion, was used in our recent papers [2,4–7] for interpretation of some behavior of the

corresponding mixtures. In this respect, the present paper forms a continuation of the earlier work dealing with the initiation mechanism of explosive mixtures containing ammonium nitrate [2]; that means that certification of the mutual relationship between chemism of the primary fragmentations in thermolysis and detonation processes of explosive mixtures is a main topic also of this paper.

Using the above-mentioned observations, including simple DTA, we try to find the above-mentioned relationship between thermal reactivity, detonation and performance characteristics of the TATP mixtures with ammonium nitrate (AN) and partly with urea nitrate (UN).

2. Experimental

2.1. Substances

The substances used (TATP, AN, and UN) were the same as those used in Part 1 of this series [1]. Also a major part of the studied mixtures (energetic materials) TATP/AN and two

* Corresponding author. Tel.: +420 46 603 8023; fax: +420 46 603 8024.
E-mail address: svatopluk.zeman@upce.cz (S. Zeman).

Table 1

Content of the triacetone triperoxide (TATP), ammonium nitrate (AN), urea nitrate (UN) and water in the studied mixtures (energetic materials—taken from Ref. [1])

Code of mixture ^a	Content of the components (wt.%)			
	TATP	AN	UN	Water
I	4.9	90.9		4.2
III	11.3	78.8		9.9
IV	11.3	88.7		
VI	22.4	15		62.6
VIII	33.0	51.5		15.5
IX	42.2	21.2		36.6
XI	44.5	34.5		21.0
XII	53.6	21.2		25.2
XIII	57.9	14.8		27.3
XX	60.0		40.0	
XXI	80.0		20.0	

^a The samples numbering according to Ref. [1].

mixtures TATP/UN were taken were taken from Part 1 [1]. A survey of samples studied is presented in Table 1.

2.2. Relative performance of TATP mixtures

The relative performance values (RP) were determined by measurements in ballistic mortar [8,9] already in Part 1 of this series [1], and the values are reported as a relative performance of TNT (RP). The RP values are given in Table 2.

2.3. Theoretical velocity of detonation

The theoretical velocity of detonation, D , of the tested mixtures, calculated using the CHEETAH code [10], was taken from Part 1 of this series [1]. The D values used for the charge density of 1000 kg m^{-3} are presented in Table 2.

Table 2

Calculated detonation velocities for charge density of 1000 kg m^{-3} , relative performance (both the data taken from Ref. [1]) and results of DTA measurements of the studied energetic materials

Code of mixture ^a	Calculated detonation velocity (m s^{-1})	Experimental relative performance (% TNT)	DTA outputs	
			$E_a R^{-1}$ (K)	r^2
I	4693	100.5	7566.3	0.9918
III	5128	100.5	8307.6	0.9443
IV	5312	114.0	6107.5	0.9983
VI	3177	6.5	4156.5	0.9900
VIII	5024 ^b	78.7	7702.2	0.9265
IX	4395	37.2	20914.0	0.9998
XI	4831 ^b	59.1	7978.2	0.9216
XII	3489	45.0	11440.0	1.0000
XIII	4669 ^b	53.1	11719.0	0.9176
XX	5032	60.9	13162.0	0.9891
XXI	5115	60.9	11556.0	0.9449
AN	4171	0	11445.0	0.9996
UN	4819	78	17285.0	0.9981
TATP	5199	61.7	20528.0	0.9915

^a The samples numbering according to Ref. [1].

^b The average value, calculated from velocities of detonation for charge densities 1100 kg m^{-3} and 900 kg m^{-3} in the paper [1].

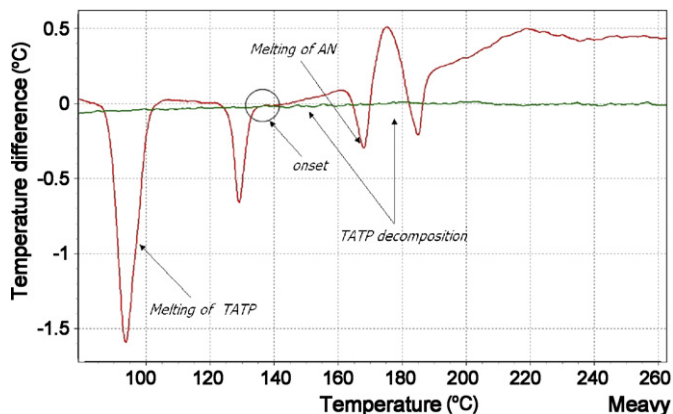


Fig. 1. Typical record from non-isothermal differential thermal analysis of the TATP/AN/water mixture (here mixture I) for linear heating rate 5°C min^{-1} —method of the onset evaluation.

2.4. Non-isothermal differential thermal analysis

We used a DTA 550 Ex apparatus [2,11] specially developed at the Institute of Energetic Materials for thermal analyses of explosives. The measurements were carried out at atmospheric pressure, in direct contact with the air atmosphere. The sample (0.02 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 glass sand. We used linear heating rates from 1 to $15^\circ\text{C min}^{-1}$. The results of these measurements were treated by means of the software delivered with the DTA apparatus [11]. An example of the corresponding DTA records is presented in Fig. 1.

In order to evaluate the reproducibility of the results, we made three analyses per sample and heating rate. For attaining a good homogeneity of the samples prepared we used a colored pigment (organic compound). The mixtures (TATP/AN/W) were hand-made, so we added a little organic pigment to them (approx. 10 mg of the Resol Orange R5 to 50 g TATP/AN/W mixture).

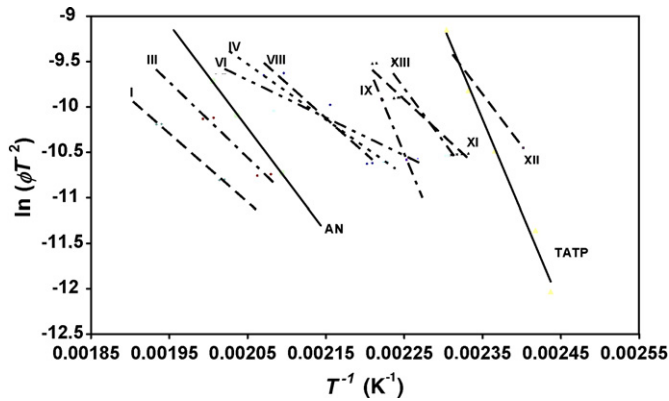


Fig. 2. Evaluation of the DTA outputs for TATP/AN mixtures by modified Kissinger method (samples of pure AN and TATP vs. mixtures TATP/AN/water).

The use of this additive made the analysis of thermograms more difficult (an influence of its “ash” on the base line); therefore, it needed some adaptations: we carried out two heating cycles with each sample, the first as the thermal decomposition and the second as the base line. We defined the onset temperature with the start of the exothermic phenomenon—point of intersection of two curves (Fig. 1).

The thermal reactivity is expressed here as the slope (activation energy) $E_a R^{-1}$ in the Kissinger relationship [12], which is used in a modified form for evaluation of results of non-isothermal differential thermal analysis:

$$\ln \left(\frac{\phi}{T^2} \right) = - \left(\frac{E_a}{R} \right) \frac{1}{T} + \ln \left(\frac{AR}{E_a} \right) \quad (1)$$

where ϕ is the rate of temperature increase, T the onset temperature of the exothermic decomposition (see Fig. 1), E_a the activation energy of the reaction, R the universal gas constant, A is the pre-exponential factor. The $E_a R^{-1}$ values obtained, together with corresponding r^2 values (coefficients of determination), are presented in Table 2. Figs. 2 and 3 represent Eq. (1) for TATP/AN mixtures and TATP/UN mixtures, respectively. Due to time problems (a possibility of ageing of the samples) it was impossible to measure all the mixtures described in Part 1 of this series (see Ref. [1]).

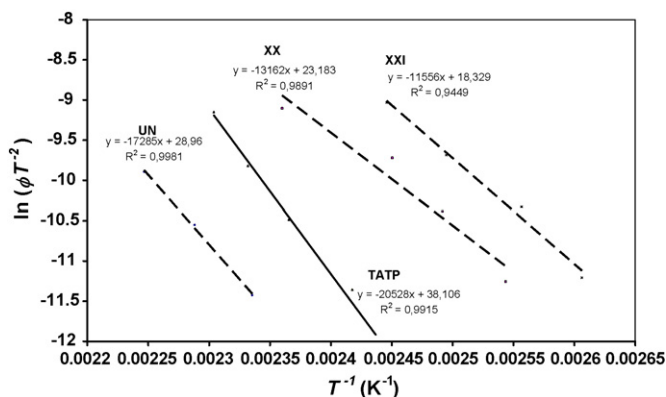


Fig. 3. Evaluation of the DTA outputs for TATP/UN mixtures by modified Kissinger method (samples of pure UN and TATP vs. mixtures TATP/UN).

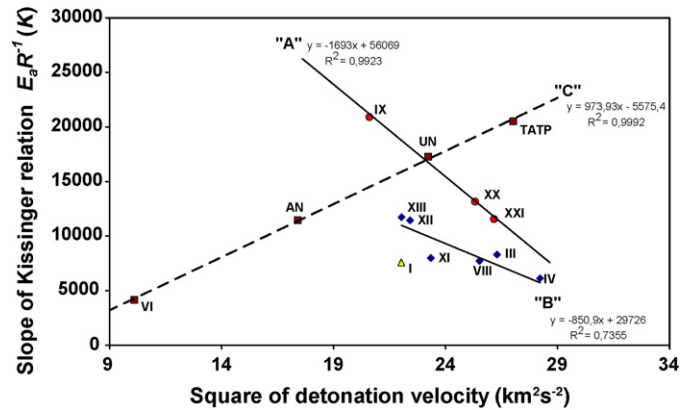


Fig. 4. Relationships between thermal reactivity, expressed as the slopes of Kissinger relation, $E_a R^{-1}$, and squares of detonation velocities of the studied energetic materials.

3. Results and discussion

3.1. Thermal reactivity and velocity of detonation

Fig. 2 shows that an addition of AN to TATP provides a mixture of higher stability than that of the starting triacetone triperoxide. The addition of UN should have an opposite effect (Fig. 3). The relationship between slopes, $E_a R^{-1}$, of Kissinger Eq. (1) and squares of experimentally determined detonation velocities, D^2 , for several kinds of ammonium nitrate explosives was successfully used to study the chemical mechanism of initiation of detonation of these mixtures [2]. The said procedure represents one of the methods of study of chemical micro-mechanism of initiation of detonation of energetic materials [2,4,5,7]. Fig. 4 is an analogy of this approach for the studied mixtures containing TATP and the calculated detonation velocities for the charge density of 1000 kg m^{-3} . In this case, the straight line “A” represents dry mixtures of TATP/UN and UN, which correlate with the data of mixture TATP/AN IX containing 36.6% of water. Straight line “B” covers the data of TATP/AN mixtures containing 0–27.3% of water; a relatively lower correlation might be caused by influence of a higher content of water in the samples VIII and XI on their $E_a R^{-1}$ values. The data of TATP/AN mixture I do not correlate with “B” because the mixture has a positive oxygen balance (the oxygen coefficient of 1.234 [1]). Line “C” corresponds to pure AN, UN, TATP, and mixture TATP/AN VI with high content of water.

Except for UN and AN, all the samples studied are characterized by the presence of TATP, which initiates the decomposition of the respective mixtures. As already stated in Part 1 of this series [1], AN and UN differ in their primary decomposition mechanisms [1,13–16] and their respective final products, which means that the subsequent reactions of mixtures containing AN (line “B”) will differ from subsequent reactions of the mixtures containing UN (line “A”). The correlation of data of mixture TATP/AN IX with data of mixtures containing UN could be explained by the high content of water in this sample—water and nitrogen compounds of UN type or guanidine nitrate act

in the detonation as “cooling admixtures” [17] (using the deuterium kinetic isotope effect it could be proved [18] that the reaction with the water, presented in the explosive mixture, is the limiting stage of complex chemical processes behind the detonation front). Straight line “C” covers the data of energetic materials exhibiting entirely different mechanisms of primary fragmentation [1,13–16], which are characterized by considerably imbalanced oxygen balance [1]; in addition to that, mixture TATP/AN VI contains 62.6% of water. The said facts indicate a dominating effect of thermochemistry of fragmentation upon the classification of the substances in group “C”. It should be noted that relationships of the type presented in Fig. 4 document that the primary fragmentation processes of molecules of energetic materials in the low-temperature thermal decomposition should be identical with those in the shock initiation [2,4,5,7].

3.2. Thermal reactivity and performance

The relationship presented in Fig. 4, as one of the forms of modified Evans–Polanyi–Semenov equation [2,4,5,7], represents a relationship between the activation energy of low-temperature decomposition and heat of explosion, Q , of energetic materials, since the definition relation between the Q and D^2 values reads as follows [19]:

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

where γ is the polytropy coefficient. The Q values also feature in the relationship for performances, A , of commercial explosives [19,20]:

$$A = Q \left(1 - \left(\frac{V_1}{V_2} \right)^{\gamma-1} \right) \quad (3)$$

where V_1 is the initial volume of gaseous products of detonation and V_2 is their final volume. Even though the detonation velocity cannot represent a criterion of performance of explosives

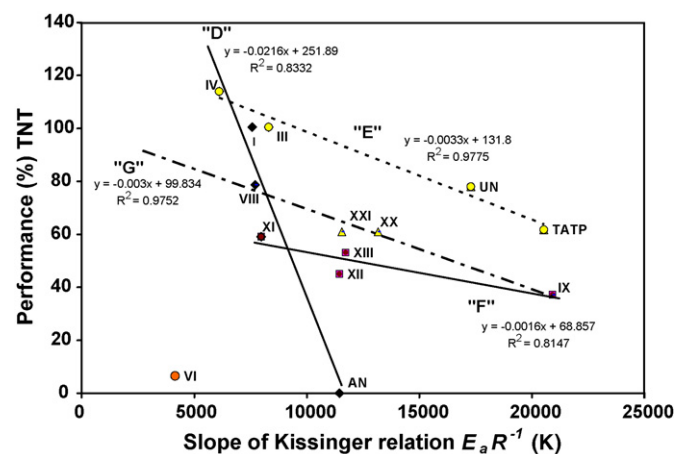


Fig. 5. Possible relationships between relative performance and thermal reactivity, expressed as the slopes of Kissinger relation, $E_a R^{-1}$, of the studied energetic materials.

[20], by using relationships (2) and (3) it should be possible to transform Fig. 4 into a potential relationship between thermal reactivity and performance (see Fig. 5).

However, the given relationship (Fig. 5) is not univocal. Line “D” combines data of TATP/AN mixtures containing more than 34.5% of AN and less than 21% of water. Line “E” covers the data of TATP alone and those of its mixtures III and IV with high AN content, and water content below 9.9%; also data of UN correlate with this line. Line “F” combines the data of TATP/AN mixtures containing more than 42% of TATP and more than 21% of water. The data of mixtures containing more than 33% of TATP and less than 36% of water constitute line “G”; the correlation here concerns the data of dry mixtures TATP/UN XX and XXI (as if UN has been partially a replacement of water here) with high content of TATP. The data of mixture VI do not fall in any of these groups because of its very high water content. The above-given facts indicate that dominant factors in these relationships (Fig. 5) are thermochemical factors of explosion transformation of the tested materials.

4. Conclusion

By means of the simple differential thermal analysis with evaluation of its outputs by modified Kissinger method it was shown that the admixture of ammonium nitrate (AN), added to triacetone triperoxide (TATP), in some degree increases thermal stability of the resulted TATP/AN mixtures; in contrast to that, urea nitrate (UN) should decrease this stability of the corresponding TATP/UN mixtures. The modified Evans–Polanyi–Semenov equation [2,4,5,7], in which the activation energy is substituted by the slope $E_a R^{-1}$ of Kissinger’s relationship and, at the same time, the heat of reaction by the square of the detonation velocity, D^2 , is valid for the studied TATP explosive mixtures. In this respect, this paper forms a direct continuation of the results of earlier analogous studies of explosive mixtures containing ammonium nitrate [2], i.e. the primary fragmentation processes in the studied mixtures during their low-temperature thermal decomposition should be identical with those during their detonation (in general see also Refs. [4,5]). A logical relationship between the $E_a R^{-1}$ values and relative performance for the tested mixtures of TATP can be found, but this relationship is not univocal. Depending on the content of “cooling components” (water or UN) in the samples studied, this relationship is composed of a number of partial linear equations. While the first mentioned correlation (modified Evans–Polanyi–Semenov equation) is connected with the primary chemical micro-mechanism of the mixtures detonation, the relationships in the second case should be connected with the thermochemical aspects of this detonation.

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References

- [1] S. Zeman, W. Trzeński, R. Matyáš, Some properties of explosive mixtures containing peroxides. Part I. Relative performance and detonation of mixtures with triacetone triperoxide, *J. Hazard. Mater.*, contribution No. HAZMAT-D-07-00852.
- [2] S. Zeman, P. Kohlíček, M. Maranda, Study of chemical micromechanism governing detonation initiation of condensed explosive mixtures by means of differential thermal analysis, *Thermochim. Acta* 398 (2003) 18.
- [3] S. Zeman, R. Varga, Study of thermal and detonation reactivities of the mixtures containing 1,3,5-trinitroso-1,3,5-triazinane (TMTA), *Cent. Eur. J. Energ. Mater.* 2 (2005) 77.
- [4] 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. B.V., 2003, p. 25 (Chapter 2).
- [5] S. Zeman, Sensitivities of high energy compounds, in: T. Klapoetke (Ed.), *High Energy Density Compounds, Structure and Bonding*, vol. 125, Springer, Heidelberg, 2007, p. 195.
- [6] S. Zeman, New aspects of initiation reactivities of energetic materials demonstrated on nitramines, *J. Hazard. Mater.* 132 (2006) 155.
- [7] S. Zeman, Usability of relationship between activation energies of the low-temperature thermal decomposition and heats of explosion or squares of detonation velocities in the study of initiation of energetic materials, in: Y. Wang, P. Huang, S. Li (Eds.), *Theory and Practice of Energetic Materials, Part B*, vol. VI, Science Press, Beijing, 2005, p. 454.
- [8] Notice of Czech Mining Authority No. 246/1996 of Law Collect, establishing more detailed conditions for allowing explosives, explosive objects and aids in use, and their testing.
- [9] M. Sućeska, *Testing Methods of Explosives*, Springer, Heidelberg, 1995, p. 176.
- [10] L.E. Fried, CHEETAH 1.39 User's Manual, UCRL-MA-117541 Rev. 3, Lawrence Livermore National Laboratory, 1996.
- [11] M. Krupka, Devices and equipment for testing of energetic materials, in: *Proceedings of the Fourth Seminar New Trends in Research of Energetic Materials*, Univ. Pardubice, April 2001, p. 222.
- [12] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.* 29 (1975) (1702).
- [13] G.B. Manelis, G.M. Nazin, Y.I. Rubtsov, V.A. Strunin, *Thermal Decomposition and Combustion of Explosives and Powders*, Izdat. Nauka, Moscow, 1996.
- [14] D.C. Sorescu, S. Alavi, L.D. Thompson, Theoretical and computational studies of energetic salts, in: M.R. Manaa (Ed.), *Chemistry at Extreme Conditions*, Elsevier B.V., Amsterdam, 2005, p. 431.
- [15] Y. Kohno, O. Takahashi, R.I. Hiyoshi, J. Nakamura, K. Saito, Theoretical study of the initial decomposition process of the energetic material urea nitrate, *J. Phys. Chem. A* 107 (2003) 6444.
- [16] I.V. Tokmakov, S. Alavi, D.L. Thompson, Urea and urea nitrate decomposition pathways: a quantum chemistry study, *J. Phys. Chem. A* 110 (2006) 2759.
- [17] L.V. Dubnov, N.S. Bakharevich, A.I. Romanov, *Promyshlennye vzryvchatye veshchestva (Industrial Explosives)*, Izdat. Nedra, Moscow, 1988.
- [18] M. Syczewski, J. Furkal, Kinetic isotope effect in detonation, *Fiz. Goreniya Vzryva* 18 (4) (1982) 117.
- [19] S.G. Andreev, A.V. Babkin, F.N. Baum, N.A. Imkhovik, I.F. Kobylkin, V.I. Kolpakov, S.V. Ladov, V.A. Odintsov, L.P. Orlenko, V.N. Okhitin, V.V. Selivanov, V.S. Solovov, K.P. Stanyukovich, V.P. Chelyshev, B.I. Shekhter, *Fizika vzryva (Physics of Explosion)*, Tom 1 (vol. 1), Fizmatlit, Moscow, 2002.
- [20] V.I. Pepekin, S.A. Gubin, O teplate vzryva promyshlennykh i brizantnykh vzryvchatykh veshchestv (On the heat of explosion of commercial and high explosives), *Fiz. Goreniya Vzryva* 43 (2) (2007) 100.