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## Electric Spark Sensitivity of Polynitro Compounds: Part II. A Correlation with Detonation Velocities of some Polynitro Arenes

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**Abstract:** The electric spark sensitivity of 32 polynitro arenes was determined as the spark energy,  $E_{ES}$ , required for 50 per cent initiation probability. A relationship between the  $E_{ES}$  values and the squares of detonation velocities of the polynitro arenes was established. This relationship represents a certain form of Evans – Polanyi – Semenov equation and, therefore, it signals an identity of chemical mechanisms of the primary fragmentation processes in the molecules of polynitro compounds during their detonation and in the initiation of their decomposition and/or explosive transformation by the action of electric spark. However, the way of energy transfer from the spark to reaction centre of molecule of the said compounds is not yet clear.

**Key words:** detonation; electric spark sensitivity; polynitro arenes

### 1 Introduction

Our previous communication<sup>[1]</sup> briefly summarised the basic effects affecting electric spark sensitivity of polynitro compounds and compared results given by several authors. but it did not deal with the mechanism of initiation of energetic materials by the action of electric spark. At present there is no unified model of the said mechanism<sup>[2]</sup>. Some authors are inclined to accept the idea of conversion of the spark energy  $E_{ES}$  into a thermal effect, i. e. thermolytic mechanism of the initiation by electric spark<sup>[3-5]</sup>. However, R. Rat et al<sup>[2]</sup> consider this initiation to be a multidisciplinary problem. From this point of view, one of the ways of specification of chemical mechanism of the given process consists in studying the relationships between the said sensitivity of energetic materials and their molecular structure<sup>[6-8]</sup>, thermal reactivity<sup>[5,6,9-11]</sup>, and sensitivity to mechanical stimuli<sup>[6,7,10,12]</sup>.

In the context of studies thus conceived, we have recently found a relationship of general form<sup>[13]</sup>:

$$(d)(E_p \cdot T_D^{-1}) = a \cdot X + b \quad (1)$$

where  $E_p$  means the Piloyan activation energy of decomposition<sup>[14-15]</sup> from the differential thermal analysis (DTA) of

polynitro compounds,  $T_D$  is the onset of their thermolysis<sup>[15-17]</sup>, and  $X$  stands for the spark energy,  $E_{ES}$ , required for 50 percent initiation probability. The general form of the equation (1), however, also defines the relationship between the results of DTA and detonation characteristics of energetic materials<sup>[16,17]</sup>. In this case,  $X$  denotes the square of detonation velocity,  $D^2$ , or explosion heat,  $Q$ , or the ratio of detonation pressure,  $p_{CJ}$ , and density,  $\rho$ , of the given material (i. e.  $p_{CJ} \cdot \rho^{-1}$ ). This fact led to specification of the following relationship<sup>[13]</sup>:

$$D^2 = A \cdot E_{ES} + B \quad (2)$$

which in the present paper has been presented and interpreted for an extend set of polynitro arenes.

### 2 Experimental

The measurements were carried out with the help of the apparatus and procedures described in the previous communication<sup>[1]</sup>. A survey of the polynitro arenes studied and the measurement results obtained are presented in Table 1. The detonation velocity values used were calculated according to Kamlet and Jacobs<sup>[18]</sup> for the theoretical maximum density (i. e. for single crystal), and they are given in Table 1, too.

Table 1 Survey of the substances measured, their code designations,  $E_{ES}$  and  $D$ .

No.	Substance Chemical name	Code design	$E_{ES}/J$	$D/km \cdot s^{-1}$
1	1,3,5-Trinitrobenzene	TNB	6.31	7.42
2	2,2',4,4',6,6'-Hexanitrobiphenyl	HNB	5.03	7.50
3	2,2',2'',4,4',4'',6,6',6''-Nonanitro- <i>m</i> -terphenyl	NONA	16.44	7.61
4	1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole	BTX	6.50	7.34
5	1,8-Dinitronaphthalene	1,8-DNN	13.99	5.38
6	1,5-Dinitronaphthalene	1,5-DNN	11.20	5.52
7	1,4,5,8-Tetranitronaphthalene	TENN	8.26	7.30
8	1,4,5-Trinitronaphthalene	TNN	10.97	6.27
9	2,2',4,4',6,6'-Hexanitrodiphenylsulfide	DIPS	2.56	7.16 <sup>a)</sup>
10	3-Methyl-2,2',4,4',6,6'-hexanitrodiphenylsulfide	MeDIPS	5.71	6.50 <sup>b)</sup>
11	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrodiphenylsulfide	DiMeDIPS	8.57	6.22 <sup>b)</sup>
12	2,2',4,4',6,6'-Hexanitro- $\alpha, \beta$ -diphenylethane	DPE	3.89	7.13
13	2,2',4,4',6,6'-Hexanitrodiphenylmethane	DPM	4.10	7.29
14	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl	BiTNT	4.28	7.10
15	2,2',4,4',6,6'-Hexanitrodiphenylamine	DPA	5.02	7.20
16	1-Methyl-3-hydroxy-2,4,6-trinitrobenzene	TNCr	5.21	7.42
17	2,2',4,4',6,6'-Hexanitrostilbene	HNS	5.32	7.27
18	1-Amino-2,4,6-trinitrobenzene	PAM	6.85	7.50
19	1-Methyl-2,4,6-trinitrobenzene	TNT	6.85	7.02
20	2,2',4,4',6,6'-Hexanitroazobenzene	HNAB	8.20	7.73
21	2,6-bis(2,4,6-Trinitrophenylamino)-3,5-dinitropyridine	PYX	8.90	7.48
22	1-Hydroxy-2,4,6-trinitrobenzene	PA	8.98	7.57
23	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB	17.75	7.95
24	2,2',4,4',6,6'-Hexanitrooxanilide	HNO	14.58	7.34
25	1,3-Diamino-2,4,6-trinitrobenzene	DATB	10.97	7.71
26	2,2',4,4',6,6'-Hexanitrodiphenylsulfone	DIPSO	10.54	6.77 <sup>c)</sup>
27	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	8.98	6.20
28	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	11.10	6.71
29	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitroazobenzene	DiMeHNAB	13.37	7.10
30	1,3-Dinitrobenzene	1,3-DNB	3.15	6.38
31	1,4-Dinitrobenzene	1,4-DNB	18.38	6.50
32	2,6-Dimethoxy-3,5-dinitropyridine	DMDNPy	20.57	6.52 <sup>b)</sup>

Notice: a) The value was taken from ref. [16];

b) Calculated by means of the Rothstein and Peterson method<sup>[25]</sup>;

c) Determined by means of the <sup>13</sup>C-NMR method<sup>[26]</sup>.

### 3 Results and discussion

In the sense of Eqn. (2), the set of polynitro arenes studied falls into several groups represented in Figs. 1 ~ 6.

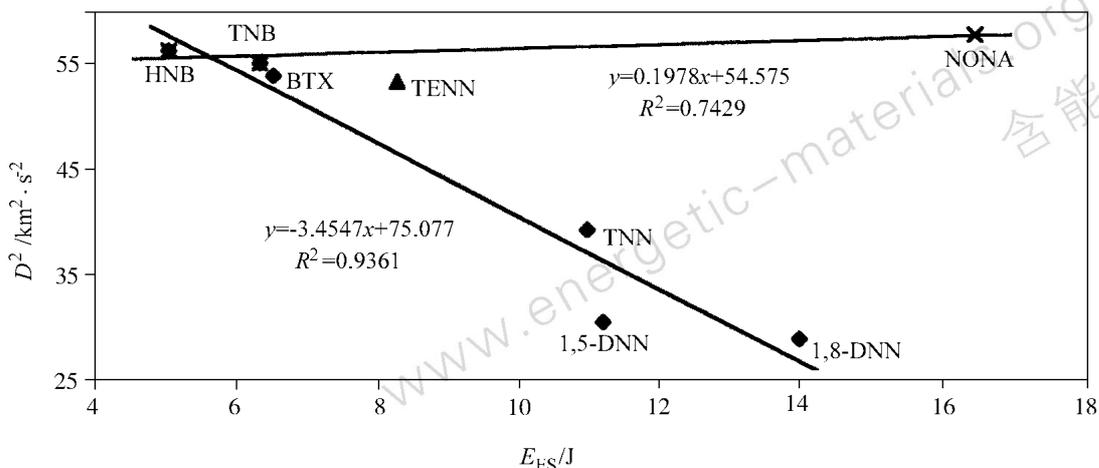


Fig. 1  $E_{ES}$  vs  $D^2$  for unsubstituted polynitro arenes (data of HNB and TNB correlating with the both forms)

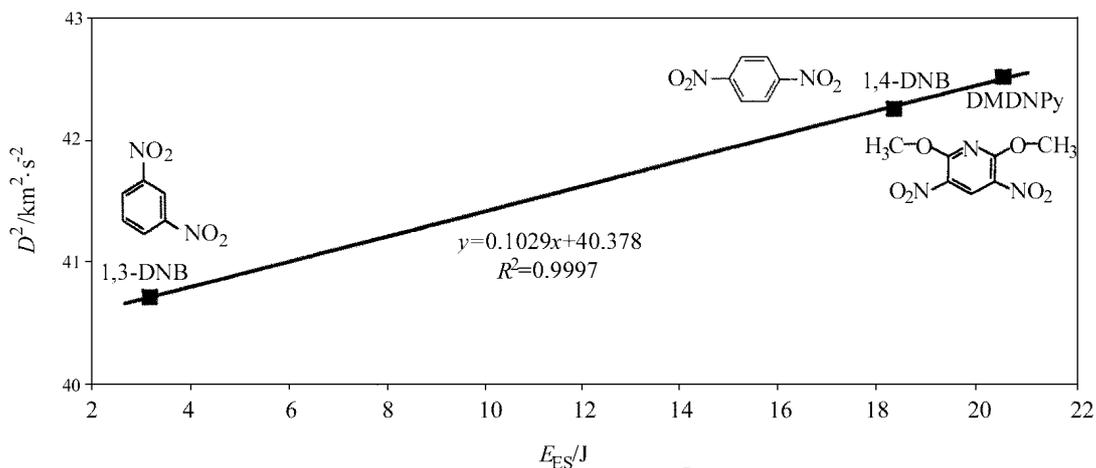


Fig. 2  $E_{ES}$  vs  $D^2$  for dinitro derivatives

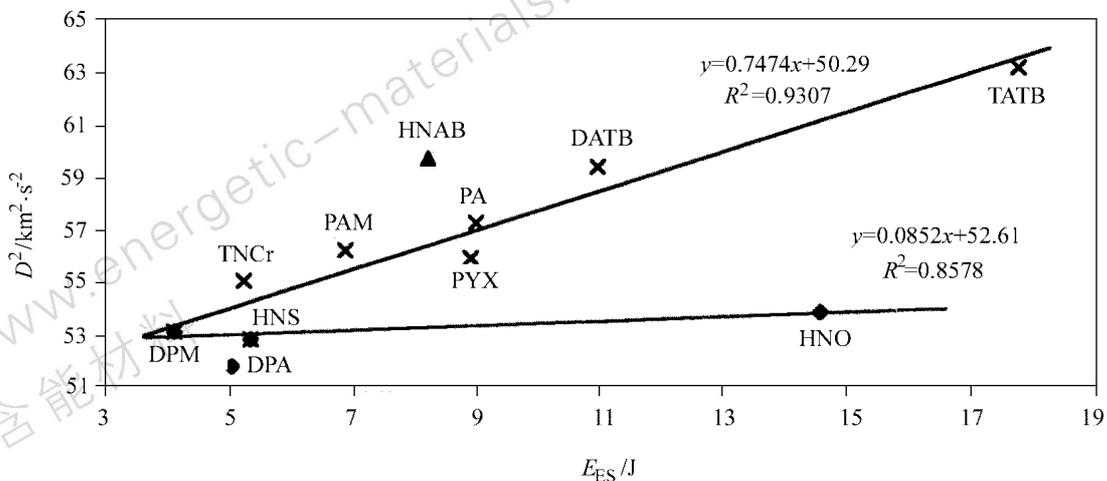


Fig. 3  $E_{ES}$  vs  $D^2$  for compounds having  $sp^2$  (or nearly  $sp^2$ ) hybridization at the central atom of thermolysis reaction centre (data of DPM and HNS correlating with the both forms)

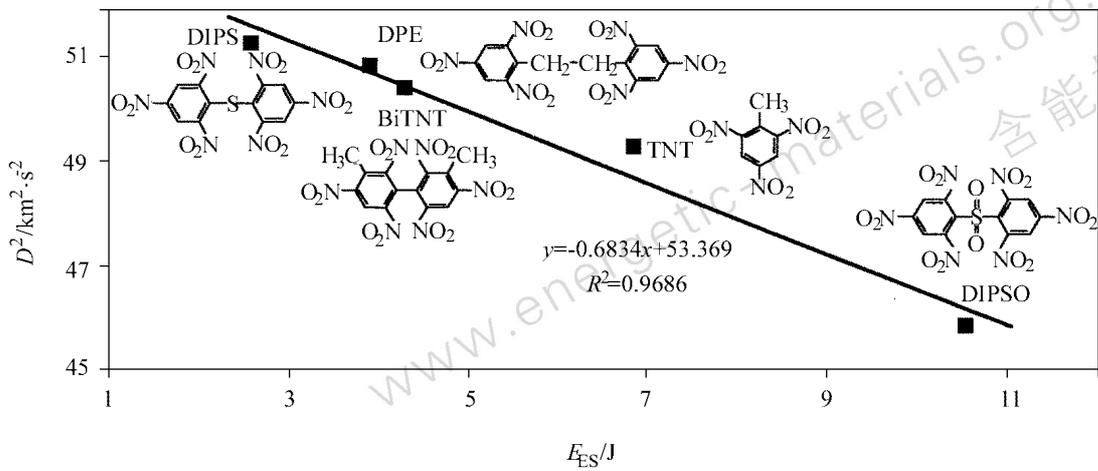


Fig. 4  $E_{ES}$  vs  $D^2$  for compounds which thermolyze via a five- or six-membered transition state involving a direct participation of ortho-nitro group

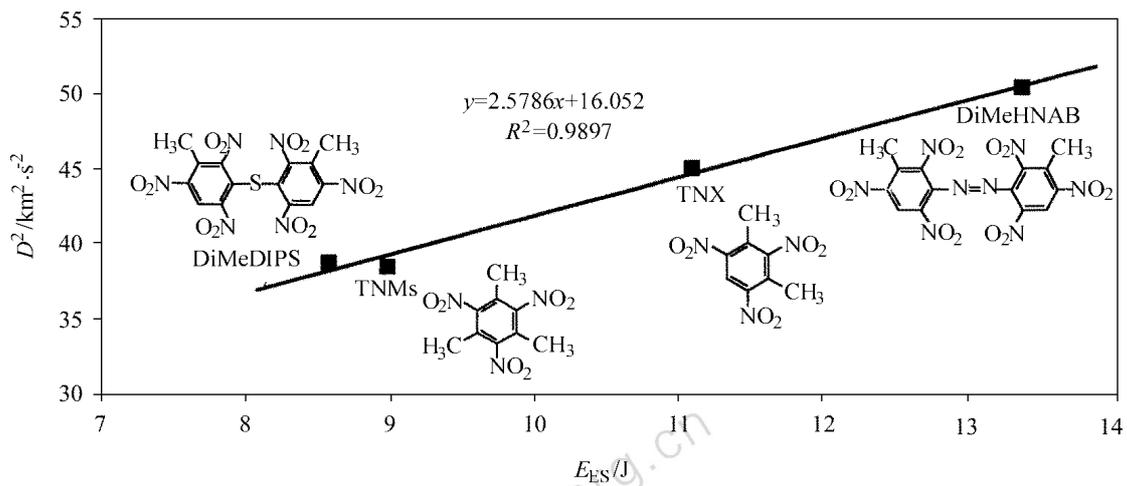


Fig. 5 Influence of polymethyl substitution upon the electric spark sensitivity

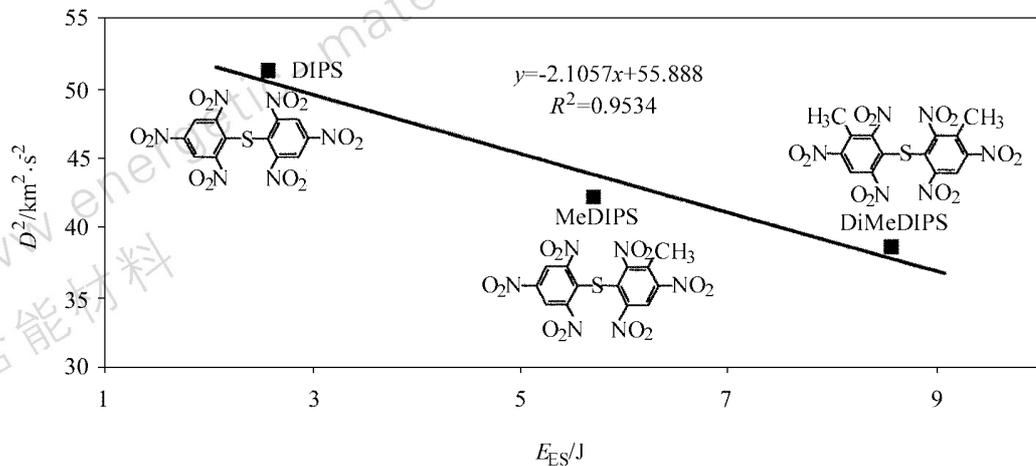


Fig. 6 Influence of polymethyl substitution upon the electric spark sensitivity

Fig. 1 documents the forms of Eqn. (2) for "genuine", i. e. unsubstituted polynitro arenes. In analogy with the impact sensitivity (see ref. [19]), also here the  $E_{ES}$  values might be affected by the intensity of intermolecular interactions in the crystals of the given substances (compounds with a more distinct interaction of this type are represented there by the straight line HNB-TNB-NONA and the position of TENN in the Figure). Data of TNB and HNB correlate with the both straight lines in the Figure.

Fig. 2 represents the dependence discussed for dinitrobenzenes and DMDNP. This is a logical group of compounds.

A relatively large group of compounds is formed by the nitro derivatives given in Fig. 3. In these compounds (with exception of HNAB) the start of thermolysis is supposed to be realised by a transfer of the hydrogen atom bound at  $\gamma$ -position to the oxygen atom of nitro group. The atoms carrying this hydrogen (i. e. carbon, oxygen or nitrogen) have  $sp^2$ , or nearly  $sp^2$  hybridization, including nitrogen atoms of azo-bridge in HNAB. This group of compounds falls into two subgroups: data of DPM and HNS correlating with the both forms of Eqn. (2) in Fig. 3. Division in this sense also might be due to the character and intensity of intermolecular interactions in the crystals of these nitroarenes. The composition of this all group of polynitro compounds is identical with that of the group corresponding to Eqn. (1) for  $X = p_{CJ} \cdot \rho^{-1}$  (see ref. [16]).

Fig. 4 presents the polynitro arenes whose thermal decomposition should start with an interaction between oxygen atom of ortho-nitro group and hydrogen atom of methyl group (TNT, BiTNT, DPE) or the connection bridge of picryls (DIPS, DIPSO). This group is also, to certain extent, similar to the nitroarene group corresponding to Eqn. (1) for  $X = p_{CJ} \cdot \rho^{-1}$  (see ref. [16]).

It is interesting to monitor the effect of polymethyl substitution in the trinitrophenyl system on the  $E_{ES}$  values, which is well documented in Fig. 5. If this substitution is connected with a marked increase of sterical effects in the molecule (TNMs, DiMeDIPS), the electric spark sensitivity increases. On the other hand, the diphenylsulfide derivatives show that multiple substitution of the said

type causes phlegmatization of these derivatives (the sensitivity decreases), which is documented by Fig. 6.

Introduction of the heat of explosion,  $Q$ , instead of the square of detonation velocity,  $D^2$ , in Eqn. (2) and subsequent modification leads to the equation:

$$E_{ES} = C \pm \alpha Q \quad (3)$$

Eqn. (3) is formally identical with the modified Evans-Polanyi-Semenov equation, which expresses the relationship between the activation energy,  $E_a$ , of thermal decomposition and heat of explosion of energetic materials<sup>[20-22]</sup>. The original equation containing the reaction heat,  $\Delta H$ , instead of  $Q$  was derived by Semenov for radical substitution reactions<sup>[23-24]</sup>; this equation is valid in narrow structural series of substances and documents the decisive importance of the bond being split for the course of the given reaction. The same validity can be observed with modified versions of the said equation, i. e. for the heat of explosion,  $Q$ <sup>[20-22]</sup>, and for the Eqn. (2) discussed here.

## 4 Conclusion

The relationship found between squares of detonation velocities and spark energies,  $E_{ES}$  required for 50 percent initiation probability can be considered another modification of the Evans-Polanyi-Semenov equation<sup>[23,24]</sup>; also with regards to the findings published<sup>[13,20-22]</sup> the described facts indicate the identity of primary fragmentation processes of molecules of energetic materials in their low-temperature thermolysis, the initiation of their detonation, and in the initiation of their decomposition and/or explosion transformation by the action of electric spark. In some cases, however, this relationship seems to be more distinctly affected by the nature of intermolecular interactions (like in the case of impact sensitivity). This suggests that the way of electric spark energy transfer to the reaction centre of molecule has not yet elucidated, which is also confirmed by the results reported by Chaumat<sup>[3]</sup> and Zeman et al<sup>[7]</sup>.

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## A Study on Initiation Mechanism of Al-containing Explosive

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**Abstract:** The processes of melting, initiation and explosion of the sample of Al-containing PETN are observed directly by a high speed photograph during impact, and the solid products of the sample after impact from the gas gun are studied by SEM analysis. The results show that the aluminum powder is oxidized and burns during detonation. After conducting the related numerical modeling by the DYTRAN code, the process of the hot spot formation in the sample around the aluminum grain is described theoretically.

**Key words:** Al-containing explosive; hot spot; impurity; shock initiation

(上接第 132 页)

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## 多硝基芳烃静电火花感度与爆速的关系

**摘要:** 通过测定 32 种多硝基芳烃的静电火花感度, 建立了 50% 发火能量  $E_{ES}$  与爆速平方值的关系式。该式不仅体现了 Evans-Polanyi-Semenov 关系, 而且表明在起爆、初始分解或由静电火花引起的能量转换过程中多硝基化合物分子初始分裂时化学机理的同一性。但电火花能转至分子反应中心的方式还不甚清楚。

**关键词:** 静电火花感度; 起爆; 多硝基芳烃

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