

New aspects of initiation reactivities of energetic materials demonstrated on nitramines^{☆,☆☆}

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Abstract

A brief survey is presented of the author's results obtained from studies of the chemical micro-mechanisms of nitramines initiation from the point of view of organic chemistry. The relationships have been presented and discussed between the characteristics of impact and electric spark sensitivities, detonation and thermal decomposition, on the one hand, and ¹⁵N NMR chemical shifts of nitrogen atoms of nitramino groups, on the other. In the case of the impact sensitivity, the said relationships involve the ¹⁵N shifts of the amino nitrogen atoms carrying the nitro group primarily split off from the molecule. In the case of the initiation by shock, heat and electric spark, the ¹⁵N shifts of nitrogen atoms in the primarily split off nitro groups themselves are involved. Also, the relationships are presented between the characteristics of thermal reactivity and values of the electronic charges at the nitro groups that are primarily split off. It has been stated that the chemical micro-mechanisms of primary fission processes of molecules of nitramines in the initiation by mechanical stimuli (inclusive the detonation course) and electric spark should be the same as in the case of their low-temperature thermal decomposition. It has been found that the electron structure and close neighbourhood of nitrogen atom of the primarily leaving nitro group is a dominant factor in initiation by shock, electric spark and heat. In the case of initiation by impact a key role plays characteristics of amino nitrogen atoms which are carriers of these most reactive nitro groups. Also mentioned is relevance of the modified Evans–Polanyi–Semenov relationship. On the basis of the findings presented it also has been stated that the detonation transformation itself of the nitramines should be preceded by an induction period.

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1. Introduction

At present, it is a generally accepted idea that nitro groups represent the primary cause of initiation reactivity of polynitro compounds. A number of papers, inclusive of some striking pieces of experimental evidence, deal with relationships between the chemism of homolytic fragmentation of these compounds in the initiation processes and the chemism of low-temperature thermal decomposition (see Introduction in Ref. [1] and references herein). However, the approaches to study of micro-

mechanism of initiation of these compounds are dominated by opinions of physicists (e.g. Refs. [2–7]). If the problems of initiation chemistry are mentioned in literature at all, then this is done very reluctantly and mostly without any broader chemical contexts. With regard to the reasons mentioned, this present paper offers a review of results of studies of initiation mechanisms obtained on the bases of approaches of physical organic chemistry to the problem given over the last seven years. These results are demonstrated on nitramines, which in their molecular structure are relatively simple polynitro compounds, and the mechanism of primary homolysis of their molecules is well understood [8–11].

2. Philosophy of approach

Recently, the relationships were found between outputs of non-isothermal differential thermal analysis and characteristics of detonation of polynitro arenes [12,13] and also nitramines,

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nitrosamines and nitric esters [13,17]. A more detailed analysis of these results for polynitro arenes shows that their classification in the sense of the relationships found is given primarily by steric conditions and electron configuration in the ground state of the reaction centre of the molecule [12,13] (see also classical French studies from this area [14–16]). In this context, by the reaction centre is meant the grouping of atoms and/or functional groups in the molecule whose primary chemical changes initiate decomposition of this molecule (see figures below, especially Fig. 7). At the same time, the said facts represent one of the basic principles of approach of organic chemistry to dealing with reactivity problems in general.

The electron configuration and steric conditions within the reaction centre of the molecule can be represented by NMR chemical shifts of the key atoms of the centre. The shifts of these atoms should correlate with characteristics of initiation reactivity of individual energetic materials [1,18–22]. It is known that the application of ^{15}N NMR chemical shifts to the study of chemical micro-mechanism of initiation of nitramines by heat [1,18], impact [1,19], shock [1,20] or electric spark [1,21,22] has given highly valuable results. It can be argued against this approach that the NMR studies carried out in solutions neglect important crystal-lattice effects that are vital in the determination of explosive properties [23]. We pointed out this possibility as early as in Ref. [24] using the particular case of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaza-isowurtzitane (HNIW). From several papers [1,18–20] and the following text, it will be seen that this fact has no fundamental significance for studies of chemical micro-mechanism of initiation of energetic materials. Also, a study of direct relation between electronic charges at

nitrogen atoms of primarily split off nitro group and thermal reactivity of nitramines [25] is a logical supplementation of this type of investigation.

Outputs from the above-mentioned studies are subsequently compared with some findings of molecular dynamic approach to problems of initiation [28–32] as well as with some results of physics of solid-state application to this problem [33,34].

3. Results and discussion

3.1. Impact reactivity

We were engaged in study of impact sensitivity, defined as the so-called “first reaction” (i.e. the first chemical change of the sample is taken as positive result), in the past [19,35]. An analysis of the relationship between the corresponding drop energies, E_{dr} , and ^{15}N NMR chemical shifts of nitrogen atoms of nitramine groups led to formulation of the relationship [19] documented in Fig. 1. The correlation involves the chemical shifts, δ_{A} , of nitrogen aza-atoms (amino nitrogen atoms) carrying the nitro groups that are leaving first during the initiation (i.e. the most reactive nitro groups). From the point of view of electron structure and close neighbourhood, the individual nitramino groups in polynitroamines are usually not equivalent to each other. Therefore, also their abilities of participation in primary initiation processes are different. This fact is documented by Fig. 1 and also by other relationships listed hereinafter.

The aza (amino)-nitrogen chemical shifts, δ_{A} , in the nitramino groups are expected to be influenced by the nitrogen hybridization, the size and conformation of molecule, and the

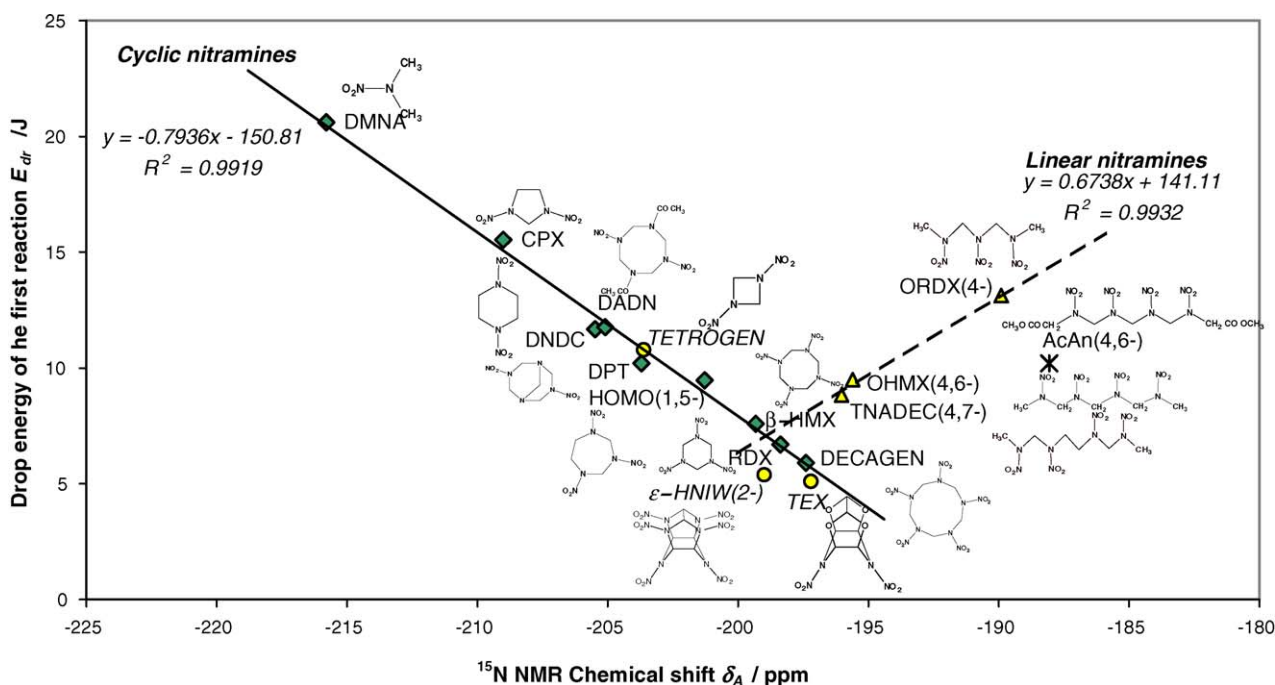


Fig. 1. Relationship between drop energy, E_{dr} , of “the first reaction” and ^{15}N NMR chemical shifts, δ_{A} , of aza-nitrogen atoms carrying the primarily leaving nitro group in the nitramine molecule (in bracket given are the respective positions in molecule, i.e. position of reaction centre); taken from Ref. [19], complemented by the data of TETROGEN, HNIW and TEX [1].

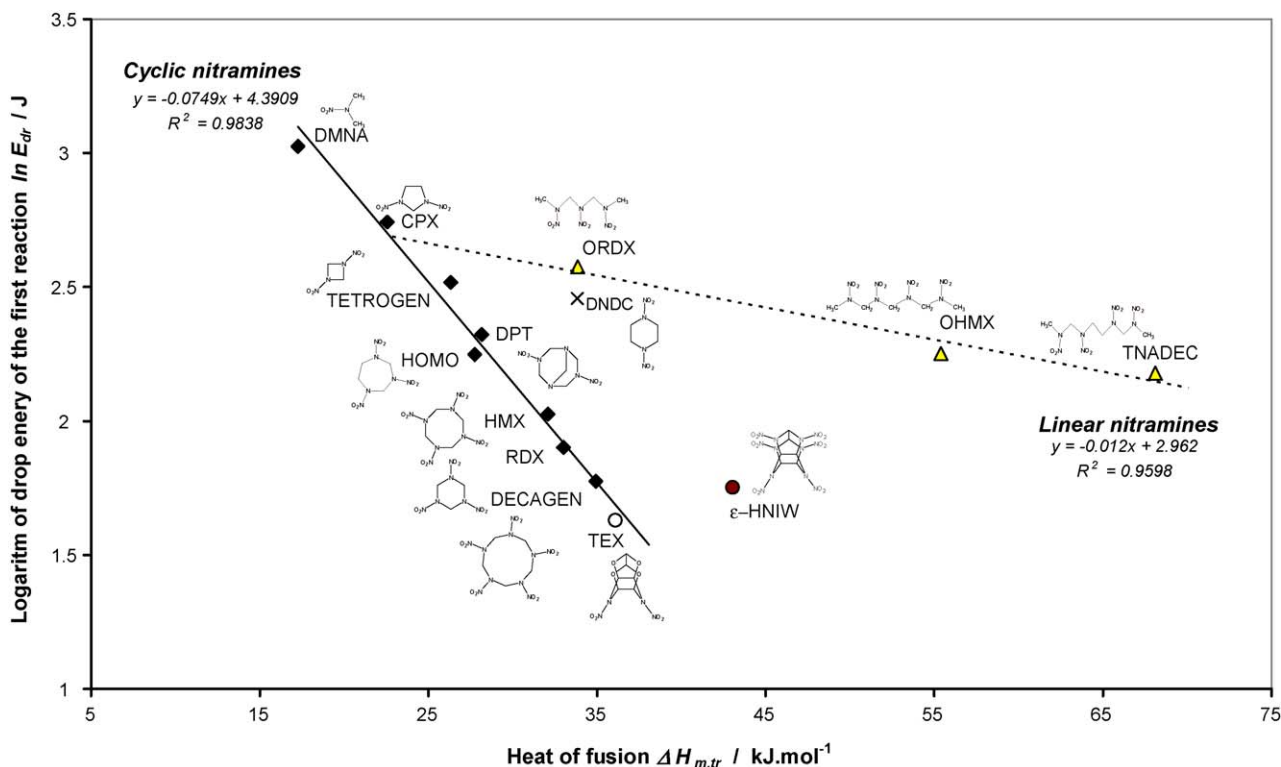


Fig. 2. Relationship between drop energy, E_{dr} , of “the first reaction” and heat of fusion, $\Delta H_{m,tr}$, of nitramines; taken from Ref. [19], completed by data of TEX [1].

extent to which the nitrogen lone pair is involved in π -bonding with NO_2 group. As the conformation and size of molecule plays dominant role in the intermolecular interactions in the corresponding crystal, the interactions should have a significant influence on the impact sensitivity. This hypothesis is verified by Fig. 2, which represents a relationship between the E_{dr} values and heats of fusion, $\Delta H_{m,tr}$, of nitramines [19]. The heat of fusion is defined here as a sum of heats of all the polymorphous transitions and of the heat of melting. As the heat represents the work needed for formation of defects in crystal lattice, the relationships found seem to stand in accordance with the ideas about the decisive role of plastic deformations of crystal [36–38] and of dislocations in energetic crystals [39,40] which they play in the initiation of energetic materials by impact or shock (also the crack temperature can be mentioned in this connection [41,42]). Here is a conjunction of approaches of the physical organic chemistry and of the physics of solid state.

3.2. Shock (detonation) reactivity

Paper [20] deals with the relationships between square of detonation velocities, D^2 , or heats of explosion, Q_{real} , on the one hand, and values of the ^{15}N NMR chemical shifts of the nitrogen atoms in nitramino groups, on the other. These relationships for the D^2 values are represented in Fig. 3. In contrast to the foregoing case, in this case such chemical shifts correlate whose values correspond to nitrogen atoms of nitro groups primarily split off during detonation [20].

3.3. Electric spark reactivity

Similarly, Fig. 4 represents the relation of the electric spark sensitivity to electronic structure and steric conditions in the reaction centre of nitramine molecules: here, the electric spark energy, E_{ES} , correlates with the ^{15}N NMR chemical shifts, δ_{N} , of nitrogen atoms of the most reactive nitro groups [1,22]. The relationships in this diagram are similar to those between the square of detonation velocity, D^2 , of nitramines and their δ_{N} values in Fig. 3. The mechanism of primary fragmentation should be identical in the two cases, even if there is no shock component present in the electric discharge. Absence of this component was justified on samples of 1,3,5-trinitro-1,3,5-triazinane (RDX) that were contaminated with crushed glass (i.e. by “hot spots”): the crushed glass markedly reduced electric spark sensitivity of the resulting mixture [43]. The said effect can be interpreted [43] on the basis of separation of RDX grains from each other by the introduced glass particles (hot spots develop here at the thinnest part of the individual solid under discharge, i.e. at contact micro-points of grains of the identical kinds [44]). An analogous effect of the introduced hot spots in lead azide was found by Stengach [45].

3.4. Low-temperature thermolysis

The ^{15}N NMR chemical shifts were used in analysis and prediction of the Arrhenius parameters of low-temperature decomposition of nitramines [18]. Fig. 5 presents the relationship between the activation energies, E_a , of this decom-

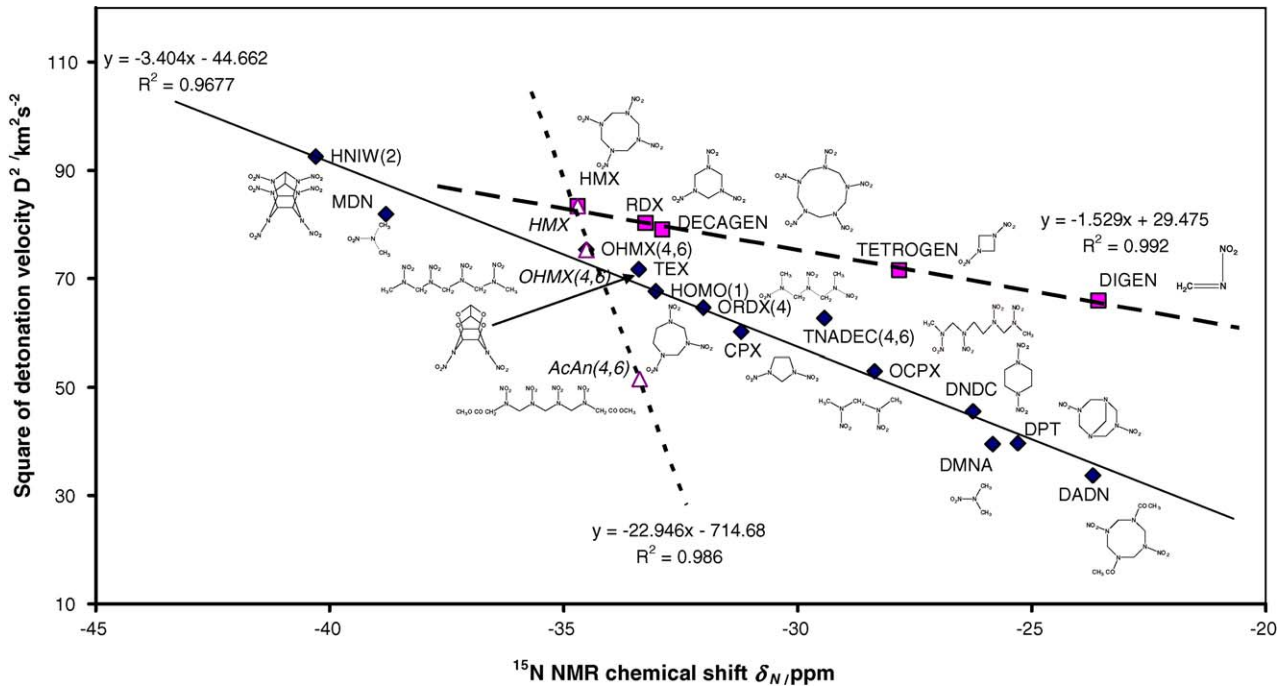


Fig. 3. Relationship between square of detonation velocity, D^2 , and ^{15}N NMR chemical shifts, δ_{N} , of nitrogen atoms of the primarily leaving nitro groups (in parenthesis given are the respective positions in molecule, i.e. position of reaction centre); repainted from Ref. [20].

position and the aforesaid chemical shifts, δ_{N} , of nitrogen atoms in the most reactive nitro groups [18]. No analogous relationship was found for the chemical shifts, δ_{A} , of azanitrogen atoms in nitramino groups. The found dependences of the type shown in Fig. 5 are discussed in detail elsewhere [18].

As was already stated, the abilities of nitramine groupings participation in primary initiation processes are different. This fact is documented also by the electronic charges at nitrogen atoms of the nitramines calculated on the basis of the Mulliken population analysis of electron densities, q^{N} , obtained by ab initio DFT B3LYP/6-31G** method [25]. The relationships

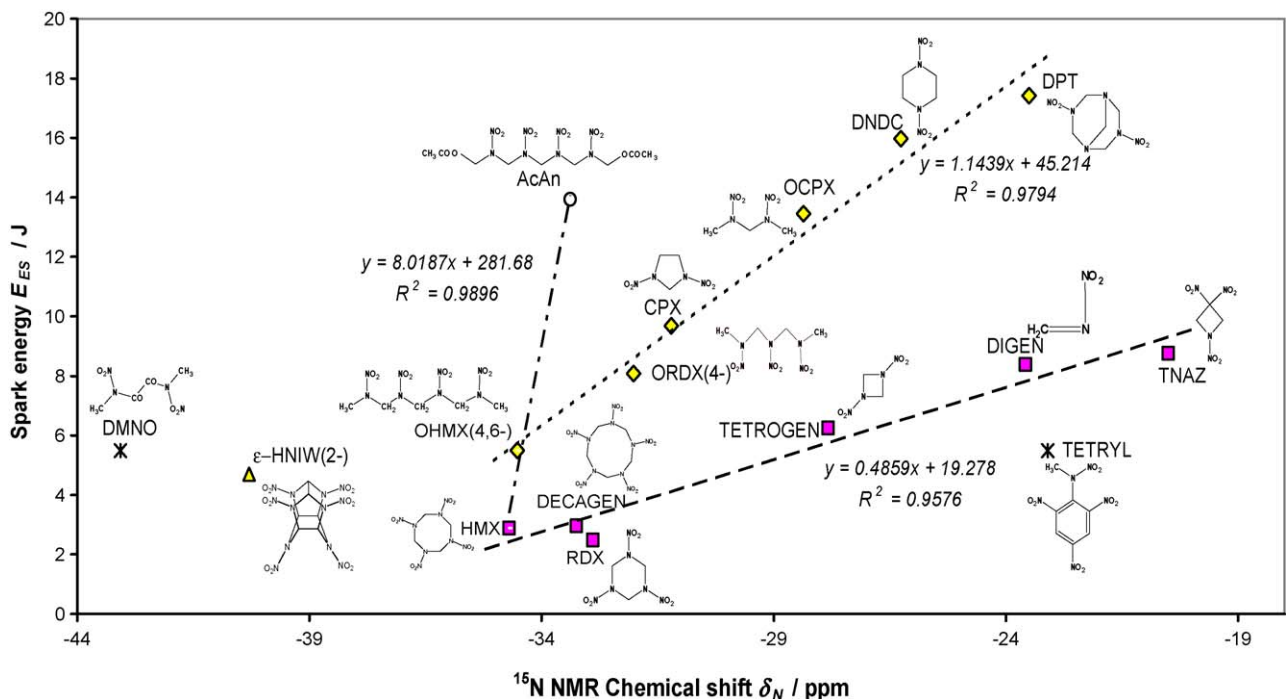


Fig. 4. Relationship between spark energy, E_{ES} (i.e. sensitivity to electric spark), and ^{15}N NMR chemical shifts, δ_{N} , of nitro-nitrogen atoms of the primarily leaving nitro groups (in parenthesis given are the respective positions in molecule, i.e. position of reaction centre) in nitramines; taken from Refs. [1,22].

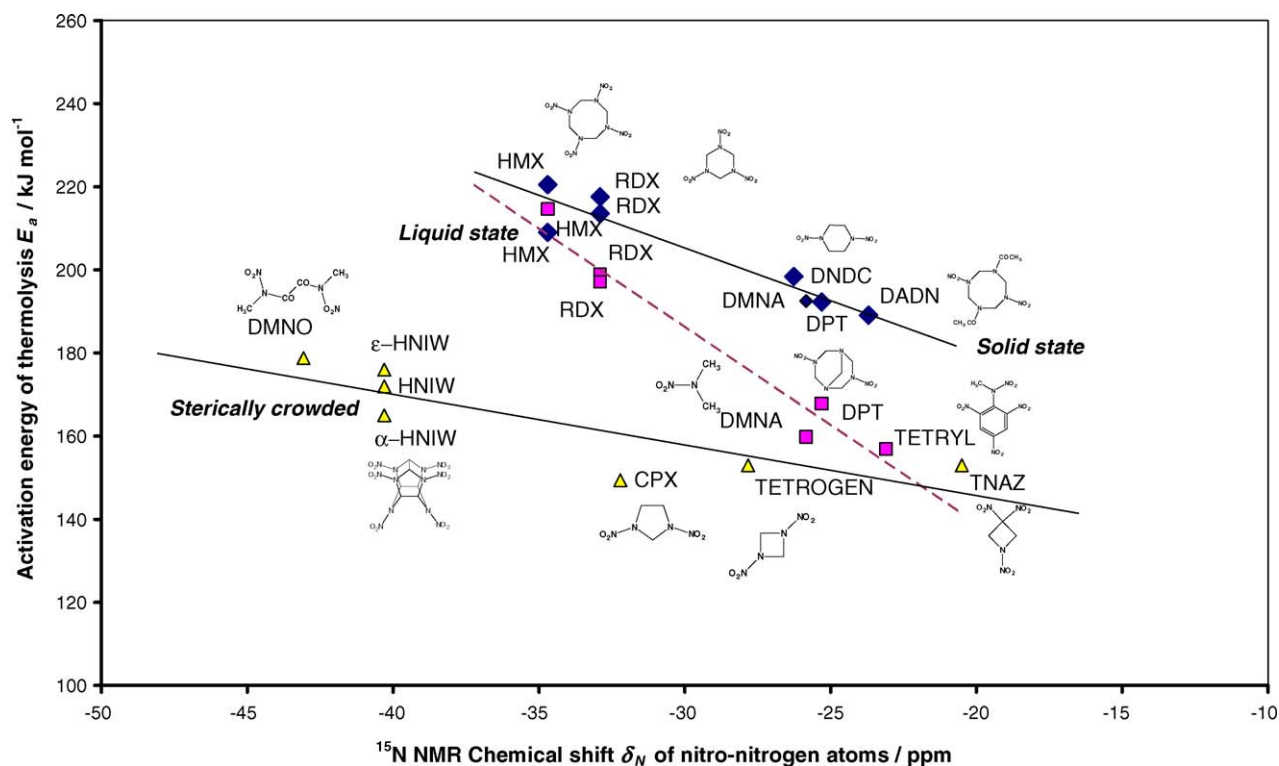


Fig. 5. Relationship between activation energy, E_a , of thermal decomposition under conditions of Russian manometric method and ^{15}N NMR chemical shifts, δ_{N} , of nitro-nitrogen of the primarily leaving nitro groups in the nitramine molecule (see Refs. [1,18]), complemented by the data of TNAZ ($E_a = 153.5 \text{ kJ mol}^{-1}$ taken from Ref. [11]; $\delta_{\text{N}} = -20.5 \text{ ppm}$ taken from Ref. [60]).

found between these charges at nitrogen atoms of primarily leaving nitro groups and thermal reactivity of a set of nitramines are documented in Fig. 6. The thermal reactivity is expressed here as the slope (activation energy) $E_a R^{-1}$ in the Kissinger relationship [46], which is used for evaluation of results of non-isothermal differential thermal analysis. The logical relationships of Fig. 6 are discussed in Ref. [25] as follows: the charge value at nitrogen atom of nitro group at 2 position in the molecules of α -HNIW and ε -HNIW correlates with both the lines A and B. This nitro group primarily leaves on shock initiation of HNIW [20] (see Fig. 3). The thermal decomposition of both polymorphous modifications of HNIW practically proceeds only after their transition to γ -HNIW [26]. The difference between mechanisms of these transitions of α -HNIW and ε -HNIW will probably cause a difference in arrangement of defects in crystal lattice in particular (i.e. a difference in intermolecular forces) in the resulting γ -modifications [26]. The different concentrations of crystal defects in the γ -modifications of HNIW, which have different histories, should make themselves felt in their different reactivity (in general).

If the N–N bond length exceeds 141.0 pm, Arrhenius parameters of the given nitramine thermal decomposition in the solid state correspond to those obtained from decomposition of this kind of substances in the liquid state [27]. Therefore, the $E_a R^{-1}$ values of HNIW (thermal decomposition in the solid state) correlate well with those of nitramines of the groups A and B (decomposition in the liquid state). From the point of view of the group B composition it may be added that 1,3-imidazolidine skeleton of CPX and 1,3,5-triazepane skeleton of HOMO form

parts of the “caged” skeleton of HNIW globular molecule. Line for group B is fulfilled by nitramine HOMO when using the charge q^{N} at nitrogen atom of nitro group at 1 position of its molecule; this nitro group also primarily leaves after shock initiation of the said nitramine [1,20] (see Fig. 3).

The composition of group C nitramines (TEX, DNDC and CPX) needs no comment. Within the group D nitramines, the data of DMEDNA and ORDX correlate with those of ε -HNIW. The molecular skeletons of these two nitramines can be considered as fragments of the molecular skeleton of HNIW (e.g. ORDX can be considered as an “open” HOMO molecule). The nitramine ORDX correlates with the data of group D by its q^{N} value of nitrogen atom of nitro group at 4 position; this nitro group also primarily leaves after shock initiation of ORDX [20,47] (see Fig. 3). The similar mechanism was also confirmed by molecular-dynamics simulation of action of shock and impact on linear nitramines [47] (see below) and by already mentioned analysis of action of these stimuli on linear and cyclic nitramines by means of the ^{15}N NMR chemical shifts (see Figs. 1, 3–5). It must be stated that linear and cyclic nitramines represent one group of chemical compounds but from the point of view of their initiation reactivity they are two different groups (see below).

3.5. Inequality of nitramino groupings (and nitrogen atoms)

From what has been given so far it follows that the initiation by impact should be dominated by the key role of the aza-atoms carrying the primarily leaving nitro groups [1] (see Fig. 1). The dominant factor in the initiation by shock, electric spark and

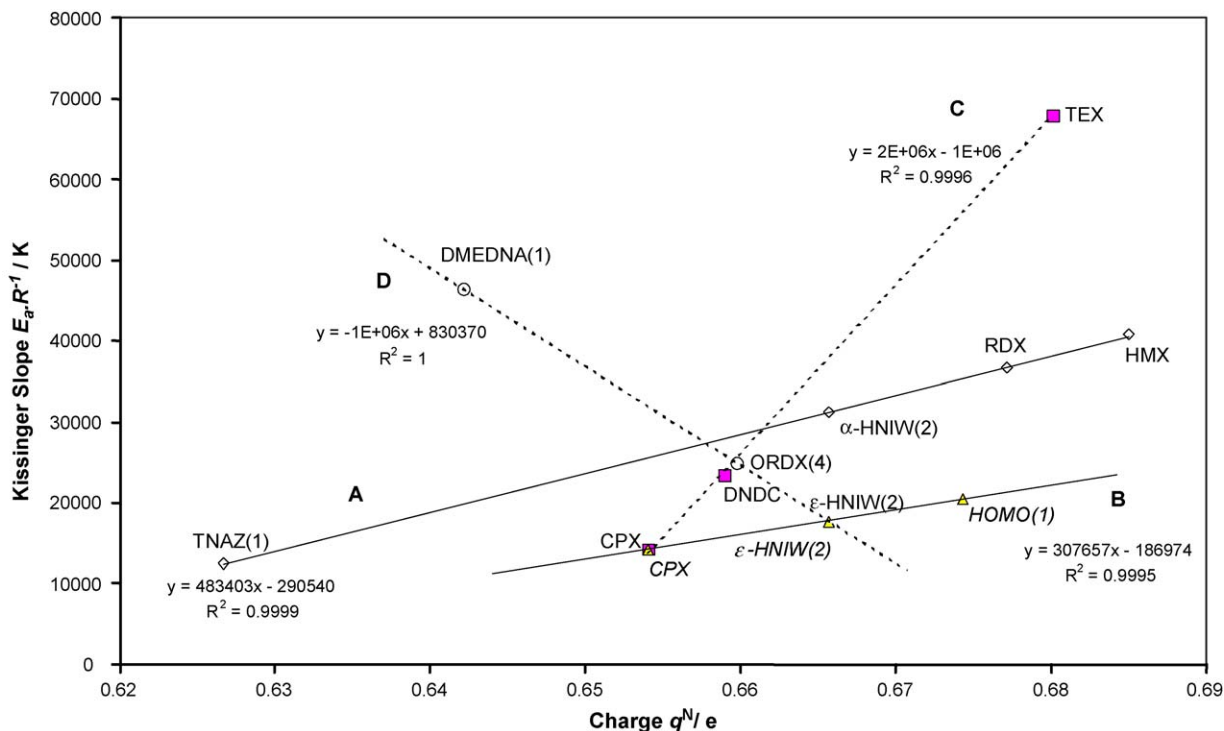


Fig. 6. Relationship between the $E_a R^{-1}$ values and Mulliken B3LYP/6-31G** charges, q^N , at the nitrogen atoms of the primarily split off nitro groups from nitramino groupings in molecule (in parenthesis given are the respective positions in molecule, i.e. position of reaction centre); taken from Ref. [25].

in low-temperature thermolysis should be the electron structure and close neighbourhood of the primarily leaving nitro group [1] (see Figs. 3–6). For nitramine molecules, whose nitrogen atoms are not isochronous, the said fact is documented in Fig. 7.

In the case of 2,4,6,8-tetranitro-2,4,6,8-tetraazanonane (OHMX) molecule, the primary reactivity of “inner” nitramino groups (positions 4 and 6) was confirmed by Kohno et al. [47] using the molecular-dynamic simulation. His paper tends to be quoted [3,5] without mentioning one of its important merits, i.e. the selectivity in the initiation reactivity of nitramino groups [47]: “in connection with action of impact or shock on a nitramine crystal, the intramolecular vibration energy is transferred into nitramino groups. There is a difference between linear and cyclic nitramines in transfer of the energy”. According to Kohno et al. [47], the linear molecule OHMX shows only low

probability of transfer of surplus energy from the “inner” to “outer” nitramino groups.

The longest N–N bond in ϵ -HNIW is that of nitramino group at 2 position of its molecule [48] (143.6 pm [48], in opposite to the single bond N–N length which is of 142.5 pm [49]). Therefore, this bond should be the first to undergo homolysis in initiation processes. This statement is supported by the findings presented in Figs. 1–4, 6 and 7.

3.6. Modified Evans–Polanyi–Semenov equation

Comparison of equations given in Figs. 3–6 leads to the relationship

$$E = aD^2 + b \quad (1)$$

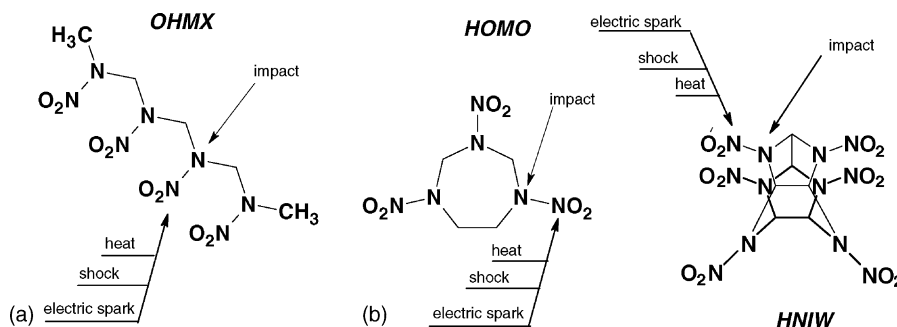


Fig. 7. Summarization of the findings about the initiation reactivities can be presented as follows: (a) dominating reactivity of “inner” nitramino groups of OHMX molecule in impact and shock was confirmed by molecular dynamics simulation [47]; (b) the most reactive nitramino group in HOMO molecule is that one at 1 position of its molecule and in HNIW molecule at position 2 (there is the longest N–N bond in molecule of its ϵ -polymorph [48]).

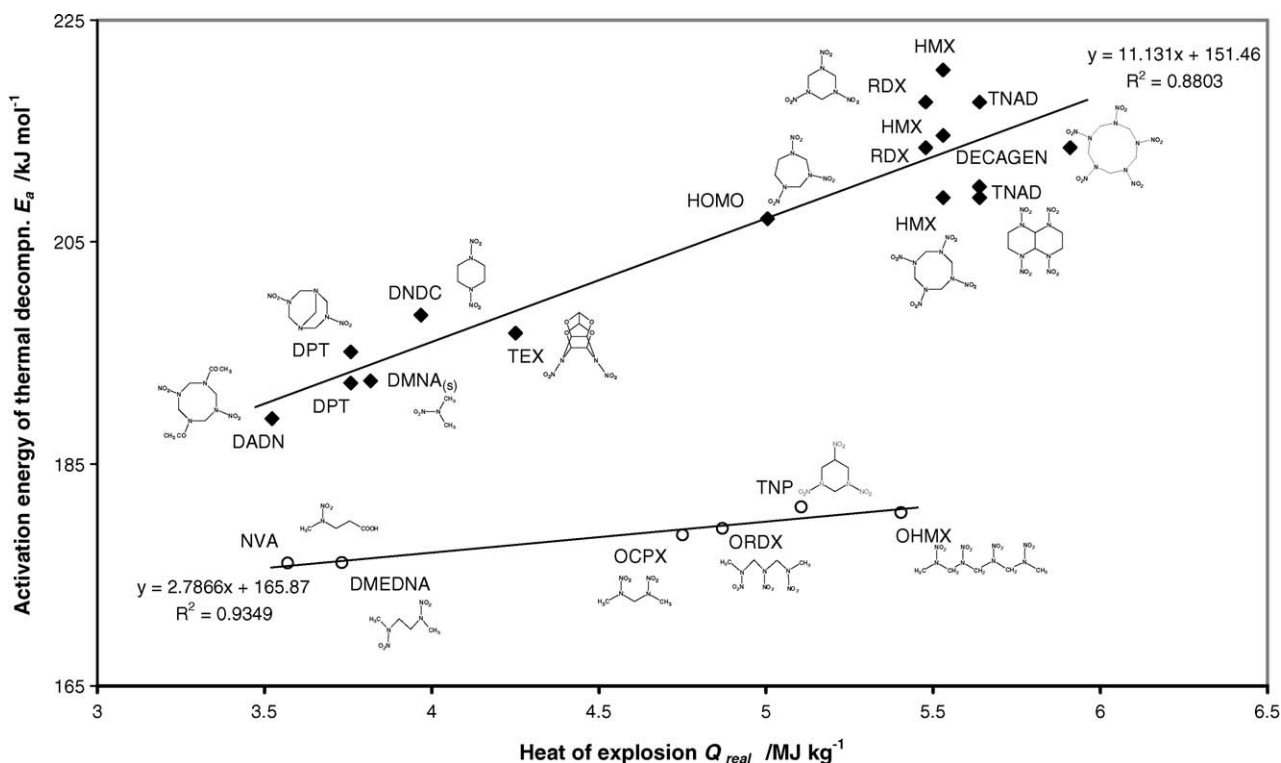


Fig. 8. Modified E–P–S equation for relationship between activation energies, E_a , of low-temperature thermolysis of nitramines (for cyclic nitramines in the solid state) and real heat of explosion, Q_{real} (calculated according to the Pepekín's semi-empirical method [59]); taken from Ref. [51].

and application of the definition relationship between detonation velocities and explosion heats Q [50] in the form

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

where γ is the polytropy coefficient, transforms Eq. (1) into the following form

$$E = \alpha Q + \beta \quad (3)$$

which is a modified Evans–Polanyi–Semenov (E–P–S) equation [51] for energetic materials. The original E–P–S describes a relationship between activation energies E of most substitution reactions of free radicals and corresponding heats of reaction ΔH of the narrow sets of substance structures [52]. The equation documents that the strength of bond being split is a decisive factor in the given reaction. A motive stimulus for study of modified E–P–S relationship was the homolytic character of primary fission in an initiation of both the detonation and low-temperature thermal decompositions of energetic materials [51] including explosive mixtures (see, e.g. Ref. [53]). Fig. 8 was taken from Ref. [51] and documents this equation for nitramines, whose activation energies, E_a , for cyclic derivatives correspond to their thermal decomposition in the solid state.

The validity of Eq. (3) was also successfully verified for the thermal decomposition of inorganic azides [55] and fulminates [56]. For azides the literature gives activation energy values, E_a ,

for thermal decomposition within various temperature ranges. In the sense of Eq. (3), however, the only E_a values correlate, which correspond to the lowest experimental temperature ranges [51,55].

We also made molecular-dynamic simulation of thermal decomposition of some individual energetic materials, including RDX, at extremely high temperatures [54]. It turned out that the primary fragmentation mechanism at these conditions is entirely different from the low-temperature variant. In the case of the RDX unimolecular decomposition, it can be mentioned that elimination of NO_2 group by homolysis of one N–N bond is observed at all the reaction conditions whereas triazinane ring fission (depolymerization to 1-nitro-1-azaethylene, Digen) occurs predominantly in the gas phase thermal decomposition of this nitramine, i.e. at higher temperatures [58].

All the above-mentioned facts mean that the effect of temperature (i.e. thermal decomposition) in classical sense has no application in the process of detonation initiation by shock or impact. Many recent papers dealt with this and related problems (for example, [5–7,28–34,57]). An idea about the initiation of detonation which could be nearest to these facts is as follows: excitation of crystal lattice vibration (phonons) after receiving impact or shock [28–30] then be converted into bond stretching frequencies (vibrons) with subsequent spontaneous localization of vibrational energy in the nitro (explosophore) groupings [31,32]. Similar, but more detailed description of this initiation is presented by another idea about electronic excita-

tions facilitated by edge dislocations in explosive solids which was obtained from application of physics of the solid-state aspect to the study of pre-explosion state of heavy metal azides [33,34].

The correlation of activation energies of low-temperature thermal decomposition (i.e. in the range up to 600 K) of nitramines and other energetic materials (in general [1,51]) in the sense of E–P–S equation thus means that the primary fission processes in this decomposition should be identical with those in the detonation transformation of these polynitro compounds [1]. The identity is confirmed by some striking pieces of experimental evidence in the case of nitramines. First of all they include the evidence (obtained with the help of Raman spectroscopy and XPS) of primary fission of N–NO₂ bond in 1,3,5-trinitro-1,3,5-triazinane exposed to shock wave [61,62]. It can be also likewise documented by experimental results of Bulusu et al. [63] which, on the basis of kinetic isotope effect, have found that the rate-determining steps in the processes of thermal decomposition RDX and HMX and the chemical process of their initiation are likely to be the same. The above-mentioned statement also means that the detonation transformation itself of the given substance should proceed at milder conditions than those present at the front of detonation wave or in its reaction zone and should have an induction period. From the point of view of physics of explosion the necessity of such induction period was also postulated by Dremin [2].

4. Conclusion

The primary fission processes of nitramine molecules in the low-temperature thermal decomposition should be identical with those in the impact, electric spark and shock initiations.

The relationships presented here focus attention on those atoms in molecules of polynitro compounds whose electron configurations and steric conditions play a key role in the primary fission processes of these molecules during initiation by mechanic stimuli, electric spark, or heat. That means that centres of initiation reactivity in molecules of nitramines can be advantageously determined by means of ¹⁵N NMR spectroscopy. From the point of view of physics of explosion the centres can be taken as “hot spots”.

Electron configuration and steric effects on aza-atoms, which are carriers of “the most reactive nitro groups” in molecule, should play a key role in the initiation by impact. The dominant factor in the initiation by shock, electric spark, and in low-temperature thermolysis should be the electron structure and close neighbourhood of nitrogen atom of the primarily leaving nitro group.

The relationships presented here, namely the modified Evans–Polanyi–Semenov equation, lead to a premise that the primary fragmentation of the studied polynitro compounds in their detonation transformation proceeds at milder conditions than those present at the front of detonation wave or in its reaction zone [1]. That means that the detonation transformation

itself of the given substances should be preceded by an induction period [1,2].

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