Friction Sensitivity of Nitramines Part Ⅱ：Comparison with Thermal Reactivity

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Abstract：The friction sensitivity（ *FS* ）of five linear and eight cyclic nitramines has been determined. Arrhenius parameters of non-autocatalyzed thermal decomposition of these nitramines were used for comparison of the *FS* values with thermal reactivity. Generally，increasing values of activation energies of non-autocatalyzed decomposition of the studied nitramines are connected with decreasing *FS* values. A similar trend was found in the relation between *FS* and hypothetical initiation temperature for 5% conversion of the nitramines after 50 μs of their thermolysis，however，if in the given series of nitramines their initiation reactivity is predominantly determined by the energy content of their molecules and closer similarity of their molecular structures，then the above-mentioned trend may be opposite. The found relationships were used for prediction and verification of the activation energy of non-autocatalyzed thermal decomposition of 2，5-dinitro-2，5-diazahexane.

Key words：physical chemistry；friction，thermal decomposition，nitramines

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1 Introduction

In the first paper [1] of this series we mentioned that the friction sensitivity is the least intensively studied kind of initiation sensitivity of energetic materials（see also Ref. [2]）. We also pointed out [1] that the results of determination of *FS* strongly depend on human error. However，careful realization of these measurements by a single researcher provides outputs that are mutually in accordance and correlate with the outputs obtained from other stability and physico-chemical tests. In this present paper，the said facts are documented by the relationship between the *FS* values of nitramines and their thermal reactivity represented by the outputs obtained from the Russian manometric method（RMM，a kind of isothermal vacuum stability test [3-5]）or outputs from the methods giving compatible data with RMM.

2 Substances and Data Sources

Table 1 presents a set of nitramines，their characteristics of thermal decomposition from RMM and friction sensitivity data. The purity of these nitramines，which were prepared in our laboratory，was checked by means of HPLC（a purity over 99.8 % wt.）. The friction sensitivity of the studied nitramines was determined by means of the BAM friction test apparatus applied at the standard test conditions [6]. Sensitivity to friction was determined by spreading about 0.01 g of the dry explosive on the surface of the porcelain plate in the form of a thin layer. Different loads were used to change the normal force between the porcelain pistil and the plate. The sample initiation was observed through sound，smoke appearance，or by the characteristic smell of the decomposition products. Using the Probit analysis [7]，only the normal force at which 50 % of initiations occur is reported as the friction sensitivity in Table 1.

3 Results and Discussion

It is known that initiation reactivity of secondary nitramines is connected with $N-NO_2$ bond homolysis（see Refs[1,17] and the references therein）. It is logical that the weakest bond will be broken as the first [1,17,19]. The $N-NO_2$ bond energy might be characterized by the energy of the nitramines' thermal decomposition from RMM（unimolecular non-autocatalyzed reaction）；this energy should correlate with the strength of initiation impulse[1,17]，in this case with the friction sensitivity. Figure 1 represents a comparison of this kind.

The straight lines *A*，*B* and *C* in Fig.1 are in accordance with the expectation：increasing bond strength is connected with decreasing *FS*. However，in the initiation of nitramines by friction（shear slide with a fixed volume）also physical properties of their crystals（i.e. their effect upon the respective shear module）play a role. This probably could explain the existence of straight line *D* in Fig.1. The Arrhenius parameters for DMEDNA were obtained from a study of its thermal decomposition in solvent（dibutyl phthalate[10]）and，therefore，they are not compatible with the data of the other nitramines. With regard to the fact that from molecular-structural point of view the data of DMEDNA should correlate with the data of straight line A（ethylenedinitramine skeleton is present in the molecular skeletons of HNIW，DNDC and HOMO），so the calculation by means of this straight line gives the E_a value for DMEDNA is equal to 165.08 kJ·mol^{-1}. The position of data for EDNA in Fig. 1 indicates that this dinitramine exhibits a somewhat higher *FS* value as compared with those of structurally cognate nitramines from the studied set of compounds；an older paper [20] states that packing in its crystal appears to be based predominantly on dipole-dipole interaction，while a newer study [21] claims that there exist weak intermolecular hydrogen bonds in the molecular crystal of EDNA. These nonbonding interactions will distinctly affect the shear module. Despite of this，data of EDNA should correlate logically in the sense of straight line *B*. Similarly，e.g.，the globular molecule of HNIW should be more strongly fixed in the crystal lattice as compared with the structurally

similar but less polar TEX molecule (also the heat of fusion of TEX is lower than that of HNIW [1]); a dash-and-dot line E indicate possible relations of TEX data.

When studying the electric spark sensitivity of explosives, Skinner et al. [22] used the idea that a substance is initiated by its mere 5% conversion after 50 μs of thermolysis; this idea should correspond with the temperature T_3, at which the rate constant k of first-order thermolysis is 103 s^{-1}; in essence, this is a hypothetical initiation temperature (characteristic feature of thermal reactivity) of the nitramines studied. Its calculation starts from the Arrhenius equation [22].

The relationship between FS and the T_3 values is not unambiguous; it is presented in Fig. 2. In this diagram, each straight line corresponds to a close molecular-structural kinship, which has to be projected into similarity of character and intensity of intermolecular force effects in the respective molecular crystals of the nitramines studied. This affects the thermal reactivity of particular nitramine and determines its inclusion into the given group. In the dependences having positive slopes in Fig. 2, increasing hypothetical initiation

temperature is connected with decreasing FS; seemingly, these dependences are dominated by the intermolecular interaction factors in the molecular crystals. On the contrary, the series DMEDNA-DNDC-RDX-HMX might be dominated by the effect of reactivity of nitramine groups as a consequence of increasing energy content of the respective molecules in the series mentioned (this is a general finding about reactivity of energetic materials [2]): the explosion temperatures calculated by the method of Pepekin et al. [23] increase in this series as follows (MJ·kg^{-1}): 3732, 3968, 5481 and 5530 (taken from [24,25]). The nitramines of this series also have close values of their heats of fusion [1]. In the case of the other groups of nitramines in Fig. 2 it is impossible to notice any similar systematic trend or closeness of the values of heat of fusion. The problem of relationship between FS and detonation characteristics is dealt with in the subsequent part of this study[25]. It is also documented on the above-mentioned series of nitramines that the Ea value predicted for DMEDNA in the sense of Fig. 1 should be close to reality.

Table 1 A survey of the studied nitramines, their friction sensitivities and Arrhenius parameters of their thermal non-autocatalyzed decomposition

Data No.	Chemical name	Code design.	Friction sensitivity /N	Arrhenius parameters					
				Method of evaluation	Temp. region/K	State of decompn.	E_a /kJ·mol^{-1}	log$A$ /s^{-1}	Ref.
1	2-Nitro-2-azapropane	DMNA	82.4	IR	298	solid	192.5	14.2	8
2	1,4-Dinitro-1,4-diazabutane	EDNA	47.4	manometric	393−418	solid	186.2	18.0	8
3	2,4-Dinitro-2,4-diazapentane	OCPX	74.9	manometric	453−503	liquid	169.6	13.5	10
4	2,5-Dinitro-2,5-diazahexane	DMEDNA	57.9	manometric	483−513	solutiona	173.8	14.2	10
4.1		DMEDNA		extrapol.		liquid	165.0−168.2		b
5	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	147.7	manometric	453−503	liquid	178.4	14.9	10
6	1,3-Dinitroimidazolidine	CPX	57.7	manometric	383−403	solid	197.8	18.7	11
7	1,4-Dinitropiperazine	DNDC	122.3	manometric	489−507	solid	198.4	17.3	12
8	1,3,5-Trinitro-1,3,5-triazinane	RDX	148.5	manometric	423−470	solid	217.6	19.1	13
9	1,3,5-Trinitro-1,3,5-triazepane	HOMO	119.9	15N NMR		(solid)	207.1	18.6	9
10	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	HMX	154.4	manometric	544−587	solid	220.5	19.5	14
11	cis-1,3,4,6-Tetranitrooctahydroimidazo[4,5-d]imidazole	BCHMX	66.1	manometric	453−473	solid	210.2	18.0	15
12	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	161.3	manometric	483−498	solid	196.8	15.4	16
13	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	HNIW	69.0	DSC	483−533	solid	176.0	15.1	17

Note: a) solution in dibutyl phthalate [10]; b) extrapolation in this paper (see in Figs. 1 and 2)
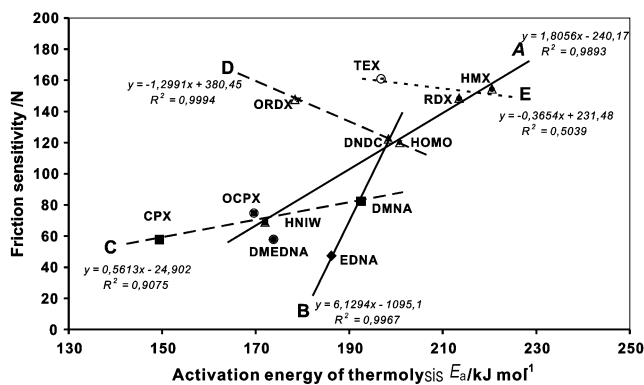

Fig. 1 Comparison of friction sensitivity of the studied nitramines with activation energies of their non-autocatalyzed thermal decomposition (This Figure was reconstructed due to error in the DMNA data)
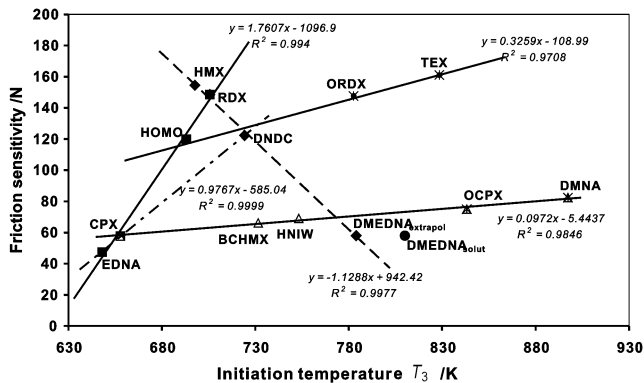

Fig. 2 Comparison of friction sensitivity of the studied nitramines with calculated temperature of the 5% conversion of the studied nitramines after 50 μs of thermolysis

4   Conclusion

The relationship between friction sensitivity and thermal reactivity of nitramines is not unambiguous. It is possible to observe in it a general trend of decrease in *FS* connected with increase in the N—NO$_2$ bond strength. This strength can be represented by the activation energies of monomolecular non-autocatalyzed thermal decomposition of the substances mentioned. Similarly, most of the nitramines studied exhibit a decrease in *FS* with increasing hypothetical initiation temperature；this temperature means the temperature for a 5% conversion of the nitramine after 50 μs of its thermolysis. However, this trend is opposite in the series DMEDNA-DNDC-RDX-HMX, which might be connected with the dominating effect of energy content of their molecules and similarity of the effect of their intermolecular interactions upon the initiation reactivity of these nitramines. The relationships found made it possible to predict and, subsequently, verify the value of activation energy of non-autocatalyzed thermal decomposition of 2,5-dinitro-2,5-diazahexane（DMEDNA）.

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