



Recent Advances in the Study of the Initiation of Energetic Materials using Characteristics of Their Thermal Decomposition Part I. Cyclic Nitramines

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Abstract: Arrhenius parameters, E_a and $\log A$, of 17 cyclic nitramines, derived from the Russian vacuum manometric method (SMM) and compatible thermoanalytical methods, have been used in this study. The detonation velocity, D , at maximum theoretical crystal density, of the nitramines in this study was taken as a characteristic of their detonation. On the basis of known relationships between their E_a and D^2 values (modified Evans-Polanyi-Semenov equation), the specific influence of some physicochemical properties on their thermal decomposition was shown. A new logarithmic relationship was found between the rate constant k , of the unimolecular thermal decomposition of the nitramines studied at 230 °C, and their D values. A fundamental characteristic of this new relationship rests on the equivalency of the primary fission processes in the low-temperature thermal decomposition and on the detonation initiation of the nitramines under study. Both these relationships confirm the problems encountered in the kinetic specification of the thermal decomposition of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX). These problems, and also the possible influence of the pre-decomposition states on the thermal decomposition of the nitramines studied, are discussed.

Keywords: Arrhenius parameters, detonation velocity, explosives, initiation, manometric method, nitramines

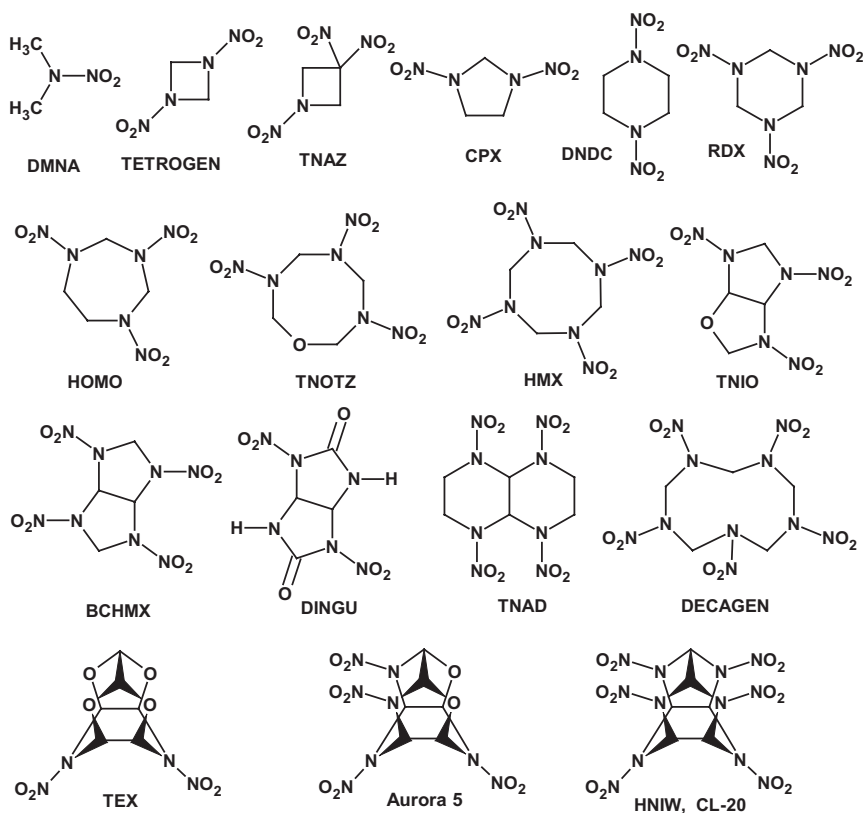
1 Introduction

Some thirty-three years ago, relationships were 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 then also for nitramines, nitrosamines and nitrate esters [3]. Later studies have shown that the most valuable thermal decomposition characteristics for the above-mentioned relationships are the Arrhenius parameters obtained by means of the Russian manometric method (SMM, see Refs. [3-7] and quotations therein) or those parameters derived from methods that give comparable results (especially differential scanning calorimetry (Refs. [2, 3, 6, 7] and quotations therein). The data obtained by the SMM method are known to correspond to the non-autocatalyzed stage of thermal decomposition of the given material, *i.e.* to the molecular structure (Refs. [6, 7] and quotations therein), and also to the absolute values of the corresponding Arrhenius parameters.

The current paper shows some new results obtained by applying the published E_a and $\log A$ values from SMM and compatible methods, in relation to the detonation velocities of the individual nitramines, together with some new conclusions in this area.

2 Data Sources

Data used for the study of the individual nitramines were taken from the published literature and are grouped in Table 1 for both the Arrhenius parameters and the detonation velocities; these velocities, for the theoretical maximum density, taken from the literature were mostly calculated by the Kamlet and Jacobs method [8] (these values were taken from papers [9, 10]), and in some cases by the method of Rothstein and Petersen [11]. The individual nitramines studied are shown in the following formulae:



In the cases of BCHMX, β -HMX, TEX, DINGU and ϵ -HNIW, heating for 30 minutes at 190 °C was carried out by means of Thermogravimetry (TG, Netzsch 209F3 instrument, Al₂O₃ crucible). The BCHMX used here was prepared in our laboratory [12], and TEX [14] and DINGU [15] were also produced in our laboratory. The β -HMX was imported from Russia. BCHMX and TEX were purified by crystallization from an acetone-water mixture, DINGU from fuming HNO₃ and CL-20 from ethyl acetate-hexane (solvent-antisolvent). HMX was used in its original state. Scanning Electron Microscope photographs of the crystals of the nitramines mentioned, before and after heating, are shown in Figures 2 and 3. The TGA recordings from heating are shown in Figure 4. For these nitramines the simple DTA readings were also made by means of a DTA 550 Ex apparatus for thermal analysis of explosives [13]: the measurements were carried out at atmospheric pressure, the tested sample being in direct contact with the ambient atmosphere. We used a linear rate of temperature increase of 5 °C min⁻¹; Figure 5 presents the cumulative DTA-readings.

Table 1. A list of the nitramines studied, showing the Arrhenius parameters (E_a in $\text{kJ}\cdot\text{mol}^{-1}$ and $\log A$ in s^{-1}) of their low-temperature thermal decomposition including the calculated rate constants k at $230\text{ }^\circ\text{C}$

Data No.	Chemical name	Code designation	Arrhenius parameters						Detonation velocity		
			Method of evaluation	Temp. region [K]	State of decompn	E_a	$\log A$	Ref.	k [s^{-1}] at $230\text{ }^\circ\text{C}$	D [km s^{-1}]	Ref.
1.1	2-Nitro-2-azapropane	DMNA	IR	298	solid	192.5	14.2	20	1.62E-06	6.29	9
1.2		DMNA	NMR	360 ^e	liquid	159.8	14.7	19	1.27E-02		
2.1	1,3-Dinitro-1,3-diazetidene	TETROGEN ^a	calcd.	450 ^e		153.1	14.1 ^c	21	1.59E-02	8.46	9
3.1	1,3,3-Trinitroazetidene	TNAZ	DSC	400-510	liquid	161.6	15.7	22	8.27E-02	8.62	10
4.1	1,3-Dinitroimidazolidine	CPX	manometric	423-473	liquid	149.4	13.5	23	9.65E-03	7.76	9
4.2		CPX	manometric	383-403	solid	197.8	18.7	24	1.44E-02		
5.1	1,4-Dinitropiperazine	DNDC	manometric	489-507	solid	198.4	17.3	23	4.97E-04	6.75	9
6.1	1,3,5-Trinitro-1,3,5-triazinane	RDX	manometric	486-572	liquid	198.9	18.5	25	6.98E-03	8.89	9
6.2		RDX	DSC	486-525	liquid	197.1	18.3	26	6.78E-03		
6.3		RDX	manometric	423-470	solid	213.5	18.6	27	2.68E-04		
6.4		RDX	manometric	423-470	solid	217.6	19.1	28	3.18E-04		
7.1	1,3,5-Trinitro-1,3,5-triazepane	HOMO	¹⁵ N NMR	490 ^e	(solid)	207.1	18.6	18	1.24E-03	8.23	9
8.1	3,5,7-Trinitro-1-oxa-3,5,7-triazocane	TNOTZ	manometric	463-498	liquid	190.1	16.4	29	4.55E-04	8.55	b
9.1	3,4,6-Trinitrohexahydro-2H-imidazo[4,5-d][1,3]oxazole	TNIO	manometric	408-428	solid	203.9	18.2	30	1.06E-03	8.90	b
9.2		TNIO	manometric	440-468	liquid	166.4	15.2	30	8.30E-03		
10.1	β -1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	β -HMX	manometric	544-587	solid	220.5	19.5	25	3.99E-04	9.13	9
10.2		β -HMX	DSC	544-558	solid	214.6	18.8	31	3.26E-04		

Data No.	Chemical name	Code designation	Arrhenius parameters						Detonation velocity		
			Method of evaluation	Temp. region [K]	State of decompn	E _a	log A	Ref.	k [s ⁻¹] at 230 °C	D [km s ⁻¹]	Ref.
10.3		β-HMX	MS	534-549	solid	209.0	17.8	32	1.25E-04		
11.1	<i>cis</i> -1,3,4,6-Tetranitrooctahydroimidazo[4,5-d]imidazole	BCHMX	manometric	453-473	solid	210.2	18.0	30	1.48E-04	9.05	10
12.1	<i>trans</i> -1,4,5,8-Tetranitrodecahydro-pyrazino[2,3- <i>b</i>]pyrazine	TNAD	DSC	477-507	solid	210.0	18.9	33	1.23E-03	8.52	10
13.1	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaaazacyclodecane	DECAGEN ^a	¹⁵ N NMR	520 ^e	solid	213.5	18.6	18	2.68E-04	8.96	9
14.1	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	manometric	483-498	solid	196.8	15.4	34	9.17E-06	8.47	9
15.1	4,8,10,12-Tetranitro-2,6-dioxa-4,8,10,12-tetraazaisowurtzitane	α-Aurora 5	manometric	463-483	solid	188.4	16.7	37	1.36E-03	8.68	17
15.2		β-Aurora 5	manometric	423-463	solid	188.8	16.8	37	1.56E-03	8.94	17
16.1	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	ε-HNIW	TGA	433-453	solid	172.0	13.8	35	8.66E-05	9.80	16
16.2		ε-HNIW	DSC	483-533	solid	176.0	15.1	36	6.64E-04		
16.3		ε-HNIW	manometric	443-473	solid	216.9	19.8	37	1.88E-03		
16.4		ε-HNIW	iso-TGA	446-484	solid	223.4	20.5	38	1.99E-03		
16.5		γ-HNIW	iso-TGA	445-467	solid	196.0	17.7	39	2.21E-03	9.40	d
17.1	1,4-Dinitrotetrahydroimidazo[4,5-d]imidazol-2,5-(1H,3H)-dione	DINGU	manometric	458-473	solid	203.0	18.5	30	2.62E-03	8.45	b

Note: a) a substance which has not yet been synthesized; b) calculated according to semi-empirical methods [11]; c) calculated in Ref. [9]; d) calculated by means of method [8]; e) the estimated value for the *k* value calculations.

3 Results and Discussion

The homolytic character of primary fission in both the detonation and the low-temperature thermal decomposition of energetic materials (for relevant quotations, see Refs. [2-5, 7]) was the original reason why Zeman chose to use the modified Evans-Polanyi-Semenov equation (E-P-S) [7] to study the chemical micro-mechanism governing initiation of energetic materials [2-5, 7]; it has the following form:

$$E_a = \alpha Q + b \quad (1)$$

and, using the relationship defined between detonation velocities and heats of explosion Q [3, 4, 7] in the form:

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

where γ is the polytropy coefficient, this transforms equation (1) into the following form:

$$E_a = aD^2 + b \quad (3)$$

The original E-P-S equation describes a relationship between the activation energy, E , of the substitution reactions of free radicals and the corresponding heat of reaction, ΔH , of a narrow set of substance structures. The equation shows that the strength of the bond being split is a decisive factor in the associated reaction. In both equations (1) and (3), the energy, E , can be the activation energy of thermal decomposition, E_a [2-5, 7], the slope $E_a \cdot R^{-1}$ of the Kissinger relationship [2-5], the energy of electric spark, E_{ES} [3-5], or the drop energy, E_p [3-5]. It may be substituted by the charge, q^N , or the ^{15}N NMR chemical shift of the nitrogen atom in the most reactive nitro group [2-5] in the molecule, by the net charge of this nitro group [4, 5], or by the half-wave polarographic potential [4, 5]. Relationship (1) for a set of nitramines has already been described [2-4], but since then new molecular structures of the said explosives have been synthesized and studied. This gives the possibility of examining equations (1) and (3) using these new nitramine structures. In this connection, Figure 1 represents equation (3) for a group of cyclic nitramines with four new compounds (BCHMX, TNIO, TNOTZ and Aurora 5).

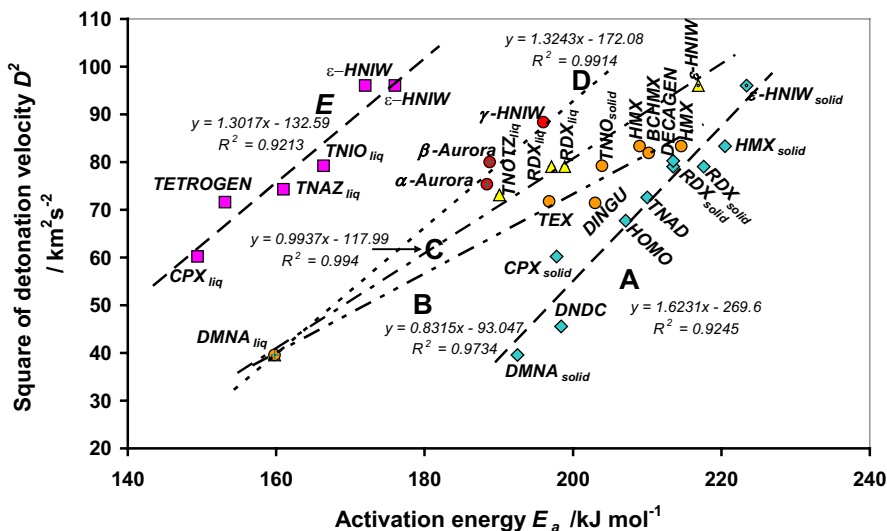
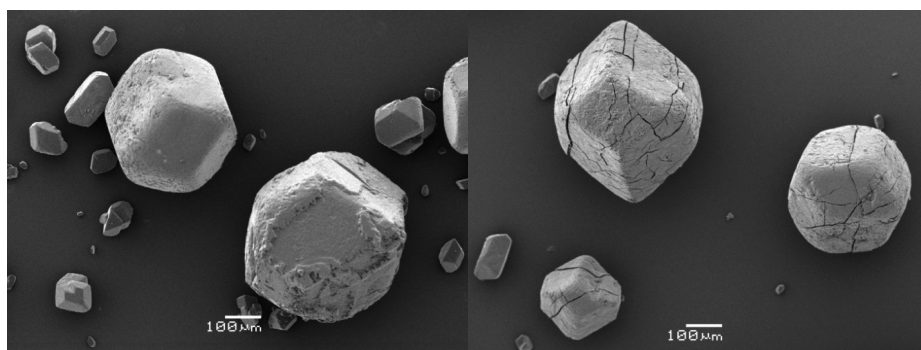


Figure 1. Relationship (3) between the squares of the calculated detonation velocities and experimental activation energies of the thermal decomposition for the nitramines studied.

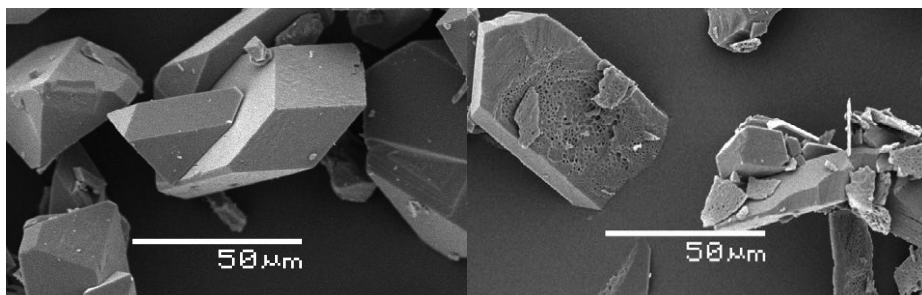
The relationships in Figure 1 generally show increasing E_a values with increasing energy content of the molecules studied. The compounds in this figure fall into several sub-groups. The nitramines, associated with line A, decompose in their solid state. Group C corresponds to compounds which decompose in the liquid state; data 16.3 of ϵ -HNIW correlate with this line (for solid state decomposition [37]). In the group around line B, nitramine HMX (data 10.2 and 10.3) might melt in its decomposition products [6]: decomposition of solid compounds very often proceeds through the liquid phase, formed as a result of the melting of impurities, the decomposition products, or their eutectic mixture with the original substance [40] – this is the problem of the differences in specification in the kinetics of the HMX decomposition in its supposed liquid and solid states [4, 6]. This might also be the case with BCHMX.

One difference between the β -HMX and BCHMX molecules lies in the presence of crowding in the latter [41] (it has a rigid structure). As Figures 2a and 2b show, the β -HMX crystal forms cracks during heating for 30 minutes at 190 °C due to the $\beta \rightarrow \delta$ transition; the process of decomposition of HMX during this polymorphous transition is signalled only by the start of a rather significant production of gas [42]. Once the β -HMX crystal surface expansion has ended, its decomposition rate is diminished [42] – see the corresponding TG readings in Figure 4.



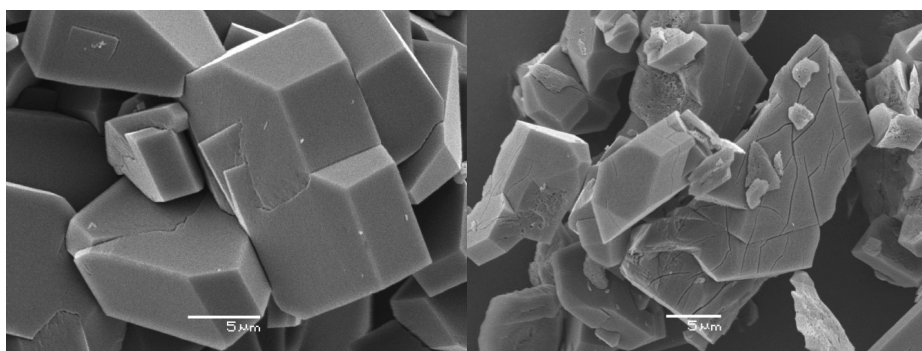
a) Original β -HMX crystals
(white colour)

b) Heated β -HMX crystals with cracks
(dark white colour)



c) Original BCHMX crystals
(white colour)

d) Heated BCHMX crystals with
bubble traces (white colour)



e) Original DINGU crystals
(white colour)

f) Heated DINGU crystals with
cracks and bubble traces
(dark green colour)

Figure 2. A comparison of the surface structures, using the SEM technique, for original crystals of HMX, BCHMX and DINGU with those of crystals heated under isothermal TG at 190 °C for 30 minutes.

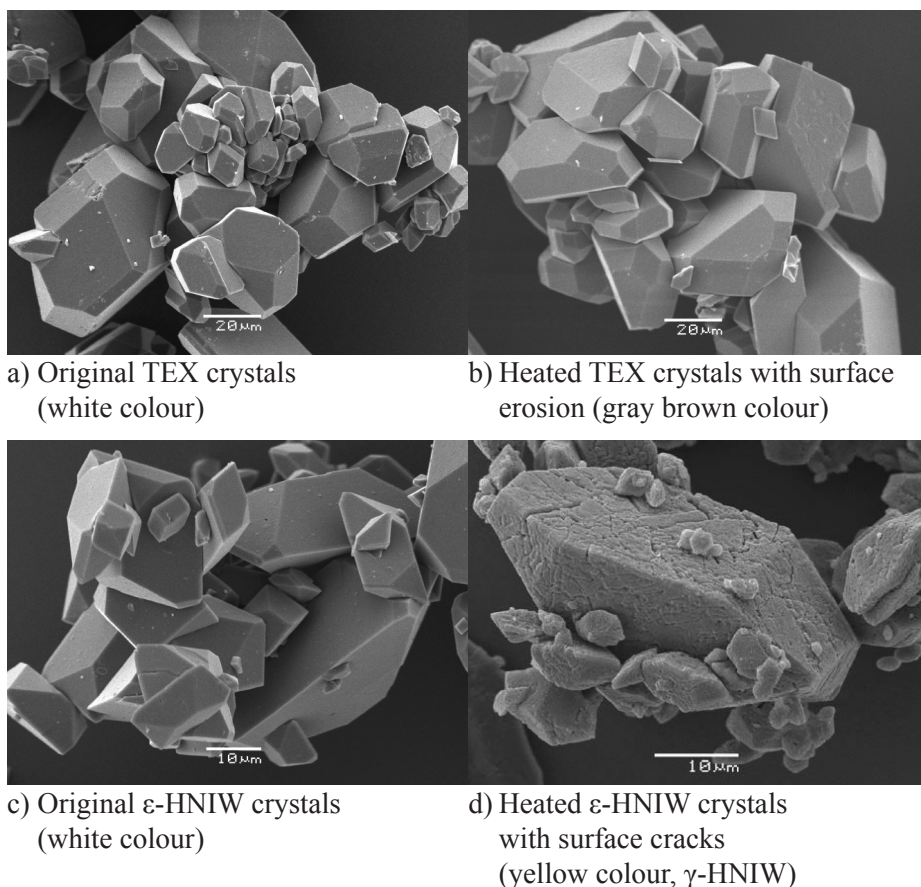


Figure 3. A comparison of the surface structures, using the SEM technique, for original crystals of TEX and ϵ -HNIW with those of crystals heated under isothermal TG at 190 °C for 30 minutes.

On the other hand, melting-dissolution of the BCHMX crystals (Figures 2c and 2d) leads to a relatively quick and more profound decomposition at 190 °C [36] (see also the corresponding TG readings in Figure 4). It should be mentioned here that the visual melting point of BCHMX is at 262 °C with decomposition [43] and, using DTA measurements, no endothermic or exothermic reaction is detected before 205 °C [42, 43] – see also Figure 5. It is possible to observe similar behavior for TNIO crystals (this nitramine is structurally similar to BCHMX). Damage to the crystals during static heating conditions is also clearly observable in DINGU (see Figures 2e and 2f), but very weakly in TEX (see Figures 3a and 3b). These substances are the most stable nitramines

according to the TG-readings in Figure 4, but under dynamic conditions there is a big difference between them (Figure 5).

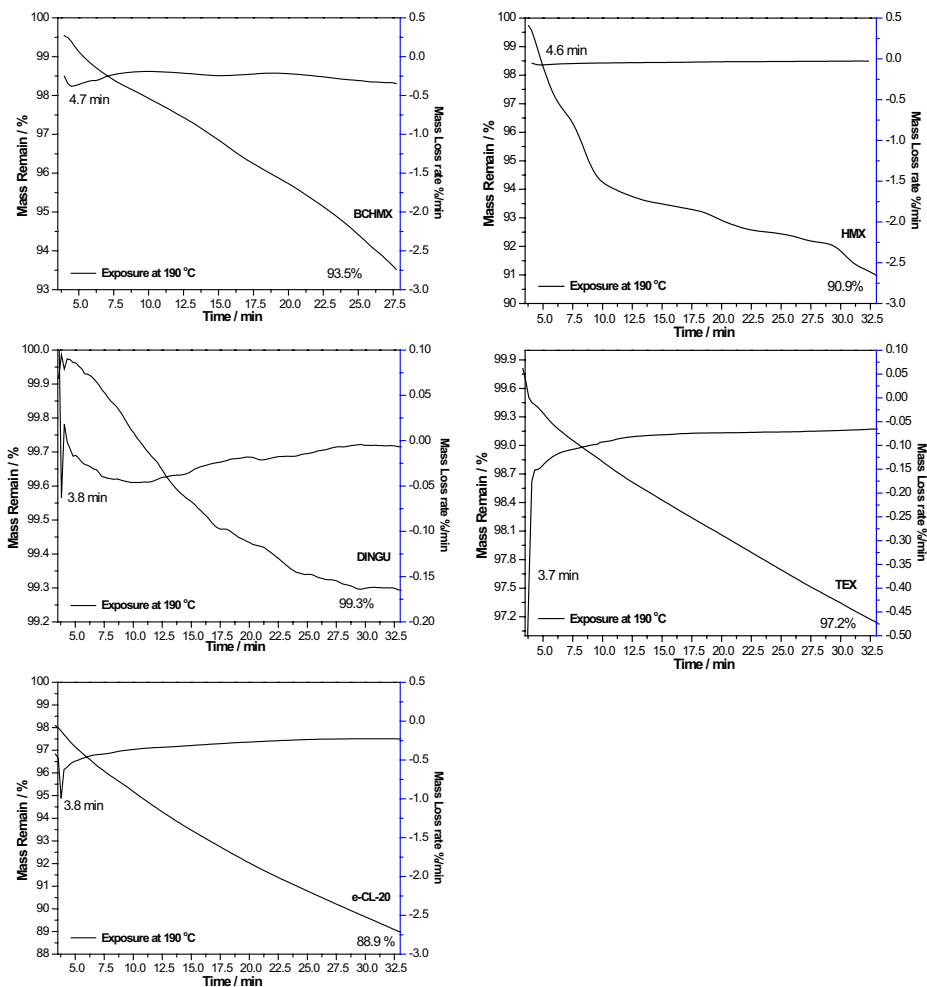


Figure 4. The TGA readings from heating under isothermal TG at 190 °C for 30 minutes of crystals according to Figures 2 and 3 – left to right and top down they are: BCHMX, β -HMX, DINGU, TEX and ϵ -HNIW. Order of decreasing reactivity in the sense of this experiment: ϵ -HNIW (ϵ -CL-20) > β -HMX > BCHMX > TEX > DINGU.

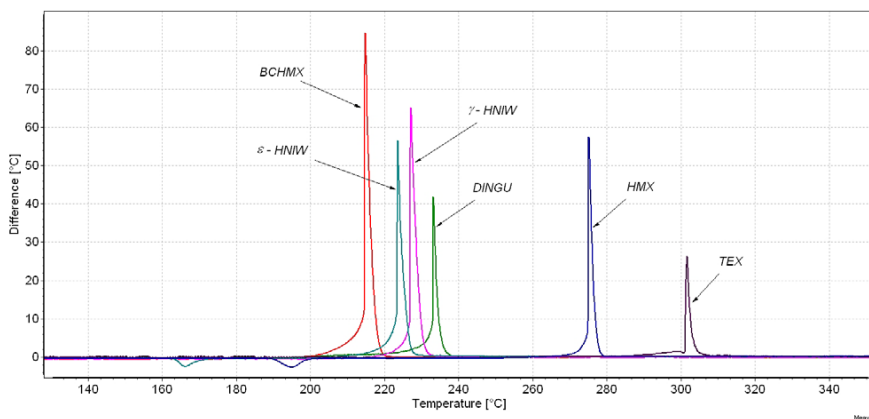


Figure 5. Cumulative DTA-readings of the nitramines studied: here the endothermic peak around 165 °C corresponds to the ϵ - γ polymorphic transition of HNIW and the one around 190 °C to the β - δ polymorphic transition of HMX.

Line D in Figure 1 probably corresponds to decomposition in the transition between the liquid and solid states; here data for γ -HNIW (*i.e.* No. 16.5) correlate well. Nedelko *et al.* [39] have studied thermal decomposition of various modifications of HNIW and have shown that all modifications are transformed into γ -HNIW before decomposition. This transformation has a complicated progression [39] and the positions of the ϵ -HNIW data, No. 16.4 (group A), and the already mentioned No. 16.3 (group B) might be connected with this fact. Chukanov *et al.* [44] stated that the ϵ - γ polymorphic transition changes the conformation in the HNIW molecule, the stressed aza atom appears and the co-linear nitrogen lone electron pair is thus differently oriented here. This change is preceded by an induction period, with the formation of active microregions which are loaded by a mechanical stress gradient [44]. Damage to the resultant γ -HNIW crystal in this way might be as shown in Figure 3d. We have not had the chance to study crystals of Aurora. It is clear that the ϵ - γ polymorphic transition should be influenced by the purity of the original ϵ -HNIW crystal. The positions of the ϵ -HNIW data in Figure 1 can be associated with this statement. Changes in the crystal lattices of BCHMX, HMX, and HNIW prior to thermal decomposition might well be a reason for the differences in the order of thermal stabilities of these nitramines under both the static (Figures 3 and 4) and the dynamic (Figure 5) conditions of the corresponding experiments in this paper.

The positions of the DMNA data, *i.e.* data for a non-cyclic nitramine, in Figure 1 are logical; all compounds belonging to lines A, B, C and D, can be derived by hypothetical substitutions from this nitramine. Assigning DMNA to the family of cyclic nitramines has already been shown in the framework of the physical stability study of nitramines [45]. However, the DINGU structure is not fully derivable from the DMNA molecule and this might be a reason for its data position in Figure 1.

Line E in Figure 1 represents nitramines with crowded molecules, mostly in the liquid state. Inclusion of data 16.1 and 16.2 for ϵ -HNIW within this group might be mainly due to crowding in its molecule, but also by the above-mentioned dissolution in impurities and products of the HNIW decomposition; in each case, data 16.1 and 16.2 correspond to the HNIW thermal decomposition in its liquid state (solution).

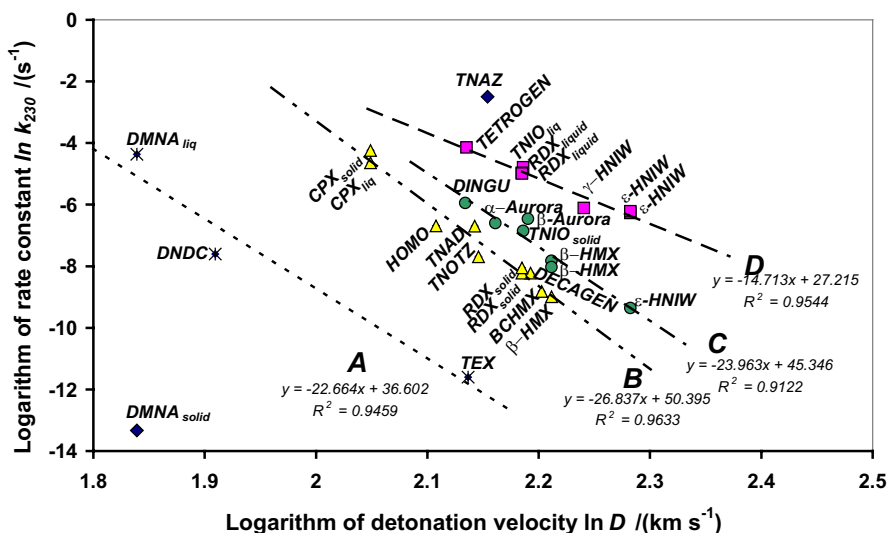


Figure 6. Logarithmic relationship of the rate constants of the monomolecular thermal decomposition at 230 °C and the detonation velocities of the nitramines studied.

An interesting relationship results from a comparison of the rate constants, k , of unimolecular thermal decomposition at 230 °C and the detonation velocities, D , at maximum theoretical crystal densities, of the nitramines in the study. This type of relationship was tentatively intimated in earlier papers [46, 47] but on the basis of only a few points obtained from just four molecular structures. More detailed studies with a greater number of data points are shown in Figure 6,

which presents such a relationship in a logarithmic form and which generally shows a reciprocal proportion between the $\ln k$ and $\ln D$ values. Also, this relationship confirms the equivalency of the primary fission chemical processes in low-temperature thermal decomposition and in the detonation of the nitramines concerned. The data positions in Figure 6 are influenced also by thermochemical factors – this is clearly shown by line A and the position of the data for TNAZ in this figure. It seems that the influence of the physical state of these nitramines on their positions is less in comparison with Figure 1. Data for the nitramines associated with line B in Figure 6 correspond to thermal decomposition largely in the solid state; it is not without interest that data 10.1 for HMX correlates with this line as well as in the case of Figure 1 (here group A). It might be concluded that data 10.1 actually corresponds to the thermal decomposition of HMX in the solid state. Group C contains nitramines for which it is not fully clear which physical state they are found in (micro-regions in their crystals) during the initial phase of their thermal decomposition (see earlier discussion on Figure 1). Line D corresponds to the thermal decomposition of compounds studied largely in the liquid state; the correlation of the γ -HNIW data with this line clearly shows that this polymorphic modification substitutes for a liquid phase of HNIW. In the case of this caged nitramine the problem of specification and interpretation of the real kinetic data at the beginning of its decomposition is again confirmed. As in the case of the impact sensitivity of HNIW, its thermal stability must strongly depend not only on its purity but also on the quality of its crystal structure. Only the presence of water in the crystal lattice of HNIW has been studied in detail from the point of view of its influence on the thermal and morphological stability of this particular nitramine [38, 39, 44].

4 Conclusions

The use of the Arrhenius parameters of newly synthesized cyclic nitramines has extended the application possibilities of the known relationship between activation energies of thermal decomposition and the square of the detonation velocity (originally referred to as the modified Evans-Polanyi-Semenov equation [3-5, 7]). This equation differentiates these parameters not only according to the molecular structure and the physical state of the energetic materials during their thermal decomposition, but it also allows certain hypotheses about the formation of reactive micro-regions (pre-decomposition states) in the heated nitramine crystals to be made. This newly found logarithmic relationship between the rate constants, k , of the unimolecular thermal decomposition and the detonation

velocities of these nitramines, generally shows decreasing k values with increasing velocities. A key part of this relationship rests on the equivalency of the primary fission processes in the low-temperature thermal decomposition and in the initiation and growth of detonation in the nitramines studied. The division of the compounds studied here is similar to the first mentioned relationship, *i.e.* the influence of the molecular structure is slightly lower, the influence of the physical state in thermal decomposition is clear and, in addition, the influence of the thermochemistry of detonation is observed. All of these relationships confirm the problems found in the kinetic specification of HMX and HNIW thermal decomposition.

5 References

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