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Electric Spark Sensitivity of Polynitro Compounds: Part Ⅲ. A Correlation with Detonation Velocities of some Nitramines

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Abstract: The electric spark sensitivity of 12 nitramines was determined as the spark energy, E_{ES}, required for 50% initiation probability. A relationship between the E_{ES} and the square of detonation velocity of these substances was specified. The relationship was used to predict the E_{ES} values of nitramines not yet synthesised, particularly, the theoretically important compounds in the field of nitramine chemistry, such as 1-nitro-1-azaethylene, 1,3-dinitro-1,3-diazacyclobutane and 1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazacyclodecane.

Key words: electric spark sensitivity; detonation; nitramine

1 Introduction

In our previous report[1] we discussed the relationship between the square of detonation velocity, D^2, and the spark energy, E_{ES}, required for 50 per cent initiation probability of some polynitro arenes; the general equation reads as follows[1,2]:

$$D^2 = A \cdot E_{ES} + B \qquad (1)$$

The relationship is presented in this paper for a group of nitramines. Attention is also paid to several substances not yet synthesised, which are very important theoretically in the field of nitramine chemistry.

2 Experimental

The measurements were carried out on the apparatus by the procedure described in ref. [3]. A survey of the nitramines studied and the results obtained are given in Table 1. The nitramines DIGEN, TETROGEN and DECAGEN have not been synthesised yet. The values of detonation velocity, D, were calculated according to Kamlet and Jacobs[4] for the theoretical maximum density (TMD, i. e. for single crystal) of the substances. In some cases the calculation was carried out by the method of Rothstein and Petersen[5], too. The D values are also presented in Table 1.

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3 Result and discussion

A common characteristic of the nitramines studied is that the homolysis of N-NO_2 occurs as the primary process in their thermolysis (see e. g. refs. [6,9]). However, in the sense of Eqn. (1) this group of substances falls into two sub-groups presented graphically in Figs. 1 and 2.

Figure 1 documents the form of Eqn. (1) for the substance having —CH_2—N(NO_2)— structure unit in their molecules, including nitramines derived theoretically from DIGEN, which has not been described yet. Therefore, this form of Eqn. (1) was used to predict the E_{ES} values of DIGEN, its dimer TETROGEN and its pentamer DECAGEN. The predicted values correspond to expectation as presented in Table 1. Eqn. (1) is also obeyed by the data for DNDC and TNAD (perhaps due to the symmetrical force influence on their rigid molecules).

Figure 2 presents the form of Eqn. (1) for the nitramines whose molecules cannot be considered as multiples of DIGEN molecule. The insufficient data and the diversity of molecular structure of these nitramines indicate a possibility of a random dependence in this case.

The discussion in our previous report[2] showed that Eqn. (1) is one of the modifications of Evans-Polanyi-Semenov equation. This equation was originally derived by Semenov to fit

radical substitution reactions[10,11], and for energetic materials it was published [12~14] in the following form at first:

$$E_a = C \pm \alpha Q \quad (2)$$

Table 1　E_{ES} and D of 15 explosives

No	substance: chemical name	code	E_{ES}/J	D/km · s^{-1}
1	2,4-dinitro-2,4-diazapentane	OCPX	13.45	7.28
2	2,4,6-trinitro-2,4,6-triazaheptane	ORDX	8.08	8.07
3	2,5-dinitro-2,5-diazahexane	DMEDNA	8.24	6.41[1)]
4	2,4,6,8-tetranitro-2,4,6,8-tetraazanonane	OHMX	5.50	8.68[1)]
5	2,4,6,8-tetranitro-2,4,6,8-tetraazanonan-1,9-diol diacetate	AcAn	13.93	7.18[1)]
6	3,5-dinitro-3,5-diazaheptane	DNDAH	12.49	5.68
7	2,5-dinitro-2,5-diazahexane-3,4-dione	DMNO	5.49	7.20[1)]
8	1-nitro-1-azaethylene	DIGEN	8.38[2)]	8.12[1)]
9	1,3-dinitro-1,3-diazacyclobutane	TETROGEN	6.25[2)]	8.46
10	1,3,5-trinitro-1,3,5-triazacyclohexane	RDX	2.49	8.89
11	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane	HMX	2.89	9.13
12	1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazacyclodecane	DECAGEN	2.96[2)]	8.96
13	1,4-dinitro-1,4-diazacyclohexane	DNDC	15.97	6.75[1)]
14	1,4,5,8-tetranitro-1,4,5,8-tetraazadecahydronaphthalene	TNAD	5.43	8.52
15	1-(methylnitramino)-2,4,6-trinitrobenzene	TETRYL	5.49	7.77

Notice: 1) The value calculated according to the ref. [5]; 2) The value predicted by means of the form of Eqn. (1) in Fig. 1.

The equation presents a relationship between activation energy, E_a, of thermal decomposition and heat of explosion, Q, of these materials. In the sense of Eqn. (2), however, the studied nitramines unambiguously fall into two groups[15]: rigid molecules of cyclic nitramines and flexible molecules of linear nitramines. This represents the fundamental difference between Eqns. (1) and (2). The said difference might resulte from the way of thermal energy transfer, i.e. the relationship between E_{ES} and E_a in the reaction centre of the molecule.

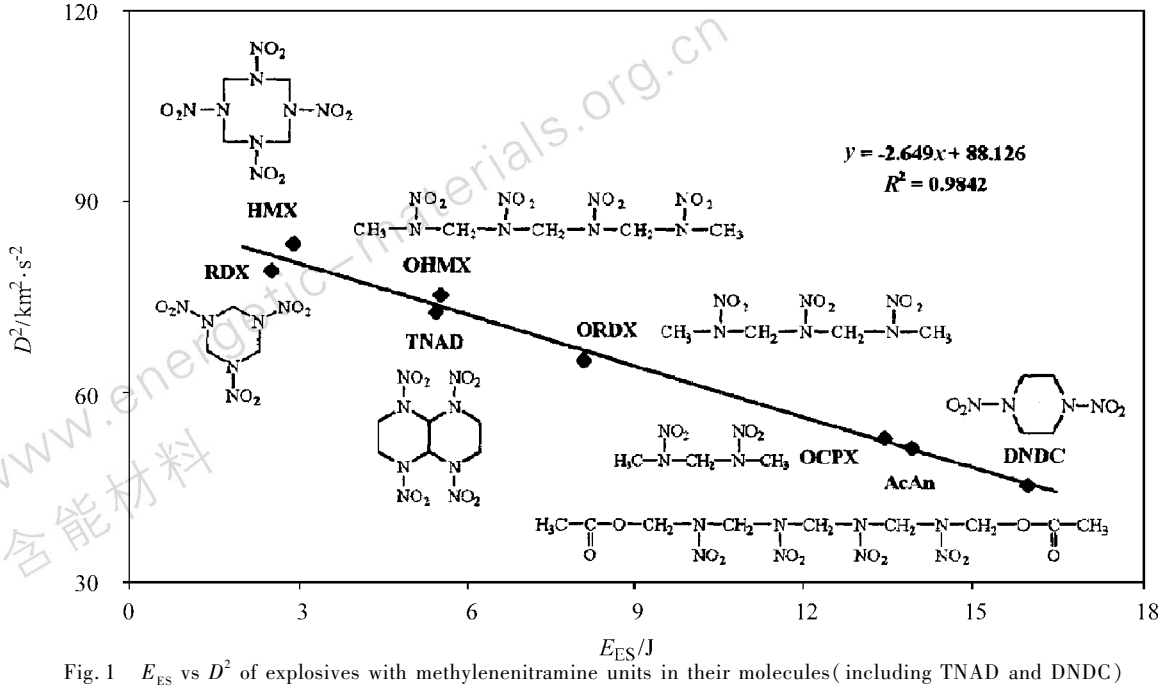

Fig. 1　E_{ES} vs D^2 of explosives with methylenenitramine units in their molecules (including TNAD and DNDC)

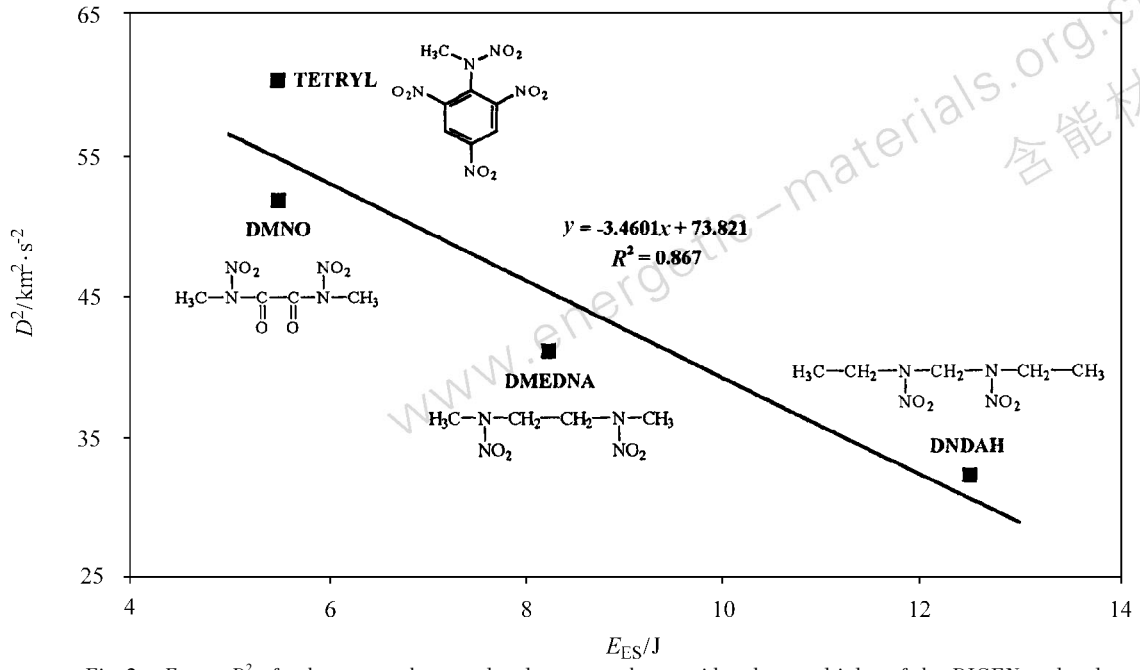

Fig. 2 E_{ES} vs D^2 of substances whose molecules cannot be considered as multiples of the DIGEN molecule

4 Conclusion

The relationship between the square of detonation velocity of nitramines and the spark energy required for 50% probability of their initiation has the same meaning as in the case of ploynitro arenes[1]. The said relationship can be used to predict the electric spark sensitivity of nitramines.

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硝胺的静电火花感度与爆速的关系

摘要：通过测定 12 种硝胺 50% 发火概率下的静电火花能 E_{ES}，建立了 E_{ES} 与爆速平方值(D^2)的线性关系，以此可预估尚未合成的硝胺化合物，尤其是那些对硝胺化学有重要意义的化合物，如 1-硝基-1-氮杂乙烯、1,3-二硝基-1,3-二氮杂环丁烷、1,3,5,7,9-五硝基-1,3,5,7,9-五氮杂环癸烷等的 E_{ES}。

关键词：静电火花感度；爆速；硝胺

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