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Analysis and prediction of the Arrhenius parameters of low-temperature thermolysis of nitramines by means of the ^{15}N NMR spectroscopy

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Abstract

The paper presents ^{15}N NMR chemical shifts δ of 24 nitramines out of which 1-nitro-1-azaethylene, 1,3-dinitro-1,3-diazacyclobutane and 1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazacyclodecane have not been synthesized yet. The relationships between the Arrhenius parameters E_a and log A of the low-temperature thermolysis under conditions of Russian manometric method and δ values of nitrogen atoms in nitro groups are specified for substances studied. The δ values correspond to nitro groups in nitramino groupings which are the first to undergo thermolysis. On the basis of the relationships specified the E_a and log A values are predicted for 13 compounds from the nitramines studied, the parameters of homolytic course of thermolysis are differentiated from those of bimolecular or another heterolytic thermal decomposition, some aspects of the thermolysis of nitramines, particularly with geometrical constraints and/or with strongly-withdrawing groups in their molecules, are interpreted and evaluation of effect of solid–liquid phase transition on the kinetics of initial stage of HMX thermolysis are made. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Nitramines; Thermolysis; Activation energy; ^{15}N NMR chemical shifts

1. Introduction

There is a great interest in the thermal reactivity of nitramines due at least in part to their importance as energetic materials. (e.g. see [1,2]). The homolysis of the N–NO$_2$ bond was proved as a primary step of thermolysis of the secondary nitramines in a condensed state [3–5]. In the case of primary nitramines the homolysis is limiting step in their thermal reactivity in gaseous state, whereas their thermolysis in the condensed state is a bimolecular autoprotolytic reaction [7]. As the valence states of nitro compounds in generally (including ground state) have a large component of biradical character [6] a bimolecular course of the primary thermolysis of the compounds, including some nitramines, cannot be fully excluded from (about the pseudomonomolecular course of their thermolysis, see [8]). All the said types of reactivity of nitramine nitro group depend upon the electron density on its nitrogen atom. The density is predominantly a function of the extend to which the amino nitrogen lone pair is involved in π-bonding with this nitro group, i.e. both the homolysis of N–NO$_2$ bond and hydrogen abstraction by an oxygen of the nitro group should be depended upon this N–N bond strength.

It is a well-known fact that ^{15}N NMR chemical shifts may be taken to indicate the degree of shielding of the ^{15}N atoms which affect the adjacent N–N bond strengths. A relationship corresponding to this has the

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following general form [9]

$$E_a = a \times \delta_N + b, \qquad (1)$$

where E_a is activation energy of non-autocatalyzed thermolysis of nitramines and δ_N is the ^{15}N NMR chemical shift of nitro group nitrogen. With respect to the kinetic compensation effect in this thermolysis [8] also this relationship was found [9]

$$\log A = a_1 \times \delta_N + b_1, \qquad (2)$$

where A means the Arrhenius preexponent of the above-mentioned decomposition. As the nitro groups play a key role in thermal reactivity of nitro compounds in general a less close correlation results from the application of the ^{15}N NMR chemical shifts δ_A of amino nitrogens of nitramino groups in the both relationships [9].

The study of thermal reactivity of nitramines is the important starting point for selection and exploitation of these nitro compounds. However, some published conclusions of the study are contradictory, which is due to both unsuitable choice of experimental conditions and a wrong interpretation of results [4,8,9]. Therefore a method is needed for mutual comparison and evaluation of results obtained in various laboratories. From the point of view of development of the new energetic materials also predicted characteristics of thermal reactivity of nitramines are significant. The relationships 1 and 2 signalize a possibility of their application not only in a prediction but also in analysis of the Arrhenius parameters resulted from the low-temperature thermolysis of nitramines. These problems are discussed in the present paper which extends the findings of the recent study [9].

2. Experimental

2.1. ^{15}N NMR *spectroscopy*

Survey of the nitramines studied and their code designation is given in Table 1. The ^{15}N NMR chemical shifts δ of the nitramines were obtained with the help of an AMX-360 Bruker apparatus using the INEPT method. The samples were dissolved in hexadeuteriodimethyl sulfoxide at a concentration of 0.2 mol nitramine per 1 dm^3 solution. For some of the substances the values of these shifts were taken from literature [11,12]; those of the substances not yet prepared were predicted. These all δ_A and δ_N values are summarized in Table 1.

2.2. *Prediction of* ^{15}N NMR *chemical shifts values*

The substance not yet prepared (i.e. 17, 18 and 19 in Table 1) are of considerable theoretical interest in the chemistry of nitramines. For the nitramines 19 and 20, the prediction of ^{15}N NMR chemical shifts δ_A of their amino nitrogen atoms starts from the equation which was found in this paper in a form

$$\sum \delta_A = -193.23 \times n - 20.78 \qquad (3)$$

with correlation coefficient r=0.9999. In this equation $\sum\delta_A$ is the sum of ^{15}N NMR chemical shifts δ_A in the molecules of substances 3, 12 and 14, i.e. in the nitramines containing –CH$_2$N(NO$_2$)– building units in their rigid molecules, and **n** is the number of these units in the molecule. The δ_A value of nitramine 17 was obtained [10] by means of its predicted heat of fusion [13]: first the drop energy E_{dr} (impact sensitivity) of the given substance was calculated from the relationship between these heats and E_{dr} values of nitramines with rigid molecules [10], and then this value was introduced into relationship between E_{dr} and δ_A values of the same nitramines to give the predicted δ_A value [10]. The prediction of ^{15}N NMR chemical shifts δ_N of nitrogen atoms of nitro groups started from the analysis (see Table 2) of the relationship between δ_A and δ_N values of nitramino groups which turned out to be describable by the following general form of relationship:

$$\delta_N = a_2 \times \delta_A + b_2. \qquad (4)$$

In the sense of relationship (4), the investigated set of substances falls naturally into several subsets as it is documented in Table 2. Data of caged molecules of nitramines 20 and 21 do not correlate with any forms of this equation. The estimate of δ_N values of all the three so far unknown nitramines was based on a subset III of substances in Table 2. The correctness of choice of particular linear dependence was verified [10] by means of relationship (1) and subsequent evaluation of reality of the E_a values thus obtained in the present paper.

Table 1
Survey of the nitramines studied, their code designation, ^{15}N NMR chemical shifts and Arrhenius parameters of their thermolysis

Nitramine			^{15}N chemical shift (ppm)			Arrhenius parameters of thermolysis					
Data no.	Chemical name	Code design	Position in molecule	Nitrogen atom		Method of thermolysis study	For the state	Temperature region (K)	E (kJ mol^{-1})	log A (s^{-1})	Reference
				Nitro	Amino						
1.1	1-Nitro-1-azaethane	MNA	1	−24.60[b]	−215.89[b]	SMM	Liquid	358–413	128.1	13.0	[7]
2.1	1,4-Dinitro-1.4-diazabutane	EDNA	1,4	−26.34	−205.47	SMM	Solid	343–368	186.2	18.0	[7]
2.2						SMM	Liquid	453–473	128.4	12.5	[7]
3.1	2-Nitro-2-azapropane	DMNA	2	−25.84[b]	−215.80[b]	IR	Solid	298	192.5	14.2	[9,17]
3.2						NMR	Liquid		159.8	14.7	[9]
4.1	2,4-Dinitro-2,4-diazapentane	OCPX	2,4	−28.36	−202.61	NMR	Liquid		178.6	16.3	[a]
5.1	2,5-Dinitro-2,5-diazahexane	DMEDNA	2,5	−27.83	−209.55	NMR	Liquid		176.1	16.1	[a]
6.1	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	2,6	−28.49	−202.29	NMR	Liquid		179.2	16.3	[a]
6.2			4	−32.02	−189.90	NMR	Liquid		195.9	17.7	[a]
7.1	2,4,6,8-Tetranitro-2,4,6,8-tetra-azanonane	OHMX	2,8	−28.77	−202.25	NMR	Solid		202.2	17.6	[a]
7.2			4,6	−34.52	−195.59	NMR	Solid		216.7	18.9	[a]
7.3		OHMX	2,8			NMR	Liquid		180.6	16.4	[a]
7.4			4,6			NMR	Liquid		207.8	18.5	[a]
8.1	2,4,7,9-Tetranitro-2,4,7,9-tetra-azadecane	TNADEC	2,9	−28.44	−202.75	NMR	Liquid		179.0	16.3	[a]
8.2			4,7	−29.43	−196.03	NMR	Liquid		183.7	16.7	[a]
9.1	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane	AcAn	2,8	−32.81	−190.52	NMR	Liquid		199.7	18.0	[a]
9.2			4,6	−33.38	−188.06	NMR	Liquid		202.4	18.2	[a]
9.3		AcAn	2,8			NMR	Solid		213.0	18.8	[a]
9.4			4,6			NMR	Solid		214.0	19.0	[a]
10.1	1,3-Dinitro-1,3-diazacyclo-pentane	CPX	1,3	−31.21	−209.01	SMM	Liquid	423–473	149.4	13.5	[18]
11.1	1,4-Dinitro-1,4-diazacyclohexane	DNDC	1,4	−26.26	−205.49	SMM	Liquid	489–507	198.4	17.3	[18]
12.1	1,3,5-Trinitro-1,3,5-triaza-cyclohexane	RDX	1,3,5	−32.90[b]	−198.10[b]	Manomet	Liquid	486–572	198.9	18.5	[19]
12.2						DSC	Liquid	486–525	197.1	18.3	[20]
12.3						TGA	Liquid	478–493	200.4	18.7	[21]
12.4						SMM	Solid	423–470	213.5	18.6	[16]
12.5						SMM	Solid	423–470	217.6	19.1	[22]
12.6						SMM	Solid	413–463	167.0	11.2	[23]
13.1	1,3,5-Trinitro-1,3,5-triazacyclo-heptane	HOMO	1,5	−33.04	−201.28	NMR	Liquid		200.8	18.1	[a]
13.2			3	−34.38	−196.32	NMR	Liquid		207.1	18.6	[a]
14.1	1,3,5,7-Tetranitro-1,3,5,7-tetra-azacyclooctane	HMX	1,3,5,7	−34.70[b]	−199.10[b]	Manomet	Solid	544–587	220.5	19.5	[19]
14.2						DSC	Liquid[c]	544–558	214.6	18.8	[24]
14.3						MS	Solid	534–549	209.0	17.8	[25]
14.4		α-HMX				SMM	Solid	403–453	159.0	10.8	[23]
14.5		β-HMX				SMM	Solid	403–413	159.0	9.2	[23]
14.6		δ-HMX				SMM	Solid	413–503	159.0	11.3	[23]

Table 1 (*Continued*)

Nitramine			^{15}N chemical shift (ppm)			Arrhenius parameters of thermolysis					
Data no.	Chemical name	Code design	Position in molecule	Nitrogen atom		Method of thermolysis study	For the state	Temperature region (K)	E (kJ mol^{-1})	log A (s^{-1})	Reference
				Nitro	Amino						
15.1	1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DADN	3,7	−23.70	−205.10	Extrapol.	Solid		189.1	16.2	[26]
16.1	1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DPT	3,7	−25.30[b]	−203.70[b]	Extrapol.	Solid		192.3	16.6	[26]
16.2						NMR	Solid		195.1	15.4	[a]
16.3						NMR	Liquid		167.8	15.4	[a]
17.1	1-Nitro-1-azaethylene	DIGEN	1	−23.58[d]	−208.52[d]	NMR	Liquid		156.0	14.5	[a]
17.2						NMR	Solid		189.0	16.4	[a]
17.3						Calcd.			146.5		[27]
18.1	1,3-Dinitro-1,3-diazacyclobutane	TETROGEN	1,3	−27.83[d]	−203.62[d]	Calcd.			153.1	14.1[e]	[28]
19.1	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaazacyclodecane	DECAGEN	1,3,5,7,9	−33.25[d]	−197.38[d]	NMR	Solid		213.5	18.6	[a]
19.2						NMR	Liquid		201.8	18.2	[a]
20.1	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	4,10	−33.40	−197.20	NMR	Solid		213.9	18.6	[a]
20.2						NMR	Liquid		202.5	18.2	[a]
21.1	2,4,6,8,10,12-Hexanitro-2,4,6,8, 10,12-hexaazaisowurtzitane	HNIW	2,6,8,12	−40.30[f]	−199.00[f]	TGA	Solid	433–453	172±26	13.8	[29]
21.2			4,10	−43.40[f]	−179.50[f]	TGA	Solid	433–453	185±7[g]	18[g]	[29]
21.3		β-HNIW				DSC	Solid	483–533	165.0	13.1	[39]
21.4		ε-HNIW				DSC	Solid	483–533	176.0	15.1	[39]
22.1	1-Methylnitramino-2,4,6-trinitro-benzene	TETRYL	N	−23.10	−208.80	SMM	Liquid	403–438	156.9	14.5	[30]
23.1	2,5-Dinitro-2,5-diazahexane-3,4-dione	DMNO	2,5	−43.07	−166.78	QSPR	Condens.		178.8		[48]
24.1	1,1-Dinitro-1-azaethane	MDN	1	−38.80[b]	−89.70[b]	NMR	Condens.		168.4	13.9	[a]

[a] Results of the present paper.

[b] The value taken from Ref. [11].

[c] The change "solid phase-liquid".

[d] The value predicted in the sense of the present paper.

[e] The value calculated according to Ref. [8] by means of the isokinetic relationship for sec. nitramines thermolysis in the liquid state.

[f] The value taken from Ref. [12].

[g] The value corresponds to autocatalysed thermolysis.

SMM – Russian (Soviet) manometric method, see Refs. [14–16].

IR – infrared spectroscopy.

MS – mass spectroscopy.

DSC – differential scanning calorimetry.

TGA – thermogravimetric analysis.

QSPR – "quantitative structure–property relationship" calculations.

Table 2
Coefficients of the individual forms of Eq. (4)[a]

No.	Group of nitramines	Coefficients		
	Structure of data[b]	a	b	r
I	3.1, 4.1, 5.1, 6.1, 8.2, 24.1	−0.095	−47.478	0.9914
II	1.1, 4.1, 6.1, 6.2, 7.1, 8.1, 9.1, 9.2, 23.1	−0.374	−104.380	0.9899
III	2.1, 4.1, 7.2, 11.1, 12.1, 13.2	−0.869	−204.740	0.9978
IV	6.1, 8.1, 14.1, 15.1, 16.1	−1.883	−409.710	0.9928
V	10.1, 13.1, 13.2	−0.248	−83.157	0.9993

[a] With exception of a line for group V of nitramines the remaining lines have a common intersection characterized by δ_A=−202.4 ppm and δ_N=−28.7 ppm.

[b] Data are numbered as in Eq. (1).

2.3. Arrhenius parameters of thermolysis

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, inter alia, both theoretical and practical results obtained by Russian scientists: they have used the isothermal manometric method [14–16] 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 (1) and (2) in [9] and in the present paper. It is possible to apply also kinetic data from other manometric method (e.g. Robertson's method [19]) or some thermoanalytical methods, particularly the differential scanning calorimetry (DSC), which are directly compatible with the SMM results. The Arrhenius parameters used are presented in Table 1.

3. Discussion

Figs. 1 and 2 are graphic representation of Eqs. (1) and (2), respectively. In these figures the dependence A corresponds to N–N bond homolysis in the solid state and the dependence B to the same fission in the liquid state. The Arrhenius parameters have been predicted by means of these dependencies (calibration curves) for nitramines whose thermolysis data have not been experimentally obtained yet (see Table 1). Predicted E_a value for liquid phase thermolysis of DIGEN agrees well with the N–N bond energy value calculated for its molecule (see data 17.1 and 17.3 in Table 1). Other predicted E_a values signalize that the introduction of another methylenenitramine grouping into nitramine molecule leads to increasing of the N–N bond energies in corresponding substances. Also introduction of electronegative acetyloxy groups into 1 and 9 positions of OHMX molecule connects with the same effect in 2 and 8 positions of the resulting AcAn.

The said E_a values also signalize higher thermal reactivity of "outer" nitramino groups, i.e. of groups in 2 and 6 positions of ORDX, 2 and 8 positions of OHMX and of AcAn, 2 and 9 positions of TNADEC, 1 and 5 positions of HOMO (lower E_a values correspond to the above-mentioned positions – see Table 1). Good correlation of the δ_N value for 2, 6, 8, or 12 positions of HNIW in the sense of Fig. 1 and Fig. 2 confirms participation of the corresponding nitramino groups in the primary thermolysis of HNIW molecule. The above-mentioned thermal reactivity is connected with the longest N–N bond in the nitramine molecule [40]. Crystalline ε-HNIW has a bond of this kind in its 2-nitramino group (0.1436 nm)[42]. It is a well-known fact that the solvation of molecules in solution of the compounds or their transition from crystalline to liquid state can be accompanied by changes of some N–N bond lengths in their molecules (the bonds are compressed in the crystal [41]). That is why, e.g., the nitro groups at positions 2, 6, 8, and 12 of ε-HNIW (in acetone-d_6 solution) appear equivalent not only in the δ_N values but also in thermal reactivity of the groups.

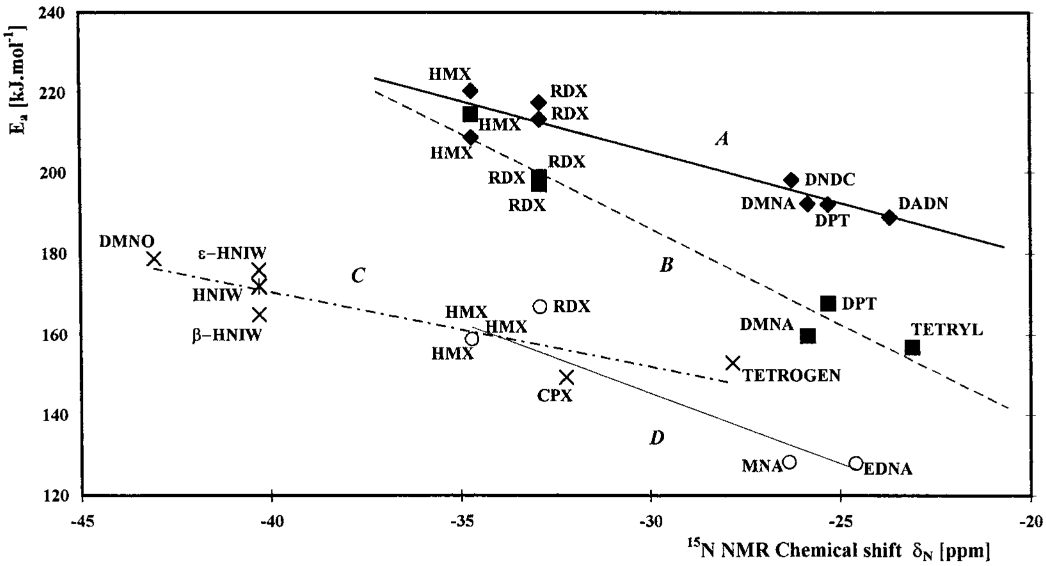

Fig. 1. Graphic representation of Eq. (1).

It must be also stated that a direct proportionality exists between the lengths of the longest N–N bonds in nitramines molecules and E_a values of their homolytic thermal decomposition [40]. In this sense CPX, TETROGEN, and HNIW make one group of nitramines [40]. Figs. 1 and 2 show that data of the same nitramines make dependences *C*. The lengths cause a trend of the dependence *C* in Fig. 2. Excessive distance between nitrogen atoms in the longest N–N bond (0.1410 nm in CPX [49] and 0.1436 nm in ε-HNIW [42], while for linear polynitramines it varies from 0.132 to 0.136 nm [4,41]), i.e. excessive suppression of the π-bonding extent of the amino nitrogen lone pair with nitro group, leads to low influence of the rest of

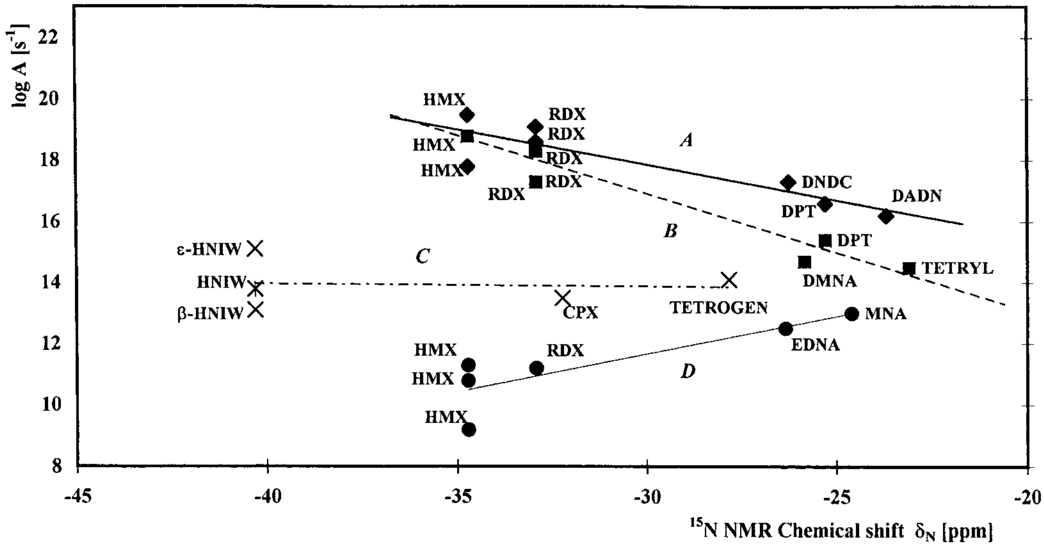

Fig. 2. Graphic representation of Eq. (2).

the molecule on the activation entropy of homolytic thermolysis of nitramines CPX, TETROGEN and HNIW type. Analogous influence, for example, exists in the case of O–NO_2 bond homolysis in the thermal decomposition of nitric esters [43]. If the N–N bond length exceeds 0.14 nm, Arrhenius parameters of the given nitramine thermolysis in the solid state correspond to those from thermolysis of this kind substances in the liquid state [40]. It may be also added that 1,3-diazacyclopentane skeleton of CPX molecule forms a part of the "caged" skeleton HNIW, hence it is logical that both these substances belong to the same dependences. This statement can be used as another explanation of the higher thermolytic reactivity of some of the nitramino groups at 2, 6, 8, or 12 positions in the HNIW molecule. Fig. 1 shows that the E_a value of DMNO is in good correlation with the dependence *C*; each from amine nitrogen atoms of the compound carries two strongly withdrawing substituents, i.e. nitro and carbonyl groups. This fact might be a reason for the creation of similar electronic configuration on these nitrogen atoms as it is in the case of aza atoms in nitramines with geometrical constraints in their molecules (predominantly in TETROGEN and HNIW). Analogous consideration can be valid for dinitramine MDN whose aza atom carries two nitro groups; therefore, the Arrhenius parameters of MDN were estimated by means dependences *C* in Figs. 1 and 2 (see Table 1).

Table 1 and Figs. 1 and 2 (here dependences *C*) show, that Arrhenius parameters of thermolysis of CPX, TETROGEN, HNIW, and MDN have significantly lower values than those of other nitramines studied. Interpretation of this fact can start from the considerations by Murray and Politzer [44] about the configuration of amine nitrogen atom in aza systems taking also the data on the bond angles at this atom in TETROGEN [28] and HNIW [42,45]. The amine (aza) nitrogen atom of the primarily thermolysed nitramino group could probably possess a rather pyramidal configuration in these substances. According to Korsoonskii et al. [46], planar nitramino groups are connected with higher E_a values of thermolysis of the corresponding compounds as compared with thermolysis of nitramines containing pyramidal nitramino groups.

Data 1.1 and 2.2 of the MNA and EDNA do not correspond to the homolytic fission of N–NO_2 bond. These two substances primarily thermolyse by a bimolecular mechanism [7] (due to an association of their molecules by hydrogen bonds [47]). However, also data 12.6, 14.4, 14.5, and 14.6 of RDX and HMX do not correspond to homolysis of this bond: activation entropies derived from them are negative (−42.02, −49.48, −79.71, and −40.47 J mol^{-1} K^{-1}, respectively) due to correspondence to thermolysis by cyclic or bimolecular mechanisms. Figs. 1 and 2 present relationships (dependences *D*) constructed on the basis of all these data.

Figs. 1 and 2 show that in case of HMX the effect of liquid phase on its thermolysis is absent [9] even if the thermolysis is realized within a temperature range above 553 (data 14.1 in Table 1). As it follows from some stability studies [31,32,35,36] and data [33,34], a demonstrable thermolysis of HMX takes places in the temperature region of formation of its δ polymorph (the liquid phase of HMX is unstable [13]). Recently Huiping and Mulan found [37] in their experiments with HMX thermolysis that nitrogen oxides begin to be released at 481 K without any thermal effect. From the point of view of this decomposition the δ polymorph of HMX represents a liquid phase of the nitramine. Therefore the opinion of Brill and Karpowicz [38], that the liquefaction of HMX at temperature above 553 K is connected with its dissolving in its thermolysis products, seems to be logical.

4. Conclusion

The earlier-described relationship [9] between the Arrhenius parameters of low-temperature thermolysis obtained at the conditions of the Russian manometric method (SMM) and the ^{15}N NMR chemical shifts of nitrogen atoms in nitro groups of their nitramino groups possesses a broader validity. The said relationship makes it possible to:

1. predict the Arrhenius parameters for the nitramines whose thermal decomposition has not been studied yet,
2. assess which nitramino group in the molecule is the first to undergo thermolysis,
3. interpretation of some aspects of the thermolysis of nitramines,
4. differentiate between the parameters of homolytic course of thermolysis of nitramines and those of

their bimolecular or another heterolytic thermal decomposition,

5. evaluate the compatibility of results of other methods of study of thermal decomposition of these nitro compounds with results of the Russian manometric method (SMM),
6. evaluate the effect of solid or liquid state on values of the Arrhenius parameters of thermolysis (in this context again the absence of effect of solid–liquid phase transition on the kinetics of initial stage of thermolysis of HMX has been confirmed).

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