Electric Spark Sensitivity of Polynitro Arenes Part I. A Comparison of Two Instruments

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Abstract: An ESZ KTTV instrument of a new, relatively simple construction has been applied to determination of electric spark sensitivity (E_{ES}) of 34 polynitro arenes and their derivatives. Results obtained are compared with those from measurements by means of older RDAD instrument. The analysis of relationship between the E_{ES} values obtained by measurements on the two instruments revealed that the relationship is not unequivocal. It is possible to come to the conclusion that the mechanisms of spark energy transfer into the reaction centre of molecule should be different in measurement on the two alternative instruments. Measurement by means of the ESZ KTTV system is more sensitive to molecular structure of the studied polynitro compounds.

Keywords: electric spark, sensitivity, polynitro arenes

Introduction

Our recent paper [1] on the electric spark sensitivity of nitramines refers also to an influence of the kind of gauging instrument on outputs of the given measurement: it is well-know that this sensitivity depends also on the configuration of electrodes, general structure of the circuit [2, 3] and finally on the discharge time [4]. 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 [5-7]. With the help of this instrument, marked as RDAD, measurements were carried out on a large set of polynitro compounds of secondary explosive type [5-13]. From the results obtained it was possible to draw conclusions on the chemical mechanisms of initiation of these compounds [1, 8-13]. 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 [7]. However, this instrument is not suitable for determination of the said sensitivity of primers and pyrotechnics. For this reason, we have developed with a financial support from Czech Ministry of Industry and Commerce [14], a new instrument [4, 15, 16], marked as ESZ KTTV [4]. This instrument is suitable for measurements of energetic materials within the whole scope of technically attractive sensitivities.

The present paper forms a continuation of our earlier work [1] and shows difference between outputs of both the instruments mentioned above. These differences are demonstrated on some polynitro arenes and their derivatives.

Experimental

Principle of the electric spark sensitivity testing

The sensitivity of polynitro arenes is determined here at conditions of undamped discharge of charged condenser into the sample tested [4]. The energy of electric spark, E_{ES}, required for 50% initiation probability is calculated (up and down method) from the know capacity C (in F) of the circuit and voltage U (in V) at the condenser by means of the well-known equation

$$E_{ES} = 0.5 \cdot C \cdot U^2 \tag{1}$$

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 ≈ 5.10^{18} W/s. The period of oscillations (from 0.5 to 20 μs) as well as the parameters of the instrument mentioned above depend considerably on the capacity value (C), testing voltage (U), and the sum of Joule losses in the test substance.

Measurement with instrument RDAD

The schemes of its wiring and its spark gap are presented in papers [5-7] (the spark gap see Scheme 1). The bottom electrode is a steel base in which centre there is attached a screw as a leak electrode. Attached to this screw is 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 carried out 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 carried out with each substance and the results were treated in the sense of eq. 1 by means of the "up and down method".

Measurements with instrument ESZ KTTV

The instrument is designed for a small-scale sensitivity testing of energetic materials [4, 14]. 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 produce 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).
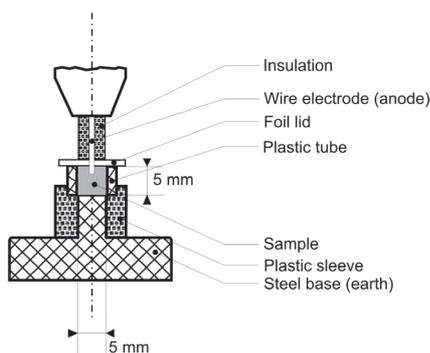
Scheme 1. A spark gap in the RDAD instrument [1, 7].
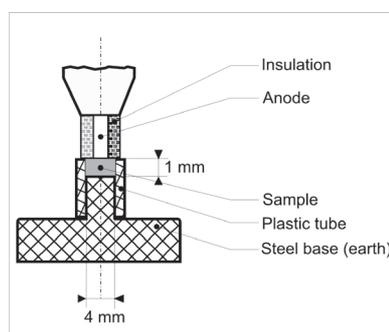
Scheme 2. A spark gap in the ESZ KTTV instrument [1, 4].

The microcontainer 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 than evaluated using a microcomputer to give the effective energy transmitted to the sample.

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

| Polynitro arene | | | E_{ES} required for 50% initiation probability obtained by instrument | | |
| | | | RDAD | | ESZ KTTV |
No.	Chemical name	Code designation	(J)	Ref.	(mJ)
1	1,3-Dinitrobenzene	1,3-DNB	3.15	12	256.7±14.4
2	1,4-Dinitrobenzene	1,4-DNB	18.38	12	403.3±14.4
3	1,3,5-Trinitrobenzene	TNB	6.31	9	108.2± 7.8
4	2,2',4,4',6,6'-Hexanitro-1,1'-biphenyl	HNB	5.03	9, 12	286.7±26.7
5	2,4,6,2',4',6',2'',4'',6''-Nonanitro-[1,1',3',1'']terphenyl	NONA	16.44	9, 12	158.2± 7.8
6	1,8-Dinitronaphthalene	1,8-DNN	13.99	12	238.2± 9.9
7	1,5-Dinitronapthalene	1,5-DNN	11.20	12	180.0±10.9
8	1,4,5-Trinitronaphthalene	TNN	10.97	12	210.0±13.3
9	1,4,5,8-Tetranitronaphthalene	TENN	8.26	12	95.0± 8.3
10	5,7-Dinitro-1-(2',4',6'-trinitrophenyl)-1H-1,2,3-benzotriazole	BTX	6.50	9, 12	135.0± 8.3
11	2,4,6-*Tris*(2,4,6-trinitrophenyl)-[1,3,5]triazine	TPT	10.61	9	283.3±27.2
12	2-Methyl-1,3,5-trinitrobenzene	TNT	6.85	9	111.8±12.9
13	2,4,6-Trimethyl-1,3,5-trinitrobenzene	TNMs	8.98	9	292.7±17.0
14	2-Amino-1,3,5-trinitrobenzene	PAM	6.85	9	156.7± 7.2
15	2,4-Diamino-1,3,5-trinitrobenzene	DATB	10.97	9, 12	175.0 ± 8.3
16	2,4,6-Triamino-1,3,5-trinitrobenzene	TATB	17.75	9, 12	293.3±14.4
17	2-Hydroxy-1,3,5-trinitrobenzene	PA	9.98	9, 12	115.5± 6.8
18	2,4-Dihydroxy-1,3,5-trinitrobenzene	TNR	12.30	9, 12	230.0±30.0
19	2-Methoxy-1,3,5-trinitrobenzene	TNA	28.59	9	436.0±29.6
20	1-Chloro-2,4,6-trinitrobenzene	CTB	6.71	9	101.0± 7.7
21	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	2.55	9	31.5± 2.8
22	(E)-Bis(2,4,6-trinitrophenyl)diazene	HNAB	8.20	9, 12	112.0± 8.6
23	(E)-Bis(3-methyl-2,4,6-trinitrophenyl)-diazene	DMHNAB	13.37	12	118.2± 7.8

Table 1.   Continuation

No.	Chemical name	Code designation	E_{ES} required for 50% initiation probability obtained by instrument		
			RDAD		ESZ KTTV
			(J)	Ref.	(mJ)
24	Bis(2,4,6-trinitrophenyl) sulfide	DIPS	2.54	9, 12	125.5± 8.6
25	Bis(2,4,6-trinitro-3-methylphenyl) sulfide	DMDIPS	8.57	9, 12	112.7± 7.1
26	Bis(2,4,6-trinitrophenyl) sulfone	DIPSO	10.24	9, 12	186.7± 7.2
27	2,4,6-Trinitro-*N*-(2,4,6-trinitrophenyl)-aniline	DPA	5.02	9	103.0± 7.6
28	Bis-(2,4,6-trinitriphenyl)methane	DPM	4.10	9, 12	136.4 ±7.6
29	1,2-Bis-(2,4,6- trinitriphenyl)ethane	DPE	3.89	9, 12	167.0± 1.5
30	3,3‘-Dimethyl-2,2‘,4,4‘,6,6‘-hexanitro-biphenyl	BITNT	4.28	9, 12	206.7± 7.2
31	2,6-Diamino-3,5-dinitropyridine	DADNP	12.40	9	358.0±10.8
32	3,5-Dinitro-*N*,*N*‘-*bis*(2,4,6-trinitro-phenyl)pyridine-2,6-diamine	PYX	8.90	9	136.7±10.
33	1,3,7,9-Tetranitro-10*H*-phenothiazine 5-oxide	TNPTM	10.68	this paper	195.0± 8.7
34	1,3,7,9-Tetranitro-10*H*-phenothiazine 5,5-dioxide	TNPTD	28.93	9	363.3±14.4

The compounds studied

     A survey of the tested polynitro arenes and their derivatives is given in Table 1. All the compounds 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 chromatography. However, the granulometry of the substances investigated was not specified.

Discussion

     The analysis of relationship between the E_{ES} values obtained by measurements on the two instruments (i.e. RDAD and ESZ KTTV) revealed that the relationship is not unequivocal. In the sense mentioned, the set of polynitro compounds tested fell into several classes, which is documented by Figures 1-3. This classification is dominated by molecular-structure factors. Thus Figure 1

presents the relationship mentioned for the data of polynitronaphthalenes having nitro groups at *peri* positions, which is logically obeyed also by the data of 1,4-dinitrobenzene. From the point of view of primary step of their thermolysis (the homolysis of C–NO$_2$ bond), however, data of 1,5-DNN also correlate: in this derivative the thermal decomposition should start by interaction of oxygen of nitro group with the adjacent *peri*-hydrogen substituent [17]. Any correlation was not found between the data of TNB, HNB and NONA, logical relationships exit between the TNB, BTX and TPT data.
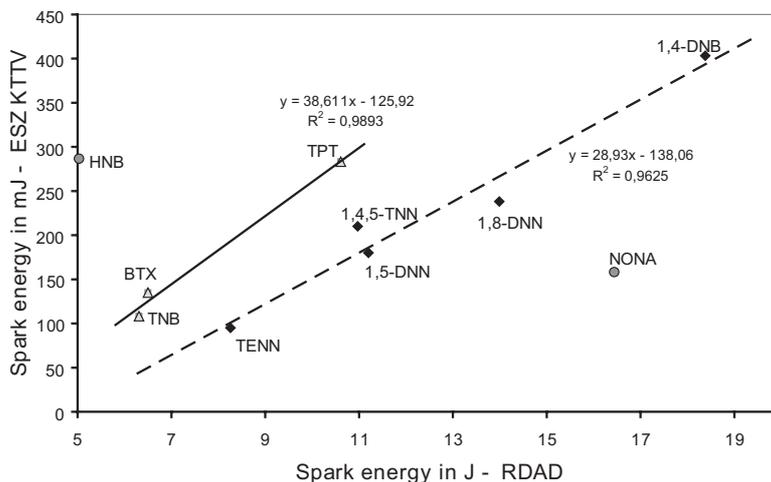
Figure 1. Relationship between outputs from ESZ KTTV and RDAD instruments for 1,4-dinitrobenzene and derivatives of naphthalene with nitro groups in *peri*-positions and for picryl substituted arenes and aza-arenes.

Figure 2 shows the class of substances which thermal decomposition begins with homolysis through five- or six-membered transition states. These include e.g. the so-called trinitrotoluene mechanism of thermal decomposition, which is obeyed by compounds having a hydrogen atom at γ-position with respect to nitro group [18-22], as well as the interaction of oxygen in *ortho*-standing nitro group with bridge heteroatom [17, 22] (e.g. in molecules of DIPS and DMDIPS) or chlorine atom [23].
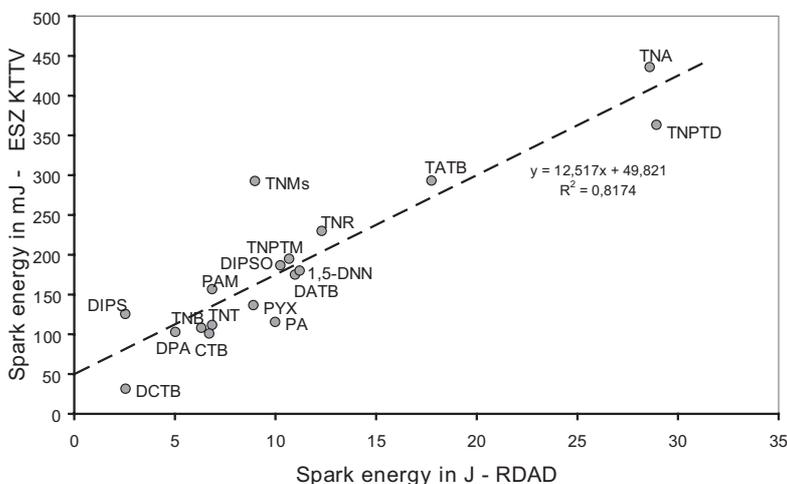
Figure 2. Relationship between outputs from ESZ KTTV and RDAD instruments for derivatives of 1,3,5-trinitrobenzene which primary step of thermolysis lies in homolysis via a five- or six-membered transition state or *aci*-form.

Figure 3 documents the effect of $-CH_2-$ linkage on the electric spark sensitivity: whereas in the measurements on the RDAD instrument the introduction of methyl groups into TNB, HNAB, and DIPS molecules produced an intermediate to distinct phlegmatising effect, this effect was negligible in measurements on the ESZ KTTV instrument. An opposite, i.e. sensitising influence of $-CH_2-$ can be seen in class *A* in Figure 3, this effect being more distinct in the measurements with ESZ KTTV instrument.

From the facts given so far it seems to follow that the mechanisms of spark energy transfer into the reaction centre of molecule could be different in the measurements on the two instruments (RDAD and ESZ KTTV) [1]. The thermal component of discharge in the first instrument may be one of the reasons of this difference. This assumption is also supported by the differences (in order of magnitude) between the E_{ES} values obtained from the individual instruments (see Table 1). Of course, the considerable electric energy losses in the area between the upper electrode and the sample surface in the RDAD system measurements contribute to the above-mentioned difference between the values.
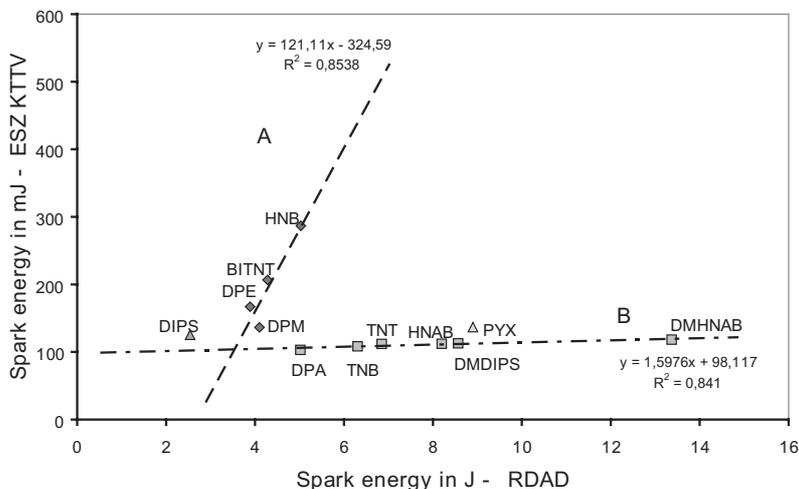
Figure 3.   Relationship between outputs from ESZ KTTV and RDAD instruments for dipicryl derivatives – an influence of $-CH_2-$ linkage upon a slope of the relationship (data of DIPS and PYX do not correlate).

Conclusions

The analysis of relationship between the E_{ES} values obtained by measurements with the two instruments (i.e. RDAD and ESZ KTTV) revealed that the relationship is not unequivocal. From the facts given above it is possible to come to the conclusion that the mechanisms of spark energy transfer into the reaction centre of molecule should be different in measurement on the two alternative instruments (see also paper [1]). The thermal component of discharge in the RDAD instrument may be one of the reasons of this difference. 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. The construction of spark gap and container in ESZ KTTV system decrease the electric energy losses. Measurement by means of this system is more sensitive to molecular structure of the studied polynitro compounds as in the case of RDAD instrument.

Acknowledgements

References

[1] Zeman S., Pelikán V., Majzlík J., Friedl Z., Electric Spark Sensitivity of Nitramines. Part I. Aspects of Molecular Structure. *Cent. Eur. J. Energ. Mater.*, **2006**, *3*(3), 27-44.

[2] Roux M., Auzanneau M., Brass C., Electric Spark and ESD Sensitivity of Reactive Solids. Part. I: Experimental Results and Reflection Factors for Sensitivity Test Optimization, *Propellants, Explos., Pyrotech.*, **1993**, *18*, 317-324.

[3] Amari S., Hosoya F., Mizushima Z., Yoshida T., Electrostatic Spark Ignitability of Energetic Materials, *Proc. 21st Int. Pyrotech. Seminar*, Moscow, Sept. **1995**, pp. 13-31.

[4] Jarman D., Prinse W., Bouma R., Electrostatic Discharge Initiation of CL-20: Effect of Discharge Time and Spark Energy, *Proc. 34th Int. Annual Conf. ICT* Karlsruhe, June **2003**, pp. 71/1-71/11.

[5] Kamenský Z., Electric Spark Sensitivity of Polynitro Compounds*, M.Sc. Thesis*, Univ. Pardubice, June **1995**.

[6] Zeman S., Kamenský Z., Valent P., Jakubko J., On the Electrostatic Spark Sensitivity of Some Organic Polynitro Compounds, in: M. Roux (Ed.) *Proc. Recueil des comunications „Journees d´etudes sur la sensibilité des composants et des substances énergét. á l´electricite statique"*, Aussois, Mai **1996**, pp. 197-206.

[7] Zeman S., Valenta P., Zeman V., Kamenský Z., Electric Spark Sensitivity of Polynitro Compounds: A Comparison of some Authors' Results*, HanNeng CaiLiao*, **1998**, *6*, 118-122.

[8] Zeman S., Zeman V., Kamenský Z., Relationship between the Electric Spark Sensitivity and the NMR Chemical Shifts of some Organic Polynitro Compounds*, Proc. 28th Int. Annual Conf. ICT*, Karlsruhe, **1997**, pp. 66/1-66/9.

[9] Kočí J., Zeman S., Spark Sensitivity of Polynitro Compounds. Part IV. A Relation to Thermal Decomposition Patrameters, *HanNeng CaiLiao,* **2000**, 8*,* 18-26.

[10] Kočí J., Zeman V., Zeman S., Spark Sensitivity of Polynitro Compounds. Part V. A Relationship between Electric Spark and Impact Sensitivities of Energetic Materials*, ibid.,* **2001**, 9, 60-65.

[11] Zeman V., Zeman S., Relationship Between the Electric Spark Sensitivity and Detonation Velocities of Some Polynitro Compounds, *Proc. 28th Int. Annual Conference of ICT*, Karlsruhe, June **1997**, pp. 67/1-67/10.

[12] Zeman V., Kočí J., Zeman S., Spark Sensitivity of Polynitro Compounds. Part II.

A Correlation with Detonation Velocities of some Polynitro Arenes, *HanNeng CaiLiao,***1999**, *7*, 127-132.

[13] Zeman V., Kočí J., Zeman S., Spark Sensitivity of Polynitro Compounds. Part III. A Correlation with Detonation Velocities of some Nitramines, *ibid.*, **1999**, *7*, 172-175.

[14] "Special Scientific and Development Activity in the Field of Energetic Materials", *Project No. FC-M2/05,* Ministry of Industry and Commerce, Prague, **2000**-**2002**, solver Univ. Pardubice.

[15] Strnad J., Majzlík J., Determination of Electrostatic Spark Sensitivity of Energetic Materials, *Proc. 4th Seminar "New Trends in Research of Energetic Materials",* Univ. Pardubice, April **2001**, pp. 303-307.

[16] Martinez Pacheco M., Bouma R., Katgerman L., Electrostatic Discharge Initiation of Ti+C Mixtures and the Thermite Al+MoO$_3$, *Proc. 35th Int. Annual Conf. ICT* Karlsruhe, June **2004**, pp. 105/1-105/12.

[17] Zeman S., Krupka M., Study of the Impact Reactivity of Polynitro Compounds. Part II. Impact Sensitivity as the First Reaction of Polynitro Arenes, *Propellants, Explos., Pyrotech.*, **2003**, *28*, 249-255.

[18] Matveev V.G., Dubikhin V.V., Nazin G.M., Soglasovanyi mekhanism razlozheniya aromaticheskikh nitrosoedinii v gazovoy faze (Thermolysis Mechanism of the Aromatic Nitrocompounds in the Gas Phase), *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1978**, 474-477.

[19] Bulusu S., Einstein D.I., Autera J.R., Anderson D.A., Velicky R.W., Deuterium Kinetic Isotope Effec: An Experimental Probe for the Molecular Processes Governing the Initiation of RDX, HMX and TNT, *Proc. 8th Int. Symp. on Detonation*, Albuquerque, NM, July, **1985**.

[20] Minier L.M., Oxley J.C., Thermolysis of Nitroarenes: 2,2',4,4',6,6'-Hexanitrostilbene*, Thermochim. Acta*, **1990,** *166*, 241-249.

[21] Wang J., Lang H.-Y., Mechanistic Study of Polynitro Compounds by XPS: Mechanism of the Thermal Decomposition of Polynitro Phenols*, Science in China*, *Ser. B*, **1990**, *33*, 257-266.

[22] Zeman S., Modified Evans-Polanyi-Semenov Relationshop in the Study of Chemical Micromechanism Governing Detonation Initiation of Individual Energetic Materials, *Thermochim. Acta*, **2002,** *384*, 137-154.

[23] Zeman S., Possibilities of Applying the Piloyan Method of Determination of Decomposition Activation Energies in the Differential Thermal Analysis of Polynitroaromatic Compounds and of their Derivatives, Part I. Polymethyl and Polychloro Derivatives of 1,3,5-Trinitrobenzene, *J. Thermal. Anal.,* **1979**, *17*, 19-29.