第 9 卷　第 2 期
2001 年 6 月

含 能 材 料
ENERGETIC MATERIALS

Vol. 9, No. 2
June, 2001

Article ID: 1006-9941(2001)02-0060-06

Electric Spark Sensitivity of Polynitro Compounds. Part V. A Relationship between Electric Spark and Impact Sensitivities of Energetic Materials

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Abstract: The spark energy, E_{ES}, required for 50 percent initiation probability of 41 polynitro compounds was determined. The relationships between the E_{ES} values and impact sensitivity, expressed as drop energies E_d of the "first reaction", were established and discussed. The conclusion is made that depending on intermolecular interaction factors in crystals of energetic materials, the mechanism of impact energy transition to the reaction centre of their molecule can be differ from that of transition of energy of electric spark.

Key words: electric spark sensitivity; impact sensitivity; energetic materials

CLC number: TQ56　　**Document code**: A

1 Introduction

A wide spectrum of the effects involved indicates that there will be problems in formulating a unique model of mechanism of electric spark initiation of energetic materials. One of the ways of specification of this mechanism can lie in studies of relationships of the said sensitivity of these materials to their molecular structure[1,2], thermal reactivity[3~7] and sensitivity to mechanic stimuli[1,3,8,9].

A routinely investigated mechanic stimulus of initiation of energetic materials is their impact sensitivity. Its relationship to the electric spark sensitivity is mentioned by Amari et al[8] and Hasegawa et al[3], the authors claim that the energies required for 50% probability of initiation in impact test and in spark test are similar for materials of medium sensitivity[8], however, highly sensitive materials are initiated by a spark more easily than by an impact. The same problem was also preliminarily dealt with by Zeman et al[1], whose findings are submitted to re-evaluation from the standpoint of testing of an extended set of polynitro compounds.

2 Experimental

2.1 Determination of Electric Spark Sensitivity

The measurements were carried out with the help of the apparatus and procedures described in the previous communication[8,10,11]. A survey of the polynitro compounds studied, their code designation and the measurement results obtained are presented in Table 1.

2.2 Determination of Impact Sensitivity

For the impact sensitivity determination in the Budapest laboratory of the Hungarian company GEOINFORM Szolnok, the standard impact tester (Julius Peters) was used with exchangeable anvil and the amount of tested substance was 0.25 cm^3 (refs. [12~14]); 2 kg and 5 kg weight drop hammers were used[12,13]. For a positive experiment was taken that connected with the first detectable decomposition[12~14] ("the first reaction", i. e. not only acoustic effect). Using up-and-down method the obtained sensitivity was expressed as drop energy E_d[12~14] whose values are presented in Table 1.

3 Results and Discussion

The relationship between impact sensitivity and electric spark sensitivity is presented in Figs. 1 ~ 3. The pictures show that the whole set of polynitro compounds studied falls into several groups, as it was the case in the preliminary study[1] too. The starting point of interpretation of this fact is the finding[7] that the initiation of energetic materials with electric spark is dominantly governed by primary chemical mechanisms of their thermolysis and by intermolecular interaction factors.

Received date: 2001-01-16

Table 1　Survey of the energetic materials studied, their electric spark (spark energy, E_{ES}) and impact (drop energy, E_d) sensitivities.

No.	Energetic material		Spark energy E_{ES}/J	Ref.	Drop energy E_d/J	Ref.
	Chemical name	Code designation				
1	1,3,5-Trinitrobenzene	TNB	6.31	10,15	5.89	13
2	2,2′,4,4′,6,6′-Hexanitrobiphenyl	HNB	5.03	10,15	2.78	13
3	1,8-Dinitronaphthalene	1,8-DNN	13.99	15	18.37	13
4	1,5-Dinitronaphthalene	1,5-DNN	11.20	15	11.01	13
5	1,4,5-Trinitronaphthalene	1.4,5-TNN	10.97	10,15	9.52	13
6	1,4,5,8-Tetranitronaphthalene	TENN	8.26	15	9.65	13
7	1,4-Dinitrobenzene	1,4-DNB	18.38	10,15	>29.43	13
8	2,2′,4,4′,6,6′-Hexanitroazobenzene	HNAB	8.20	10,15	8.57	13
9	3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitro-azobenzene	DiMeHNAB	13.37	10,15	6.18	13
10	1-Methyl-2,4,6-trinitrobenzene	TNT	6.85	10,15	>29.43	13
11	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	11.10	10,15	9.94	13
12	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	8.98	10,15	7.41	13
13	2,4,6-Trinitrobenzoic acid	TNBA	11.49	a	8.26	13
14	1-Methyl-3-hydroxy-2,4,6-trinitrobenzene	TNCr	5.21	15	9.45	13
15	2,2′,4,4′,6,6′-Hexanitrodiphenylamine	DPA	5.02	10,15	10.17	13
16	2,2′,4,4′,6,6′-Hexanitrooxanilide	HNO	14.58	15	8.72	13
17	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfide	DIPS	2.56	10,15	2.94	13
18	3-Methyl-2,2′,4,4′,6,6′-hexanitro-diphenylsulfide	MeDIPS	5.71	10,15	21.83	13
19	3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitrodiphenyl-sulfide	DiMeDIPS	8.57	10,15	>29.43	13
20	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfone	DIPSO	10.54	10,15	3.87	13
21	2,2′,4,4′,6,6′-Hexanitrobibenzyl	DPE	3.89	10,15	5.79	13
22	2,2′,4,4′,6,6′-Hexanitrostilbene	HNS	5.32	10,15	3.64	13
23	1,3,7,9-Tetranitrophenoxazine	TENPO	5.12	10,7	9.84	13
24	1,3,7,9-Tetranitrophenothiazine-5-oxide	TNPTM	10.68	a	7.22	13
25	1,3,7,9-Tetranitrophenothiazine-5,5-dioxide	TNPTD	5.78	7	4.51	13
26	3-Nitro-1,2,4-triazole-5-one	NTO	8.98	10,11	15.86	13
27	Pentaerythritol tetranitrate	PETN	1.74	10	3.60	13
28	1-Nitro-1-azaethylene	DIGEN	8.38	16	14.73	12
29	2,2-Dinitro-2,4-diazapentane	OCPX	13.45	10,16	>29.43	13
30	2,5-Dinitro-2,5-diazahexane	DMEDNA	8.24	10,16	>29.43	13
31	2,5-Dinitro-2,5-diazahexane-3,4-dione	DMNO	5.49	10,16	11.77	13
32	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	8.08	10,16	13.13	13
33	2,4,6,8-Tetranitro-2,4,6,8-tetraazanonane	OHMX	5.50	16	9.50	12
34	1,9-Diacetoxy-2,4,6,8-tettranitro-2,4,6,8-tetraazanonane	AcAn	13.93	16	10.20	13
35	1,3-Dinitro-1,3-diazacyclobutane	TETROGEN	6.25	16	10.78	12
36	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	2.49	10,16	6.69	13
37	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX	2.89	10,16	7.59	13
38	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaaza-cyclodecane	DECAGEN	2.96	16	5.90	12
39	1,5-Endomethylene-3,5-dinitro-1,3,5,7-tetra-azacyclooctane	DPT	17.42	7	10.20	13
40	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaaza-isowurtzitane	ε-HNIW	4.70^{b}	a	4.60^{b}	c
41	1,3,3-Trinitroazetidine	TNAZ	8.76	a	18.9	c

Notes: a) The result of this paper;

b) The value correspond to substance with min. 97 percent wt. of ε-HNIW (E_d value for pure ε-HNIW was predicted to be of 5.38 J[12]);

c) The value was determined by Accredited Trial Lab. No. 1025 of Sci. Res. Institute of Coal, Ltd., in Ostrava according to method[17] (practically in the sense of method[14]).

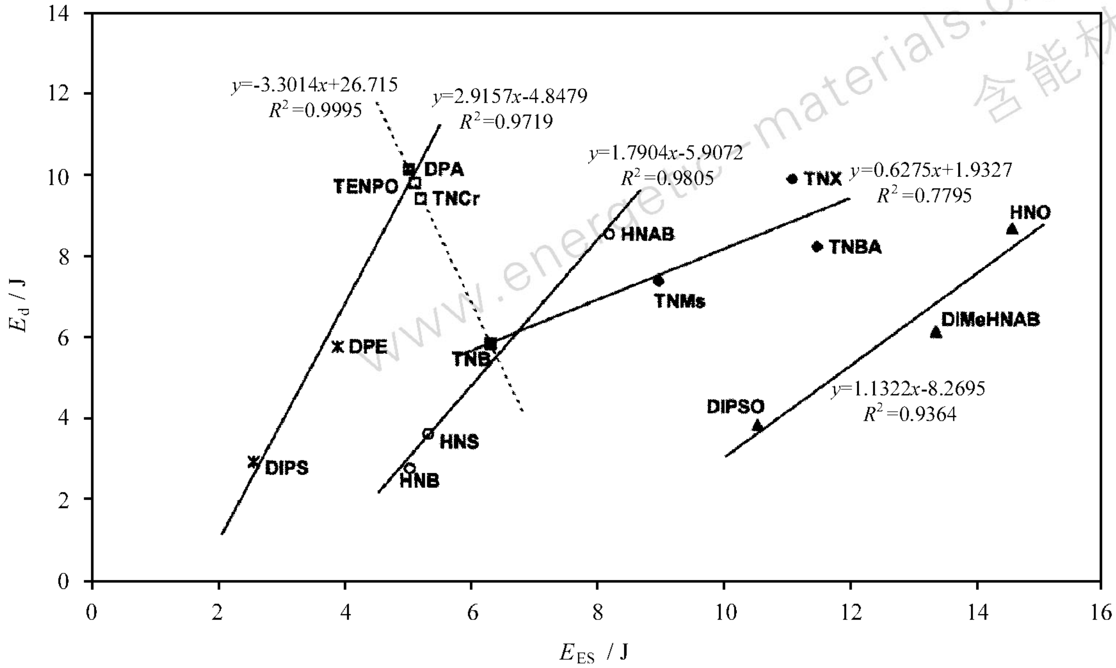

Fig. 1 Relationship between drop energy (E_d) and spark energy (E_{ES}) for substances with 2,4,6-trinitrofenyl building units in their molecules and for TENPO.

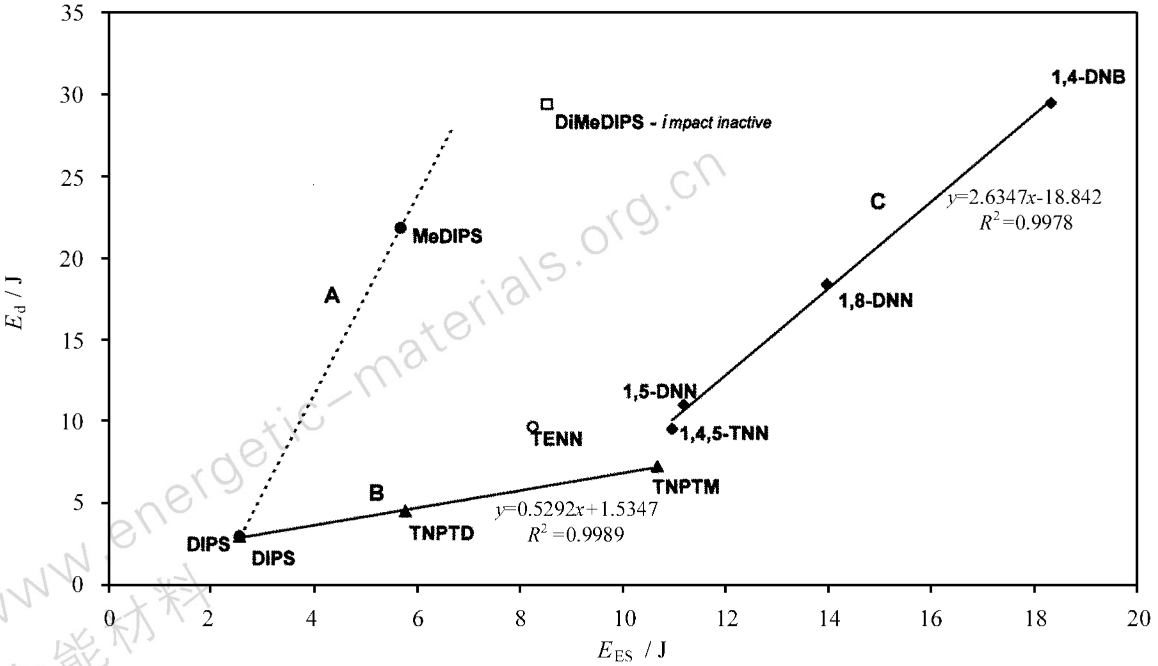

Fig. 2 Relationship between drop energy (E_d) and spark energy (E_{ES}) for substances with a sulphur hetero-atom in their molecules (groups A and B), and for "genuine" polynitro arenes.

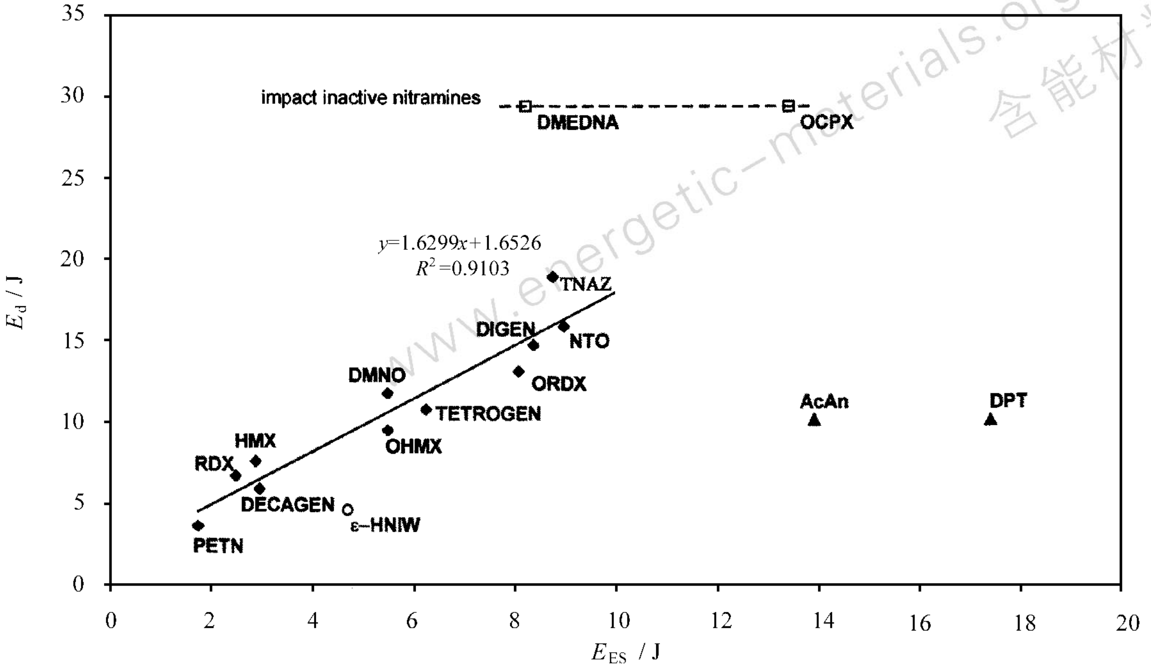

Fig. 3 Relationship between drop energy (E_d) and spark energy (E_{ES}) for nitramines, NTO and PETN.

Groups in Fig. 1 mainly consist of polynitro compounds having a hydrogen substituent bound at γ position to nitro group, i. e. compounds exhibiting the so-called "trinitrotoluene mechanism" of their primary thermolysis[18~20]. TNT was inactive at the conditions of the impact test applied. TNB and HNB represent "genuine" polynitro arenes with C—NO_2 bond primary fission in their thermolysis. Primary homolyses of C—S bonds in DIPS and DIPSO[21,22] and C—N_2 (azo-bridge) bond in HNAB[23] were originally presumed for thermolysis of these compounds: corresponding activation entropy values prove, however, that primary thermolysis of the said compounds goes by cyclic mechanism[24] (see also in ref. [7]).

The studied polynitro compounds are divided into individual groups on the basis of distinct characteristics of molecular structure in Fig. 2. Here the substances of groups *A* and *B* contain a sulphur hetero-atom in their molecules. Group *A* in the Fig. 2 includes DiMeDIPS, which is inactive at the conditions of the impact test applied. Substances of group *C* are "genuine" polynitro arenes, largely polynitro naphthalenes: data of TENN, whose molecule is centrosymmetrical, do not correlate with the group.

From what has been said so far it follows that the individual groups in Figs. 1 and 2 are not homogenous from the point of view of primary fission. The group of polynitro compounds in Fig. 3, on the other, is more homogeneous from this point of view. Data of AcAn do not correlate due to presence of two acetyls in its molecule; from the point of view of the electrostatic intermolecular interactions acetyl groups cannot be taken equivalent to nitro groups. Data of the globular nitramine molecules HNIW and DPT are alike different from other nitramines in Fig. 3. E_{ES} and E_d values of TNAZ signalise that unlike the most nitramines it is less vulnerable[25].

The inactivity of some of the polynitro compounds investigated in the impact test signals that the transfer of impact energy to the reaction centre of molecule will not be identical with the way of transfer of electric spark energy. The hypothesis of energy transfer differences between the two tests is also supported by the findings by Stengach[26], who studied the electric spark sensitivity of lead(II) azide and found out that an addition of hard inert admixtures to this azide (up to 10% by wt.) has practically no effect on the electric spark sensitivity (whereas the impact sensitivity is increased). On the other hand it should be noted that an introduction of methyl group into the DIPS molecule results in lowering of both impact sensitivity and electric spark sensitivity.

On the basis of above-mentioned facts it is possible to arrive at the conclusion that a common feature of the division of the polynitro compounds studied into the groups depicted in Figs. 1 ~ 3 primarily lies in the molecular structure, while the chemical mechanism of primary thermolysis is subsidiary here. Hence the reason of differences between the energy transfer from electric spark and that from impact to the reaction centre of molecule seems to be primarily given by intermolecular interaction factors in crystals of the energetic materials.

4 Conclusion

The results obtained confirm that the mutual relationship between the electric spark sensitivity and impact sensitivity of polynitro compounds is not unambiguous. Depending on intermolecular interaction factors in crystals of energetic materials, the impact energy transfer mechanism to the reaction centre of the molecule can be different from the electric spark energy transfer.

Acknowledgement

The authors are indebted the management of the Austin Detonator (former Zbrojovka Indet, Inc.), CZ-755 37 Vsetín, for its kind interest in and support of realization of this study. The author also expresses his gratitude to the Hungarian company GEOINFORM Szolnok for affording the impact tester and sponsoring the respective measurements.

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Thermal Decomposition and Reaction of Binary Mixtures of Fuels and Oxidants

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Abstract: By using the DTA technique, the thermal decomposition of fuels (MEL, PVA, MC, AC) and thermal reactions of mixtures of these fuels and oxidants were investigated. The results show that MEL decomposed endothermally, PVA, AC, MC – exthothermally. The mixtures react more complicatedly. From the view of processing DTA data with the help of famous Kissinger method, some mixtures do not follow the conditions of Kissinger's equation. The reason of such phenomena may be is that the gaseous products of thermal reaction do not influence the reaction process, in one hand, and the reaction happens in pure solid phase, in another hand. These phenomena are important for estimating the ignition ability of combustion and stability combustion of such gas generation compositions (GGC), The value of reaction constants of mixtures demonstrates the possibility and stability of ignition and combustion of mentioned mixtures. Because that MEL and its mixture with oxidants mentioned above decompose and react endothermally, MEL does not be used singly as fuel of pyrotechnic composition. MC, AC and PVA may be used as component of GGC.

Key words: gas generation compositions (GGC); oxidant; fuel; decomposition; combustion