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Modified Evans–Polanyi–Semenov relationship in the study of chemical micromechanism governing detonation initiation of individual energetic materials

Svatopluk Zeman*

Department of Theory and Technology of Explosives, University of Pardubice, CZ-532 10 Pardubice, Czech Republic

Abstract

The paper deals with basic problems of the study of the thermal reactivity of individual energetic materials with special attention on the compatibility of results obtained using different methods. It is shown that the activation energies for thermal decomposition of these materials, obtained under comparable conditions, correlate with the respective detonation heats through a modified Evans–Polanyi–Semenov equation. These correlation relationships apply within groups of molecules with closely related structures and underline the importance of the bond that is primarily split in the molecule for the detonation of a given material. They also indicate that the primary fragmentation processes during low-temperature thermal decomposition are the same as those controlling the detonation reaction. It is shown that the correlation relationships found are also valid in the case of electric spark initiation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Energetic materials; Thermal decomposition; Detonation

1. Introduction

The influence of shock on energetic materials results in adiabatic compression of the molecular layer struck. According to Klimenko and Dremin [1–4], the kinetic energy of the shock in this compression is accumulated, through translational–vibrational relaxation processes, by translational and vibrational modes of molecular crystals of the material within 10^{-13} to 10^{-12} s. This causes a considerable quasi-overheating (20 000–40 000 K [3,4]) especially of vibrational modes. A nonequilibrium state is established with concomitant primary fission of the energetic material into ions and radicals [2–4]. Chemical reactions of these active particles causes the shock front to spread and evoke a second equilibrium stage of detonation behind the front. This or similar ideas of transformation of low-frequency vibrations of crystal lattice (acoustic phonons) into high-frequency vibrations (vibrons), with subsequent spontaneous localization of vibrational energy in the explosophore groupings [10,11], have been applied by a number of authors in their studies of shock reactivity of energetic materials (for representative papers see [5–11]). Conclusions of this type also correspond to the older simplified idea, which was formulated by Bernard [12,13] on the basis of the kinetic theory of detonation, that only explosophore groups are compressed ahead of the shock front, as a result of the activation of explosive molecules.

Since the middle 1970s, the studies of impact and shock reactivities and the chemical micromechanism of the initiation of organic polynitro compounds have also been adopting quantum chemistry methods (see,

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* Fax: +42-40-6038024.
E-mail address: svatopluk.zeman@upce.cz (S. Zeman).

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e.g. [13–27]). From the findings thus obtained it follows that the principal reactive mojety is the nitro group or, more specifically, $C–NO_2$, $N–NO_2$ or $O–NO_2$ bonds [16–29]. There exist direct experimental [28–30] as well as indirect semi-empirical [33–50] pieces of evidence for the above-mentioned facts.

It is well known that the above-mentioned groupings are carriers also thermal reactivity of corresponding energetic materials (i.e. polynitro compounds, see [18–21,31–63]). The mechanisms of primary fragmentation in thermal decomposition of organic polynitro and polynitroso compounds can be divided into [64] the following:

- homolysis of $C–NO_2$, $N–NO_2$, $O–NO_2$ [18–21,31–40,42,46–48,62,63] and N–NO [35,65] bonds;
- homolysis via a five- or six-membered transition state or aci-form [38,49–53];
- in a few cases homolytic fragmentation without a primary participation of a nitro group [66–69].

From what has been said so far it follows that the primary fragmentations in both the detonation and thermal decomposition of explosive molecules are similar. The similarity or identity between the primary mechanism of low-temperature and detonation reactions is a topic of numerous papers [32–35,38–48,69,70]. The identity is also confirmed by some striking pieces of experimental evidence. First of all they include the evidence (obtained with the help of Raman spectroscopy and XPS) of primary fission of $N–NO_2$ bond in 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) exposed to shock wave [28,29]. On the basis of deuterium kinetic isotope effect (DKIE) it was proved [54,71] that the rate-limiting step for the thermal decomposition of 2,4,6-trinitrotoluene (TNT) in the condensed state and that for the initiation of its detonation are identical. The presence of furoxanes and furazanes in the XPS spectrum of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) exposed to shock [30,72,73] provides the further evidence—the pyrolysis of *ortho*-nitroanilines is a method of synthesis of benzofurazane [74] and in the case of 1,3-diamino-2,4,6-trinitrobenzene (DATB) this reaction leads to 4-amino-5,7-dinitrobenzofurazane [75]. The identity is also reflected in a relationship between the kinetics of the low-temperature thermal decomposition of the energetic materials and reaction rates in the reaction zone of their detonation [76,77].

The homolytic character of primary fission in both the detonation and low-temperature thermal decompositions of energetic materials was a motive for Zeman et al. [34] to use the Evans–Polanyi–Semenov (E–P–S) equation [78,79] to study the chemical micromechanism governing initiation of energetic materials [34,35,40–42,44–46,69,70,80]. The original E–P–S equation describes a relationship between activation energies E of most substitution reactions of free radicals and corresponding heats of reaction DH:

$$E = B + \alpha' \Delta \mathrm{H} \tag{1}$$

where B is a constant. Eq. (1) is valid for closely related molecules and indicates that the strength of bond being split is a decisive factor in the given reaction [78,79]. Substitution of ΔH by real heat of explosion Q_{real} and E by activation energy E_{a} of the low-temperature thermal decomposition has led to first version of modified E–P–S equation [34, 35,40,69,70] in the general shape (here C is a constant):

$$E_{\mathrm{a}} = C + \alpha Q_{\mathrm{real}} \tag{2}$$

which is applicable for the detonation of energetic materials. The present paper re-examines some aspects of Eq. (2) from the point of view of new findings and reviewed applications of this equation to the study of the chemical micromechanism of initiation of individual energetic materials.

2. Data selection

2.1. Thermal decomposition of energetic materials

2.1.1. Basic methods of following the thermal decomposition (thermal reactivity)

The course of the primary fission processes in thermal decomposition of the energetic materials is generally followed by studying secondary effects of them, i.e. the type and quantity of gaseous products, and/or thermal effects, and/or the mass decrease accompanying the reaction. The thermal decomposition of individual energetic materials thus can be divided into two limiting types [61]:

1. Fission the products of which have low molecular weight; its mechanism does not involve too many

intermediate stages (nitramines, polynitroaliphatic compounds).

2. Fission whose intermediates are relatively stable compounds; its induction period need not necessarily be linked with a more pronounced development of gaseous products (polynitro arenes and polynitro heteroarenes).

Reaction kinetics of the first type of fission can be studied by methods based on following the quantity of reaction products with time. Reaction kinetics of the second type can best be studied by methods based on following thermal effects of the reaction. Regardless of the difference in these limiting types, the gasometric and thermoanalytical methods are the most widespread in the study of the thermal stability of energetic materials [81,82]. However, differences in the underlying principles and the physical conditions of the methods makes them difficult to compare results obtained in different laboratories.

2.1.2. Basic problem of thermal reactivity specification

From the practical point of view, an understanding of the thermal stability and mechanisms of thermal decomposition of energetic materials in the condensed state are the most significant. The influence of the condensed phase is expected to make itself felt in the reactivity through the changed character of bond hybridization of the molecule, due to intermolecular interactions [83]. In solid-phase decomposition, moreover, the hinder influence of the closely arranged molecules within the crystal upon the formation of the activated complex should also be considered [85,86]. The fragments of the primary homolysis and/or products of subsequent reactions, can attack the neighboring unchanged molecules (intermolecular redox processes in thermal decomposition of polynitroarenes were documented by means of the ESR spectroscopy [87]), and can enter into various reactions with each other, such chemical interactions depend very strongly upon temperature and pressure.

The effect of temperature on the kinetics and mechanism of chemical reactions is well known [88]. In the case of thermal decomposition of polynitro arenes this effect can be very well documented using the modified Piloyan DTA method in the study of this process [61,89], including the specification of temperature region in which autocatalytic course of the process is started [89].

Like temperature, pressure also affects the thermal decomposition of energetic materials, either directly, by influencing its kinetics and mechanism [55,92,93], through its effect on chemical interaction of the primary fragments, or on the reaction of the decomposition products with the starting material [84,90,91,93]. An increase in pressure produces, for example a decrease in the decomposition reaction rate of solid HMX and RDX [55,92,93], an increase in decomposition rate of liquid RDX [55], and a dramatic change in the reaction mechanism for the thermal decomposition of nitromethane above 4 GPa [55]. The well-known effect of filling of the reaction volume on the kinetics [84,90,91,93–97,111] and on the reaction heat [98] of thermal decomposition of polynitro and polynitroso compounds is connected with the above-mentioned effects of pressure (together with the reaction products) on the decomposition. The dependence of the kinetics and heat of the decomposition process on pressure and/or temperature must affect the quantity and quality of final products of thermal decomposition of energetic materials. In this field, however, no systematic research has been done yet, in particular any research has been done on the composition of the condensed products.

With respect to the homolytic nature of thermal decomposition of polynitro and polynitroso compounds in particular, the construction materials that are in contact with the sample can also significantly affect the kinetics. For example, the effect of stainless steel and several sorts of glass on the results of thermostability measurements using non-isothermal DTA was demonstrated in [89] for polynitro arene derivatives. Contact of polynitro arenes with glass when reacted in the gas phase stimulates formation of low-volatile polynuclear compounds [99] and can distort the effect of molecular structure on the reaction rate [100]. Sial glass markedly increases thermal reactivity of liquid TNT compared to pure iron [101]; after being coated with nickel, the iron becomes more inactive in the above-mentioned sense [101]. The effect of some metal oxides on thermal reactivity of several high explosives is documented in [102].

Table 1
Survey of the compounds studied, their code designations, heats of detonation and activation energies of thermal decomposition

Substance			Heat of detonation, Q_{real} (MJ kg^{-1})	Activation energy, E_a			
Data no.	Chemical name	Code designation		Method of evaluation	State of decomposition	(kJ mol^{-1})	Reference
1	1-Methyl-2,4-dinitrobenzene	2,4-DNT	3.653	SMM	Liquid	139.56	[106]
2	1-Methyl-2,6-dinitrobenzene	2,6-DNT	3.832	SMM	Liquid	198.87	[106]
3	1-Methyl-3,5-dinitrobenzene	3,5-DNT	3.763	SMM	Liquid	186.08	[106]
4.1	1-Methyl-2,4,6-trinitrobenzene	TNT	4.277	SMM	Liquid	144.44	[107]
4.2		TNT		DSC	Liquid	143.30	[108]
5	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	4.074	SMM	Liquid	146.95	[107]
6	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	3.801	SMM	Liquid	185.08	[107]
7	3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitrobiphenyl	DMHNB	4.468	SMM	Solid	106.40	[110]
8	α,β-bis(2,4,6-Trinitrophenyl)ethane	DPE	4.369	Calculated	Liquid	124.00	[32]
9	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfide	DIPS	4.185[a]	SMM	Liquid	131.80	[112]
10	1-Chloro-2,4,6-trinitrobenzene	CTB	4.479[b]	SMM	Liquid	118.07	[106]
11	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	4.039[b]	SMM	Liquid	177.09	[106]
12	1,3,5-Trichloro-2,4,6-trinitrobenzene	TCTB	3.866[b]	SMM	Liquid	185.77	[106]
13	3-(2,4,6-Trinitrophenylamino)-1,2,4-triazole	PATO	4.182	DSC	Solid	134.72	[108]
14	1-Amino-2,4,6-trinitrobenzene	PAM	4.263	SMM	Liquid	129.79	[96]
15.1	1,3-Diamino-2,4,6-trinitrobenzene	DATB	4.138	SMM	Solid	196.80	[113]
15.2		DATB		DSC	Solid	193.72	[108]
16.1	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB	3.990	DSC	Solid	250.62	[108]
16.2		TATB		SMM	Solid	175.00	[113]
17	3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl	DIPAM	4.420	Extrapolated	Solid	190.23	[32]
18	2,2′,4,4′,6,6′-Hexanitrodiphenylamine	DPA	4.438	DTA	Solid	177.76	[114]
19	2,2′,4,4′,6,6′-Hexanitrooxanilide	HNO	4.189	SMM	Solid	215.62	[113]
20	2,4,6-tris(2,4,6-Trinitrophenylamino)-1,3,5-triazine	TPM	4.064	SMM	Solid	257.06	[113]
21	2,6-bis(2,4,6-Trinitrophenylamino)-3,5-dinitropyridine	PYX	4.341	SMM	Solid	213.00	[115]
22	2,6-Diamino-3,5-dinitropyridine	DADNP	3.700	SMM	Solid	224.50	[115]
23.1	2,2′,4,4′,6,6′-Hexanitrostilbene	HNS	4.480	SMM	Solid	183.80	[113]
23.2		HNS	4.480	DSC	Liquid	123.00	[116]
24	2,2′,4,4′,6,6′-Hexanitroazobenzene	HNAB	4.835	SMM	Liquid	121.83	[113]
25	1-Hydroxy-2,4,6-trinitrobenzene	PA	4.372	SMM	Liquid	161.18	[96]
26	1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	4.130	SMM	Liquid	144.86	[96]
27	1,3,5-Trihydroxy-2,4,6-trinitrobenzene	TNPg	3.960	SMM	Liquid	114.64	[113]
28	Benzotrifuroxane	BTF	5.772	SMM	Solid	284.51	[117]
29	1,3,5-Trinitrobenzene	TNB	4.754	SMM	Liquid	180.03	[107]
30	2,2′,4,4′,6,6′-Hexanitrobiphenyl	HNB	4.689	SMM	Liquid	207.24	[96]
31	2,2′,2‴,4,4′,4″,6,6‴-Octanitro-*m*-terphenyl	ONT	4.547	SMM	Solid	281.58	[118]
32	2,2′,2″,4,4′,4″,6,6′,6″-Nonanitro-*m*-terphenyl	NONA	4.798	DTA	Solid	214.11	[32]
33	2,2′,2″,2‴,4,4′,4″,4‴,6,6′,6″,6‴-Dodecanitro-*m*-quaterphenyl	DODECA	4.800	Extrapolated	Solid	217.48	[34]
34	Azo-bis(2,2′,4,4′,6,6′-hexanitrobiphenyl)	ABH	4.859	Extrapolated	Solid	223.56	[34]

35	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfone	DIPSO	3.773	SMM	Solid	106.76	[119]
36	2,4,6-tris(2,4,6-Trnitrophenyl)-1,3,5-triazine	TPT	4.259	SMM	Solid	269.45	[118]
37	1,4,5,8-Tetranitronaphthalene	TENN	4.422	DTA	Solid	223.05	[32]
38	1,3,7,9-Tetranitro-1,3a,4,6a-tetraazapentalene	TACOT-1	4.372	SMM	Solid	234.30	[113]
39	1,3,8,10-Tetranitro-1,3a,6,6a-tetraazapentalene	TACOT-2	4.310	SMM	Solid	189.95	[113]
40	1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole	BTX	4.364	Extrapolated	Solid	214.85	[34]
41	Nitromethane	NM	4.522	DTA	liquid	173.60	[120]
42	Dinitromethane	DNM	6.814	Extrapolated	liquid	163.00	[121]
43	Tetranitromethane	TENM	2.259	SMM	liquid	159.2	[122]
44	1,1,1-Trinitroethane	1,1,1-TNEt	6.599	SMM	liquid	178.24	[123]
45	1,1-Dinitropropane	1,1-DNPr	4.517	SMM	liquid	182.00	[124]
46	2,2-Dinitropropane	2,2-DNPr	4.435	SMM	liquid	140.20	[124]
47	1,1,1-Trinitropropane	1,1,1-TNPr	5.419	SMM	liquid	174.91	[124]
48	1,1,1,3-Tetranitropropane	TENPr	6.250	SMM	liquid	205.43	[124]
49	2-Methyl-1,1,1,3-tetranitropropane	MeTENPr	5.458	SMM	liquid	175.7	[123]
50	1,1,1,2,2-Pentanitropropane	PNPr	7.373	SMM	liquid	166.10	[123]
51	1,1-Dinitro-1-azaethane	MDN	6.780	NMR	Liquid	168.40	[103]
52.1	1-Nitro-1-azaethylene	DIGEN	4.914	NMR	Liquid	156.00	[103]
52.2		DIGEN		Calculated		146.50	[125]
53.1	2-Nitro-2-azapropane	DMNA	3.817	NMR	Liquid	159.80	[103]
53.2		DMNA		IR	Solid	192.50	[126]
54	2,4-Dinitro-2,4-diazapentane	OCPX	4.750	NMR	Liquid	178.60	[103]
55	2,5-Dinitro-2,5-diazahexane	DMEDNA	3.732	NMR	Liquid	176.10	[103]
56	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	4.870	NMR	Liquid	179.20	[103]
57	2,4,6,8-Tetranitro-2,4,6,8-tetraazanonane	OHMX	5.404	NMR	Liquid	180.60	[103]
58	4-Nitro-4-azavaleric acid	NVA	3.570	SMM	Liquid	176.06	[127]
59	1-Methylnitramino-2,4,6-trinitrobenzene	TETRYL	4.830	SMM	Liquid	156.90	[128]
60	1,3-Dinitro-1,3-diazacyclobutane	TETROGEN	5.350	Calculated		153.10	[129]
61	1,3-Dinitro-1,3-diazacyclopentane	CPX	4.603	SMM	Liquid	149.40	[130]
62	1,4-Dinitro-1,4-diazacyclohexane	DNDC	3.968	SMM	Liquid	198.40	[130]
63	1,3,5-Trinitro-1,3-diazacyclohexane	TNP	5.105	IR	Liquid	181.10	[145]
64.1	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	5.477	Manomet.	Liquid	198.90	[131]
64.2		RDX		DSC	Liquid	197.10	[109]
64.3		RDX		SMM	Solid	213.50	[96]
64.4		RDX		SMM	Solid	217.60	[132]
65	Mixture of 59.5% RDX, 39.5% TNT and 1% wax	Comp. B	4.700	DSC	Liquid	180.20	[109]
66	1,3,5-Trinitro-1,3,5-triazacycloheptane	HOMO	5.005	NMR	Liquid	207.10	[103]
67.1	1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DPT	3.756	Extrapolated	Solid	192.30	[34]
67.2		DPT		NMR	Solid	195.10	[103]
68	1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DADN	3.523	Extrapolated	Solid	189.10	[34]
69.1	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX	5.530	Manomet.	Solid	220.50	[131]
69.2		HMX		DSC	Solid	214.60	[133]
69.3		HMX		MS	Solid	209.00	[134][c]
70.1	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaazacyclodecane	DECAGEN	5.910	NMR	Liquid	201.80	[103]
70.2		DECAGEN		NMR	Solid	213.50	[103]

Table 1 (*Continued*)

Substance			Heat of detonation, Q_{real} (MJ kg^{-1})	Activation energy, E_a			
Data no.	Chemical name	Code designation		Method of evaluation	State of decomposition	(kJ mol^{-1})	Reference
71.1	1,4,5,8-Tetranitro-1,4,5,8-tetraazadecahydronaphthalene	TNAD	5.639	Extrapolated	Solid	217.60	[34]
71.2		TNAD		DSC	Solid	210.00	[135]
71.3		TNAD		DSC	Solid	209.00	[135]
72	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	4.260	SMM	Solid	196.80	[146]
73.1	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	HNIW	5.956	TGA	Solid	172.26	[136]
73.2		α-HNIW	5.980	DSC	Solid	176.00	[137]
73.3		β-HNIW	6.020	DSC	Solid	165.00	[137]
74	bis(2,2,2-Trinitroethyl)-N-nitrosamine	BTN	7.171	SMM	Liquid	148.11	[138]
75	1,4-Dinitroso-1,4-diazacyclohexane	DNSP	3.946	DSC	Liquid	143.94	[35]
76.1	1,3,5-Trinitroso-1,3,5-triazcyclohexane	TMTA	4.829	SMM	Liquid	144.35	[139]
76.2		TMTA		DSC	Liquid	146.94	[35]
77	1,5-Endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane	DNPT	3.999	DSC	Solid	144.20	[35]
78.1	1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecahydronaphthalene	TNSAD	4.600	DSC	Solid	149.15	[35]
78.2		TNSAD		IR	Solid	150.10	[36]
79	Ethylnitrate	EtN	4.349	SMM	Liquid	167.36	[65]
80	1,4-Butylene glycol dinitrate	1,4-BGDN	4.620	SMM	Liquid	163.18	[140]
81	Nitrocellulose 13.35% N	NC-13.35	4.489	SMM	Solid	164.12	[141]
82	1,1,1-Trimethylolpropane trinitrate	ETRYNIT	4.687	Extrapolated	Liquid	165.29	[34]
83	Penterythritol tetranitrate	PETN	5.729	SMM	Liquid	163.17	[85]
84	Ethylene glycol dinitrate	EGDN	6.229	SMM	Liquid	163.28	[142]
85	Glycerol trinitrate	NG	6.264	SMM	Liquid	163.30	[143]
86	Erythritol tetranitrate	ETN	6.217	SMM	Liquid	160.25	[124]
87	Manitol hexanitrate	MHN	6.485	SMM	liquid	159.10	[142]
88	Trimethylolnitromethane trinitrate	NIBNG	6.739	Manomet.	Liquid	152.30	[144]

[a] Predicted on the basis of results of ^{13}C NMR spectroscopy [164].

[b] Taken from [34].

[c] Cited in [154].

The basic problem of defining the thermal reactivity of energetic materials thus lies in the strong dependence of the resulting kinetic parameters on temperature, pressure, and construction materials in contact with the sample decomposed. Hence, the mutual compatibility of results obtained from thermal analyses of energetic materials using different methods and/or different types of apparatus of different origin is very rare [64,103].

The resulting stability and/or kinetic characteristics are complicated by the effects of consecutive reactions of intermediates and products of thermal decomposition both with each other and with the starting energetic material, which can be minimized by dilution and by removal of gaseous intermediates from the sample measured. This can to a certain extent be achieved by carrying out the respective measurement in vacuum and made isothermal conditions. In this sense, the most sophisticated method is the Russian isothermal manometrical method (named Soviet Manometric Method in the past [32]), making use of Bourdon's glass compensation manometer [96, 104,105].

2.1.3. Activation energies of thermal decomposition

The data obtained by the Russian manometric method (called SMM [32]) are known to correspond to the primary non-autocatalyzed stage of thermal decomposition of the energetic materials [67,85,86, 96,104,121,122,132]. In the case of thermal decomposition in the condensed state, only the results of some methods of the differential scanning calorimetry (DSC, e.g. [108,109,116,133]) are directly comparable with the results of SMM [34,35,64,103], whatever is documented also by this paper (see Section 3). Results of the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) can be converted to comparable values if a relationship exists between them and the results of the SMM (for DTA see [33,40,41,61,89,114] and for TGA [38,40,147]). The above-mentioned E_a values can be also obtained by prediction on the basis of Eq. (2) (see this paper and [34]) or by means of outputs of the ^{15}N NMR spectroscopy [40,103,163]. Within the framework of the present paper activation energies E_a of thermal decomposition of polynitro and polynitroso compounds are preferred whose values are compatible with those resulting from SMM application (see Table 1).

2.2. Heats of detonation

The heats of detonation, Q_{real}, used in the present paper, were calculated for monocrystals by means of semi-empirical relationships devised by Pepekin et al. [148]. These values correspond to the experimentally determined heats of detonation in the calorimetric bomb [148,160]. The Q_{real} values for polynitro compounds with Cl and S heteroatoms in their molecules were obtained by means of prediction methods (see notes to Table 1).

3. Results and discussion

3.1. Polynitro arenes and polynitro heteroarenes

The set of polynitro arenes and polynitro heteroarenes in Table 1 is divided—in the sense of Eq. (2)—into several groups documented by Figs. 1–3. The substances given in Fig. 1 are characterized by the presence of a hydrogen atom at γ-position with respect to the nitro group, i.e. they are polynitro compounds exhibiting the so-called trinitrotoluene mechanism of thermal decomposition [38,50–52]. Exceptional is polychlorinated derivatives of TNB (i.e. CTB, DCTB, and TCTB). Their thermal decomposition, however, represents a certain analogy with the decomposition of polymethyl derivatives of TNB [61,107]. The primary step of the chloro-derivatives thermal decomposition could perhaps be connected with the chemical interaction between chlorine atom and oxygen of *ortho*-standing nitro group (which is also indicated by negative values of the respective activation entropy $\Delta S^{\ddagger}$ [32]). An analogous interaction of this oxygen atom with sulphur atom in DIPS molecule could also start the decomposition of this substance (again the respective $\Delta S^{\ddagger}$ value is negative [32]), even though the primary homolysis of C–S bond was originally presumed in this case [66,67]. The activation energies E_a of the substances of group I correspond to their thermal decomposition in liquid state: exceptional is TATB, whose E_a value was obtained in solid state. The E_a was obtained on the basis of the SMM [113] in temperature region above hypothetical melting point of TATB [38] (this E_a value, which is very close to the heat of sublimation of TATB, is discussed in [38]). Sets II is logically formed by polyamino derivatives of

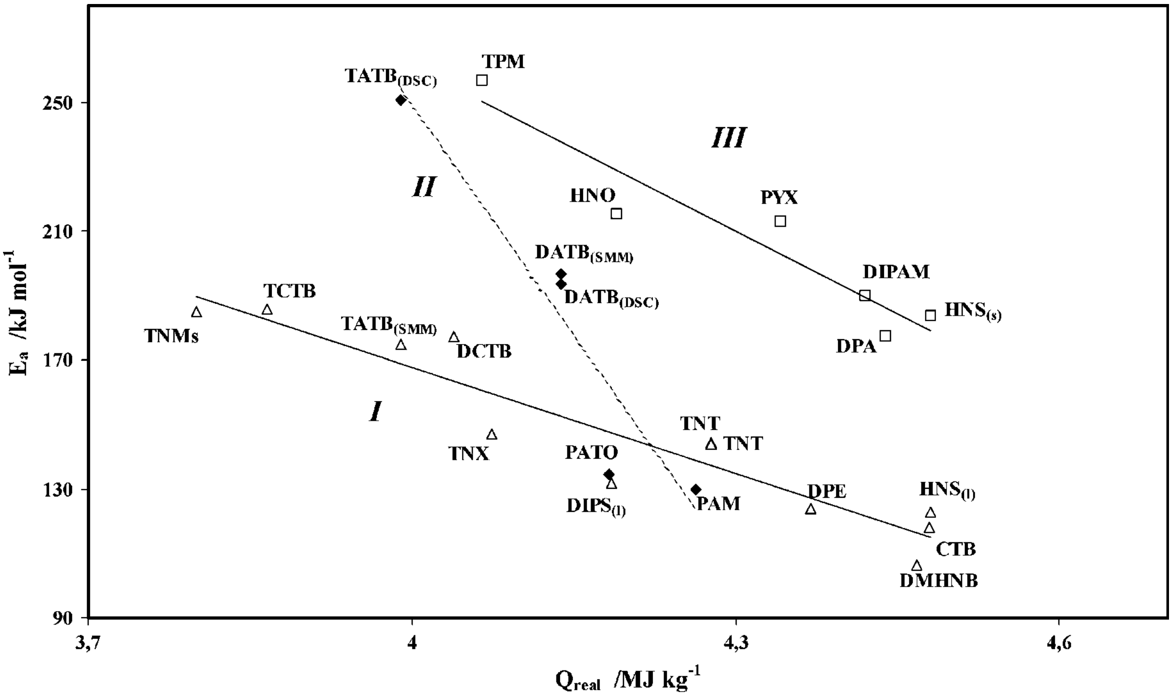

Fig. 1. Forms of Eq. (2) for polynitro arenes: majority from them have hydrogen atom in γ-position with respect to nitro group in their molecules.

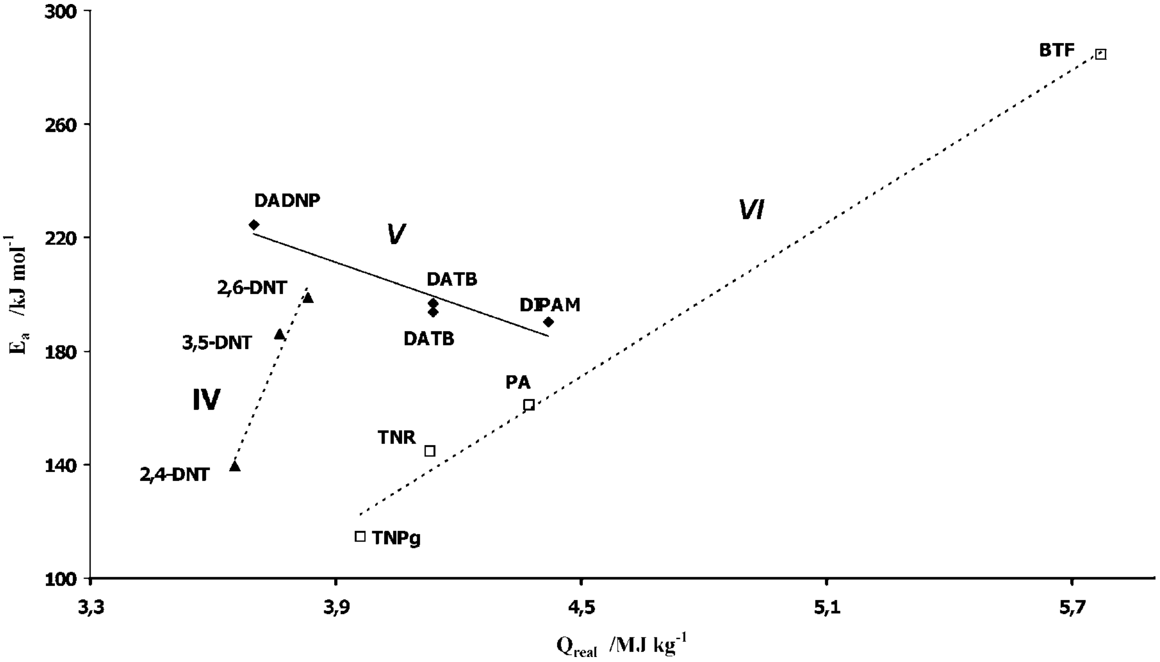

Fig. 2. Forms of Eq. (2) for polynitro arenes.

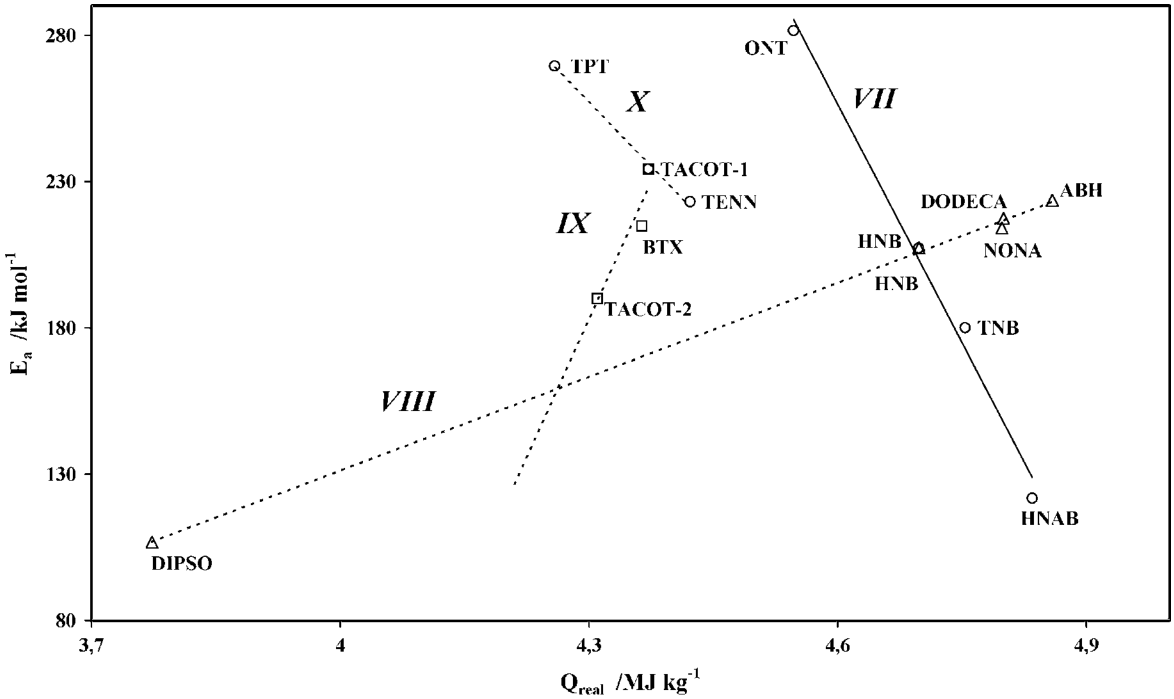

Fig. 3. Forms of Eq. (2) for polynitro arenes: lines with positive slope correspond with the groups of substances with high melting points.

1,3,5-trinitrobenzene. Likewise to this, group V in Fig. 2 includes logical set of diamino polynitro arenes. The data of polypicryl derivatives of group III correspond to their thermal decomposition in the solid state. Figs. 1 and 2 indicate that the both primary steps and physical state of thermal decomposition (i.e. intermolecular interactions) influence positions of the above-mentioned groups in the coordinates of these Figs. The same can be said about groups IV and VI in Fig. 2: here 2,4- and 2,6-DNT, PA, TNR and TNPg should have to produce radicals with –NO* grouping in molecule as primary intermediates of their thermal decomposition (the trinitrotoluene mechanism of the primary thermal splitting [49–54,132]). The same radicals result from the primary thermal fission of BTF [132] (by opening of the furazan cycle). C–N bond should be primarily homolyzed in the thermal decomposition of 3,5-DNT; however, activation entropy of this reaction in liquid state is negative [32] which means, that this decomposition may be a pseudo-monomolecular fission (to find more about this type of fission see in [32,64]).

Polyhydroxy derivatives of TNB (group VI) have chelate cycles in their molecules which are formed by the intramolecular hydrogen bonds. These six-membered cycles have similar space arrangement as five-membered cycles of furoxans, i.e. intermolecular interactions in polynitro-benzofuroxanes should be similar to those in polynitro analogues of phenols. It is possible reason for correlation of BTF data with group VI. Hence, the classification of individual substances into the groups mentioned is given by similarity of basic molecular structure, i.e. character of intermolecular interactions. Similarly, the forms of Eq. (2) with positive slopes in Fig. 3 should have to correspond with the groups of substances showing the dominant effect of intermolecular interactions on their thermal decomposition, because substances of groups VIII and IX possess high melting points.

3.2. Nitro paraffins

Thermal reactivity of polynitro paraffins in condensed state has received little attention so far [64]. The data published in this field were used to construct the forms of Eq. (2) presented in Fig. 4. Groups XII and XIII are related to derivatives of nitromethane and

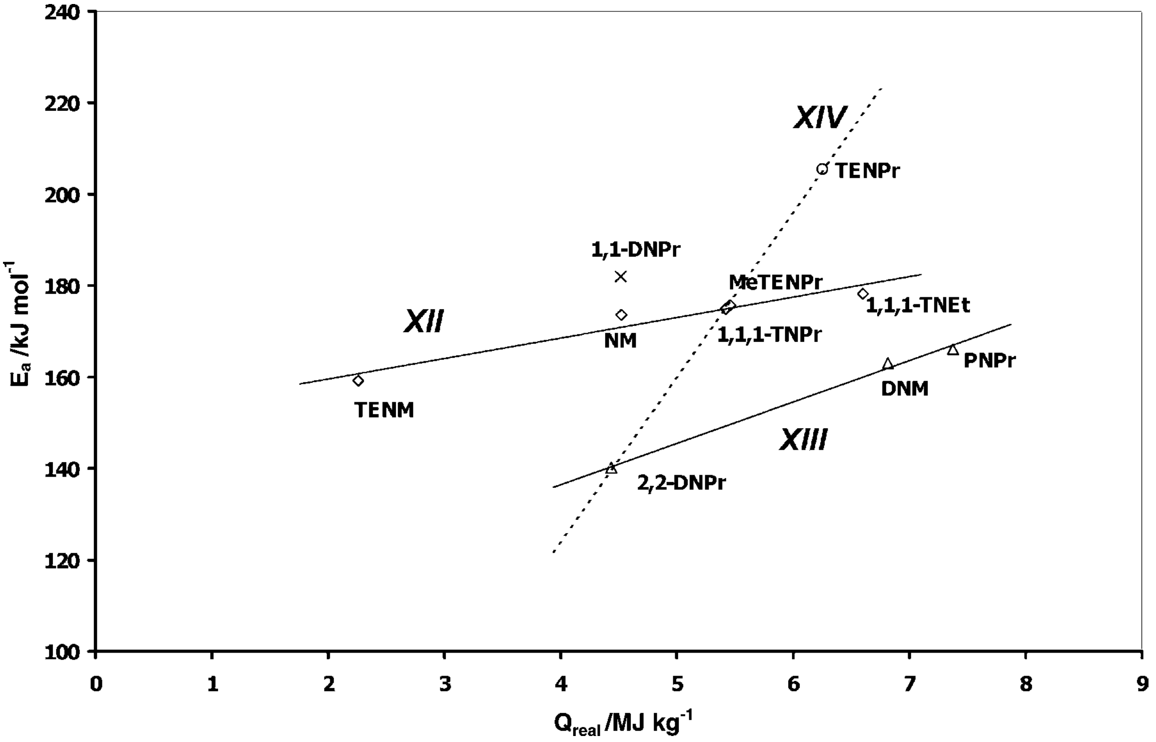

Fig. 4. Forms of Eq. (2) for polynitro paraffins.

dinitromethane, respectively. The data group XIV corresponds to polynitro derivatives of propane.

3.3. Nitramines

The technically attractive polynitramines represent a group of nitro compounds characterized by higher crystal densities than those usually encountered with polynitro arenes. This fact indicates better intermolecular interactions in crystals of nitramines, although the values of the corresponding crystal lattice energies [149] do not greatly differ from those of polynitro arenes [150]. It appears that the longest N–N bonds are responsible for the homolytic reactivity of nitramines [151]. The corresponding nitramine groups contribute strongly to the intermolecular potential in the crystal state [152]. In the case of HMX, e.g. [154] claims that its thermal decomposition is supposed to be controlled rather by the braking of intermolecular interactions than by the extinction of the intramolecular covalent bonds. Hence, the dominant effect of intermolecular interactions during thermal decomposition and initiation of detonation could be the main reason for positive slopes of the forms of Eq. (2) for the nitramines in Figs. 5 and 6. The data for substances of group XV correspond to thermal decomposition of cyclic nitramines in the solid-phase including of DMNA (a reason for its involvement, see [153]. Group XVI corresponds to the data for the decomposition of linear nitramines in the liquid phase, including of the "nitroparaffinic nitramine" TNP. Group XVII in Fig. 6 corresponds to the data of thermal decomposition of cyclic nitramines RDX and DECAGEN in the liquid state, again including DMNA. The data for RDX solution in TNT (Comp. B) correlate well with it, too. Group XVIII includes the data of nitramines with geometrical constraints in their molecules. A part of these substances form a separate group also in the sense of the relationships between the Arrhenius parameters of their thermal decomposition and the lengths of the longest N–N bond in their molecules [151] or between these parameters and ^{15}N NMR chemical shifts of nitrogen atoms in their most reactive nitro groups [103].

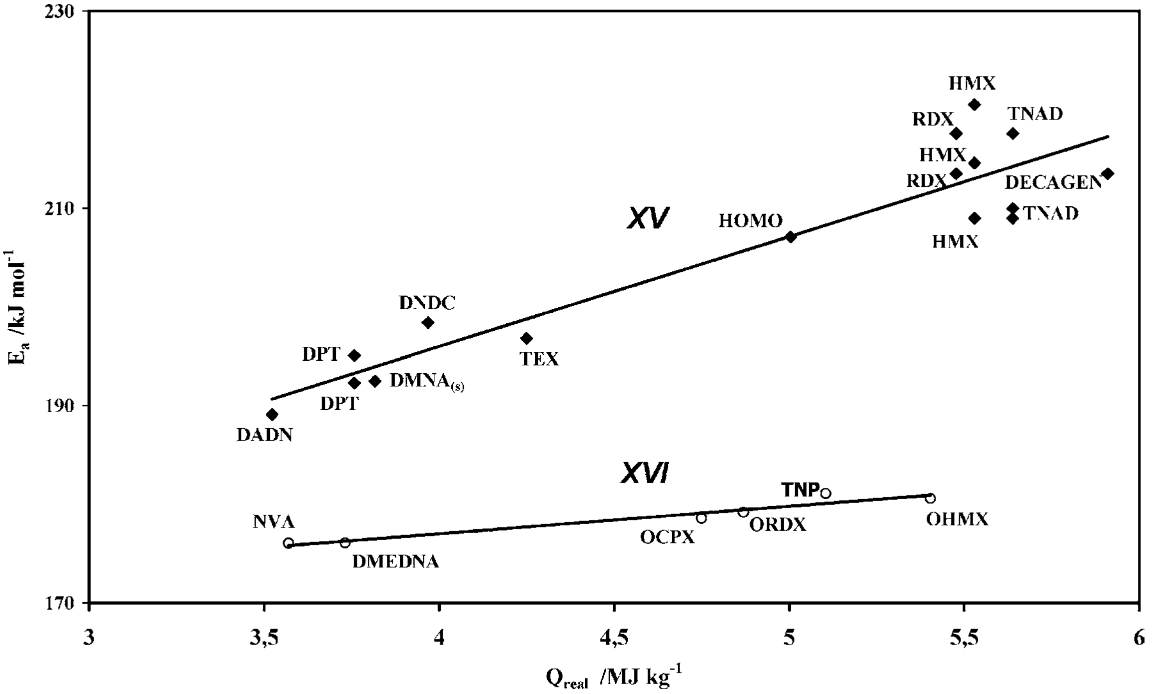

Fig. 5. Forms of Eq. (2) for cyclic and linear polynitramines.

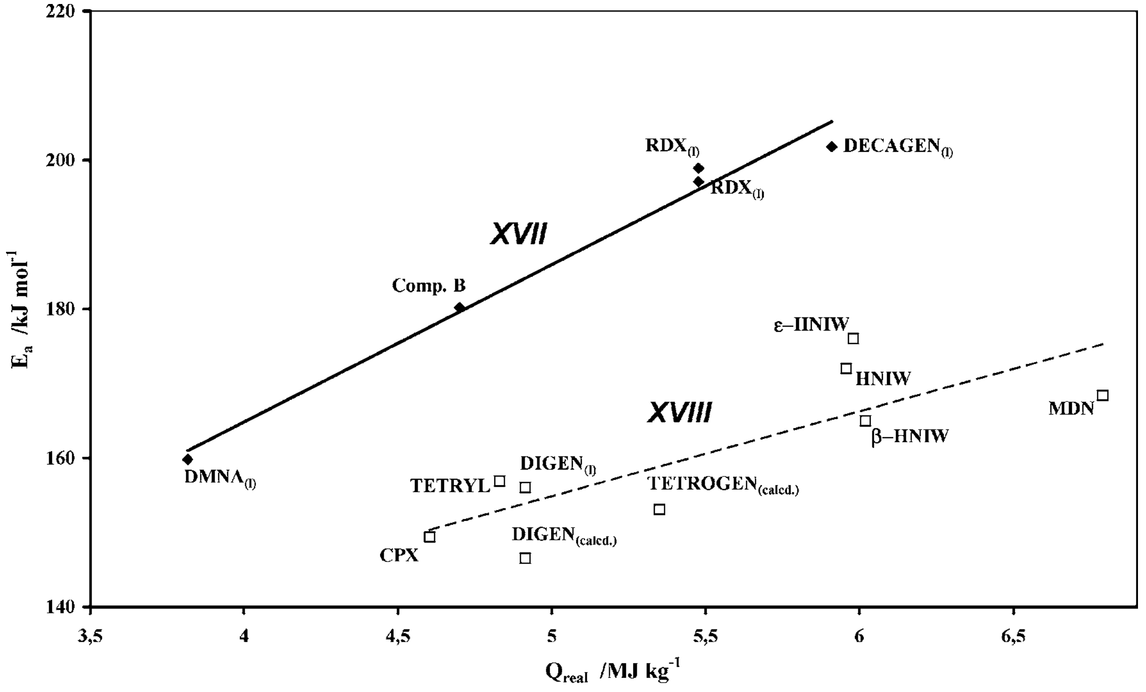

Fig. 6. Forms of Eq. (2) for cyclic nitramines in liquid state and for nitramines with geometrical constraints in their molecules.

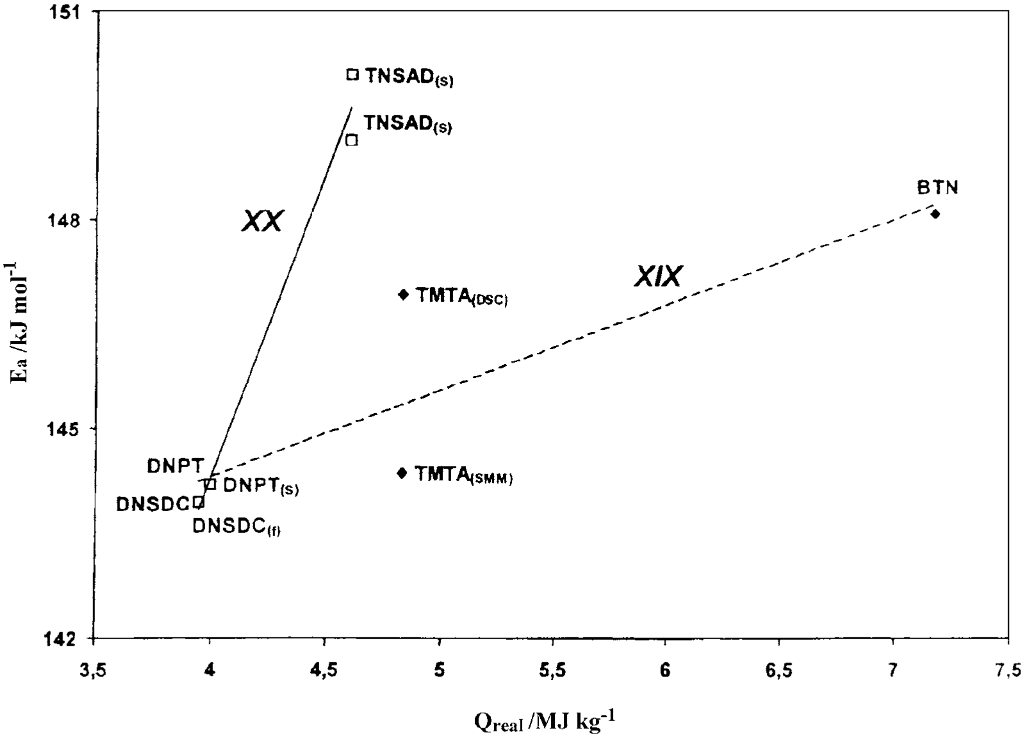

Fig. 7. Forms of Eq. (2) for nitrosamines.

3.4. Nitrosamines

Thermal reactivity of nitrosamines in general has been given insufficient attention so far. The published values of Arrhenius parameters for their thermal decomposition in the condensed state correspond to the homolysis of N–N bond in the molecule [35,39,55,139]. The forms of Eq. (2) for this group of compounds are indicated in Figs. 7 and 8. The data for group XIX correspond to thermal decomposition in the liquid state, those of group XX corresponding to the solid state. As in the case of nitramines, the positive slope of these plots indicates the dominant effect of intermolecular interactions on the thermal decomposition and initiation of nitrosamines.

3.5. Nitrate esters

Generally, the substances of this type represent the most reactive group of polynitro compounds with regard to both homolysis and heterolysis. Therefore, it is logical that increasing the number of nitro groups in their molecules is connected with a decrease in the activation energy, E_a, and an increase in the heat of detonation, Q_{real}.

3.6. Primers

The validity of Eq. (2) was also successfully verified for the thermal decomposition of inorganic azides [69] and fulminates [70], and the photolysis of fulminates [70]. The results are presented in Fig. 9, data compiling [69,70]. For azides the literature gives activation energy values, E_a, for thermal decomposition within various temperature ranges. In the sense of Eq. (2) (Fig. 9), however, the only E_a values which correlate, correspond to the lowest experimental temperature ranges [69,155–158]. Slopes of forms of Eq. (2) for thermal decomposition of both groups of primers signal a dominant effect of mechanisms of primary splitting in this decomposition and initiation of their detonation. The slightly positive value of slope in the form of Eq. (2) given for the photolysis of fulminates in Fig. 9 is probably connected with the solvating of

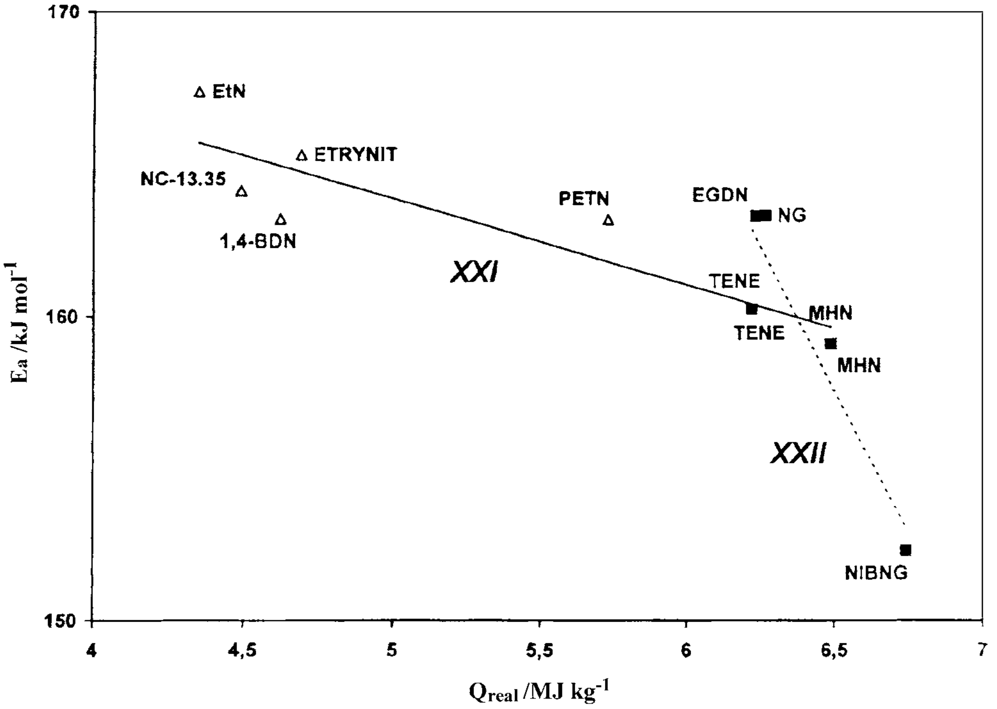

Fig. 8. Forms of Eq. (2) for nitrate esters.

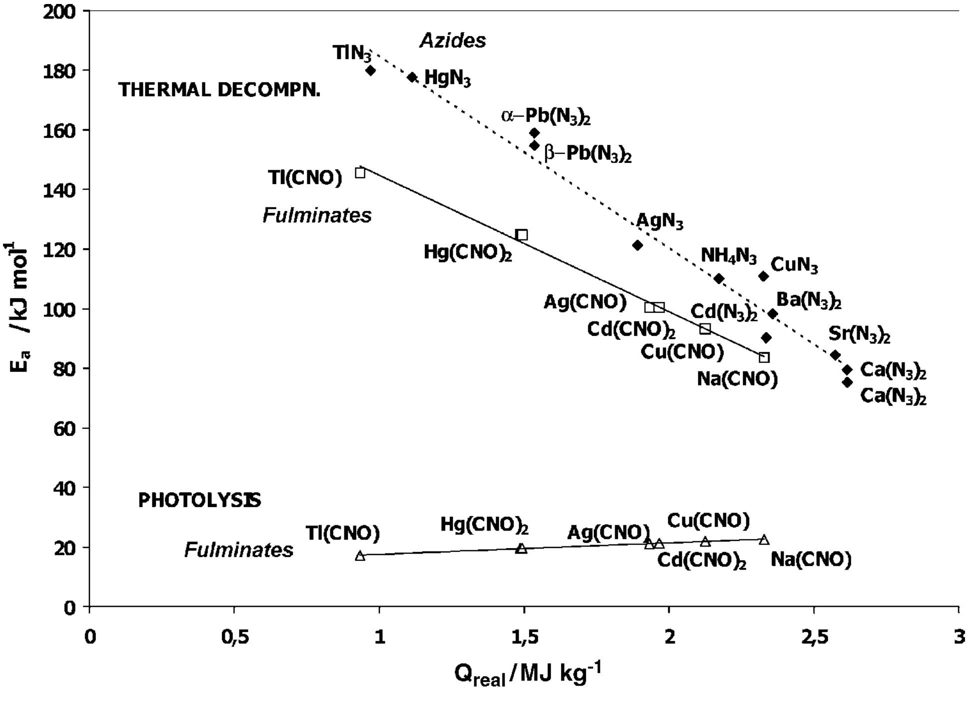

Fig. 9. Forms of Eq. (2) for primers (constructed on the basis of data from [69,70]).

their molecules, because the photolysis was carried out in solution [159].

3.7. Application to study of electric spark sensitivity

The relationship in the general form

$$D^2 = aE_{ES} + b \tag{3}$$

was found between square of detonation velocities, D^2, and spark energies, E_{ES}, required for 50% initiation probability, for polynitro arenes [42,44] and nitramines [42,45]. As the square of detonation velocity and explosion heat in the Chapman–Jouguet plane are related by definition [161,162]:

$$Q = D^2\{2(\gamma^2 + 1)\}^{-1} \tag{4}$$

(where γ is the polytropy coefficient), also Eq. (3) can be considered another modification of the E–P–S equation [42,44,45]. Relationship (3) is valid in very narrowly delimited molecular-structural series of polynitro compounds (an example see in Fig. 10 [44]) and seems to be more distinctly affected by the nature of intermolecular interactions [44,45].

3.8. Electronic structure and initiation of detonation

Using results of DTA measurements, [31,40,41] pointed out the relationship between electronic structure of ground state at the reaction center of molecule and the detonation parameters of polynitro arenes. As already mentioned in Section 1, this finding stands in accordance with the conclusions of applications of quantum-chemistry methods to the study of the micro-mechanism of initiation of detonation. From among the recent papers in this field we have to mention study [103] presenting a description of the relationship between ^{15}N NMR chemical shifts, δ_N, of nitrogen atoms in nitro groups and the Arrhenius parameters of low-temperature thermal decomposition of nitramines: for the activation energy, E_a, it has the following form:

$$E_a = a_1\delta_N + b_1 \tag{5}$$

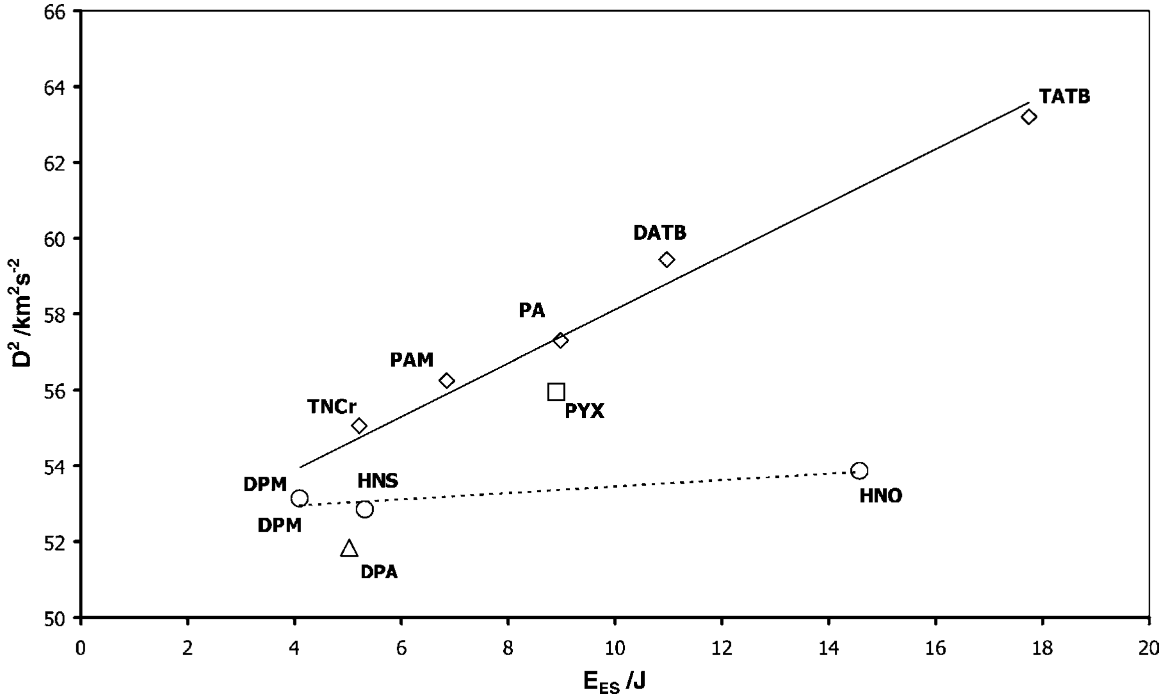

Fig. 10. An example of graphic representation of Eq. (3), taken from [44]. Here DPM is 2,2′,4,4′,6,6′-hexanitrodiphenylmethane and TNCr is 1-hydroxy-3-methyl-2,4,6-trinitrobenzene.

An analogous relationship found between these chemical shifts and velocities or heats of detonation of nitramines [46,163], specifying the most reactive nitramine grouping in the molecule, has the following general form:

$$X = A\delta_N + B \tag{6}$$

where X stands for square of detonation velocity, D^2, or detonation heat, Q. A superposition of Eqs. (5) and (6) can lead to Eq. (2) (the meaning of Eq. (6) was interpreted on the basis of Eq. (2) [46]). This means that also Eqs. (5) and (6) can be considered certain modifications of the E–P–S relationship [46]. As the above-mentioned chemical shifts, δ_N, are directly connected with the electron configuration at the reaction center of molecule, Eqs. (2), (5) and (6) thus represent the relationships between this configuration and detonation reactivity of polynitro compounds in general. It must be mentioned that primary considerations of Evans and Polanyi have risen from the quantum-chemical characteristics of the reaction abilities of molecules and radicals [78,165].

4. Conclusion

The homolytic fragmentations or reactions of the C–NO_2, N–NO_2, N–NO, and O–NO_2 groupings, or other bearers of explosibility [14,69,70] (i.e. explosophores), are common primary fission processes of energetic materials under thermal [31–41], impact [17,18,29,30,40,48], shock [14–17,25,29,40,46], and electric spark [42–45,47] stimuli.

A mechanism of the thermal decomposition processes of these materials is generally specified by means of study of their secondary manifestations. Reactions of this type, however, strongly depend upon temperature and pressure and, also upon the construction materials that the reacting material is in contact with. Therefore, in the great majority of cases it is impossible to directly compare the results obtained by various methods used for studies of thermal reactivity of energetic materials; this is particularly true in case of the Arrhenius parameters. The disproportionate influence of secondary reactions of thermal decomposition upon experimental results can be eliminated to a large extent by carrying out the thermal decomposition in vacuum at isothermal conditions (e.g. by the Russian manometric method).

The activation energies for thermal decomposition of individual energetic materials, obtained under mutually compatible conditions, correlate with the respective detonation heats in the sense of the modified E–P–S relationship (Eq. (2)). Like the original E–P–S relationship, also Eq. (2) is valid in narrowly delimited molecular-structural series of energetic materials and documents that the primarily split bond is a decisive factor in their detonation. As the results from the study of detonation reactivity of nitramines by means of ^{15}N NMR spectroscopy [46] show, Eq. (2) represents the relationship between this reactivity and electron configuration in the reaction center of corresponding molecules. This equation also indicates the identity of chemical mechanisms of primary splitting in low-temperature thermal decomposition and in detonation reactions.

Due to common character of primary fission processes, taking place in energetic materials after above-mentioned stimuli, it can be expected, that equations of type (2) and (3) will also be valid in the case of electric spark initiation [42,44,45].

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