



Recent Advances in the Study of the Initiation of Energetic Materials Using the Characteristics of Their Thermal Decomposition

Part II. Using Simple Differential Thermal Analysis

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Abstract: Simple Differential Thermal Analysis (DTA), with evaluation of its output by the Kissinger method, was used in the case of emulsion explosives and, as an advanced application, for several plastic bonded explosives (PBXs). In both of these kinds of explosive the square of their detonation velocities, D^2 , is used as their performance characteristic. A relationship between the slope of the Kissinger equation, $E_a T^1$, and the D^2 values makes it possible to formulate a possible mechanism for the initiation of emulsion explosives. Regarding PBXs, it would seem possible to postulate a change in the detonation chemistry of plastic bonded nitramines, depending on the pressure and temperature in the zone of the detonation wave, particularly in the case of CL-20 fillers. Binders with aromatic building units in their macromolecular structure seem to be less-favoured in terms of their thermal reactivity and performance than the final PBXs. These findings document the advantages of the above-mentioned application of simple DTA.

Keywords: activation energy, detonation velocity, DTA, explosives, initiation, nitramines, PBX, thermal decomposition

1 Introduction

Relationships have been found between the output of non-isothermal, differential thermal analysis (DTA, *i.e.* low-temperature, non-autocatalyzed thermolysis) and the detonation characteristics of polynitroarenes [1, 2], and also nitramines,

nitrosamines and nitrate esters [3]. The choice of methodology for evaluating the DTA recordings was based on the fact that a higher brisance of an individual explosive is usually connected with a steeper DTA exothermal curve for its decomposition [1, 2]. Another, recently verified, source of reactivity data is the simple DTA, whose output has been evaluated by means of the Kissinger method [4] represented by the following relationship:

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

where: ϕ is the rate of temperature increase and T is the peak temperature of the exothermic decomposition, E_a is the activation energy and A is the pre-exponent. The reactivity was expressed as the $E_a R^{-1}$ slope from this relationship. One of the uses of this characteristic is in the modified Evans-Polanyi-Semenov equation [5-8], used to study the chemical micro-mechanism governing initiation of energetic materials [2, 3, 5-8]. Use of this equation, represented in its modified forms, has been dealt with in a recent paper [8], where particular attention was paid to the following form:

$$\frac{E_a}{R} = aD^2 + b \quad (2)$$

It is well known that D^2 corresponds to the heat of explosion [8, 9] in units of MJ per kg. This kind of relationship belongs to the group of general relationships between “sensitivity and performance” which are still awaiting scientific interpretation [10]. We have found that a better representative of the above mentioned performance is the energy per unit volume of explosive [11], which, in the case of Equation (2), can be represented by Equation (3); here ρ is the density of the given explosive (the product of this density and D^2 can be taken as a representative of the detonation pressure). Thus the modified Equation (2) is, used in this paper for the first time.

$$\frac{E_a}{R} = \alpha\rho D^2 + \beta \quad (3)$$

The present paper, therefore, shows some new results from applying the $E_a R^{-1}$ values, taken from the simple non-isothermal DTA approach, to the study of explosive mixtures, as well as PBXs. Above all the second case represents an advantage in the application of simple DTA. This paper is a continuation of the study in [8].

2 Data Sources

2.1 Differential thermal analysis

A DTA 550 Ex apparatus was used for differential thermal analysis [12]. The measurements were carried out at atmospheric pressure, with the tested sample in direct contact with the air. The sample (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm long. The reference standard was 0.05 g aluminum oxide. A linear heating rate of 5 °C min⁻¹ was used. The output of these measurements was evaluated by the Kissinger relationship (1) [4]. In the case of the emulsion explosives, only the dry oxidizing systems, or alternatively their mixture with high explosives (in the fortified mixtures), were measured by DTA [13, 14]. The $E_a R^{-1}$ values of the plastic bonded explosives measured are presented in Table 1.

Table 1. Experimental detonation velocities, charge densities and slopes of the Kissinger equation (1) of the PBXs studied with 91 wt.% of nitramine fillers

Explosive code designation	Density [kg/m ³]	Detonation velocity [km/s]	Ref.	Slope of Kissinger relationship [K]	
				$E_a R^{-1}$	R ²
RDX	1760	8.750	15	32127	0.9478
HMX	1900	9.100	15	37233	0.9979
BCHMX	1770	8.700	15	29355	0.9978
CL-20	1980	9.473	15	52123	0.9759
RDX-C4	1610	8.055	11,15	19274	0.9879
HMX-C4	1670	8.318	11,15	30171	0.9992
BCHMX-C4	1660	8.266	11,15	25203	0.9984
CL-20-C4	1770	8.594	11,15	25687	0.9948
RDX-PA	1620	8.045	15	24358	0.9994
HMX-PA	1690	8.386	15	30912	0.9993
BCHMX-PA	1670	8.293	15	25285	0.9933
CL-20-PA	1780	8.567	15	25772	0.9391
RDX-V9	1760	8.285	11,16	23629	0.9059
HMX-V9	1840	8.602	11,16	35826	0.9998
BCHMX-V9	1810	8.474	11,16	28843	0.9995
CL-20-V9	1940	9.023	11,16	24911	0.9824
RDX-FL	1740	8087	16	38156	0.9990
HMX-FL	1810	8398	16	35532	0.9877
BCHMX-FL	1790	8270	16	38718	0.9244
CL-20-FL	1920	8855	16	25285	0.9933

Note: suffix C4 means a binder based on softened polyisobutylene;
 suffix PA means a binder based on softened poly(methyl methacrylate);
 suffix V9 means binder Viton A 200;
 suffix FL means binder fluoroelastomer Dyneon FT 2481 (Fluorel).

2.2 Materials

A series of plastic bonded explosives (PBXs) was measured using a DTA 550 Ex apparatus. The following nitramines were used as fillers for the PBXs studied: RDX (1,3,5-trinitro-1,3,5-triazinane), β -HMX (β -1,3,5,7-tetranitro-1,3,5,7-tetrazocane), BCHMX (*cis*-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole) and ϵ -HNIW (ϵ -2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, or ϵ -CL-20); the origin of these nitramines is described in papers [11, 15, 16]. Their content in these plastic explosives was 91 wt.% and they were bonded with one of the following: a softened polyisobutylene binder (C4 matrix) [14], a softened poly(methyl methacrylate) (PA matrix) [15], Viton A (V9 matrix) [15] and a fluoroelastomer Dyneon FT 2481 (Fluorel) [16]. The preparation of these PBXs is described in papers [15, 16]. Experimental data for the explosives mentioned are summarized in Table 1, where the details for the PBXs are also presented (detonation velocities and densities [15, 16]).

3 Results and Discussion

Equation (2) has recently been applied to a study of explosive mixtures (see Figure 1, which is a compilation of three individual Figures from Refs. [2, 6, 13, 14, 17, 18]); the thermal reactivities of several oxidizing systems for emulsion explosives and some commercial explosives with different nitrate ester content have been specified in the literature [2, 6, 13, 14]; attention has also been paid to explosive mixtures containing peroxides [17, 18]. The main component of these oxidizing systems is ammonium nitrate (AN). In Figure 1, line *B* corresponds to classical W/O emulsion explosives, line *A* to W/O emulsions fortified by the addition of at least 30 wt.% of the high explosives RDX and PETN, and line *C* to W/O mixtures fortified with demilitarized Composition B (60% RDX/40% TNT) in amounts ranging from 30 to 50 wt.%. The group around line *A* indicates that a critical amount of admixed nitrate ester or nitramine exists for the mixtures (*i.e.* about 30 wt.%): the decomposition of the explosive mixture is not influenced by the physical state (*i.e.* solution or crystalline) of the oxidizing system when the high explosive content in these fortified mixtures is above the critical value (line *C*). Line *A* also contains data for commercial gelatinous explosives whose nitrate ester content exceeds 30 wt.% (black dots in Figure 1).

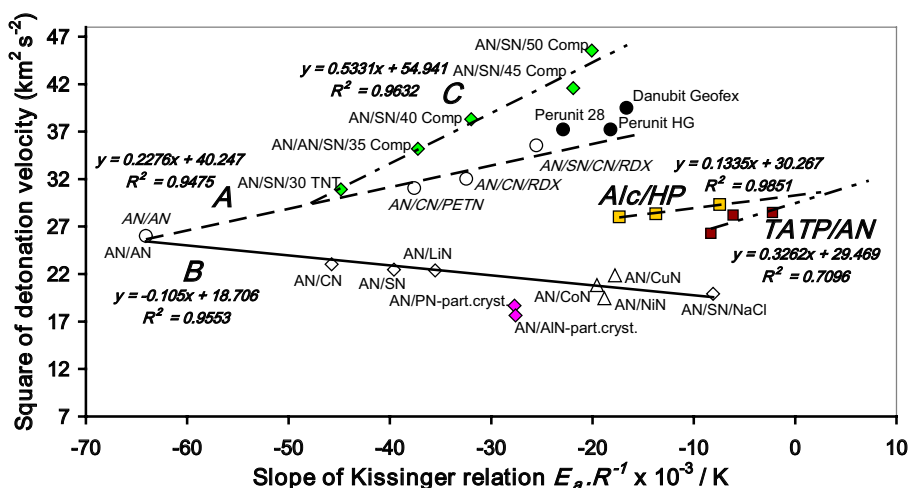


Figure 1. Compilation of the graphical representations of the relation (2) between the squares of the experimental detonation rates of the explosive mixtures and the slopes, $E_a R^{-1}$, of the Kissinger relationship (1). Here lines *A* and *B* are taken from paper [13], line *C* from paper [14] and lines for Alc/HP and TATP/AN from study [18]. Oxidizing systems for groups *A*, *B*, *C* and TATP/AN explosives are based on ammonium nitrate (AN) and its mixtures with sodium nitrate (SN), potassium nitrate (PN), calcium nitrate (CN), aluminum nitrate (AlN), lithium nitrate (LiN), and sodium chloride-sodium nitrate (NaCl/SN), nickel(II) nitrate (NiN), copper(II) nitrate (CuN) and cobalt(II) nitrate (CoN). The oxidizing system in Alc/HP liquid mixtures is hydrogen peroxide, and the fuels are ethanol, glycol and glycerine.

This effect is analogous to the well-known influence of shock pressure on initiation and propagation of detonation, in which the critical pressure plays a decisive role [19]. If the initiation pressure is lower than the critical value, then the initiation and growth of the detonation will depend on the micro-structure of the given charge ("hot spots"). If the pressure is higher than the critical value, then the initiation will depend only on the chemical composition of the charge [19]. The pressure during the detonation process is also given by the amount and reactivity of the molecular fragments which come into the reaction zone of the detonation wave. It has been stated that, in the explosive mixtures studied, the thermal reactivity of the oxidizing system and/or its mixture with a high explosive (for example: AN increases the thermal reactivity of RDX) replaces

the primary thermal reactivity of the explosophoric groups in the individual energetic material [13]. Mixtures with peroxides (Alc/HP and TATP/AN), presented here for comparison, also contain water, from their preparation; 74% hydrogen peroxide and wet triacetone triperoxide (TATP) were used respectively.

Applying Equation (2) to the study of plastic bonded explosives (PBXs) can lead to Figure 2, and in its modified form (3) to Figure 3 (see also Table 1); in the second case a product of the loading density, ρ , and the square of the detonation velocity can be taken as representative of the detonation pressure [11, 15]. These figures were drawn with the same coordinate system as in the older Figure 1 (for comparison purposes). Group *I* in Figure 2 includes the PBXs studied, with the exception of the CL-20 analogues. The CL-20-V9 point is wholly outside the PBX groups in both figures. What could be the reason for this? It has been stated [20] that, in fluorine containing explosives, there is very little difference between oxygen and fluorine as oxidizing elements from a thermodynamic point of view. However, the thermochemistry of detonation depends on the products actually formed in the reaction zone. In this respect, one needs to mention that a certain pressure should exist in the detonation of the nitramine PBXs with polyfluorinated binders, which induces a shift in the fluorine chemistry of these binders during detonation [21]. This statement about mechanism shift might be valid also for CL-20-C4 and CL-20-PA (in both figures, data for these PBXs correlate with data for group *II*). This exclusivity of the CL-20 mixtures can be connected with its brisance, which is higher than in the cases of the other nitramine fillers used.

Line *III* in Figure 2 corresponds to PBXs with the Fluorel binder, which is a terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, with a fluorine content of 68.6 wt.%; it also contains aromatic building units. In comparison with the copolymer of vinylidene fluoride with hexafluoropropene, *i.e.* Viton A (66 wt.% fluorine), Fluorel binder influences the chemistry of the decomposition of the corresponding PBXs differently, as Figure 2 shows. According to this figure, a relationship should exist between the mechanisms of low-temperature thermal decomposition and the primary fragmentation in the detonation of these PBXs. At the same time, data for CL-20-FL lie close to data for CL-20-V9 in the coordinate system of Figure 2.

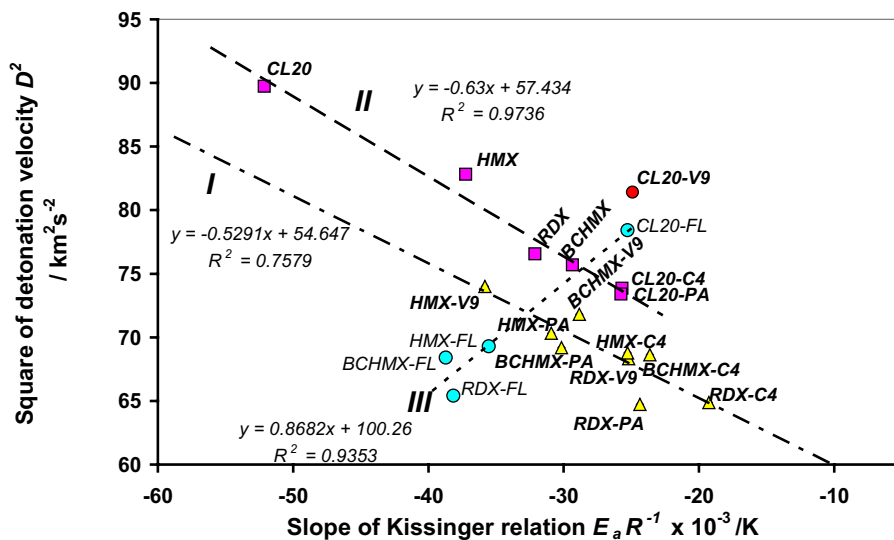


Figure 2. Relationship (2) between the square of experimental detonation velocities and the slope of the Kissinger relation for the PBXs studied.

If the square of the detonation velocity is substituted by a representative of the detonation pressure (*i.e.* by the product ρD^2), Figure 2 will be simplified – see Figure 3: PBXs bonded by Viton A are displaced from group *II* in Figure 2 into group *I* in Figure 3 – and the mixtures with the Viton binder are comparable with those of pure fillers. This fact agrees with practical experience [18]. On the other hand, PBXs with the Fluorel binder remain in group *I*; data for CL-20-FL are again situated near to data for CL-20-V9. That means that the chemical mechanisms of RDX-FL, HMX-FL and BCHMX-FL should be comparable with those for explosives bonded by the C4 and PA matrices. This should be due to the presence of the non-fluorinated aromatic building units in Fluorel. By reason of this fact (*i.e.* lower performance), and also due to the lower density of pressed charges of the corresponding PBXs [16], this binder is not very suitable for this kind of PBX. The unfavourable influence of the aromatic units in the binder structure is also shown by a comparison of the thermal reactivity of the C4 PBXs (*i.e.* bonded by polyisobutylene) with those bonded by a styrene-polybutadiene resin [22]; here the latter have a higher reactivity.

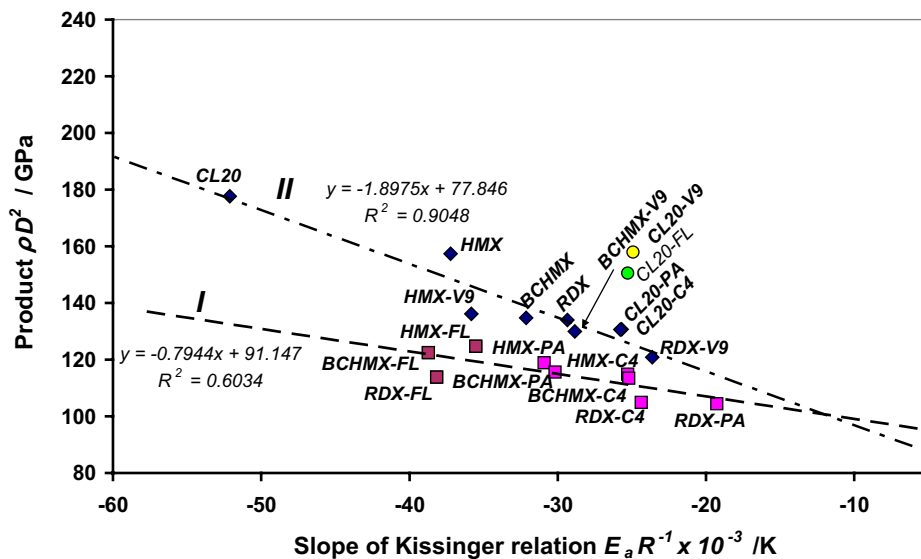


Figure 3. Relationship (3) between the product of the density and the square of the experimental detonation velocities, on the one hand, and the slope of the Kissinger relation for the PBXs studied, on the other.

Regarding the slope lines in Figures 1, 2 and 3, it can be seen that a negative slope corresponds to decomposition in which only one of the mixture components plays a decisive role. In emulsion explosives it is ammonium nitrate and in PBXs it is the nitramine. In the fortified emulsion explosives, decomposition of the nitrate might be also complicated by the decomposition of the admixed high explosive (influence of AN on nitramine decomposition – see paper [22]). There might also be synergistic effects at work with the oxidiser and the explosive affecting each other. This effect is clearly visible in the liquid mixtures of hydrogen peroxide with alcohols, mainly with ethanol (this alcohol slowly decomposes the peroxide and is itself oxidized to acetaldehyde, already at normal temperature [18]).

4 Conclusions

The known relationship between the activation energies of thermal decomposition and the squares of the detonation velocities of energetic materials (EMs) [1-3, 5-8] belongs in the area of relationships of the type “Performance – Sensitivity”; applying this relationship to the mixed EMs, it is possible to say that:

- a) considering the above mentioned relationship and using the output from simple DTA, evaluated by the Kissinger method, it is possible to estimate that part of the condensed explosive mixture, which is why it is a main trigger of the explosive reaction in the given mixture;
- b) considering the above mentioned relationships and using the output from simple DTA, evaluated by the Kissinger method, it might be possible to postulate a difference between the chemistry of detonation in PBXs with CL-20 fillers, on the one hand, and that for explosive mixtures with other nitramine fillers, on the other;
- c) considering the above mentioned relationships in the case of polyfluorinated binders, it might be postulated which of them should be preferable for achieving a higher performance; here polyfluoropolymers with non-fluorinated aromatic building units in their compositions seem to be less-favoured in comparison with polyfluoroparaffinic-olefins.

5 References

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