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# A New Aspect of Relationships between Electric Spark Sensitivity and Thermal Stability of Some Polynitro Arenes

Svatopluk Zeman

(*Institute of Energetic Materials (IEM), Faculty of Chemical Technology, University of Pardubice, CZ-*532 10 *Pardubice, Czech Republic*)

**Abstract:** An ESZ KTTV instrument of a new, relatively simple construction has been applied to determination of electric spark sensitivity of 29 polynitro arenes, expressed as spark energy, $E_{ES}$, required for 50-percent initiation probability. The thermal stability thresholds, $T_{max}$, were calculated from the published Arrhenius parameters of monomolecular thermal decomposition of the studied compounds, predominantly obtained under the conditions of the Russian manometric method. An approximate relationship has been found between the ln $E_{ES}$ values and threshold $T_{max}$ values. In the sense of this relationship, the compounds studied fall into several sub-groups. The reason of the said diversification lies in the decomposition reaction rate at the temperature of onset of their thermal decomposition. It has been found that in each sub-group increasing thermal stability of polynitro arenes is accompanied by increasing electric spark sensitivity of these substances. This fact must be taken into account if we deal with the problem of electric spark energy transfer into the reaction centre of the molecule.

**Key words:** electric spark sensitivity; explosive; thermal stability; polynitro arene

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## 1　Introduction

So far, there has not existed any unique idea of mechanism of initiation of energetic materials by electric spark[1-3]. The results of studies carried out by Zeman et al.[2-3] indicate that the primary fragmentation reactions in this initiation should be identical with the primary splitting processes of low-temperature thermolysis and detonation transformation of molecules of these materials. However, the mechanism of energy transfer from electric spark to the reaction centre of molecule is not fully understood yet[2-6]. Some authors are inclined to accept the idea of conversion of the electric spark energy into a thermal effect, i. e. to a thermolytic principle of the electric spark initiation[2-3,6-9]. However, Rat et al[1] consider this initiation a multidisciplinary problem. Auzanneau et al[7] stated that the "hot spots" during the initiation by electric spark should develop at the thinnest part of the solid, i. e. at intergrain points. On the basis of relationships between the electric spark sensitivity and heats of fusion of nitramines we supposed[4] that also dislocations in the crystals have some effect on the initiation of these compounds by spark. From this point of view, one of the ways of specification of mechanism of the said spark energy transfer consists in studying the relationships between the title sensitivity and molecular structure of the polynitro compounds[2-4], or thermal reactivity[8-12], sensitivity to mechanic stimuli[11,13-15] and parameters of their detonation[3-4,15-17].

Two different instruments were available for studies of electric spark sensitivity at the University of Pardubice: they differ by configuration of electrodes and structure of circuit[3-5]. In our recent papers[4-5] attention has been focused on mutual comparison of results of the measurements by means of these instruments. It was shown[4-5] that one of them, developed with a financial support from the Czech Ministry of Industry and Trade[18] (referred to as ESZ KTTV[4-5,19-20]), provides results that are more closely connected with molecular structure. This instrument gives $E_{ES}$ values that are lower in order of magnitude as compared with most earlier-published results obtained with other instruments[4-5,8-12,21], the highlighted influence of thermal component of discharge in these instruments is one of the reasons of this difference[3-5]. The outputs obtained from the ESZ KTTV instrument have not yet been investigated from the standpoint of their relationship to thermal reactivity of energetic materials. Therefore, this present paper focuses on their relation to the thermo-

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**Corresponding Author:** e-mail: svatopluk. zeman@ upce. cz

stability thresholds of polynitro arenes. These threshold values represent a significant characteristic feature of thermally stable explosives.

## 2 Experimental

### 2.1 Materials and their thermal decomposition data

The polynitro arenes used were synthesized in the framework research work described in papers[22-24,26-27] and earlier research activities at IEM. Their purity was checked by thin-layer chromatography using Silufol UV 254 with acetone-cyclohexane as the mobile phase. Their survey is presented in Table 1. The data on the onset of exothermic decomposition of most polynitroarenes studied, (see Table 1), were obtained by means of differential thermal analysis (DTA) described in Refs [22-24]: these DTA onsets, $T_D$, correspond to a linear temperature increase of 5 ℃ · $\min^{-1}$ and the sample magnitude of 0.09-0.11 g[22-24] or 0.05 g[25-26].

Some of the $T_D$ values were obtained within the work described in this present paper (it concerns ONT, DODECA, NTFA, BTX and PYX). The measurements were carried out on a DTA 550 Ex apparatus[25-26] specially developed for thermal analysis of explosives at our Institute. The apparatus represents a considerably modernized version of one used in the research described in paper[25]. The measurements were realized at ambient pressure, the sample being in direct contact with atmospheric air. The weighed sample (0.05 g) was placed in

**Table 1 Survey of the studied compounds, their code designations and thermal decomposition data**

| polynitro arene | | | thermal decomposition data | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | DTA onsets | | arrhenius parameters | | | | |
| data No. | chemical name | code design | $T_D$ /K | reference | method of evaluation | state of decompn | $E_a$ /kJ · $mol^{-1}$ | $\log(A/s^{-1})$ | reference |
| 1 | 1,3,5-trinitrobenzene | TNB | 579 | 24, 43 | SMM | liquid | 180.03 | 10.9 | 32, 38 |
| 2 | 2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl | HNB | 534 | 24, 43 | SMM | liquid | 207.24 | 16.1 | 30, 32 |
| 3 | 2,4,6,4′,6′,2″,4″,6″-octanitro -1,1′:3′,1″-terphenyl | ONT | 575 | a) | SMM | solid | 281.58 | 19.5 | 32, 36 |
| 4 | 2,4,6,2′,4′,6′,2″,4″,6″-nonanitro-1,1′:3′,1″-terphenyl | NONA | 578 | 24, 43 | TGA | solid | 236.29 | 15.2 | 32 |
| 5 | 2,4,6,2′,4′,6′,2″,4″,6″,2‴,4‴,6‴-dodecanitro-1,1′:3′1″:3″,1‴-quaterphenyl | DODECA | 550 | a) | extrapol. | solid | 217.48 | 15.2 | 37 |
| 6 | 1,8-dinitronaphthalene | 1,8-DNN | 558 | 23 | | liquid | b) | b) | |
| 7 | 1,5-dinitronapthalene | 1,5-DNN | 569 | 23 | | liquid | b) | b) | |
| 8 | 1,4,5-trinitronaphthalene | TNN | 549 | 23 | | liquid | b) | b) | |
| 9 | 1,4,5,8-tetranitronaphthalene | TENN | 579 | 23,24,43 | DTA | solid | 223.05 | 15.0 | 32 |
| 10 | 5,7-dinitro-1-(2,4,6-trinitrophenyl)-1H-1,2,3-benzotriazole | BTX | 545 | c) | extrapol. | solid | 214.85 | 13.9 | 37 |
| 11 | 2,4,6-tris(2,4,6-trinitrophenyl)-[1,3,5] triazine | TPT | 593 | 24, 43 | SMM | solid | 269.45 | 18.2 | 33, 36 |
| 12 | 2-methyl-1,3,5-trinitrobenzene | TNT | 526 | 24, 43 | SMM | liquid | 144.44 | 9.3 | 32, 39 |
| 13 | 2,4,6-trimethyl-1,3,5-trinitrobenzene | TNMs | 488 | 24, 43 | SMM | liquid | 185.05 | 12.3 | 32, 39 |
| 14 | 2-amino-1,3,5-trinitrobenzene | PAM | 514 | 24, 43 | SMM | liquid | 129.79 | 7.1 | 31, 41 |
| 15 | 2,4-diamino-1,3,5-trinitrobenzene | DATB | 527 | 24, 43 | SMM | solid | 196.80 | 13.2 | 32, 37 |
| 16 | 2,4,6-triamino-1,3,5-trinitrobenzene | TATB | 561 | 24, 43 | SMM | solid | 175.00 | 11.6 | 32, 37 |
| 17 | 2-hydroxy-1,3,5-trinitrobenzene | PA | 498 | 24, 43 | SMM | liquid | 161.18 | 11.7 | 29, 31 |
| 18 | 2,4-dihydroxy-1,3,5-trinitrobenzene | TNR | 447 | 24, 43 | SMM | liquid | 144.86 | 11.2 | 30, 31 |
| 19 | 1-chloro-2,4,6-trinitrobenzene | CTB | 569 | 24, 43 | SMM | liquid | 118.07 | 5.7 | 33, 42 |
| 20 | 1,3-dichloro-2,4,6-trinitrobenzene | DCTB | 570 | 24, 43 | SMM | liquid | 177.09 | 10.5 | 32, 42 |
| 21 | (E)-bis(2,4,6-trinitrophenyl)diazene | HNAB | 515 | 24, 43 | SMM | solid | 121.83 | 6.8 | 38 |
| 22 | bis(2,4,6-trinitrophenyl) sulfide | DIPS | 526 | 24, 43 | SMM | solid | 178.77 | 12.0 | 30, 35 |
| 23 | bis(2,4,6-trinitrophenyl) sulfone | DIPSO | 530 | 24, 43 | SMM | solid | 106.76 | 5.6 | 32, 35 |
| 24 | 1,1′-methylenebis(2,4,6-trinitrobenzene) | DPM | 461 | 24, 43 | DTA | solid | 92..95 | 5.2 | 22, 32 |
| 25 | 1,1′-ethane-1,2-diylbis(2,4,6-trinitrobenzene) | DPE | 514 | 24, 43 | SMM | liquid | 153.13 | 9.9 | 33 |
| 26 | 3,3′-dimethyl-2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl | BITNT | 487 | 24, 43 | SMM | liquid | 129.90 | 8.1 | 32, 40 |
| 27 | 2,4,6-trinitro-*N*-(2,4,6-trinitrophenyl)aniline | DPA | 507 | 24, 43 | DTA | solid | 177.76 | 11.0 | 22, 32 |
| 28 | *N*,*N*-bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline | NTFA | 542 | a) | SMM | solid | 187.00 | 11.5 | 35 |
| 29 | 3,5-dinitro-*N*,*N*′-bis(2,4,6-trinitrophenyl)-pyridine-2,6-diamine | PYX | 581 | c) | SMM | solid | 213.00 | 13.6 | 32, 41 |

Notes: a) the value taken from paper[26] and divided by 1.06 (see in text); b) the value was not specified yet;
c) the $T_D$ value from DTA 550 Ex apparatus, divided by 1.06 (see in text).

a Simax test tube of 5 mm diameter and 50 mm length. The reference standard was aluminium oxide (0.05 g). However, the sensitivity of this apparatus was lower than that in the case of the recent measurements[22-24], i. e. the corresponding $T_D$ values were 1.010 - 1.13 times higher as compared with these measurements[22-24]. Therefore, the $T_D$ values obtained from the DTA 550 Ex apparatus for ONT, DODECA and NTFA[26] and also for BTX and PYX (measured now and described in this paper) were divided by a factor of 1.06. The $T_D$ values of the compounds examined are given in Table 1.

### 2.2 The kinetic data

So far the most reliable kinetic results in the area of thermal decomposition of polynitro compounds are both theoretical and practical findings obtained by Russian scientists on the basis of their manometric method (see Refs[29-30,33]). The data obtained by this method (code abbreviation SMM[31]) are known to correspond to the non-autocatalyzed stage of thermal decomposition of the given material (i. e. to molecular structure[27-28]), and also to the absolute values of corresponding Arrhenius parameters. These data formed the main source of the Arrhenius parameters (i. e. $E_a$ and $\log A$) of thermal decomposition of the substances studied[32-33]. In some of these cases it is possible to apply also these kinetic data from the differential scanning calorimetry (DSC), which are directly compatible with the SMM results in many cases[2-3,31,34]. Results of differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) can be converted into compatible values by means of calibration curves[22-23,31-32]. The above-mentioned $E_a$ and $\log A$ parameters can also be obtained by prediction on the basis of modified Evans-Polanyi-Semenov equation[37]. The said parameters of the compounds studied are given in Table 1.

### 2.3 The thermostability threshold

The threshold, $T_{max}$, whose data presents in Table 2, is the maximum temperature that is applied to the given explosive for 6 hours without destroying its functionality (this roughly corresponds to a chemical change of max. 2% of the explosive)[35]. The calculation of this threshold starts from the Arrhenius equation in the form:

$$T_{max} = \frac{E_a}{2.303 \cdot R \cdot (\log A - \log k)} \qquad (1)$$

Semi-empirically it was found for thermally stable polynitro aromatic explosives that at the condition mentioned the rate constant $k$ is $10^{-6}$ $s^{-1}$[35]. However, the real $T_{max}$ values of a given explosive, depending upon the hydrostatic pressure of the medium as well as upon the size of the explosive charge, can be lower than the calculated limit by 50 - 80 K[35]. In the cases of 1,8-DNN, 1,5-DNN and TNN, whose Arrhenius parameters have not been specified yet, the thermostability thresholds were specified by means of their $T_D$ values[23] and a relationship between the $T_D$ and $T_{max}$ quantities[24].

Another limiting condition on the use of polynitro arenes in technological practice as thermostable explosives can be due to their physical thermal stability[24]. In Table 2, this stability is characterized by the melting points of the studied compounds whose values were taken from literature[22-24,33].

### 2.4 Electric spark sensitivity data

These data were obtained by means of the ESZ KTTV instrument and are presented in recent papers[4-5,8-20]. The instrument is designed for a small-scale sensitivity testing of energetic materials[4-5,18]. A high voltage power supply (the operating voltage of 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 ranging 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 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 an oscilloscope and then evaluated by means of a microcomputer to give the effective energy transmitted to the sample. The resulting electric spark sensitivity taken from paper[5] is presented in Table 2 as the spark energy (in mJ) for 50% probability of initiation. More details about the sensitivity determination are given in the papers[4-5].

## 3 Discussion

### 3.1 Relationships between electric spark sensitivity and thermal reactivity

Skinner et al[8] found a semi-logarithmic relationship between their $E_{ES}$ values and reciprocal temperatures $T_3$, which correspond with the rate constants $k = 10^{-3}\,s^{-1}$ of the first-order thermolysis of investigated explosives (the $k$ values were calculated from the published Arrhenius parameters[8]). The application of this approach to polynitro compounds shows[9] that this relationship is not unambiguous: both the chemical mechanism of primary thermolysis of energetic materials and intermolecular interaction factors in their crystals play decisive roles in classification of these compounds in the sense of the above-mentioned relation[9]. The Arrhenius parameters of thermal monomolecular decomposition are also present in Eq. (1) for prediction of the thermostability threshold, $T_{max}$. With regard to the fact that intermolecular interaction factors are significantly manifested in molecular crystals of thermally stable polynitro arenes[24,43], these factors are included in the resulting $T_{max}$ values due to the way of deriving Eq. (1)[35]. That means that with the polynitro arenes lacking a distinct stabilizing effect of crystal lattice the application of Eq. (1) gives higher $T_{max}$ values than are the values of the corresponding melting points (see Table 2). However, these practically nonrealistic $T_{max}$ values correspond with thermal stability of the compounds studied[24] and in this way give a certain idea of their thermal reactivity.

**Table 2　Survey of the electric spark sensitivities, $E_{ES}$[5] thermostabilty thresholds, $T_{max}$, melting points and calculated logarithms of hypothetical rate constants, ln*k*, for the temperatures of decomposition onsets, $T_D$, of the studied compounds**

| polynitro arene | | | thermostability threshold $T_{max}$/K | melting point /K | $E_{ES}$[5] /mJ | logarithm of the rate constant for temperature $T_D$ (Table 1) |
|---|---|---|---|---|---|---|
| class of compds. (Fig. 1) | data No. a) | code designation | | | | |
| A | 2 | HNB | 518 | 515.1 - 516.1 | 286.7 ± 26.7 | -9.5812 |
| | 3 | ONT | 563 | 567 - 569 | 128.9 ± 28.0 b) | -14.0011 |
| | 4 | NONA | 557 | above 643.1 | 158.2 ± 7.8 | -14.1885 |
| | 5 | DODECA | 543 | above 643.1 | 157.8 ± 8.6 b) | -12.5612 |
| | 6 | 1,8-DNN | 531 a) | 443.5 - 444.6 | 238.2 ± 9.9 | |
| | 7 | 1,5-DNN | 540 a) | 488.7 - 489.6 | 180.0 ± 10.9 | |
| | 8 | TNN | 523 a) | 421.1 - 421.9 | 210.0 ± 13.3 | |
| | 10 | BTX | 561 | 536.1 - 537.5 | 135.0 ± 8.3 | -15.3222 |
| | 13 | TNMs | 528 | 504.1 - 505.1 | 292.7 ± 17.0 | -17.3255 |
| | 15 | DATB | 537 | 560.1 - 563.1 | 175.0 ± 8.3 | -14.5393 |
| | 16 | TATB | 521 | dec. 573 | 293.3 ± 14.4 | -10.7968 |
| | | | averaged ln*k* value | | | -14.5038 |
| B | 1 | TNB | 556 | 395.1 - 396.1 | 108.2 ± 7.8 | -12.2940 |
| | 14 | PAM | 518 | 461.1 - 461.6 | 156.7 ± 7.2 | -13.9997 |
| | 18 | TNR | 441 | 382.1 - 382.6 | 230.0 ± 30.0 | -13.1727 |
| | 22 | DIPS | 519 | 507.1 - 508.1 | 125.5 ± 8.6 | -13.2867 |
| | 23 | DIPSO | 481 | dec. 614.1 | 186.7 ± 7.2 | -11.3200 |
| | 25 | DPE | 488 | 491.1 - 492.6 | 167.0 ± 1.5 | -13.0377 |
| | 26 | BITNT | 483 | 512.6 - 513.6 | 206.7 ± 7.2 | -13.4581 |
| | 29 | PYX | 523 | 603 - 608 | 136.7 ± 10.0 | -12.7803 |
| | | | averaged ln*k* value | | | -12.9186 |
| C | 9 | TENN | 556 | dec. 581.1 | 95.0 ± 8.3 | -11.8127 |
| | 12 | TNT | 493 | 354.6 - 355.1 | 111.8 ± 12.9 | -11.6021 |
| | 17 | PA | 476 | 394.1 - 394.6 | 115.5 ± 6.8 | -12.0199 |
| | 19 | CTB | 527 | 355.1 - 356.1 | 101.0 ± 7.7 | -11.8205 |
| | 21 | HNAB | 480 | 495.1 - 496.1 | 112.0 ± 8.6 | -12.7784 |
| | 24 | DPM | 434 | dec. 503.1 | 136.4 ± 7.6 | -12.2675 |
| | 27 | DPA | 484 | 516.1 - 517.6 | 103.0 ± 7.6 | -11.0687 |
| | | | averaged ln*k* value | | | -11.9099 |
| D | 1 | TNB | 556 | 395.1 - 396.1 | 108.2 ± 7.8 | -12.2940 |
| | 9 | TENN | 556 | dec. 581.1 | 95.0 ± 8.3 | -11.8127 |
| | 11 | TPT | 556 | dec. 621.5 | 283.3 ± 27.2 | -12.7643 |
| | 20 | DCTB | 561 | 421.1 - 422.1 | 31.5 ± 2.8 | -13.1786 |
| | 28 | NTFA | 558 | 616.1 - 618.1 | 50.2 ± 4.4 b) | -14.9805 |
| | | | averaged ln*k* value | | | -13.0060 |

Note: a) the value calculated from the $T_D$ value by means of relationship between the $T_D$ and $T_{max}$ values from paper [24]; b) the value calculated in the sense of paper [24].

An approximate relationship between the results obtained from the measurements by means of the ESZ KTT instrument and the thermostabilty thresholds of the compounds studied is presented in Fig. 1: like in Ref. [9] this semi-logarithmic relationship between the $E_{ES}$ and $T_{max}$ values is divided into several sub-groups. From the standpoint of primary fragmentation mechanism, these sub-groups represent heterogeneous aggregates of compounds. The polynitro arenes TATB, DATB, and 1,5-DNN in sub-group A should undergo homolysis via the six-membered transition state [2-3,46] which is connected with the presence of a hydrogen atom at $\gamma$-position with respect to the nitro group (the so-called trinitrotoluene mechanism of thermal decomposition[31,44-45]). In the molecules of the remaining members of this sub-group, the homolysis should primarily split the C—$NO_2$ bonds[2-3,47-48]. A strong stabilizing effect of crystal lattice can eliminate the effect of primary fragmentation mechanism upon the classification of polynitro compounds in the sense of relationships of the type "molecular structure-initiation reactivity"[2-3,49], which was clearly proved also in Ref. [43]. From among the polynitro arenes studied, TPT exhibits the most distinct stabilization of the mentioned type: its mixture with TNB has the onset of thermal decomposition lower by 143.5 K than the onset of pure TPT[24,43].

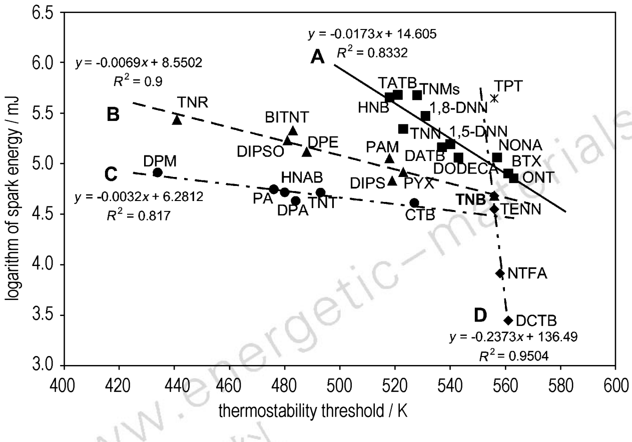

Fig. 1 Semilogarithmic relationship between electric spark sensitivity (expressed as the spark energy in mJ) and thermostability thresholds of the studied polynitro arenes

The members of sub-groups B and C are compounds whose primary homolysis proceeds via a five- or six-membered transition state[2-3] except for TNB and TENN: in their molecules the C—$NO_2$ is the first to be split. The straight line D approximately represents the limit of thermal stability of polynitro arenes including trinitrophenyl building units in their molecules: from this point of view, this area should also include the data of TPT, NONA, ONT, and BTX.

### 3.2 Reasons for classification of compounds studied

Now, if the mechanism of primary fragmentation of molecule is not the reason for the classification of polynitro arenes in the sense of Fig. 1, what other reason(s) exist(s)? A similar problem was encountered when we interpreted the classification of polynitro compounds in the sense of mutual relationship between the impact sensitivity detected by sound and impact sensitivity detected as "the first reaction"[3,50]. The interpretation of the relationships shown in Fig. 1 could start from the onset values, $T_D$, of thermal decomposition of the compounds studied. The rate of thermal decomposition of the studied polynitro arenes at this temperature might be the reason of their diversification in the sense of Fig. 1. These $T_D$ values (see Table 1) are easily specified by means of simple DTA. From the Arrhenius parameters of thermal decomposition given in Table 1, we then calculated the logarithms of hypothetical rate constants, ln$k$, for the temperatures of their decomposition onsets $T_D$. The results are presented in Table 2. The averaged ln$k$ values in Table 2 for each sub-group of the studied compounds lucidly show differences between these sub-groups. Comparison of these averaged ln $k$, values shows that the straight line $D$ should represent a broken section of the straight line $B$. It need not be emphasized that sub-group A includes highly thermostable polynitro arenes of technological importance (particularly ONT and NONA[28]).

An interesting finding is the following fact: in each sub-group an increasing thermal stability is connected with increasing electric spark sensitivity. This behavior could be due to the intensity of intermolecular interactions in molecular crystals of the compounds studied: on the basis of the decrease in the $T_D$ values of the mixtures of some of the polynitro arenes studied with TNB—compared with these values of pure substances—the highest stabilizing effect of the crystal lattice was found for TPT, NONA, TATB and TENN; slightly less distinct effect was found with DPA, DIPSO and DPM[26, 43]. Hence, in this sense the trend of electric spark sensitivity of polynitro arenes is opposite to their trend of thermal sensitivity. This fact has to be taken into account if we deal with the problem of electric spark energy transfer to the reaction centre of the molecule.

## 4 Conclusion

There exists an approximate linear dependence between the logarithm of electric spark sensitivity (expressed as spark energies, $E_{\mathrm{ES}}$, required for 50-percent initiation probability) and thermal stability thresholds of polynitro arenes. These compounds are diversified in the sense of this relationship and fall into several sub-groups. Each of them includes compounds with characteristic range of the values of their hypothetical thermolysis rate constants at the temperatures of onsets of their exothermic decomposition, $T_{\mathrm{D}}$, which are determined by means of differential thermal analyses. In each sub-group, increasing thermal stability is connected with increasing electric spark sensitivity. This fact could be due to the intensity of intermolecular interactions in molecular crystals of the polynitro arenes studied, and it has to be taken into account when dealing with the problem of the electric spark energy transfer to the reaction centre of molecule.

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