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Kinetic compensation effect and thermolysis mechanisms of organic polynitroso and polynitro compounds

Svatopluk Zeman

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

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Abstract

The present study starts from the published values of the Arrhenius parameters E_a and $\log A$ of thermolysis in the condensed state of seven nitrosamines and one hundred organic polynitro compounds. On the basis of the linear relationship between E_a and $\log A$, the set studied has been divided into several reaction series, each of which is characterized by a mechanism of primary thermolysis. For compounds with intense intermolecular interactions in a crystal, the classification mentioned is codetermined by the stabilizing effect of the crystal lattice. In the context of this effect, the absence of an effect of solid–liquid transition on thermal reactivity of octogen (HMX) has been confirmed. The idea also presented is that, in the primary homolysis in thermolyses of polynitro compounds, there takes place a mutual interaction of molecules of the given compound, which is analogous to termination interactions of nitroarenes in radical polymerizations. © 1997 Elsevier Science B.V.

Keywords: Explosives; Kinetics; Nitramines; Nitrate esters; Nitroarenes; Nitrosamines; Reaction mechanism; Thermolysis

1. Introduction

Organic polynitro compounds occupy the most important place in technological practice because of their unique and irreplaceable application, being active components (explosives and propellants) of various categories of charges for both military and industrial purposes (e.g. [1–4]) including exploration and exploitation of space [5]. Their polynitroso analogues, specially *N*-nitrosamines and *N*-nitrosamides, can be made use of in the rubber and plastic technology as blowing agents [6,7], as medicaments in the treatment of malign tumors (e.g. [8]) and can serve as a means for introducing mutation in plants (by chromosomal aberration), resulting in new species of agricultural plants (e.g. [9]).

The data on stability of the aforementioned nitrogen compounds, which can be characterized as 'pseudo-stable substances' or energy-source materials, are inevitably necessary to avoid undesirable decomposition or self-initiation during their handling, storing and the application itself. An important starting point in the stability evaluation is the study of thermal reactivity of these compounds. These reactivity data can be obtained by various methods of thermal analysis and gasometry or by a variety of methods based on thermal explosion.

The discrepancy in principles and physical conditions of corresponding measurements, however, prevents a uniform classification of a large majority of results obtained in various laboratories all over the world. This field of considerable importance involves,

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inter alia, both theoretical and practical results obtained by Russian scientists dealing with the thermolysis kinetics and mechanism of the polynitro and polynitroso compounds.

The Russian authors have used the isothermal manometric method (e.g. [4,26,72,76]) with a glass compensating manometer of the Bourdon type to examine the kinetics of thermolysis of energetic materials in vacuum; this method was called the Soviet Manometric Method (SMM) by Zeman in the past [58]. The data obtained by this method are known to correspond to the primary non-autocatalyzed stage of thermal decomposition of the given compounds, and also to the absolute values of the corresponding Arrhenius parameters (i.e. activation energies, E_a, and logarithm of preexponential factor, $\log A$ (e.g. [18,21,47,67]). In the case of thermolysis in condensed state, only the results of some methods of the differential scanning calorimetry (DSC) (e.g. [18,22,23,25]) are directly comparable with the results of SMM [10,15,17]. Results of the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) can be converted to comparable values (in the aforementioned sense) if a relationship exists between them and the results of the SMM, as for instance, by means of a calibration curve (for DTA see [55,56,64,80,83,86] and for TGA [63,65]).

From the point of view of technological practice, the knowledge of the thermal stability and thermolysis mechanisms of polynitro and polynitroso compounds in the condensed state are the most significant. The existing literature, however, lacks a more complete survey of the published Arrhenius parameters of the monomolecular non-autocatalyzed thermal decomposition of these nitrogen compounds in the condensed state classified according to the primary thermolytic fissions.

In the present paper, the aforementioned parameters have been classified on the basis of published mechanisms of the primary steps of thermolysis and by means of the kinetic compensation effect between values E_a and $\log A$ [51,61,64] described by the following [77–80]:

$$E_a = e_0 + 2.303 * R * \beta * \log A \quad (1)$$

where β is the isokinetic temperature [78,79]. The compensation effect results from the application of the Arrhenius law to non-homogenous kinetics both in isothermal and non-isothermal conditions, if there is only one factor determining the rate of the reaction [77]. Eq. (1) could help in defining with more precision the term of reaction series in a proper sense [78]. Four classes of the series are known [78]: isoentropic ($\beta^{-1} = 0$), isoenthalpic ($\beta^{-1} = 0$), with compensation (β>0) and with anticompensation (β<0). Validity of Eq. (1) is necessary but not a sufficient condition for a set of reactions to form a 'series' [78].

2. Data sources

2.1. Substances

A survey of the polynitro and polynitroso compounds studied and corresponding Arrhenius parameters of their thermolysis are given in 1–6.

2.2. Arrhenius parameters of thermolysis

The basic data on the Arrhenius parameters of the non-autocatalyzed thermal decomposition in the condensed state of the nitrogen compounds studied in the present paper have been taken from the Russian authors working at the Mendeleev University of Chemical Technology and the Institute of Chemical Physics of the Russian Academy of Sciences, Moscow. The parameters were obtained by the treatment of the results from the manometric method (SMM, e.g. [4,26,76]) applied for determining the thermolysis kinetics of the aforementioned compounds. Another important source of data are those obtained by the DSC method by Rogers from the Los Alamos National Laboratory [10,22–25]. Results of some other thermoanalytical methods have also been included (see Tables 1,2,3,4,5 and 6). Within the framework of the present paper, it must be added that such Arrhenius parameters are preferred whose absolute values approach the real E_a and $\log A$ values of the primary thermolysis processes (see also [11,66,67]).

3. Results and discussion

When studying the interrelations of E_a and $\log A$ values, we can divide the set of nitrogen compounds studied (given in Tables 1,2,3,4,5 and 6) into several groups (reaction series). Each group is characterized

Table 1
Arrhenius parameters of the Nitrosamines thermolysis

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(K)	E/(kJ mol^{-1}) (s^{-1})	log A/(s^{-1})	Reference
1.1	1,4-Dinitroso-1,4-diazacyclohexane	DNSDC	DSC	Liqid	490–510	143.94	14.0	[10]
1.2	1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecaline	TNSAD						
1.2.1			DSC	Solid	460–480	149.15	15.5	[10]
1.2.2			IR	Solid	443–458	150.10	14.3	[123]
1.3	1,3,5-Trinitroso-1,3,5-triazacyclohexane	TMTA						
1.3.1			SMM	Liquid	383–433	144.35	13.1	[11]
1.3.2			DSC	Liquid	455–470	146.94	15.5	[10]
1.4	1,5-Endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane	DNPT	DSC	Solid	470–485	144.20	13.9	[10]
1.5	bis(2,2,2-Trinitro-ethyl)-*N*-nitrosamine	BTN	SMM	Liquid	388–433	148.11	15.3	[12]
1.6	Bis(2,2-Dinitropropyl)-*N*-nitrosamine	BDPN	SMM	Liquid	418–470	123.84	11.4	[12]
1.7	bis(2,2-Dinitro-2-fluoroethyl)-*N*-nitrosamine	BDFN	SMM	Liquid	448–495	125.94	10.3	[12]

by a different form of Eq. (1). The members of these groups and corresponding e_0, β, and r (correlation coefficient) values are presented in Table 7.

Group I in Table 7 includes *N*-nitrosamines. The Arrhenius parameters of thermolysis of the nitrosamines 1.1–1.5 from Table 1 correspond to the N–N bond homolysis [10,11,91,120]. On the other hand, the data of the nitrosamines 1.6 and 1.7 correlate neither with the Eq. (1) form valid for group I nor with the relation between E_a values and oxygen balance values [91] or detonation characteristics [10] for these nitro compounds, i.e. they do not correspond to the aforementioned homolysis: perhaps the primary splitting in the substances 1.6 and 1.7 starts in the nitroparaffinic portions of their molecules.

The data of II A group of Table 7 correspond with the thermolysis of primary nitramines in liquid phase. The respective primary thermolysis is considered to have an autoprotolytic bimolecular course [10]. However, the values of 2.3.1 and 2.3.2 (solid-phase thermolysis of ethylenedinitramine) correspond to the N–NO_2 bond homolysis and, hence, do not correlate with the form of Eq. (1) – valid for the group I. The bimolecular course of primary thermolysis can also be expected in the case of salts of primary nitramines, i.e. substances of group IIB.

In terms of Eq. (1), the Arrhenius parameters of thermolysis of secondary nitramines in the condensed state (Table 3) are split into the groups III A and III B corresponding to the thermolyses in solid and liquid states, respectively (see Table 7). The thermolysis mechanisms of secondary nitramines, particularly hexogen and octogen (substances 3.5 and 3.6) have frequently been discussed in literature. Often the conclusions are contradictory, which is due to both unsuitable choice of experimental conditions [15,34] and a wrong interpretation of results [15,91] (in particular, interpretation of the deuterium isotope effect [91]). Nevertheless, at present there are enough convincing pieces of evidence in favour of the N–NO_2 bond homolysis as the primary thermolytic splitting of secondary nitramines even in condensed state [15,17,82,85,91,94–96]. The data for 3.5.7 and 3.6.4–3.6.7 do not correspond to the N–NO_2 bond homolysis [15,91] (the respective activation entropy values are negative [58]).

In terms of Eq. (1), the data 3.6.1 through 3.6.3 and 3.6.8 correlate well with those of both groups III B and

Table 2
Arrhenius parameters of the prim-Nitramines thermolysis

Data No.	Substance	Code designation	Method of thermolysis following	State of thermal decomposition	Temperature range/(K)	E (kJ mol^{-1})	log A (s^{-1})	Reference
2.1	*N*-Monomethylnitramine	MNA	SMM	Liquid	358–413	128.00	13.0	[13]
2.2	Methylenedinitramine	MEDINA						
2.2.1			SMM	Solid	343–368	148.10	16.2	[13]
2.2.2			SMM	Liquid	383–408	148.10	16.2	[13]
2.2.3			SMM	Liquid	423–473	142.25	14.2	[13]
2.2.4			SMM	Liquid	383–403	148.10	15.6	[20]
2.3	Ethylenedinitramine	EDNA						
2.3.1			SMM	Solid	393–418	186.20	18.0	[13]
2.3.2			TGA	Solid	393–418	186.20	19.5	[13]
2.3.3			SMM	Liquid	453–473	128.45	12.5	[13]
2.3.4			SMM	Liquid	457–527	127.61	12.8	[20]
2.4	1,3,5,7,9-Pentanitrazanonane or 1,3,5,7,9,11-hexanitrazaundecane							
2.4.1			TGA	Solid	413–443	140.58	14.0	[13]
2.4.2			SMM	Solid	373–454	147.28	14.7	[13]
2.5	Potassium monomethyl-nitraminate	KMNA						
2.5.1			TGA	Liquid	497–516	124.26	9.4	[13]
2.5.2			SMM	Solid	476–495	177.82	14.3	[13]
2.6	Dipotassium ethylene-dinitraminate	KEDNA						
2.6.1			TGA	Liquid	593–618	160.66	10.4	[13]
2.6.2			SMM	Solid	493–518	196.65	14.7	[13]
2.6.3			SMM	Solid	522–560	186.20	13.3	[13]

Table 3
Arrhenius parameters of the sec-Nitramines thermolysis

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(*K*)	$E/(\text{kJ mol}^{-1})$	$\log A/(\text{s}^{-1})$	Reference
3.1	*N*,*N*-Dimethylnitramine	DMNA						
3.1.1			IR	Solid	298	192.50	14.2	[14,15]
3.1.2			Calculated [a]	Liquid		159.80	14.7	[15]
3.2	1,3-Dinitro-1,3-diazacyclopentane	CPX	SMM	Liquid	423–473	149.46	13.5	[16]
3.3	1,4-Dinitro-1,4-diazacyclohexane	DNDC						
3.3.1			SMM	Liquid	489–507	198.45	17.3	[16]
3.3.2			Extrapolated	Solid		211.50	18.9	[17]
3.4	trans-1,4,5,8-tetranitro-1,4,5,8- tetraazadecaline	TNAD						
3.4.1			DSC	Solid	477–507	210.0	18.9	[18]
3.4.2			DSC	Solid	477-507	209.0	18.8	[18]
3.4.3			Extrapolated	Solid		217.6	19.6	[17]
3.5	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX						
3.5.1			MANOMETRIC	Liquid	486–572	198.9	18.5	[24]
3.5.2			DSC	Liquid	495–525	197.1	18.3	[25]
3.5.3			TGA	Liquid	478–493	200.4	18.7	[19]
3.5.4			DSC	Liquid	487–513	211.8	19.6	[23]
3.5.5			SMM	Solid	423–470	213.5	18.6	[26]
3.5.6			SMM	Solid	423–470	217.6	19.1	[27]
3.5.7			SMM	Solid	413–463	167.0	11.2	[28,29]
3.5.8			[b]	Liquid	480–530	200.5	18.4	[15]
3.5.9			[b]	Solid	420–470	213.0	18.8	[15]
3.6	1,3,5,7-Tetranitro-1,3,5,7-tetraaza-cyclooctane	HMX						
3.6.1			MANOMETRIC	Solid	544–587	220.5	19.5	[24]
3.6.2			DSC	Solid	544–558	214.6	18.8	[22]
3.6.3			MS	Solid	534–549	209.0	17.8	[75]
3.6.4			SMM	Solid	449–503	158.7	11.2	[27]
3.6.5		α-HMX	SMM	Solid	403–453	159.0	10.8	[28,29]
3.6.6		β-HMX	SMM	Solid	403–413	159.0	9.2	[28,29]
3.6.7		χ-HMX	SMM	Solid	413–503	159.0	11.3	[28,29]
3.6.8			[d]	Solid	448–483	201.7	18.2	[131]
3.6.9			[b]	Solid	530–590	211.0	19.1	[15]
3.7	3,7-Dinitro-1,3,5,7-tetraazacyclooctane	DPT						
3.7.1			Extrapolated	Solid		192.00	16.6	[17]
3.7.2			[a]	Solid		195.10	15.4	[15]
3.7.3			[a]	Liquid		168.70	15.4	[15]
3.8	1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DADN						
3.8.1			DSC	Solid	523–533	178.60	15.3	[31]
3.8.2			Extrapolated	Solid		189.14	16.2	[17]

Table 3
(Continued)

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(*K*)	*E*/(kJ mol^{-1})	log *A*/(s^{-1})	Referenc e
3.9	1,4-Dinitrotetrahydro-imidazo[4,5-d]imidazol-2,5 (1H,3H)-dione	DINGU						
3.9.1			DSC	Solid	498–518	217.82	20.9	[31]
3.9.2			Extrapolated	Solid		189.14	16.2	[17]
3.10	4-Nitrazavaleric acid	NVA	SMM	Liquid	453–493	176.06	14.7	[32,33]
3.11	1-(Methylnitramino)-2,4,6-trinitrobenzene	TETRYL						
3.11.1			SMM [c]	Liquid	403–438	156.9	14.5	[32]
3.11.2			[a]	Solid		190.4	14.6	[15]

[a] The values determined by means of ^{15}N NMR spectroscopy.

[b] The values averaged on the basis of relationships between the Arrhenius parameters and the ^{15}N chemical shifts of nitrogen in nitrogroups.

[c] The averaged values from [32].

[d] The values of induction period of thermolysis – obtained by means of the simultaneous thermogravimetric modulated beam mass spectrometry.

III B. The same ambiguity was also confirmed for nitramine 3.6 (i.e. HMX) in the case of study of relation of the Arrhenius parameters of thermolysis and the ^{15}N chemical shifts of nitrogen in nitro groups of nitramines [15] and was interpreted by the absence of an influence of solid–liquid transition on this decompositions [15]. According to Maycock and Pai Verneker [89,90] the thermolysis of the HMX takes place in the temperature interval of formation of its δ polymorph, i.e. above 443 K. Huiping and Mulan [88] in their experiments with the HMX thermolysis found that the formation of nitrogen oxides at 481 K occured without any thermal effect. The opinion of Macock and Pai Verneker [89,90] is also shared by Karpowicz and Brill [106] but the critical temperature given by the latter authors is 521 K. In this case, the problem lies in providing a more precise specification of temperature of formation of δ modification since the measured temperature values of polymorphic transitions of the HMX depend not only on the method and technique of their specification [104] but also on the HMX grain size [106,107] and applied pressure [107]. The alleged melting point of this substance is about 553 K. However, another paper [124] predicts the theoretical melting point of the HMX in the interval from 463.4 to 465.2 K, which corresponds to its polymorphic transition $\beta \rightarrow \delta$, currently determined by means of DSC [124–126] at atmospheric pressure. As a consequence of intermolecular interactions in the crystal (see [107–110]), this nitramine has an unstable liquid phase represented by its δ polymorph. This is the reason of the aforementioned absence of the influence of solid–liquid transition. Therefore the opinion of Brill and Karpovicz [110], that the liquefaction of the HMX at temperatures above 553 K is connected with its dissolution in its thermolysis products, seems to be logical.

In terms of Eq. (1), the nitrate esters presented in Table 4 can very approximately be divided into two groups (see Table 7). Those in group IV A, predominantly generated from ethylene glycol or hydroxypropane derivatives, show the compensation in their thermolyses, whereas those in group IV B, involving predominant derivatives of long-chain polyols, show anticompensation, i.e. an opposite change of activation enthalpy as compared with entropy. Some of the data of the nitrate esters can be included into both the groups, as it is particularly seen in the cases of the data

Table 4
Arrhenius parameters of the Nitroesters thermolysis

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(*K*)	*E*/(kJ mol^{-1})	log *A*/(s^{-1})	Reference
4.1	Methylnitrate	MN	SMM	Liquid	485–512	165.27	14.4	[34]
4.2	Ethylene glycol dinitrate	EGDN						
4.2.1			SMM	Liquid	343–413	163.28	14.5	[35]
4.2.2			MANOMETRIC	Liqiud	358–378	163.18	15.9	[36,37]
4.2.3			SMM	Liquid	[a]	165.27	15.5	[30]
4.3	Diethylene glycol dinitrate	DEGN	SMM	Liquid	353–413	175.72	16.5	[38]
4.4	1,2-Propylene glycol dinitrate	1,2-PGDN						
4.4.1			SMM	Liquid	345–413	168.72	15.8	[39]
4.4.2			MANOMETRIC	Liquid	353–373	156.48	15.2	[36,37]
4.5	1,3-Propylene glycol dinitrate	1,3-PGDN						
4.5.1			SMM	Liquid	345–413	163.70	14.9	[39]
4.5.2			MANOMETRIC	Liquid	363–383	159.41	15.2	[36,37]
4.6	1,4-Butylene glycol dinitrate	1,4-BGDN	SMM	Liquid	373–413	163.18	15.1	[39]
4.7	2,3-Butylene glycol dinitrate	2,3-BGDN	SMM	Liquid	353–413	174.05	16.7	[39]
4.8	2-Hydroxy-1,3-propylene glycol dinitrate		SMM	Liquid	353–413	177.40	16.8	[39]
4.9	Glycerol trinitrate	NG						
4.9.1			SMM	Liquid	343–413	163.3	15.4	[40]
4.9.2			SMM	Liquid	[a]	164.4	15.7	[30]
4.10	Erythritol tetranitrate	ETN	SMM	Liquid	[a]	160.25	16.3	[30]
4.11	Xylitol pentanitrate	XPN	SMM	Liquid	[a]	159.00	16.7	[30]
4.12	Pentaerythritol tetranitrate	PETN						
4.12.1			SMM	Liquid	353–413	165.29	15.8	[35]
4.12.2			SMM	Liquid	353–413	163.17	15.6	[41]
4.12.3			SMM	Solid	[a]	173.64	15.2	[41]
4.13	Manitol hexanitrate	MHN						
4.13.1			SMM	Liquid	353–413	159.10	15.9	[35]
4.13.2			SMM	Liquid	[a]	161.10	16.9	[30]
4.14	Dipentaerythritol hexanitrate	DPHN	Extrapolated	Liquid		164.59	15.0	[17]
4.15	Nitrocellulose 13.35% N	NC (13.35%)	SMM	Solid	408–433	164.12	15.0	[42]
4.16	*N*,*N*-Diethanolnitramine dinitrate	DINA	SMM	Liquid	373–433	173.75	16.5	[43]
4.17	Trimethylolnitromethane trinitrate	NIBNG						
4.17.1			MANOMETRIC	Liquid	348–368	152.30	15.3	[36,37]
4.17.2			Calculated	Liquid	348–368	166.07		[44]
4.18	Ethylnitrate	EN						
4.18.1			SMM	Liquid	343–383	167.36	14.7	[45]
4.18.2			SMM	Liquid	[a]	165.27	14.5	[30]
4.19	1,1,1-Trimethylolpropane trinitrate	ETRYNIT	Extrapolated	Liquid		165.29	14.9	[17]

[a] Not presented in original paper.

Table 5
Arrhenius parameters of the Nitroparaffins thermolysis

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(*K*)	*E*/(kJ mol^{-1})	log *A*/(s^{-1})	Reference
5.1	Nitromethane	NM						
5.1.1			DTA	Liquid	443–524	173.63	12.8	[46]
5.1.2			Extrapolated	Liquid		174.0	12.8	[47]
5.2	Dinitromethane	DNM	Extrapolated	Liquid		163.00	14.4	[47]
5.3	Trinitromethane	TNM	Extrapolated	Liquid		159.00	15.1	[47]
5.4	Tetranitromethane	TENM						
5.4.1			SMM	Liquid	353–413	156.48	15.5	[48]
5.4.2			SMM	Liquid	359–450	159.23	16.3	[21]
5.5	1,1,1-Trinitroethane	TNE	SMM	Liquid	353–413	178.24	16.2	[48]
5.6	1-Nitropropane	1-MNP	SMM	Liquid	[a]	205.90	13.9	[30]
5.7	2-Nitropropane	2-MNP	SMM	Liquid	[a]	163.18	11.1	[30]
5.8	1,1-Dinitropropane	1,1-DNP	SMM	Liquid	[a]	182.00	14.8	[30]
5.9	2,2-Dinitropropane	2,2-DNP	SMM	Liquid	[a]	140.16	11.9	[30]
5.10	1,1,1-Trinitropropane	1,1,1-TNP	SMM	Liquid	[a]	174.91	16.9	[30]
5.11	1,1,1,3-Tetranitropropane	TENP	SMM	Liquid	[a]	205.43	17.6	[50,30]
5.12	2-Methyl-1,1,1,3-tetranitropropane	METENP	SMM	Liquid	[a]	175.73	17.7	[50]
5.13	1,1,1,2,2-Pentanitropropane	PNP	SMM	Liquid	[a]	166.10	19.2	[50]
5.14	Hexanitroethane	HNE						
5.14.1			IR	Solid	333–373	162.75	16.3	[49]
5.14.2			SMM	Solid	[a]	149.80	16.4	[41]
5.14.3			SMM	Liquid	363–408	149.80	17.3	[21,41]
5.15	1-Fluoropentanitroethane	FPNE	SMM	Liquid	361–413	152.71	17.3	[21]

[a] Not presented in original paper.

Table 6
Arrhenius parameters of the Polynitroarenes thermolysis

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(K)	E/(kJ mol^{-1})	log A /(s^{-1})	Reference
6.1	2,4-Dinitrotoluene	2,4-DNT	SMM	Liquid	^{a}	139.56	9.0	[51]
6.2	2,6-Dinitrotoluene	2,6-DNT	SMM	Liquid	^{a}	198.87	14.3	[51]
6.3	3,5-Dinitrotoluene	3,5-DNT	SMM	Liquid	^{a}	186.08	12.4	[51]
6.4	2,4,6-Trinitrotoluene	TNT						
6.4.1			SMM	Liquid	463–523	144.44	9.3	[52]
6.4.2			DSC	Liquid	^{a}	143.90	11.4	[53,54]
6.5	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	SMM	Liquid	493–533	146.95	9.1	[52]
6.6	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	SMM	Liquid	514–545	185.05	12.3	[52]
6.7	3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitrobiphenyl	DMNHB						
6.7.1			DTA	Solid	491–496	148.18	10.0	[55,56]
6.7.2			SMM	Solid	488–513	106.40	5.3	[57]
6.7.3			SMM	Liquid	518–538	129.90	8.1	[57]
6.8	2,2′,4,4′,6,6′-Hexanitrodiphenyl-methane	DPM	DTA	Solid	462–473	92.95	5.2	[55,56]
6.9	α,β-bis(2,4,6-Trinitrophenyl)ethane	DPE						
6.9.1			Calculated	Liquid		124.00	6.3	[58]
6.9.2			DTA	Solid	518–528	209.03	15.3	[55,56]
6.10	2,2′,4,4′,6,6′-Hexanitrostilbene	HNS						
6.10.1			DSC	Liquid	590–628	126.77	9.2	[53]
6.10.2			SMM	Solid	533–573	183.80	12.0	[61]
6.10.3			DSC	Liquid	628–648	123.00	8.8	[59]
6.10.4			MANOMETRIC	Liquid	593–633	125.00	8.3	[59]
6.11	1-Chloro-2,4,6-trinitrobenzene	CTB	SMM	Liquid	^{a}	118.07	5.7	[51]
6.12	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	SMM	Liquid	^{a}	177.09	10.5	[51]
6.13	1,3,5-Trichloro-2,4,6-trinitrobenzene	TCTB	SMM	Liquid	^{a}	185.77	11.4	[51]
6.14	1-Hydroxy-2,4,6-trinitrobenzene	PA	SMM	Liquid	456–543	161.18	11.7	[26,62]
6.15	1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	SMM	Liquid	453–473	144.86	11.2	[26]
6.16	1,3,5-Trihydroxy-2,4,6-trinitrobenzene	TNPg						
6.16.1			SMM	Solid	418–438	226.77	22.0	[61,74]
6.16.2			SMM	Liquid	440–453	114.64	10.2	[74]
6.17	1-Hydroxy-3-methyl-2,4,6-trinitrobenzene	TNCr	SMM	Liquid	471–513	192.46	15.6	[62]
6.18	1-Methoxy-2,4,6-trinitrobenzene	TNA	SMM	Liquid	449–505	113.80	6.9	[62]
6.19	1-Amino-2,4,6-trinitrobenzene	PAM	SMM	Liquid	523–573	129.79	7.1	[26]
6.20	1,3-Diamino-2,4,6-trinitrobenzene	DATB						
6.20.1			SMM	Solid	493–543	196.80	13.2	[61]
6.20.2			DSC	Solid	^{a}	193.72	15.1	[60]

Table 6
(Continued)

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(*K*)	*E*/(kJ mol^{-1})	log *A* /(s^{-1})	Reference
6.21	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB						
6.21.1			SMM	Solid	557–593	175.00	11.6	[61]
6.21.2			DSC	Solid	[a]	250.62	19.5	[60]
6.22	3-(2,4,6-Trinitrophenylamino)-1,2,4-triazole	PATO	DSC	[b]	[a]	134.72	10.2	[60]
6.23	2,2′,4,4′,6,6′-Hexanitrooxanilide	HNO	SMM	Solid	503–568	215.62	16.0	[61]
6.24	2,2′,4,4′,6,6′-Hexanitrodiphenylamine	DPA						
6.24.1			DTA	Solid	506–515	177.76	11.0	[55,56]
6.24.2			TGA	[b]	473–573	153.30	11.0	[63]
6.25	3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl	DIPAM	Extrapolated	Solid		190.23	12.8	[58]
6.26	2,2′,4,4′,6,6′-Hexanitroazobenzene	HNAB	SMM	Liquid	463–493	121.83	6.8	[61]
6.27	2,4,6-Tris(2,4,6-trinitrophenylamino)-1,3,5-triazine	TPM	SMM	Solid	523–563	257.06	19.0	[61]
6.28	2,4,6-Tris(3-methyl-2,4,6-trinitrophenylamino)-1,3,5-triazine	TMPM	DTA	Solid	507–515	116.18	7.2	[55,56]
6.29	2,2′,4,4′,6,6′-Hexanitrobenzophenone	HNBF	SMM	Liquid [c]	533–565	174.05	11.7	[67]
6.30	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfide	DIPS						
6.30.1			SMM	Liquid	508–528	131.80	7.4	[68]
6.30.2			SMM	Solid	473–493	178.77	12.0	[26]
6.31	2,2′,4,4′,6,6′-Hexanitrodiphenylsulfone	DIPSO	SMM	Solid	473–563	106.76	5.6	[69]
6.32	1,3,5-Trinitrobenzene	TNB	SMM	Liquid	523–583	180.03	10.9	[52]
6.33	2,2′,4,4′,6,6′-Hexanitrobiphenyl	HNB	SMM	Liquid	513–573	207.24	16.1	[26]
6.34	2,2′,2″,4,4′,4″,6,6′,6″-Nonanitro-*m*-terphenyl	NONA						
6.34.1			DTA	Solid	572–596	214.11	14.1	[56,64]
6.34.2			TGA	Solid	523–623	236.29	15.2	[65]
6.35	2,2′,2″,4,4′,6,6′,6″-Octanitro-*m*-terphenyl	ONT	SMM	Solid	573–623	281.58	19.5	[66]
6.36	2,4,6-Tris(2,4,6-trinitrophenyl)-1,3,5-triazine	TPT	SMM	Solid	573–623	269.45	18.2	[66]
6.37	1,4,5,8-Tetranitronaphthalene	TENN	DTA	Solid	572–605	223.05	15.0	[56,64]
6.38	Benzotrifuroxane	BTF						
6.38.1			SMM	Liquid	473-523	173.64	14.2	[70]
6.38.2			SMM	Solid	443–463	284.51	23.0	[70]
6.39	1,3,7,9-Tetranitrodibenzo-1,3,*a*,4,6 *a*-tetraazapentalene	TACOT-1	SMM	Solid	583–623	234.30	15.4	[61]
6.40	1,3,8,10-Tetranitrodibenzo-1,3*a*,6,6 *a*-tetraazapentalene	TACOT-2	SMM	Solid	583–623	189.95	11.7	[61]

Table 6
(Continued)

Data No.	Substance	Code designation	Method of thermolysis	State of thermal decomposition	Temperature range/(K)	E/(kJ mol^{-1})	log A /(s^{-1})	Reference
6.41	1,3,7,9-Tetranitrophenothiazine-5,5-dioxide	TNPTD	SMM	Solid	523–573	200.96	11.7	[61]
6.42	3-Nitro-1,2,4-triazol-5-one	NTO						
6.42.1			Chemiluminiscence	Solid	273–313	140.00	6.7	[60]
6.42.2			TGA	Solid	502–5193	186.00	16.6	[130]
6.42.3			IR	Solid	468–483	206.00	20.6	[130]
6.43	2,6-Diamino-3,5-dinitropyridine	DADNP	SMM	Solid	538–558	224.50	15.3	[127]
6.44	2,6-bis(2,4,6-Trinitrophenylamino)-3,5-dinitropyridine	PYX						
6.44.1			SMM	Solid	563–588	213.0	13.6	[127]
6.44.2			Extrapolated	Solid		203.3	14.2	[17]
6.45	Pottassium picrate	KPA	SMM	Solid	[a]	183.26	11.4	[69]
6.46	Magnesium picrate	MgPA	SMM	Solid	[a]	212.55	13.9	[69]
6.47	Lead tricinate	LTNR	Chem. anal.	Solid	433–493	138.1	10.3	[71]
6.48	Potassium 2,2′,4,4′-6,6′-hexanitrodiphenylaminate	KDPA	DTA	Solid	497–509	107.57	5.18	[17,55]
6.49	Sodium 3,5-dinitro-1,2,4-triazolate	SDNT	SMM	Solid	503–528	175.3	12.0	[127]
6.50	Potassium 3-oxi-2,4,6-trinitropyridinate	KOTNP	SMM	Solid	453–483	136.00	9.8	[127]

[a] Not presented in original paper.

[b] Thermolysis within the temperature range near the melting.

[c] Thermolysis in the solid state has the same kinetic parameters as in the liquid state [67].

Table 7
A distribution of compounds studied into groups and coefficients of corresponding shapes of Eq. (1)

Group of substances				Coefficients of Eq. (1)		
Entity		No.	Structure [a]	e_0/(kJ mol^{-1})	β/(K)	r
Nitrosamines		I	1.1, 1.2, 1.3.1, 1.3.2, 1.4, 1.5	117.6	102.1	0.885
prim-Nitramines	Liquid	II A	2.1, 2.2.1, 2.2.2, 2.2.3, 2.2.4, 2.3.3, 2.3.4, 2.4	52.8	316.3	0.934
	Salts	II B	2.5.1, 2.5.2, 2.6.1, 2.6.2, 2.6.3	34.2	567.4	0.914
sec-Nitramines	Solid	III A	3.1.1, 3.3.2, 3.4.1, 3.4.2, 3.4.3, 3.5.5, 3.5.6, 3.5.9, 3.6.1, 3.6.2, 3.6.3, 3.6.8, 3.6.9, 3.7.1, 3.7.2, 3.8.1, 3.8.2, 3.9.1, 3.9.2, 3.11.2	96.7	315.0	0.911
	Liquid	III B	3.1.2, 3.2, 3.3.1, 3.5.1, 3.5.2, 3.5.3, 3.5.4, 3.6.1, 3.6.2, 3.6.3, 3.6.8, 3.7.3, 3.10, 3.11.1	7.7	556.7	0.960
Nitrate esters		IV A	4.3, 4.3.2, 4.4.1, 4.7, 4.8, 4.9.1, 4.9.2, 4.12.1, 4.12.3, 4.16	47.8	398.1	0.766
		IV B	4.1, 4.2.1, 4.2.2, 4.5.1, 4.6, 4.9.1, 4.10, 4.11, 4.12.3, 4.13.1, 4.13.2, 4.14, 4.15, 4.18.1, 4.19	204.6	−138.7	0.575
Nitro-paraffins		V A	1.6, 5.8, 5.9, 5.11	−15.6	670.4	0.983
		V B	5.1.1, 5.1.2, 5.2, 5.3, 5.4.1, 5.4.2, 5.14.1, 5.14.2, 5.14.3, 5.15	233.5	−248.8	0.908
		V C	5.5, 5.6, 5.10, 5.12, 5.13	302.4	−380.2	0.945
Nitroarenes		VI A	6.32, 6.33, 6.34.1, 6.34.2, 6.35, 6.36, 6.37, 6.39, 6.40, 6.42.1	62.8	566.3	0.962
		VI B	6.1, 6.2, 6.3, 6.4.1, 6.4.2, 6.5, 6.6, 6.7.1, 6.7.2, 6.7.3, 6.9.1, 6.9.2, 6.11, 6.12, 6.13, 6.29, 6.30.1, 6.30.2, 6.31	53.3	536.9	0.956
		VI C1	6.8, 6.10.1, 6.10.2, 6.10.3, 6.10.4, 6.14, 6.15, 6.16.2, 6.17, 6.18, 6.19, 6.20.2, 6.21.2, 6.22, 6.23, 6.24.2, 6.25, 6.26, 6.28, 6.38.1, 6.38.2	36.2	556.8	0.968
		VI C2	6.20.1, 6.21.1, 6.24.1, 6.27, 6.41, 6.43, 6.44.1	73.1	511.3	0.957
Nitroarene salts		VII	6.45, 6.46, 6.47, 6.48, 6.49, 6.50	33.4	628.3	0.925

[a] Numbered as in Tables 1,2,3,4,5 and 6.

of 4.2.3, 4.9.1, and 4.12.3. The very poor correlation of the two groups of data in terms of Eq. (1) is connected with the low influence of the rest of nitrate ester molecule on the activation entropy [44]. This is due to the way of bonding of nitro group in this molecule and to the primary step of thermolysis which consists in the O–NO_2 bond homolysis in this case [17,44,90,93,121,122].

In terms of Eq. (1), the polynitro derivatives of aliphatic hydrocarbons in Table 5 can be divided into three groups (see Table 7). Group V A predominantly includes geminal dinitropropane derivatives inclusive of *N*-nitrosamine 1.6, whose classification in this group can indicate a primary thermolysis in the 2,2-dinitropropyl section of its molecule. Group V B again predominantly involves the nitropropane derivatives with nitro groups cumulated most often at position 1. Nitromethane and nitroethane derivatives are found in group V C. As it can be seen from Table 5, the cumulation of nitro groups at a single carbon atom in the molecule of substances of groups V B and V C corresponds with a decrease in the activation enthalpy with concomitant increase in activation entropy, i.e. an anticompensation. The primary process of thermolysis of these nitro compounds in condensed state involves the C–NO_2 bond homolysis [47,48] which also holds true in the case of thermolysis of mononitromethane under pressures lower than 4 GPa [47,111]. However, it is not excluded that, in the case of substances 1.6, 5.7, and 5.9, the thermolysis goes by a heterolytic mechanism with participation of hydrogen at the β-position with respect to nitro group (i.e. elimination of HNO_2).

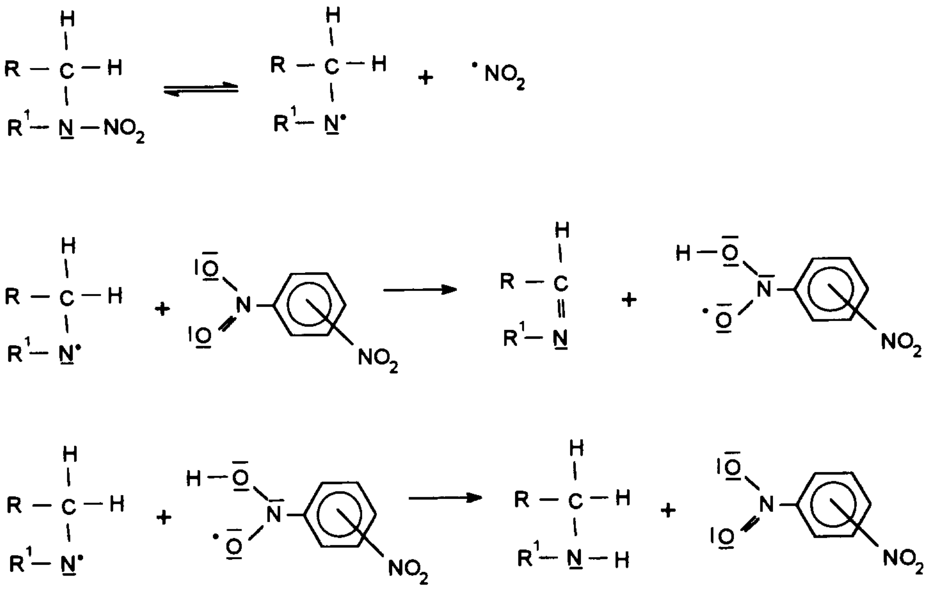
Nitro groups in aliphatic nitro compounds interact with the rest of the molecule as a substituent with -I effect, whereas in nitroarenes their effect is predominantly -M. This generally results in lowered thermal reactivity of polynitroarenes as compared with the above-discussed polynitro compounds. The intensity of the interaction as mentioned and the manner of its transmission to the other substituents in the aromatic system codetermine the mechanism of primary thermolysis of the given polynitroarene.

The data 6.32, 6.33, 6.34.1, 6.34.2, 6.35, 6.36, 6.37, 6.39–6.42 from Table 6, except perhaps the date 6.41, correspond to 'pure' (nonsubstituted) polynitroarenes whose primary thermolytic process should consist in the C–NO_2 bond homolysis. In some cases this is also indicated by the respective activation entropy values [58,92].

For all derivatives of 1,3,5-trinitrobenzene with hydrogen at the χ-position to nitro group (i.e. with alkyl, amino, and hydroxy substituents) the accepted mechanism of primary thermolysis is the so-called 'trinitrotoluene mechanism'. It involves migration of the said hydrogen (through a six-membered transition state) to the oxygen of nitro group [97–100] with subsequent homolysis of the N–OH bond thus formed. A stable intermediate of this splitting of 2,4,6-trinitrotoluene (substance 6.4) is dinitroanthranil [52,100] showing a strong catalytic influence on further thermolysis. An analogous mechanism of primary splitting has been suggested for the thermolysis of hexanitrostilbene [59] (substance 6.10). With the help of X-ray photoelectron spectroscopy (XPS), the mechanism of primary fragmentation in the above-given sense was also confirmed for polynitrophenols [101]. An analogous course of splitting of (poly)amino derivatives of 1,3,5-trinitrobenzene [101] (substances 6.19–6.21) leads to nitrobenzofurazanes and nitrobenzofuroxanes as stable intermediates [84,102]: the pyrolysis of *o*-nitrophenyl carbamate has been described [103] as a method for synthesizing benzofurazane.

In the case of polychloro derivatives of 1,3,5-trinitrobenzene, it was pointed out by Maksimov et al. [52] that in a way their thermolysis resembles that of their polymethyl analogues. This similarity was fully confirmed by some published results [81,83]: here, a primary interaction between chlorine substituents and oxygen atoms of ortho-nitro groups may operate, a fact which is supported by the activation entropy values [58].

There are a few substances in the polynitroarene series whose primary thermolysis is supposed to proceed without participation of the nitro group. Thus Maksiomov et al. suppose that C–S bond is primarily split [72] in the thermolyses of hexanitrodiphenyl sulfide (substance 6.30) and hexanitrodiphenyl sulfone (substance 6.31), and the C–CO bond [76] in the case of hexanitrobenzophenone (substance 6.29). Similarly, Hoffsommer and Feiffer presume a primary homolysis of C–N_2 bond [105] in hexanitroazobenzene. However, from the activation entropies of these substances [58] it can be deduced that the primary fragmentation goes via a cyclic transition state: even from the results [81,83] for substances 6.26 and 6.30 it



Scheme 1. The probable mechanism of the polynitroarene interaction with the primary products in the thermolysis of nitramines [58].

is reasonable to presume a primary interaction between oxygen of ortho-nitro group and the bridge heteroatom (five-membered transition state).

A detailed analysis of relationships between thermal reactivity of polynitroarenes and their detonation characteristics [81] showed a strict classification of these substances into three groups: nonsubstituted 'pure' polynitroarenes, derivatives with alkyl and chloro substituents or –S– or $-SO_2-$ bridges at the ortho position to nitro group, and derivatives having sp^2 (or nearly sp^2) ground-state hybridization at the central atom of thermolysis reaction centre (–OH, –NH–, –N=N–, –CH=CH– and similar groups). The application of Eq. (1) to the data on polynitroarenes in Table 6 arrives at practically identical classification of this set of substances (see Table 7) although far less rigid than that in the previous case: a summary (traditional [51,61,64]) treatment of the data on polynitroarenes (i.e. groups VI A–VI C) results in a single form of Eq. (1) with $e_0 = 44.27$ kJ mol^{-1}, $\beta = 581.51$ K, and the correlation coefficient $r = 0.952$.

Group VI A of substances in Table 7 includes 'pure' polynitroarenes; the kinetic data of their thermolyses were predominantly obtained with the help of SMM. This group represents highly thermostable explosives. The NTO data 6.42.1 (one of the representatives of LOVA explosives) correlate well with it, while data 6.42.2 is near to VI C_1 group and 6.42.3 does not correlate with any polynitroarenes data. It must be added, that only O-aci form of NTO has an aromatic character.

Polynitroarene derivatives of group VI B are characterized by the interaction of oxygen of the nitro group with ortho-standing substituent as the primary step of thermolysis. This interaction can be realized by a hydrogen transfer from alkyl substituent via a six-membered transition state or through a five-membered transition state involving a direct participation of ortho-substituent.

Group VI C is divided into two subgroups denoted as VI C_1 and VI C_2 and includes the substances exhibiting primary thermolysis by the trinitrotoluene mechanism but having an sp^2 (or nearly sp^2) ground-state hybridization at the central atom of ortho-substituent. The form of Eq. (1) valid for VI C_1 subgroup is well obeyed by the Arrhenius parameters of thermolysis of DATB (substance 6.20) and TATB (substance 6.21) obtained from DSC measurements, whereas the parameters derived from SMM (in vacuum) correlate with the data of VI C_2 subgroup. The reason of the difference has been discussed in [63] for TATB. The substances of VI C_2 subgroup are characterized by a distinct stabilizing effect of crystal lattice which was experimentally proved in [56] for some of them. This effect predominates here over that of the molecular structure itself, which brings these derivatives (possessing an –NH– grouping in the molecule and showing strong intermolecular interactions in the crystal) close (from the stability point of view) to the 'pure' polynitroarenes: some authors (e.g. Maksimov and Kogut [61] for the substance 6.41 or Maksimov et al. [128] and Sharma et al. [87] for TATB (substance 6.21)) consider the C–NO_2 bond homolysis to be the primary step of thermolysis of substances of subgroup VI C_2. However, the activation entropies derived from the data of 6.21.1 and 6.41 have negative values and thus do not correspond to this type of homolysis [58].

The Arrhenius parameters of salts involving polynitroarene and polynitroheterocyclic anions correlate well in terms of the form of Eq. (1) valid for group VII of the substances. This group of salts exhibit negative values of activation entropy, and a significant stabilizing effect of crystal lattice can be presumed here too.

In the past, the attempts at studies of relationships between molecular structure and thermal reactivity of organic polynitro compounds used to adopt the so-called inert solvents [26,32] involving, e.g. 1,3-dinitrobenzene [16,26,32], 1,3,5-trinitrobenzene [26,105,112–114], hexachlorobenzene [73], and even 2,4,6-trinitrotoluene [26,32]. The Arrhenius parameters resulting from such studies could not be used to derive their relationships to the detonation characteristics of the respective polynitro compounds [17,58].

In hexachlorobenzene solutions, a bimolecular course of thermolysis was observed with polynitroarenes, this character gradually vanishes with increasing dilution of the solution [73]. Some 'inert' solvents, although structurally quite cognate with the substance thermolyzed, exhibited a distinct influence on the splitting itself (see also citations and partial conclusions in [56,58]): e.g. 1,3,5-trinitrobenzene inhibits the thermolysis of hexanitroazobenzene [105]. A study [114] of thermolysis of RDX (substance 3.5) in 1,3,5-trinitrobenzene solution revealed formation of 2,4,6,3′,5′-pentanitrobiphenyl from the solvent molecules. It was also found that the reaction rate of thermolysis of 1,3,5-trinitrobenzene derivatives in the condensed phase is higher than that in benzene solution [129]. The facts given indicate a pseudo-monomolecular course of thermolysis of organic polynitro compounds.

The problem of solvent effect and/or that of participation of bimolecular interactions in the initial phases of thermolysis [52,73,115,116] has been interpreted with application [58] of the findings by Urbanski and Bužniak concerning the retarding effects of polynitroarenes in radical polymerizations [117–119]. In [58], this consideration is demonstrated on a dinitrobenzene-nitramine mixture (see Fig. 1). Correctness of the application cited can be verified on the basis of a typical a reaction condensation products. However, the problem lies in the fact that till now the manometric methods have monitored the amounts and composition of only the gaseous products, little attention being paid to condensed products.

Beside the possibility of pseudo-monomolecular course (or its suppression depending on the solvent type), the results of studies of thermal reactivity of polynitroarenes in solution also reflect the loss of stabilizing effect of the crystal lattice: thus, the highly thermostable TPT (substance 6.36) changes into a thermally reactive substance (more reactive than, e.g., DPA (substance 6.24.) on transferring it into 1,3,5-trinitrobenzene solution [56].

The pseudo-monomolecular course of thermolysis cannot be excluded even among molecules of a single kind. In this way, it would perhaps be possible to interpret the published considerations [115,116] about the bimolecular course of thermolysis by trinitrotoluene mechanism, or the already mentioned concentration dependence of the value of effective rate constant of thermolysis of polynitroarenes in hexachlorobenzene solution [73] or even the lowering of the thermolysis reaction rate in benzene solution [129]. The course discussed can also be documented by the attempt at interpretation [47] of the finding of Piermarini et al. [120] concerning the effect of pressure on the thermolysis kinetics of nitromethane: here an agreement with practice was reached even with regard to the characteristic products of thermolysis [47].

4. Conclusion

On the basis of the linear relationship between the activation energies, E_a, and logarithm of preexponential factor, $\log A$, which result from monomolecular non-autocatalyzed thermolysis of organic polynitroso and polynitro compounds in condensed state, these substances can be classified into several reaction series. For the compounds with intensive intermolecular interaction in the crystal, such as nitramines and highly thermostable polynitroarenes with –NH– grouping in the molecule, the classification mentioned is also determined by the influence of crystal lattice. Each series of substances exhibits its characteristic chemical mechanism of primary thermolysis. A compensation effect between the E_a and $\log A$ values is typical of most series. However, an anticompensation corresponds to a cumulation of nitro groups in the molecule and lengthening of carbon chain in nitrate esters, and to a cumulation of nitro groups at a single carbon atom in nitroparaffins.

Although with the aliphatic and heteroaliphatic polynitro compounds the reaction series are relatively sharply delimited in terms of the aforementioned relation, this is not the case with polynitroarenes. The main reason for that can lie in the dominating effect of conjugation of nitro group with the π-electron system of the arene on the thermal reactivity of the nitroarenes. Traditionally, polynitroarenes have been included in a single reaction series [51,61,64]. However, a detailed analysis given in the present paper, starting from the relationship between the thermal reactivity of the given compounds and their detonation characteristics [81], confirms the classification of the polynitroarenes studied into three subgroups [81]:

1. Nonsubstituted 'pure' polynitroarenes;
2. Derivatives containing alkyl or chloro substituents or –S– or $-SO_2-$ bridges at ortho position to a nitro group; and
3. Derivatives having sp^2 (or nearly sp^2) ground-state hybridization at the central atom of the thermolysis reaction centre (i.e. $-NH_2$, –NH–,–OH, –CH=CH–, –N=N–, activated $-CH_2-$).

Whereas in the case of the first two groups the stabilizing effect of crystal lattice is not markedly projected into the interrelation of the respective E_a and $\log A$ values, the third group is split into two reaction series by this effect.

In the context of the said stabilizing effect in the thermolysis of nitramines, on the basis of the relation discussed, it has again been possible to confirm the absence of the effect of solid–liquid transition on the thermal reactivity of the HMX (i.e. substance 3.6): the reason lies in the instability of liquid phase of this nitramine. This phase is 'represented' by the δ-polymorphic modification of the HMX.

In the primary homolytic fragmentation of thermolysis of the polynitro compounds, particularly polynitroarenes, one can anticipate a mutual interaction of molecules [47,58] analogous to the termination reactions of nitroarenes in radical polymerizations. This hypothesis [47,58] follows from the comparison of results of the study of thermal reactivity of organic polynitro compounds in the so-called inert solvents [16,26,32,73,105,112–114,129] with those in the condensed state (see [47,52,58,73,115,116] and references in Tables 1,2,3,4,5 and 6), taking into account the conclusions by Urbanski and Bužniak about the retardation action of polynitroarenes in the said polymerizations [117–119].

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