第 8 卷　第 1 期
2000 年 3 月

含　能　材　料
ENERGETIC MATERIALS

Vol. 8, No. 1
March, 2000

Article ID: 1006-9941(2000)01-0018-09

Electric Spark Sensitivity of Polynitro Compounds: Part IV. A Relation to Thermal Decomposition Parameters

Svatopluk ZEMAN, Jiří KOC■

(*Department of Theory and Technology of Explosives*, *University of Pardubice CZ* – 532 10 *Pardubice*, *the Czech Republic*)

Abstract: The spark energy, E_{ES}, required for 50 percent initiation probability of 53 polynitro compounds was determined. It was found that semi-logarithmic relationship by Skinner et al (1998) between the E_{ES} values and reciprocal temperatures for thermolysis rate constants $k = 10^3\ s^{-1}$ has different forms for different groups of the compounds. The fact is discussed and conclusion is made that both the chemical mechanism of primary thermolysis of energetic materials and intermolecular interaction factors in their crystals play decisive roles in their initiation by electric spark.

Key words: electric spark sensitivity; energetic materials; polynitro compounds; thermal decomposition

CLC number: TQ560.7　　**Document code**: A

1 Introduction

So far, there exists no unique idea of initiation mechanism of energetic materials by electric spark[1]. The results carried out by Zeman et al[2~4] indicate that the primary fragmentation reactions in this initiation can 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[3~6]. Some authors are inclined to the idea of conversion of the electric spark energy into a thermal effect, i. e. to a thermolytic principle of the electric spark initiation[6~8]. However, Rat et al[1] consider the initiation as a multidisciplinary problem. From this point, one of the ways of specification of mechanism of the said spark energy transfer connects with the relationships between the title sensitivity and mole-cular structure of the polynitro compounds[2,5,9], or thermal reactivity[8~12], sensitivity to mechanic stimuli[5,9,11,13] and parameters of their detonation[3,4,14].

In the context of studies thus conceived, we have found (in the case of thermal reactivity characteristics) a relationship[3] between the expression $E_P \cdot T_D^{-1}$ and the spark energy E_{ES} for 50% probability of initiation. Where, E_P stands for the Piloyan activation energy of decomposition[15,16] from differential thermal analysis (DTA) of polynitro compounds, and T_D stands for the start temperature of their thermolysis[16~18]. The expression ($E_P \cdot T_D^{-1}$) represents the entropy of thermolysis onset of energetic materials[19,20] and correlates well with the characteristics of their detonation[17~20].

We failed in finding the direct relationship between the E_P values or values of thermolysis activation energy, E_a obtained from the Russian Manometric Method (SMM, see e. g. refs [21, 22]) and the E_{ES} values found by us[9]. However, Skinner et al[8] described a poor correlation between their E_{ES} values and reciprocal values of thermolysis activation energies. On the other hand addition, Roux et al found a good linear correlation between the E_a values (taken from ref. [23]) and their own E_{ES} values[10]; they obtained the same result also when applying the reciprocal values of E_a[24]. However, the E_{ES} values by Roux et al are incompa-tible with those obtained from our measurements, which is due to different construction of the spark gap and arrangement of the sample measured[25].

Skinner et al[8] used construction parameters and sample different from ours. They found a semi-logarithmic relationship between E_{ES} and the reciprocal temperatures, which

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Received date: 1999-05-21

correspond to the rate constants $k = 10^3\ s^{-1}$ of the first-order thermolysis of the investigated substances. This temperature was calculated[8] with the help of the Arrhenius parameters (i. e. E_a and log A) published by various authors and under the assumption that 5% conversion of the substance after 50 μs of thermolysis is sufficient for its initiation. Skinner et al[8] found a good correlation between the E_{ES} and the reciprocal critical temperatures calculated from the Frank-Kamenetskii relationship.

In view of the above facts, the attention in the following text will be paid to re-evaluate the relationship between the spark energies specified by us and the thermal decomposition parameters of organic polynitro compounds. For this purpose we shall particularly adopt the findings by Skinner et al[8].

2 Experimental

2.1 Electric spark sensitivity

The measurements were carried out with the help of the apparatus and procedures described in ref. [25]. Experiment results of the polynitro compounds studied are presented in Table 1.

Table 1 E_{ES} and Arrhenius parameters[26,27] of the polynitro compounds studied

No.	Polynitro compound		E_{ES}/J	Arrhenius parameters of thermolysis					
	Chemical name	Code		Method	State	T/K	E_a/(kJ · mol^{-1})	log$A$	Ref.
1	1,3,5-Trinitrobenzene	TNB	6.31	SMM	Liquid	523 ~ 583	180.03	10.9	[28]
2	2,2′,4,4′,6,6′-Hexanitrobiphenyl	HNB	5.03	SMM	Liquid	513 ~ 573	207.24	16.1	[29]
3	2,2′,2′′,4,4′,4′′,6,6′,6′′-Nonanitro-*m*-terphenyl	NONA	16.44	DTA	Solid	572 ~ 596	214.11	14.1	[30]
4	1,4,5,8-Tetranitronaphthalene	TENN	8.26	DTA	Solid	572 ~ 605	223.05	15.0	[30]
5	1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole	BTX	6.50	a	Solid		214.80	13.9	[31]
6	2,4,6-tris(2,4,6-Trinitrophenyl)-*s*-triazine	TPT	10.61	SMM	Solid	573 ~ 623	269.45	18.2	[32]
7	2,2′,4,4′,6,6′-Hexanitroazobenzene	HNAB	8.20	SMM	Liquid	463 ~ 493	121.83	6.8	[33]
8	1-Methyl-2,4,6-trinitrobenzene	TNT	6.85	DSC	Liquid		143.90	11.4	[34]
9	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	11.10	SMM	Liquid	493 ~ 533	146.95	9.1	[28]
10	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	8.98	SMM	Liquid	514 ~ 545	185.05	12.3	[28]
11	1-Hydroxy-2,4,6-trinitrobenzene	PA	8.98	SMM	Liquid	456 ~ 543	161.18	11.7	[29]
12	1-Methoxy-2,4,6-trinitrobenzene	TNA	28.59	SMM	Liquid	449 ~ 505	113.80	6.9	[35]
13	1-Methyl-3-hydroxy-2,4,6-trinitrobenzene	TNCr	5.21	SMM	Liquid	471 ~ 513	192.46	15.6	[35]
14	1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	12.30	SMM	Liquid	453 ~ 473	144.86	11.2	[29]
15	1-Amino-2,4,6-trinitrobenzene	PAM	6.85	SMM	Liquid	523 ~ 573	129.79	7.1	[29]
16	1,3-Diamino-2,4,6-trinitrobenzene	DATB	10.97	SMM	Solid	493 ~ 543	196.80	13.2	[33]
17	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB	17.75	DSC	Solid		250.62	19.5	[34]
18	2,6-Diamino-3,5-dinitropyridine	DADNPy	12.40	SMM	Solid	538 ~ 558	224.50	15.3	[36]
19	2,6-bis(2,4,6-Trinitrophenylamino)-3,5-dinitro-pyridine	PYX	8.90	SMM	Solid	563 ~ 588	213.00	13.6	[36]
20	2,4,6-tris(3-Methyl-2,4,6-trinitrophenylamino)-*s*-triazine	TMPM	6.84	DTA$^{b)}$	Solid	507 ~ 515	116.18	7.2	[26]
21	2,2′,4,4′,6,6′-Hexanitrodiphenylamine	DPA	5.02	TGA	c	473 ~ 573	153.30	11.0	[37]
22	2,2′,4,4′,6,6′-Hexanitrooxanilide	HNO	14.58	SMM	Solid	503 ~ 568	215.62	16.0	[33]
23	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfide	DIPS	2.56	SMM	Solid	473 ~ 493	178.77	12.0	[29]
24	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfone	DIPSO	10.54	SMM	Solid	473 ~ 563	106.76	5.6	[38]

Continuning Table 1

No.	Polynitro compound		E_{ES}/J	Arrhenius parameters of thermolysis					
	Chemical name	Code		Method	State	T/K	E_a/(kJ·mol^{-1})	log$A$	Ref.
25	2,2′,4,4′,6,6′-Hexanitrodiphenylmethane	DPM	4.10	a	Solid	462～473	177.55	11.8	[31]
26	2,2′,4,4′,6,6′-Hexanitrodiphenylethane	DPE	3.89	Calcd.	Liquid		124.00	6.3	[39]
27	2,2′,4,4′,6,6′-Hexanitrostilbene	HNS	5.32	SMM	Solid	533～573	183.80	12.0	[33]
28	3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitrobiphenyl	BiTNT	4.28	SMM	Liquid	518～538	129.90	8.1	[40]
29	1-Chloro-2,4,6-trinitrobenzene	CTB	6.71	SMM	Liquid		118.07	5.7	[41]
30	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	2.55	SMM	Liquid		177.09	10.5	[41]
31	1,3,7,9-Tetranitrophenoxazine	TENPO	5.12	DTA	Solid	509～517	158.55	10.0	[23]
32	1,3,7,9-Tetranitrophenothiazine-5,5-dioxide	TNPTD	5.78	SMM	Solid	523～573	200.96	11.7	[33]
33	1,1,1-Trimethylolpropane trinitrate	ETRYNIT	2.46	a	Liquid		165.29	14.9	[31]
34	Pentaerythritol tetranitrate	PETN	1.74	SMM	Solid		173.64	15.2	[42]
35	*N*,*N*-bis(2-Nitroxyethyl)-nitramine	DINA	5.85	SMM	Liquid	373～433	173.75	16.5	[43]
36	1-Nitro-1-azaethylene	DIGEN	$8.38^{d)}$	NMR	Liquid		156.00	14.5	[27]
37	2,4-Dinitro-2,4-diazapentane	OCPX	13.45	NMR	Liquid		178.60	16.3	[27]
38	2,5-Dinitro-2,5-diazahexane	DMEDNA	8.24	NMR	Liquid		176.10	16.1	[27]
39	3,5-Dinitro-3,5-diazaheptane	DNDAH	12.49	NMR	Liquid		185.90	16.9	d
40	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	8.08	NMR	Liquid		179.20	16.3	[27]
41	2,4,6,8-Tetranitro-2,4,6,8-tetraazanonane	OHMX	5.50	NMR	Liquid		180.60	16.4	[27]
42	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane	AcAn	13.93	NMR	Liquid		199.70	18.0	[27]
43	1,4-Dinitro-1,4-diazacyclohexane	DNDC	15.97	SMM	Liquid	489～507	198.40	17.3	[44]
44	1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline	TNAD	5.43	DSC	Solid	477～507	210.00	18.9	[45]
45	1,3-Dinitro-1,3-diazacyclobutane	TETROGEN	$6.25^{d)}$	Calcd.	Cond.		153.10	$14.1^{e)}$	[46]
46	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	2.49	f	Solid	420～470	213.00	18.8	[47]
47	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX	2.89	f	Solid	448～483	201.70	18.2	[47]
48	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaaza-cyclodecane	DECAGEN	$2.96^{d)}$	NMR	Solid		213.50	18.6	[27]
49	1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DPT	17.42	NMR	Solid		195.10	15.4	[31]
50	2,5-Dinitro-2,5-diazahexane-3,4-dione	DMNO	5.49	QSPR$^{g)}$	Cond.		178.80	$13.8^{h)}$	[27]
51	1,4-Dinitrotetrahyroimidazo[4,5-d]imidazol-(1H,3H)-dione	DINGU	15.19	a	Solid		189.19	16.2	[31]
52	1-(Methylnitramino)-2,4,6-trinitrobenzene	TETRYL	5.49	SMM	Liquid	403～438	156.9	14.5	[48]
53	3-Nitro-1,2,4-triazol-5-one	NTO	8.98	IR	Solid	468～483	206.00	20.6	[49]

Notice: a) The values extrapolated by means of the modified Evans-Polanyi-Semenov equation[31];

b) DTA means the differential thermal analysis whose results were transformed to parameters compatible to SMM outputs by means calibration curves[30]-analogously results of TGA (i. e. the thermogravimetric analysis) were treated[37];

c) The temperature region of the phase change "solid phase-liquid";

d) The value predicted[14];

e) The value taken from ref. [27];

f) Gasometric methods and DSC whose results were averaged by means of calibration curves on the basis of ^{15}NNMR outputs[47];

g) QSPR means "Quantitative Structure-Property Relationship" calculation and the E_a value was obtained by Pivina T S[50];

h) The value calculated by means of relationship between log$A$ and ^{15}NNMR chemical shifts of nitro group nitrogens (ref. [27]).

2.2 Arrhenius parameters

The discrepancy in principles and physical conditions of kinetics measurements in the thermolysis of energetic materials prevents a uniform classification of a large majority of results obtained in various laboratories all over the world. This field of considerable importance involves both theoretical and practical results obtained by Russian scientists: they have used the isothermal manometric method[21,22,29] with a glass compensating manometer of the Bourdon type to examine the kinetics of thermolysis of energetic materials in vacuum. The data obtained by this method (which was code designated as SMM) are known to correspond to the non-autocatalyzed stage of thermal decomposition of the given materials, and also to the absolute values of the corresponding Arrhenius parameters. The parameters, i. e. values E_a and log A, were used in construction of the relationships in the present paper. It is possible to apply also kinetic data from the differential scanning calorimetry (DSC), which are directly compatible with the SMM results. Results of the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) can be converted to compatible values by means of the calibration curves[26,37]. The above-mentioned E_a and log A parameters can be also obtained by prediction on the basis of modified Evans-Polanyi-Semenov equation[19,31] or by means of outputs of the ^{15}NNMR spectroscopy[19,27,47]. The Arrhenius parameters used are presented in Table 1.

3 Results and discussion

In the sense of the semi-logarithmic relationship found by Skinner et al [8] between the E_{ES} and T_3, the group of polynitro compounds of Table 1 fell into several subgroup depicted in Figs 1 ~ 4.

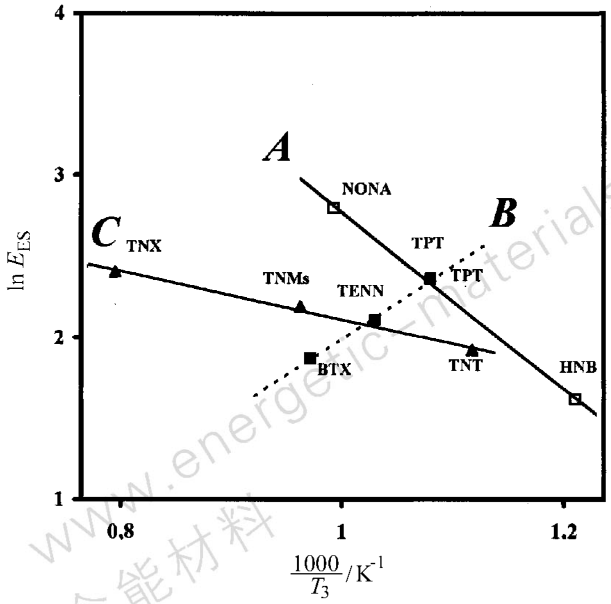

Fig. 1 Relationship between E_{ES} and reciprocal temperatures T_3 for thermolysis rate constant $k = 10^3$ s^{-1} unsubstituted polynitro arenes (lines A and B); polymethyl derivatives of TNB (lines C)

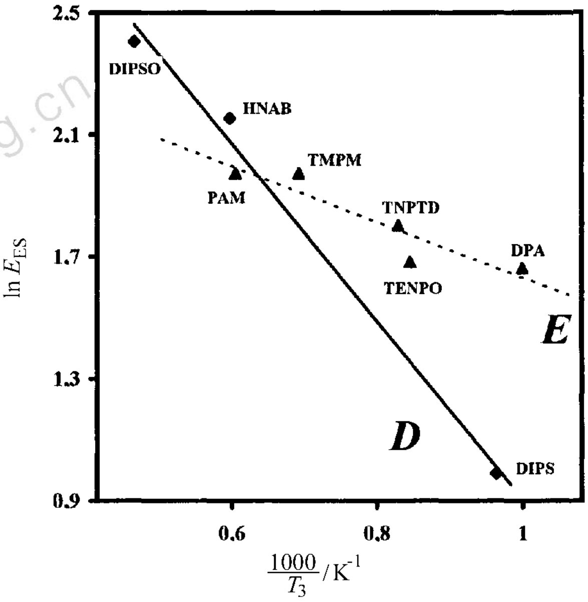

Fig. 2 Relationship between E_{ES} and reciprocal temperatures T_3 for thermolysis rate constant $k = 10^3$ s^{-1} dipicryl derivatives with primarily thermolysed C – S and C – N_2 bonds, respective (line D); amino-polynitro arenes (line E)

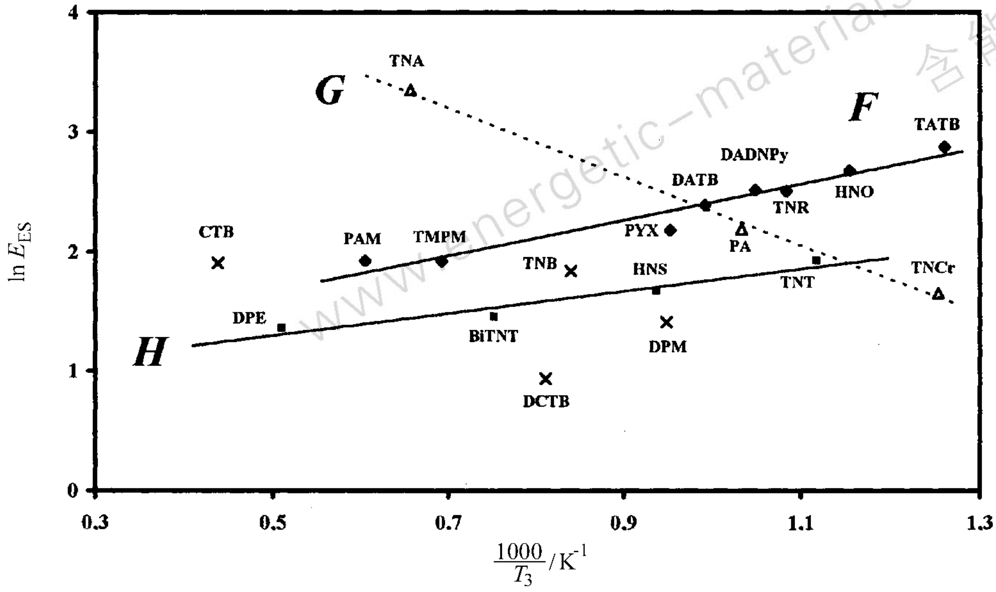

Fig. 3 Relationship between E_{ES} and reciprocal temperatures T_3 for thermolysis rate constant $k = 10^3$ s^{-1} derivatives of picric acid (line G) ; amino- and polyamino- polynitro arenes (line F) ; dimers of TNT (line H)

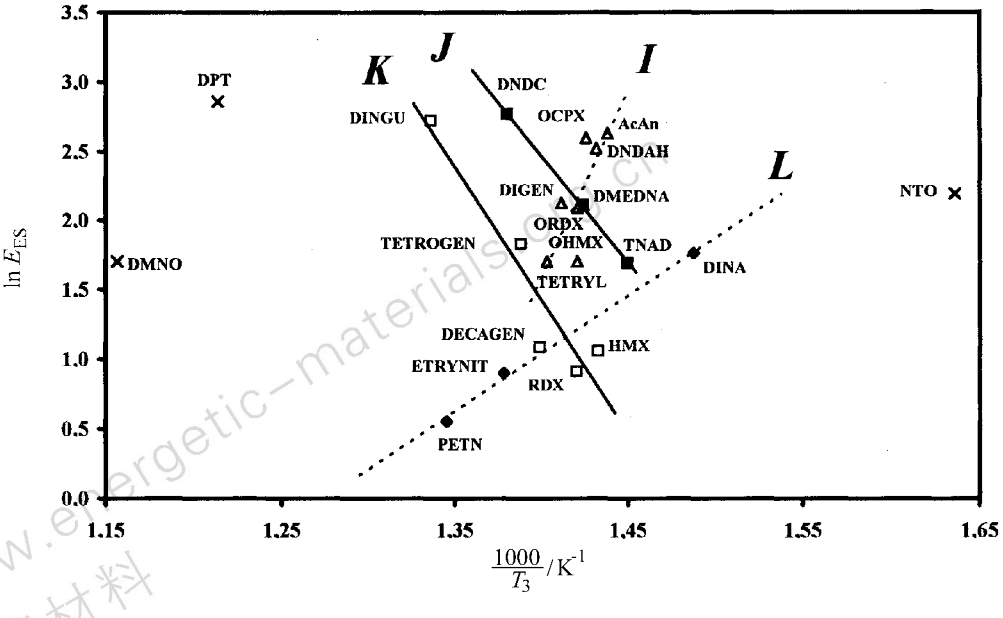

Fig. 4 Relationship between E_{ES} and reciprocal temperatures T_3 for thermolysis rate constant $k = 10^3$ s^{-1} polynitramines (lines I, J and K) ; nitric esters (line L)

The dependences *A* and *B* in Fig. 1 include polynitroarenes whose primary thermolysis consists in homolytic decomposition of $C-NO_2$ bond (in some cases this is also indicated by the respective activation entropy values[39,51]). The molecules of polynitroarenes of group *B* are more rigid than the polypicryl derivatives of group *A*. The steric hindrance in the TPT molecules can be a probable reason of the correlation of its data with both the relationships.

According to some authors, the primary thermolysis of the substances involved in relationship *D* of Fig. 2 is not connected with the reactivity of nitro group[26], e. g. Maksimov presumes[52] that the C – S bond is primarily split in the thermolysis of DIPS and DIPSO. Similarly, Hoffsommer and Feiffer presume[53] the primary thermolysis of $C-N_2$ bond in HNAB. However, from the activation entropy values it can be presumed that the primary fragmentation of the said substances goes by a cyclic mechanism[39]. The results obtained from the thermlolysis of DIPS and DIPSO indicate that the first step of thermolysis consists in the primary interaction between the oxygen atom of ortho-nitro group and the bridge heteroatom[17].

The dependences *C* (Fig. 1), *E* (Fig. 2), *F*, *G*, and *H* (Fig. 3) involve the data pertaining to the polynitroarenes whose molecules contain a hydrogen atom bound at the γ-position with respect to the nitro group (i. e. there are alkyl, amino or hydroxy substituents adjacent to the nitro group). For these substances the accepted mechanism of primary thermolysis is the so-called "trinitrotoluene mechanism"[54]. It involves migration of the said hydrogen (through a six-membered or, in the case of TNA, a seven-membered transition state) to the oxygen of nitro group with subsequent homolysis of the N – OH bond thus formed[54~57].

The dependences *E* (Fig. 2) and *F* (Fig. 3) predominantly summarise the data of amino- or polyamino-polynitroarenes. Their different courses are probably due to different character and intensity of intermolecular interactions in the crystals of both the groups of substances. The dependences *C* (Fig. 1) and *H* (Fig. 3) are same; the latter should also involve the data of DPM. The dependence *G* (Fig. 3) includes derivatives of picric acid. In the case of polychloro derivatives of TNB (here CTB and DCTB in Fig. 3), it was pointed by Maksimov et al[28] that their thermolysis resembles that of their polymethyl analogues in a way (see dependence *C* in Fig. 1). Therefore, for these derivatives, a course of the relationship discussed should be similar to dependence *C*.

Data of TNB do not correlate with any dependence in Figs. 1 ~ 3. A substitution in TNB nucleus connects probably with greater change in thermal reactivity than the change will be in spark energy transfer to reaction centre of molecule of resulting derivative. This might be a reason for the above-mentioned fact.

The effect of intermolecular interactions in crystals (through the molecular structure and its rigidity) upon the above-discussed relationship is also well illustrated in the dependences *I*, *J*, and *K* (Fig. 4). These involve the data of the polynitramines group whose primary thermolysis occurs in a homolytic splitting of N – N bond[58,59]. The dependence *I* contains the data of the linear polynitramines whose flexible molecules are formed by multiples of DIGEN structure units. The dependence *J* summarises the data of ethy-lenedinitramine derivatives. The data pertaining to rigid molecules of cyclic polynitramines, i. e. cyclo-polymers of DIGEN building units, correlate with the dependence *K*. It is worth mentioning that an analogous difference between polynitramines with flexible and rigid molecules is also encountered in the case of the relationship between their impact sensitivities and heats of fusion[19,60].

From the point of molecular structure, the data of DPT and DMNO do not correlate with any dependence in Fig. 4. The same is valid for NTO.

The homolysis of $O-NO_2$ bond forms the primary step in thermolyses of nitrate esters[61]. These substances are well depicted by the dependence *L* (Fig. 4).

4　Conclusion

It is not general validity that the semi-logarithmic relationship between the E_{ES}, for 50% probability of initiation, and the reciprocal temperatures T_3 (which correspond to the thermolysis rate constants $k = 10^3\ s^{-1}$) found by Skinner et al[8] for secondary explosives. This relationship has different forms for different groups of energetic materials. The analysis of the respective individual polynitro compounds in these forms of relationships shows that besides the chemical mechanism of primary thermolysis step, there is another decisive factor operating, viz. the intermolecular interaction factors in crystals of these materials. This conclusion should be valid for outputs of all methods whose results are compatible[25] with that of our method of electric spark sensitivity specification[2~5,9,14,25].

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多硝基化合物的静电火花感度与热分解参数的关联

摘要：通过测定53种多硝基化合物在50%发火概率下的静电火花感度E_{ES}，发现由Skinner等人在热分解速率常数$k = 10^3$ s^{-1}下建立的E_{ES}与温度倒数的半对数关系表达式随着化合物种类的不同而不同。分析结果表明，含能材料初始热分解的化学机理及其晶体中分子的相互作用对电火花点火起决定性的作用。

关键词：静电火花感度；含能材料；多硝基化合物；热分解