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Friction Sensitivity of Nitramines. Part III: Comparison with Detonation Characteristics

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Abstract: The friction sensitivities (FS) of five linear and eight cyclic nitramines have been determined. These FS values were compared with the respective detonation velocities, D , and with the dimensionless ratio created by relating the heat of explosion, Q_{real} , to the activation energy, E_a , of non-autocatalyzed thermal decomposition of the explosives concerned. For the nitramines studied, these comparisons show a general trend of FS decreasing with increasing energy content.

Key words: friction; detonation; heat of explosion; nitramines

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1 Introduction

In the first papers^[1,2] of this series we mentioned reasons why we are interested in a more detailed study of friction sensitivity (FS). We also stated that careful measurements by a single researcher can provide outputs that are mutually consistent and correlate well with the output of other stability and physico-chemical tests. In the current paper, the data are documented by the relationship of FS of the nitramines with their detonation parameters at the maximum theoretical crystal density; these parameters include the detonation velocities, D (calculated by the method of Kamlet & Jacobs^[3,4]) and heats of explosion, Q_{real} (according to the semi-empirical method of Pepekín et al.^[5]). The heats of explosion are involved in the relationship together with the activation energies, E_a , of thermal decomposition obtained by means of the Russian manometrical method (RMM), a kind of isothermal vacuum stability test^[6-12], and methods that are compatible with it^[14,15] and commonly used in studies of thermal decomposition of explosives.

2 Substances and Data Sources

Table 1 presents a set of nitramines with their detonation characteristics^[3-5], thermal decomposition^[6-15] and friction sensitivity data. The purity of the nitramines, which were prepared in our laboratory, was checked by means of HPLC (a purity greater than 99 % by weight-preparation of several from the studied nitramines, together with method of HPLC analysis, is a part of Ref. 16). The determination of FS by means of the BAM friction test apparatus under standard test conditions^[17] using the probit analysis^[18] is described in Refs [1,2]. All the above-mentioned data are shown in Table 1. The heats of explosion, Q_{real} , calculated according to Pepekín et al.^[5], should correspond to the values determined in a detonation calorimeter, i. e. they involve the effect of the charge density. Since the Kamlet & Jacobs method^[4] was derived for charge densities in the range of $1.3 - 1.9 \text{ g} \cdot \text{cm}^{-3}$,

for HNIW we used the value D obtained by extrapolation of experimental data on the values of the theoretical maximum crystal density of HNIW^[20].

3 Results and Discussion

It is interesting to compare the FS values of the nitramines studied with their calculated detonation velocities (see Fig. 1). Generally, the dependencies indicated show a decrease in FS with increasing detonation velocity of the nitramines studied. If we take the D values also as an indicator of performance, then the above-mentioned trend does not correspond with the finding that high performance is usually accompanied by an increased sensitivity (an insensitive explosive will not exhibit good performance)^[21]. The difference between the groups in Fig. 1 should be due first, to the difference in character and intensity of intermolecular interactions and, secondly, to the difference in initiation reactivity of the nitramines constituting the groups. This reactivity and close molecular-structural similarity are dominant in the group including HNIW; molecular skeletons of these substances contain the ethylenedinitramine grouping. EDNA itself does not correlate well, due to the presence of the "acidic hydrogen atoms" in its molecule (it has a higher sensitivity in this case, similar, for example, to the case of the thermal reactivity of primary nitramines in general^[22]).

The dissociation energy of the weakest bond in the molecule of energetic material is thought to play an important role in initiation events. In the case of impact sensitivity, however, some authors accept the idea that the correlation between bond strength and this sensitivity is not generally limited to certain classes of molecules^[23,24]. Fried et al.^[24] state that the energy content of the material must also play a role in determining the impact sensitivity. The same should hold true for friction sensitivity, too. If we take the heat of explosion, Q_{real} , as a representative of the energy content of the nitramine, and the activation energy, E_a , of its non-autocatalyzed thermal decomposition as a typical feature of the strength of its weakest bond^[22], then we can obtain—in a way similar to that used by Fried et al.^[24]—the dimensionless ratio $Q_{\text{real}} E_a^{-1}$. The relationship between FS and this ratio is presented in Fig. 2, which appears similar to Fig. 1.

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Table 1 A table of the nitramines studied, their calculated detonation velocities, $D^{[3]}$, heats of explosion, $Q_{\text{real}}^{[3]}$, experimentally determined friction sensitivities (50% probability of initiation), and the activation energies, E_a , of thermal non-autocatalyzed decomposition of nitramines^[6-15]

data No.	chemical name	code design	$D^{[3]}$ /m · s ⁻¹	$Q_{\text{real}}^{[3]}$ /MJ · kg ⁻¹	friction sensitivity/N	conditions of thermal decomposition				
						method of evaluation	temp. region/K	state of decomp	E_a /kJ · mol ⁻¹ ref.	
1	2-nitro-2-azapropane	DMNA	6.29	3817	82.4	IR	298	solid	192.5	6
2	1,4-dinitro-1,4-diazabutane	EDNA	8.42	4874	47.4	manometric	393-418	solid	186.20	6
3	2,4-dinitro-2,4-diazapentane	OCPX	7.28	4367	74.9	manometric	453-503	liquid	169.6	13
4	2,5-dinitro-2,5-diazahexane	DMEDNA	6.42	3732	57.9	manometric	483-513	solution ^{a)}	173.8	13
4.1		DMEDNA				extrapol.		liquid	168.2	2
5	2,4,6-trinitro-2,4,6-triazaheptane	ORDX	8.04	4870	147.7	manometric	453-503	liquid	178.4	13
6	1,3-dinitroimidazolidine	CPX	7.76	4708	57.7	manometric	383-403	solid	197.8	7
7	1,4-dinitropiperazine	DNDC	6.75	3968	122.3	manometric	489-507	solid	198.4	8
8	1,3,5-trinitro-1,3,5-triazinane	RDX	8.89	5481	148.5	manometric	423-470	solid	217.6	9
9	1,3,5-trinitro-1,3,5-triazepane	HOMO	8.23	5005	119.9	¹⁵ N NMR ^{b)}		(solid)	207.1	14
10	1,3,5,7-tetranitro-1,3,5,7-tetrazocane	β -HMX	9.13	5530	154.4	manometric	544-587	solid	220.5	10
11	cis-1, 3, 4, 6-tetranitrooctahydroimidazo-[4,5-d]imidazole	BCHMX	9.05 ^{c)}	5758 ^{c)}	66.1	manometric	453-473	solid	210.2	11
12	4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-isowurtzitane	TEX	8.47	4538	161.3	manometric	483-498	solid	196.8	12
13	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	ε -HNIW	9.80 ^{d)}	5956	69.0	DSC	483-533	solid	176.0	15

Note: a) solution in dibutyl phthalate; b) extrapolation method on the basis of ¹⁵N NMR chemical shifts^[14]; c) the value taken from^[19] (calculated by the Kamlet & Jacobs method^[4]); d) the extrapolated value from experimental data, taken from^[20].

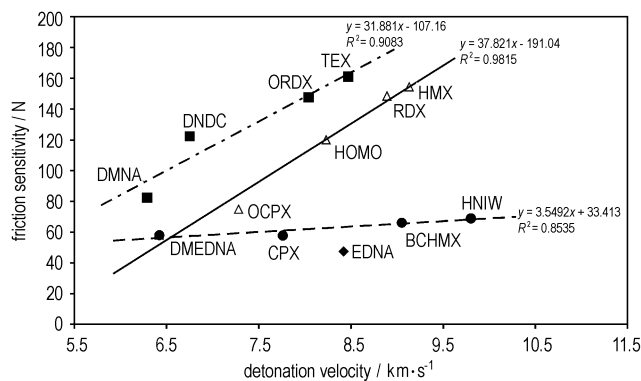


Fig. 1 Comparison of friction sensitivity of the nitramines studied with their detonation velocities calculated for maximal theoretical crystal density

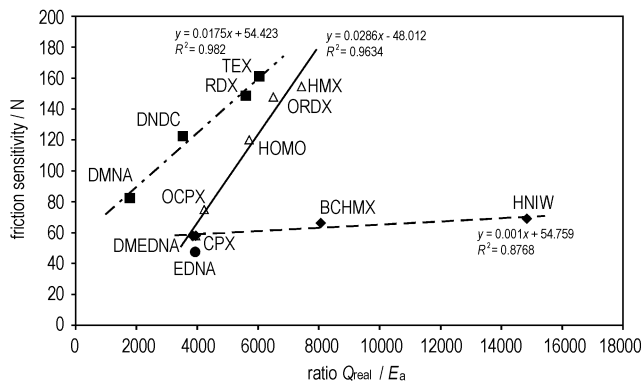


Fig. 2 Comparison of friction sensitivity of the nitramines studied with ratio of their heats of explosion and thermal decomposition activation energies

In the case of DMEDNA, Fig. 2 presents the E_a value predicted and verified in Ref. [2] (in Table 1 data 4.1). The same holds true (as in Fig. 1) for the trend of the indicated relationships in Fig. 2. However, the classification of the nitramines studied into individual groups is different. While the group containing HNIW is identical with the corresponding group in Fig. 1, the remaining two groups differ in the rigidity of molecular skeleton; the group DMNA-DNDC-RDX-TEX should represent more rigid molecules (the DMNA molecule has the characteristic of a rigid molecule^[25]) as compared with the group containing HMX, which includes three linear nitramines (a certain flexibility of the HMX molecule skeleton can be explained by the existence of its four polymorphs). The presence of “acidic hydrogen atoms” in the EDNA molecule again places this nitramine outside the groups in Fig. 2.

4 Conclusion

The relationship between friction sensitivity (FS) and the detonation parameters of nitramines is not unequivocal. There is a general trend of decreasing FS with increasing energy content of the nitramines studied. The character of intermolecular interactions and the initiation reactivity of structurally cognate nitramines may represent the reason for the division of the nitramines into groups on the basis of comparing their friction sensitivities with their detonation velocities. A better indicator of energy content of nitramines was found in the dimensionless ratio, $Q_{\text{real}} E_a^{-1}$, i. e. the ratio of heats of explosion to the activation energies of their non-autocatalyzed thermal decomposition. According to the relationship between FS and this ratio, the nitramines studied divided into groups on the basis of similarity and rigidity of their molecular skeletons. The presence of “acidic hydrogen atoms” in the molecule of 1,4-dinitro-1,4-diazabutane (ethylene dinitramine) somewhat

increases its FS as compared with structurally cognate secondary nitramines.

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