



Electric Spark Sensitivity of Nitramines. Part I. Aspects of Molecular Structure^{*)}

Svatopluk ZEMAN, Vojtěch PELIKÁN, Jiří MAJZLÍK

Institute of Energetic Materials, University of Pardubice

CZ-532 10 Pardubice, Czech Republic

E-mail:svatopluk.zeman@upce.cz

Zdeněk FRIEDL

Faculty of Chemistry, Brno University of Technology

CZ-612 00 Brno, Czech Republic

Jiří KOČÍ

Austin Detonator, Ltd., CZ-755 01 Vsetín, Czech Republic

Abstract: An ESZ KTTV instrument of a new, relatively simple construction has been applied to determination of electric spark sensitivity (E_{ES}) of 16 nitramines. Results obtained are compared with those from measurements by means of an older RDAD instrument. Attention was focused both on the relationships between the E_{ES} values from both the instruments and theoretical B3LYP/6-311+G(d,p) N-NO₂ bond dissociation energies, B3LYP/6-31G(d,p) Mulliken net charges of the nitro group, heats of fusion and ¹⁵N NMR chemical shifts of the nitrogen atoms of the most reactive nitro groups, respectively. It is stated a larger difference between results of both instruments. The E_{ES} values from both the instruments correlate with such characteristics of molecular structure which correspond to the primarily leaving nitro group in the nitramine molecule. It has been found that these relationships for ESZ KTTV results are strongly affected by molecular structure factors. It is also pointed out that the dislocations in the crystals should have some relation to electric spark sensitivity.

Keywords: bond dissociation energy, electric spark, sensitivity, nitramines

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Introduction

Recent studies on sensitivity of energetic materials to the electric spark [1-23] have shown that this sensitivity depends not only on the chemical entity of the material given [1, 4, 6, 8, 9, 12, 14-16], its granulometry [1-3, 12, 16] and grain shape [3], mechanical properties [5, 6], temperature [1, 13], moisture content [2, 4], its thermal [2, 6, 7, 12, 17, 19] and impact [7, 16, 20] reactivities but also on the configuration of electrodes, general structure of the circuit [2, 4] and finally on the discharge time [26]. Consequently, it has not yet been possible to devise an international standard test specifying this stability [9, 10, 18]. Irrespective of the mentioned spectrum of effects influencing the said sensitivity, a linear relationship between the tests results obtained with various apparatuses can be found [9-11].

Our Institute in cooperation with the R&D Department of Austin Detonator Ltd., (Vsetín, Czech Republic) took part in constructing of an instrument for determination of electric spark sensitivity [8-10]. With the help of this instrument, marked as RDAD, measurements were made on a large set of polynitro compounds of secondary explosive type [8-10, 14, 19-23]. From the results obtained it was possible to make conclusions on the chemical mechanisms of initiation of these compounds [14, 19-23]. The outputs from the RDAD instrument correlate satisfactory with those obtained by other methods of determination of the electric spark sensitivity in some recognized laboratories [10]. However, this instrument is not suitable for determination of the sensitivity of primers and pyrotechnics. For this reason, we have developed, with a financial support from Czech Ministry of Industry and Commerce [24], a new instrument [25-27], marked as ESZ KTTV [26]. This instrument is suitable for measurements of energetic materials within the whole scope of technically attractive sensitivities.

The present paper shows difference between outputs of both instruments from the point of view not only numerical values but also molecular structure. These differences are demonstrated on some nitramines – theirs molecular structure is relatively simple and a mechanism of primary homolysis of N-NO₂ bonds is well understood [28-31].

Experimental

Principle of the electric spark sensitivity testing

The sensitivity of nitramines is determined here under conditions of undamped discharge of charged condenser into the sample tested [25, 26]. The

energy of electric spark, E_{ES} , required for 50% initiation probability is calculated (up and down method) from the known capacity C (in F) of the circuit and voltage U (in V) at the condenser by means of the well-known equation

$$E_{ES} = 0.5 \cdot C \cdot U^2. \quad (1)$$

Beside the working condenser and test chamber with sample, the series resonance circuit consists of the loss resistor of circuit (whose value varies from 0.27 to 10.0 Ω) and total parasitic inductance (ranging from 1 to 1.6 μH). In the course of oscillation discharge, the increase in output in the space between the electrodes of testing spark gap reaches the values of $dP/dt \approx 5 \cdot 10^{18}$ W/s. The period of oscillations (from 0.5 to 20 μs) as well as the parameters of the instrument depend considerably on the capacity value (C), testing voltage (U), and the sum of Joule losses in the test substance.

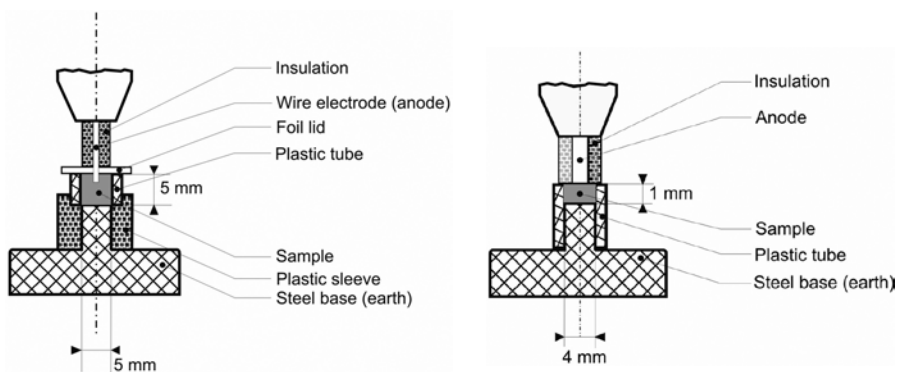
Measurement with the instrument RDAD

The schemes of its wiring and its spark gap are presented in papers [8-10] (the spark gap see Scheme 1). The bottom electrode is a steel base which has in the centre an attached screw as a leak electrode. To this screw is attached a plastic cylinder with a cut for fastening a piece of flexible tubing of 5 mm height and 5 mm diameter serving as a container of the sample tested. The top electrode is a steel cylinder of conical shape with attached resistance wire protected by a plastic distance stop, which presses an Umafol lid to the flexible tubing. The capacity of the capacitors was chosen so as to allow measurements in the voltage interval from 8 to 14 kV. If the initiation was successful, the next measurement was made with a voltage lowered by 0.2 kV; if it was unsuccessful, the voltage was increased by the same value. We considered an initiation to be successful if the sample disappeared or the flexible tubing was torn. Altogether 25 measurements were made with each substance and the results were treated in the sense of eq. 1 by means of the "up and down method".

Measurements with the instrument ESZ KTTV

The instrument is designed for a small-scale sensitivity testing of energetic materials [25-27]. A high voltage power supply (operating voltage 4-10 kV) and a set of capacitors of overall capacity in the range from 100 pF to 350 nF produces an electrostatic discharge of total energy from 10 mJ to 16 J. A sample of 1 mm height is fitted into an isolation tube mounted on the lower cylindrical metal electrode. The upper electrode is equipped with manual vertically adjustable positioner (the spark gap see Scheme 2). The micro container itself is placed in

a separate test box with ventilation. The time behavior of voltage and current at the spark gap is registered with a scope and then evaluated using a microcomputer to give the effective energy transmitted to the sample.



Scheme 1: A spark gap in the RDAD instrument [10].

Scheme 2: A spark gap in the ESZ KTTV instrument [26].

The nitramines studied

A survey of the tested nitramines is given in Table 1. All the nitramines were purified by crystallization in motion, and often by precipitation crystallization (with a good stirring) from organic solvents. The crystallization was carried out in such a way as to obtain the product appearing as individual in thin layer chromatograph (Silufol, hexane-acetone eluent and developing the chromatograms with 2% diphenylamine in ethanol with UV detection). However, the granulometry of the substances investigated was not specified.

Molecular structure characteristics

In connection with our recent results of initiation reactivity of energetic materials [15] the electronic charges at nitro groups, N-NO₂ bond dissociation energies, heats of fusion and ¹⁵N NMR chemical shifts of NO₂ nitrogen atoms were chosen as characteristics of molecular structure of the nitramines studied (see in Table 2).

The N-NO₂ bond dissociation energies, $DH(N-N)$, were calculated at *ab initio* level by DFT B3LYP/6-311+G(d,p) method [32]. The calculation by total optimization gave the equilibrium geometries of isolated molecules in the gas phase at 0 K. The optimized structures were verified by normal mode frequency analysis to exclude imaginary frequencies for the remaining 3N-6 vibrational degrees of freedom. The net charges of the nitro group, Q_{nitro} , of the nitramines

investigated were obtained by means of Mulliken population analysis of electron densities obtained at *ab initio* level by DFT B3LYP/6-31G(d,p) method [32] without frequency analysis. The relevant data are summarized in Table 2.

Discussion

The analysis of relationship between the E_{ES} values obtained by measuring on RDAD and ESZ KTTV instruments revealed that the relationship is not unequivocal as is illustrated in Figure 1. Similar trends in E_{ES} values obtained from the two instruments are exhibited by class *A* of high-energetic cyclic nitramines. On the other hand, class *C* of linear nitramines and particularly class *B* of cyclic nitramines show opposite trends in E_{ES} values. DMEDNA data correlate with the last class probably due to a fact that its molecular skeleton can be found as a part of skeletons of remaining members of this class. Surprisingly TETRYL data correlate with the data of *A* class and TNAZ is unexpectedly more sensitive in measurements by means of ESZ KTTV instrument.

Large difference between outputs of measurements on RDAD instrument on the one hand, and those from ESZ KTTV instrument, on the other (both the values see Table 1), should be due to mutual difference in construction namely spark gaps of each instrument; scheme of this gap in the first instrument is presented in Ref. 10 and in the second one in Ref. 26 (see also Schemes 1 and 2). Large energetic losses in the spark gap of the RDAD instrument might manifest oneself as a strong thermal effect of the relevant electric discharge, i.e., outputs of this measurement connected with thermolysis of the given samples. This statement should be valid for all equipments whose outputs are in good unambiguous correlation with those of DRAD instrument (see in Ref. 10).

Table 1. Summary of the studied nitramines, their code designation and sensitivities to electric spark E_{ES} (RDAD and ESZ KTTV instruments)

Nitramines			E_{ES} required for 50% initiation probability obtained by instrument		
			RDAD		ESZ KTTV
No.	Chemical name	Code designation	[J]	Ref.	[mJ]
1	<i>N</i> -Methyl- <i>N</i> ,2,4,6-tetranitroaniline	TETRYL	5.49	23	574.2 ± 7.6
2	2,5-Dinitro-2,5-diazaheptane	DMEDNA	8.24	23	392.0 ± 51.7
3	3,5-Dinitro-3,5-diazaheptane	DNDAH	12.49	23	225.0 ± 11.3
4	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	8.08	23	243.3 ± 14.4
5	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane	AcAn	13.93	23	206.7 ± 14.4
6	1,3-Dinitroimidazolidine	CPX	9.68	23	403.3 ± 14.4
7	1,3-Dinitro-1,3-diazetidene	TETROGEN	6.25	23	494.0 ^a
8	1,4-Dinitropiperazine	DNDC	15.97	23	190.0 ± 8.3
9	1,3,5-Trinitro-1,3,5-triazinane	RDX	2.49	23	216.4 ± 15.6
10	1,3,5-Trinitro-1,3,5-triazepane	HOMO	3.70	23	431.3 ± 19.3
11	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	β -HMX	2.89	23	236.4 ± 10.1
12	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentazecane	DECAGEN	2.96	23	276.5 ^a
13	<i>trans</i> -1,4,5,8-Tetranitrodecahydro-pyrazino[2,3- <i>b</i>]pyrazine	TNAD	5.43	23	520.0 ± 53.3
14	1,3,3-Trinitroazetidene	TNAZ	8.76	20	78.3 ± 7.2
15	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	ϵ -HNIW	4.70	20	462.0 ± 41.4
16	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaaisowurtzitane	TEX	13.10 ^b	this paper	285.5 ± 25.3

^a The value predicted by means of Fig. 1 (here line A for DECAGEN and line B for TETROGEN);

^b Predicted on the basis of molecular structural congeniality by means of the line B relation in the Fig. 1.

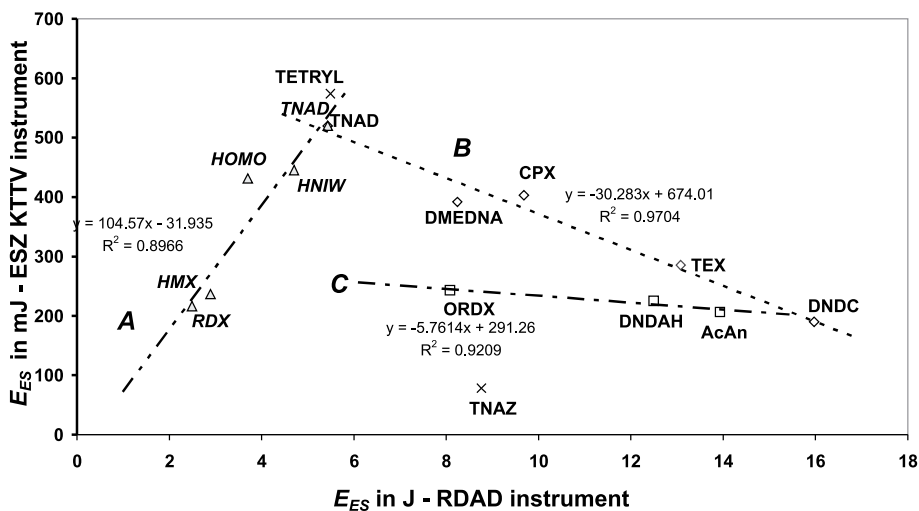


Figure 1. Relationship between outputs from ESZ KTTV and RDAD instruments.

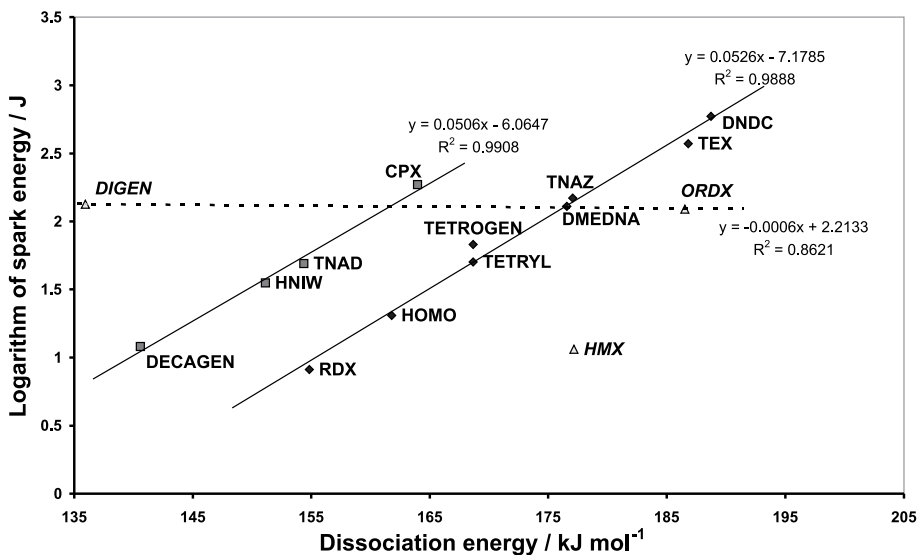


Figure 2. Relationship between E_{ES} values from RDAD instrument and $DH(N-N)$ energy.

Table 2. Calculated N-NO₂ bond dissociation energies, $DH(N-N)$, Mulliken net charges of the nitro group, Q_{nitro} , heat of fusion, $\Delta H_{m,tr}$, and ¹⁵N NMR chemical shifts, δ_N , of NO₂ nitrogen atoms

Code designation	Bond dissociation energies ^a Mulliken net charges ^b			Heat of fusion ^c		¹⁵ N NMR chemical shifts ^d		
	position in molecule	DH(N-N) [kJ mol ⁻¹]	Q_{nitro} [e]	$\Delta H_{m,tr}$ [kJ mol ⁻¹]	Ref.	position in molecule	δ_N [ppm]	Ref.
TETRYL	N(CH ₃)	130.95	-0.135261	25.850	34	N(CH ₃)	-23.1	37
DMEDNA	2,5-	176.55	-0.201818	29.409	34	2,5-	-27.8	37
ORDX	2-	194.86	-0.176718	34.031	34	2,6-	-28.5	37
	4-	186.50	-0.178246			4-	-32.0	
	6-	186.83	-0.198959					
CPX	1,3-	163.96	-0.167031	22.570	34	1,3-	-31.2	37
TETROGEN	1,3-	168.65	-0.154150	26.320	34	1,3-	-27.8	37
DNDC	1,4-	188.72	-0.165965	33.823	34	1,4-	-26.2	37
RDX	1,3,5-	154.84	-0.127376	33.012	34	1,3,5-	-32.9	37
HOMO	1,5- (ax)	161.78	-0.133985	27.738	34	1,5-	-33.0	37
	3- (eq)	177.70	-0.142745			3-	-34.4	
β -HMX	1,3- (eq)	177.16	-0.107995	32.100	34	1,3,5,7-	-34.7	37
	2,4- (ax)	179.05	-0.120368					
DECAGEN	1-	168.09	-0.127184	34.930	34	1,3,5,7,9-	-33.2	37
	3-	167.16	-0.143869					
	5-	167.29	-0.128259					
	7-	140.58	-0.118018					
	9-	176.05	-0.093269					
TNAD	1,3- (ax)	154.36	-0.156531	46.400	34			
	2,4- (eq)	175.24	-0.144025					
TNAZ	1-	177.06	-0.152032	30.310	36	1-	-20.5	38
ϵ -HNIW	2,6,8,12-	151.12	-0.080958	43.030	35	2,6,8,12-	-40.3	37
	4,10-	169.46	-0.074584			4,10-	-43.4	
TEX	4,10-	186.79	-0.111044	36.100	35	4,10-	-33.4	37

^a Calculated by B3LYP/6-311+G(d,p) method; ^b Calculated by B3LYP/6-31G(d,p) method;

^c Heats of fusion taken from literature [34-36]; ^d ¹⁵N NMR chemical shifts taken from literature [37, 38].

It is known that initiation reactivity of secondary nitramines is connected with N-NO₂ bond homolysis (see Ref. 15 and reference therein). It is logical that the weakest bond will be broken as the first. Therefore, energy of electric spark, E_{ES} , should correlate with the lowest values of the bond dissociation energy $DH(N-N)$. The verification can be found in Figures 2 and 3. While the relationships for outputs from RDAD instrument have a logical regularity (Figure 2), the opposed direction of these relationships is beyond expectation

typical for ESZ KTTV measurements (Figure 3). Some authors are inclined to accept the idea of conversion of the spark energy into a thermal effect, i.e., thermolytic mechanism of the initiation by electric spark [3, 6, 15, 17, 19]. However, Rat *et al.* [5] consider this initiation to be a multidisciplinary problem. Results of this paper give these authors [5] the truth. Namely facts in Figure 3 signalize the multidisciplinary and that the thermal component of electric discharge does not participate in the ESZ KTTV measurements; the reversed relationships in Figure 3 still wait for an interpretation (the most probably by means of quantum chemical simulation method).

Mulliken net charges of the total nitro group, Q_{nitro} , were used in the study of impact sensitivities of nitro compounds [33]. Application of this approach to electric spark sensitivity gave in this study correlations which are present in Figures 4 and 5. The most positive Q_{nitro} charges of each nitramine were used in both cases. The outputs of the RDAD instrument are relatively scattered even though some relationships are intimated here (Figure 4). As a large part of discharge is enacted in the air, also other factors should have an influence on the nitramines initiation (they might be partly in floatation during the discharge). The E_{ES} values from ESZ KTTV measurements, on the other hand, gave the relationships (Figure 5) which are strongly determined by molecular structure (namely for compounds along the lines with positive slope).

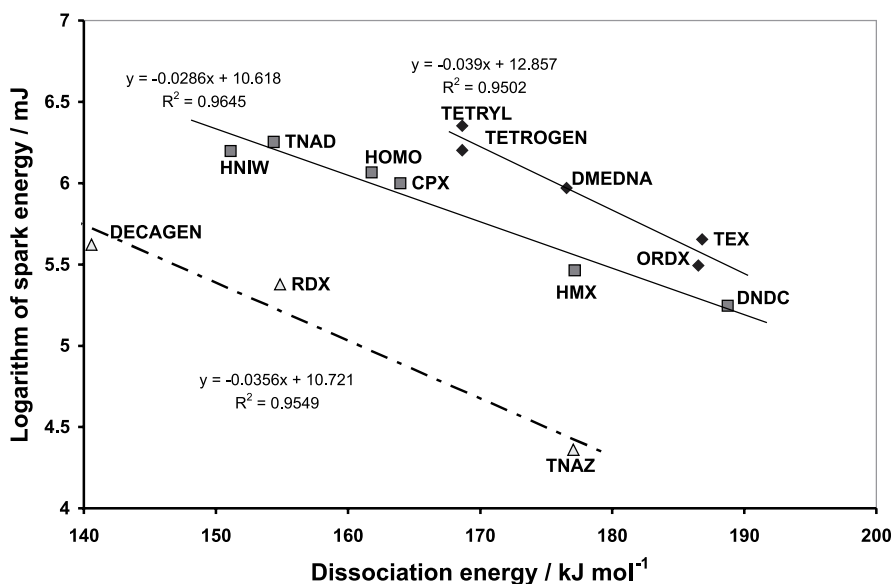


Figure 3. Relationship between E_{ES} values from ESZ KTTV instrument and $DH(N-N)$ energy.

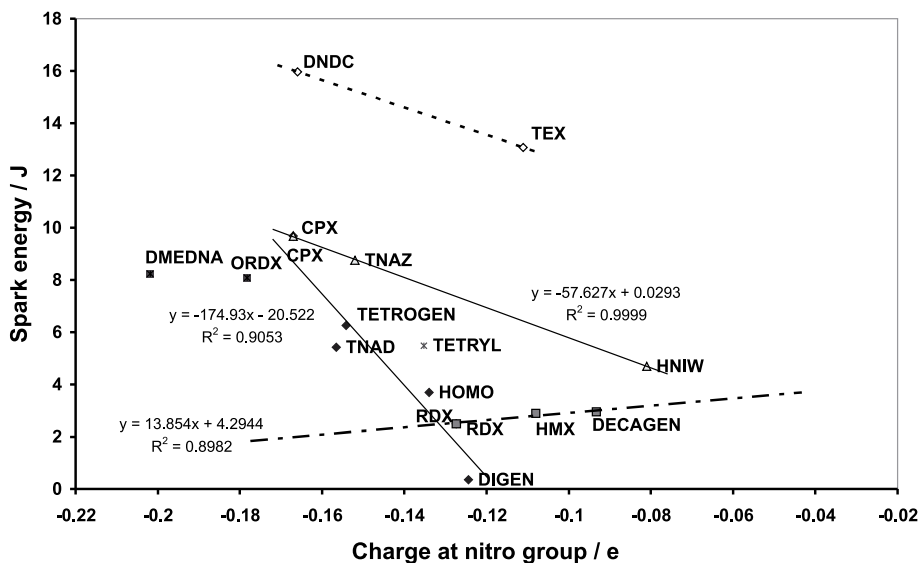


Figure 4. Relationship between E_{ES} values from RDAD instrument and net electronic charge of the nitro group Q_{nitro} .

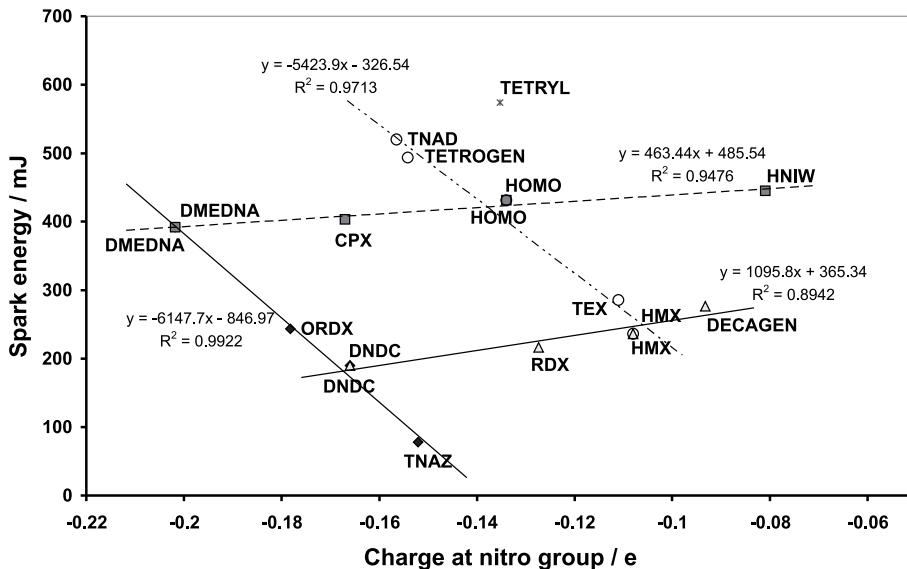


Figure 5. Relationship between E_{ES} values from ESZ KTTV instrument and net electronic charge of the nitro group Q_{nitro} .

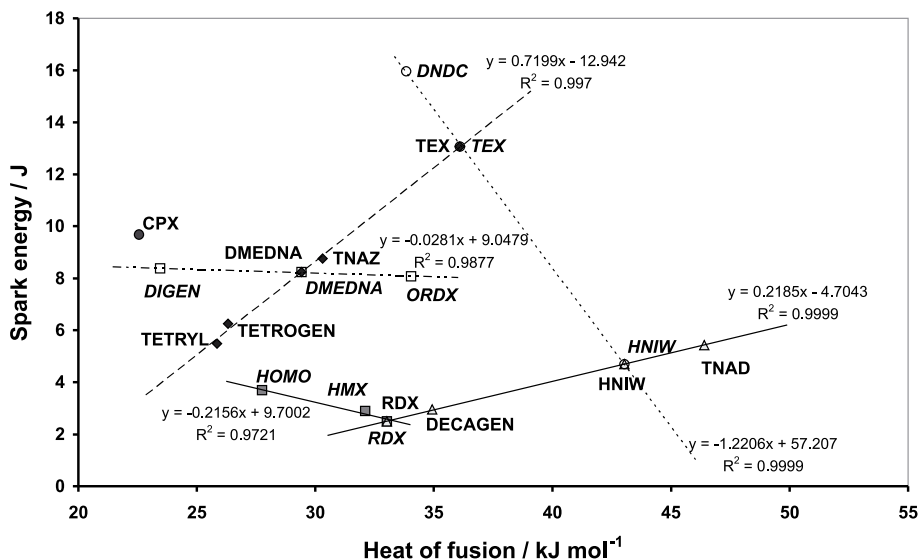


Figure 6. Relationship between E_{ES} values from RDAD instrument and heats of fusion.

Figures 6 and 7 document an interrelationship of the E_{ES} values and intermolecular interactions which are represented here by heats of fusion, $\Delta H_{m,tr}$, of the nitramines studied. This approach was successfully applied in the study of influence of an intermolecular interaction on the impact sensitivity of polynitro compounds [15, 39-41]. The heat of fusion is defined as a sum of heat of all the polymorphous transitions and of the heat of melting [34, 43] and it can represent here the work needed for formation of defects in crystal lattice [15, 39-41]. Figure 6, analogous to Figure 4, documents again complexity of the initiation in the spark gap of the RDAD instrument.

Figure 7 reminds of analogous relationships between impact sensitivity (taken as the first reaction) and the $\Delta H_{m,tr}$, values of nitramines [15, 39, 41]. These relationships strongly differentiate cyclic and linear nitramines while according to the Figure 7 this differentiation is not evident. It might mean that a role namely of plastic deformations of crystal does not need to be significant in the initiation by electric spark as in the case of impact or shock. But the dislocations should be a reason for existence of the relationships in Figure 7. That means that results from measurements by means of ESZ KTTV instrument should be more depended on the shape and size of crystals as in case of RDAD. Satisfactory correlation of the data from the first mentioned instrument with characteristics of nitramine molecular structure might be caused by wide spectrum of their

granulometry (given by the method of samples crystallization) which can lead to the “averaged” E_{ES} values.

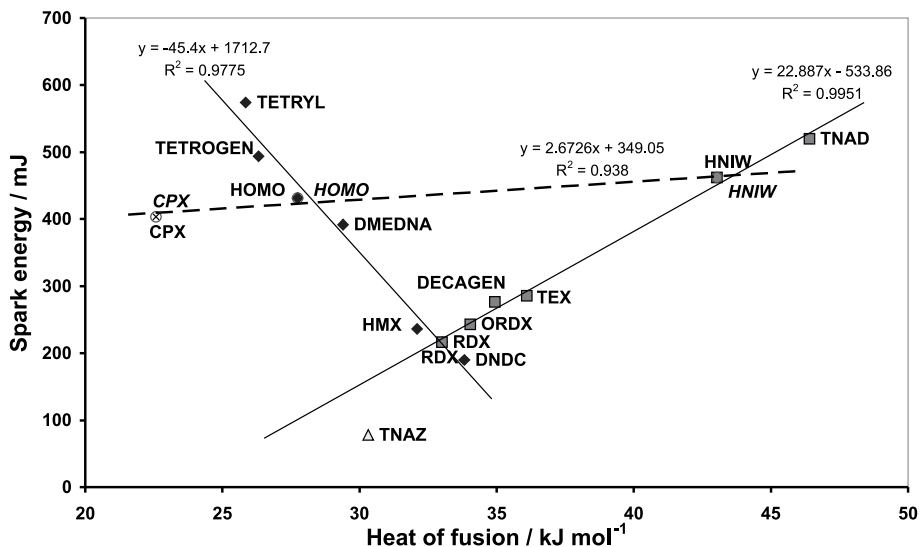


Figure 7. Relationship between E_{ES} values from ESZ KTTV instrument and heats of fusion.

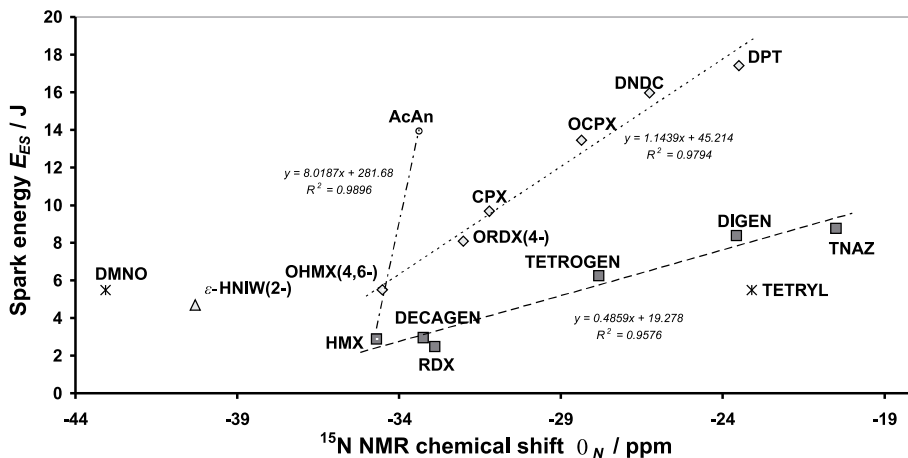


Figure 8. Relationship between E_{ES} values from RDAD instrument and ^{15}N NMR chemical shifts of nitrogen atoms of the primarily split off nitro groups (taken from [15, 41]).

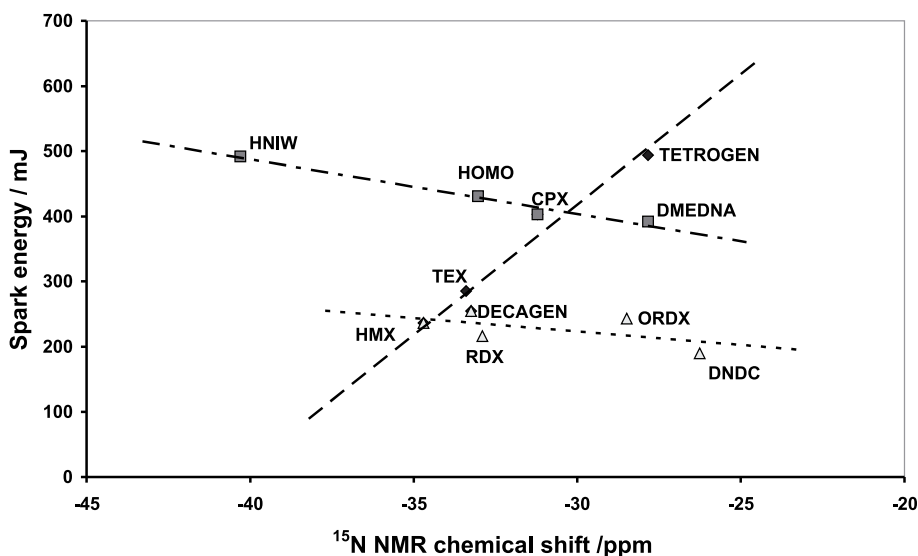
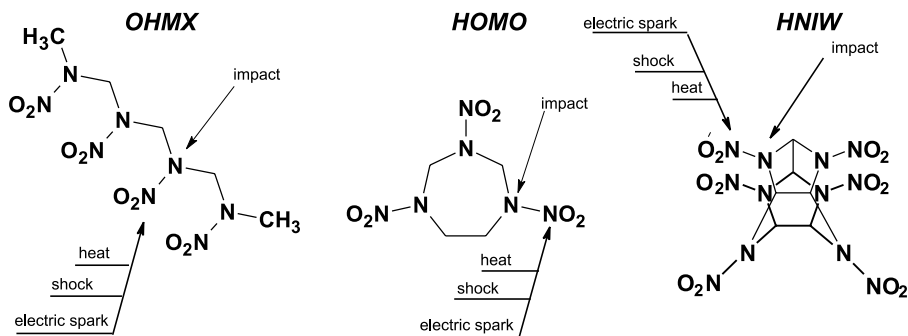


Figure 9. Relationship between E_{ES} values from ESZ KTTV instrument and ^{15}N NMR chemical shifts of nitrogen atoms of the primarily split off nitro groups (values of these shifts were taken from Ref. 42).

Completely mutually different are data in the Figures 8 and 9 which represent relationships between ^{15}N NMR chemical shifts of nitrogen atom in the most reactive nitro groups (i.e., primarily split off nitro groups) and the E_{ES} values. Figure 8 somewhat reminds the relationship between these shifts and square of detonation velocities of nitramines [15, 41]. On the other hand, relationships in Figure 9 go near to those in Figure 5. It seems the outputs from ESZ KTTV instrument have more close relation to molecular structure as those from RDAD instrument.

Results presented so far correspond to our recent findings [39, 41]: from point of view of the electron structure and close neighbourhood, the individual nitramino groups in polynitramines are usually not equivalent to each other. Therefore, also their abilities of participation in primary initiation processes are different even with respect to individual nitrogen atoms in the given nitramino group (see Ref. 41 and Scheme 3).



Scheme 3. Summarization of the findings about the initiation reactivities of nitramines [41].

The 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. However, the dominant factor in the initiation by shock, electric spark, and in low-temperature thermolysis should be the electron structure and close neighborhood of nitrogen atom of the primarily leaving nitro group [41]. As it is shown from this paper the second statement is valid also for the ESZ KTTV instrument outputs.

Conclusions

From the facts given above it is possible to deduce that the mechanisms of spark energy transfer into the reaction centre of molecule should be different in measurement on the two alternative instruments (RDAD and ESZ KTTV). The thermal component of discharge in the RDAD instrument may be one of the reasons of this difference. This assumption is also supported by the differences (in an order of magnitude) between the E_{ES} values obtained from the individual instruments (see Table 1). Further, the considerable electric energy losses in the area between the upper electrode and the sample surface in the RDAD system measurements contribute to the difference mentioned above – most likely a large part of discharge is enacted in the air.

Data from ESZ KTTV instrument have close relation to the molecular structure of measured polynitro compounds [16]. In a line with knowledge about reactivity initiation of polynitro compounds [15, 41] the E_{ES} values correlate with such characteristics of molecular structure which correspond to the primarily leaving nitro group in the nitramine molecule. Reversed relationship between

the E_{ES} values and dissociation energies $DH(N-N)$ (Figure 3) waits for a detailed, preferably quantum chemical interpretation so far. The E_{ES} values also correlate with heats of fusion of the studied nitramines, probably due to the influence of dislocations in their crystals on electric spark sensitivity. This assumption can have some relation to the significant influence of the crystals' shape and size on the electric spark sensitivity of the energetic compounds in general.

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