Theoretical prediction of electric spark sensitivity of nitroaromatic energetic compounds based on molecular structure

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Abstract

A new simple correlation is introduced for predicting electric spark sensitivity of nitroaromatic compounds. This approach is based on the number of carbons and hydrogens as well as the ratio of hydrogens to oxygens and the presence of certain groups, i.e. alkyl or alkoxy groups, attached to an aromatic ring. The model is optimized using a set of 17 polynitroaromatic explosives as training set and then it is applied to 14 explosives from a variety of chemical families as test set in order to assess the predictive capability of new method. Predicted results are reasonably close to the measured values for both training and test sets.
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1. Introduction

Organic explosives are substances containing metastable molecules capable of undergoing very rapid and highly exothermic reactions. A major goal within the energetic materials community has been to predict various aspects of a notional energetic compound including sensitivity, performance, physical and thermodynamics properties. The study of explosives by various empirical methods has provided a considerable insight into the understanding of factors affecting their behavior [1,2]. However, an effort has been made significantly world-wide in order to understand better the relationship between the molecular structures of energetic compounds and their sensitivities.

Sensitivity of an energetic compound is very complex which is a consequence of the kinetics and thermodynamics of thermal decomposition of the explosive. Response to specific stimulus such as impact and shock depends on the ease with which a detectable reaction of any kind can be initiated in an explosive. Then, establishment of the tendency of small reaction can grow to destructive proportions and the ease with which a high-order detonation can be established in an explosive.

The negative effects of munitions on the environment and the cost associated with both facility clean-up as well as disposal of synthesis waste can be introduced into the factors that are considered before investing in synthesis and testing. Therefore, the development of theoretical and empirical methods to predict properties related to performance and sensitivity allows such screening upon the conception of a new energetic material. The purpose of this work is to determine a new correlation between electric spark sensitivity and molecular structure of nitroaromatic energetic compounds. The paper shows success in finding a reasonable good correlation between electric spark sensitivity and elemental composition as well as the existence of alkyl or alkoxy groups attached to an aromatic ring. In this study, two training and test sets are used to establish a good correlation and its application to complex molecular structures of nitroaromatic explosives where their experimental data have been reported. It will be shown that predicted results are reasonably close to the measured values for both training and test sets.

2. Theory

Many kinds of sensitivity have been identified in terms of stimuli causing detonation. Some of stimuli include impact, shock, electric spark, heat and friction. Three of the most commonly used measures are impact, shock and electric spark or

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electrostatic sensitivity [1,3]. However, electric spark sensitivity will be discussed in the following sections.

2.1. Electric spark sensitivity and its measurement

The electric spark or electrostatic sensitivity (E_{ES}) of an energetic compound can be defined as the degree of sensitivity to the electrostatic discharge, which can be determined by subjecting the explosive to a high-voltage discharge from a capacitor. It is an important quantity which can be determined by the electrostatic discharge energy required for 50% probability of initiation [3]. This energy is calculated from the known capacitance C (in F) of the circuit and voltage U (in V) at the condenser by means of the well-known equation $E_{ES} = 0.5CU^2$. Since electric spark sensitivity depends on the configuration of the electrodes and structure of circuit, one can expect that different results must be obtained by different test specification of electrode energy used by different authors [4]. For instance, the surface area of the tip of electrode will affect the energy density of the spark. The structure of the electrical circuit will affect the shape and duration of the electrical pulse, which in turn affect the rate and duration of the delivery of energy to the sample. Also, it should be mentioned that confinement of the sample (or lack thereof) can have a dramatic effect on the measured electrostatic sensitivity due to the tendency of some samples to form dust clouds when unconfined. Zeman and co-workers [4,5] used an instrument marked as RDAD, which was constructed in the R&D Department of Zbrojovka Indet, Inc., Vsetín, Czech Republic [4], to measure electric spark sensitivity for a large set of polynitro compounds of the secondary explosive class type. In RDAD instrument, the capacitance of the capacitor is chosen so as to allow measurements in the voltage from 8 to 14 kV. If the initiation is successful, the next measurement is carried out by 0.2 kV. In contrast, if it is unsuccessful, the voltage is increased by the same value (up and down method). Fortunately, they have found [4] a linear relationship between their experimental data of RDAD instrument with some of those obtained by the other methods of determination of the electric spark sensitivity in some recognized laboratories. However, the RDAD instrument is not suitable for determination of the sensitivity of primers and pyrotechnics [5]. Later, Zeman and co-workers [5,6] also developed a new instrument, with a financial support from Czech Ministry of Industry and Commerce [5], marked as ESZ KTTV, which is suitable for both primary and secondary explosives. Details of the apparatus and procedure for two instruments of RDAD and ESZ KTTV were described elsewhere [4–6].

2.2. Detonation performance and electrostatic sensitivity

There is no unique idea of initiation mechanism of energetic materials by electric spark [7]. Zeman and co-workers [8] have indicated that the primary fragmentation reactions in this initiation can be supposed identical with the primary splitting processes of low-temperature thermolysis and detonation transformation of molecules of these materials. However, the mechanism of energy transfer from electric spark to the reaction center of molecule is not fully understood yet [7,8]. Some

authors were inclined to the idea of conversion of the electric spark energy into a thermal effect, i.e. to a thermolytic principle of the electric spark initiation [9,10]. However, the initiation can be considered as a multidisciplinary problem [7]. From this point, mechanism of the spark energy transfer can be related to molecular structure, thermal reactivity, sensitivity to mechanic stimuli and parameters of their detonation [7–12]. Zeman et al. [7,8,12,13] indicated that there are some correlations for special groups of energetic compounds among detonation velocity, the Piloyan activation energy of decomposition from the differential thermal analysis (DTA) and electric spark sensitivity. They found that there was a linear relationship between the electric spark energy values and the squares of detonation velocities of some special groups of explosives. Wang and co-workers [14,15] also used quantum chemistry methods to optimize molecular geometries and electronic structures of some classes of explosives. They also indicated that there were quantitative relationships between the experimental electrostatic spark sensitivity values and the theoretical values of detonation velocity and pressure for some special groups of energetic compounds.

3. Results and discussion

3.1. Deriving new correlation

The study of electric spark sensitivity of nitroaromatic compound has shown that it is possible to predict electric spark sensitivity from structural parameters. It was found that the same as impact [16–21] and shock sensitivity [22,23] correlations, elemental composition can be used to determine electric spark sensitivity. The results have indicated that the following general equation with four variables is suitable for various types of nitroaromatic compounds:

$$E_{ES} = z_1 + z_2 n_C + z_3 n_O + z_4 R_{n_H/n_O} + z_5 C_{R,OR} \qquad (1)$$

where z_1, z_2, z_3, z_4 and z_5 are adjustable parameters which can be obtained by the best fit to experimental electric spark sensitivities data via multiple linear regression method [24], n_C, n_O and n_H are the number of carbon, oxygen and hydrogen in molecular formula of explosive, respectively, R_{n_H/n_O} is the ratio of n_H to n_O, and $C_{R,OR}$ is the presence of certain groups such as alkyl (–R) or alkoxy (–OR) groups attached to an aromatic ring. It was found that the number of carbons and oxygens as well as the ratio of the number of hydrogens to oxygens in molecular formula of explosive are suitable descriptors for elemental composition in finding a good correlation. The contribution of the number of nitrogens is small which can be neglected. Among the various structural parameters, the existence of alkyl or alkoxy functional groups can be found appreciable effect in predicting electric spark sensitivity. Experimental data of electric spark sensitivity for 17 explosives, which are given in Table 1 , were used to find adjustable parameters. Multiple linear regression method [24] was used for this purpose. Since the equation set is overdetermined [24], the left-division method for solving linear equations uses the least squares method. It should be mentioned

Table 1
Comparison of predicted electric spark sensitivity (J) of nitroaromatic compounds of training set with the experimental data [12]

Name	Molecular structure	Molecular formula	$C_{R,OR}$	E_{ES} (exp)	E_{ES} (cal)	Dev
2-Methyl-1,3,5-trinitrobenzene (TNT)		$C_7H_5N_3O_6$	1	6.85	6.31	0.54
2,4,6-Trinitrophenol (PA)		$C_6H_3N_3O_7$	0	8.98	9.20	−0.22
2-Methoxy-1,3,5-trinitrobenzene (TNA)		$C_7H_5N_3O_7$	−2	28.59	21.36	7.23
1,5-Dinitronaphthalene (1,5-DNN)		$C_{10}H_6N_2O_4$	0	11.2	13.91	−2.71
1,4,5-Trinitronaphthalene (TNN)		$C_{10}H_5N_3O_6$	0	10.97	9.25	1.72
1,4,5,8-Tetranitronaphthalene (TENN)		$C_{10}H_4N_4O_8$	0	8.26	7.64	0.62
1,3,5-Trinitro-2-(2,4,6-trinitrobenzyl)benzene (DPM)		$C_{13}H_6N_6O_{12}$	1	4.1	3.20	0.90
2,6-Dimethoxy-3,5-dinitropyridine (DMDNPy)		$C_7H_7N_3O_6$	-2	20.57	24.78	−4.21
1,3,5-Trinitrobenzene (TNB)		$C_6H_3N_3O_6$	0	6.31	9.13	−2.82
2,4,6-Trinitrobenzene-1,3,5-triamine (TATB)		$C_6H_6N_6O_6$	0	17.75	13.71	4.04
N,N-Bis(2,4,6-trinitrophenyl)amine (DPA)		$C_{12}H_6N_7O_{12}$	0	5.02	9.07	−4.05
2,4,6-Trinitroaniline (PAM)		$C_6H_4N_3O_6$	0	6.85	10.65	−3.80
1,1′-(1,2-Ethenediyl)bis[2,4,6-trinitrobenzene] (HNS)		$C_{14}H_6N_6O_{12}$	1	5.32	2.47	2.85
2,2′,4,4′,6,6′-Hexanitro-1,1′-biphenyl (HNB)		$C_{12}H_4N_6O_{12}$	0	5.03	7.54	−2.51

Table 1 (*Continued*)

Name	Molecular structure	Molecular formula	$C_{R,OR}$	E_{ES} (exp)	E_{ES} (cal)	Dev
2,4-Dimethyl-1,3,5-trinitrobenzene (TNX)		$C_8H_7N_3O_6$	1	11.1	8.63	2.47
Bis(2,4,6-trinitrophenyl)diazene (HNAB)		$C_{12}H_4N_8O_{12}$	0	8.2	7.54	0.66
3-Methyl-2,4,6-trinitrophenol (TNCr)		$C_7H_5N_3O_7$	1	5.21	5.94	-0.73

that an overdetermined system is a set of equations that has more independent equations than unknowns. However, in this situation, the matrix inverse method and Cramer's method will not work [24]. Thus, the left-division method can be used. Furthermore, the left-division method is based on Gauss elimination so that it uses fewer internal multiplications and divisions than the matrix method inversion. Thus, optimized correlation has the following form:

$$E_{ES} (J) = 4.60 - 0.733n_C + 0.724n_O + 9.16R_{n_H/n_O} - 5.14C_{R,OR} \qquad (2)$$

The value of $C_{R,OR}$ can be determined as follows:

(a) $C_{R,OR} = 1.0$ for alkyl group attached to nitroaromatic ring, e.g. 2-methyl-1,3,5-trinitrobenzene.
(b) $C_{R,OR} = -2.0$ for alkoxy group attached to nitroaromatic ring, e.g. 2-methoxy-1,3,5-trinitrobenzene.

Since the existence of the variety of different factors that influence the electric spark sensitivity, R-squared value or the coefficient of determination of this correlation is 0.77 [24]. As seen in Table 1, predicted electric spark sensitivity of 17 different nitroaromatic compounds were also calculated and compared with the experimental values. To test the validity of the correlation, electric spark sensitivity for 14 nitroaromatic energetic compounds as test set are also calculated and compared with measured values, which are given in Table 2. Differences of the predictions from the experiments for various methods are given in Tables 1 and 2. As indicated in Tables 1 and 2, the estimated electric spark sensitivity of different nitroaromatic compounds by new correlation are within ± 4.0 J of 26 measured values and more than ± 4.0 J for remainder 5 experimental data. Moreover, Eq. (2) can be used easily for nitroaromatic energetic compounds which have complex molecular structure, e.g. 5,7-dinitro-1-(2,4,6-trinitrophenyl)-1H-1,2,3-benzotriazole.

A visual comparison of the predictions with experiment for training and test sets is also given in Figs. 1 and 2. As evident in Figs. 1 and 2, the new method shows relatively good results as compared to experimental data for both training and test sets.

3.2. Known limitations of the correlation

Since electric spark sensitivity depends on shape and size of crystals that might connect with dislocations in theses crystals [5,6,9], the new method cannot predict electrostatic sensitivity versus the grain and size. For some isomeric compounds, the difference of their sensitivities may be large which can be attributed to different behavior of nitro groups in different positions. For example, electric spark sensitivity for 1,3-dinitrobenzene and 1,4-dinitrobenzene are 3.15 and 18.38 J [12], respectively. However, new method can predict only the value 12.26 J that is close to the average value of two measured values.

Due to different behavior of electric spark sensitivity of nitramines with respect to nitroaromatic compounds [3,6,12–15], Eq. (2) cannot be applied for nitroaromatic compounds which have N-NO_2 groups, e.g. 1-(methylnitramino)-2,4,6-trinitrobenzene or TETRYL. Moreover, the new method
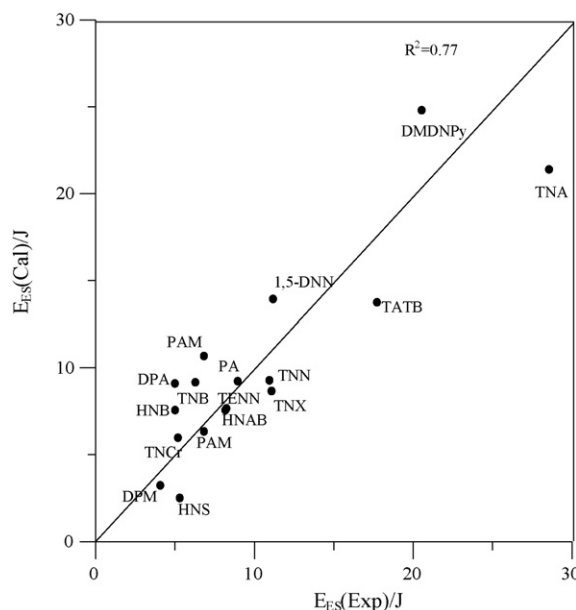

Fig. 1. Calculated electric spark sensitivity of training set versus experimental data for nitroaromatic energetic compounds. Compound names for abbreviations are given in Table 1.

Table 2
Comparison of predicted electric spark sensitivity (J) of nitroaromatic compounds of test set with the experimental data [12]

| Name	Molecular structure	Molecular formula	$C_{R,OR}$	E_{ES} (exp)	E_{ES} (cal)	Dev
3,5-Dinitropyridine-2,6-diamine (DADNPy)		$C_5H_5N_5O_6$	0	12.4	15.28	−2.88
2-Chloro-1,3,5-trinitrobenzene (CTB)		$C_6H_2N_3O_6Cl$	0	6.71	7.60	−0.89
2-Methyl-1,3,5-trinitro-4-[(2,4,6-trinitrophenyl)thio]benzene (MEDIPS)		$C_{13}H_6N_6O_{12}S$	1	5.71	3.20	2.51
2-Methyl-4-[(3-methyl-2,4,6-trinitrophenyl)thio]-1,3,5-trinitrobenzene (DIMEDIPS)		$C_{14}H_8N_6O_{12}S$	1	8.57	3.99	4.58
1,3,5-Trinitro-2-[(2,4,6-trinitrophenyl)sulfonyl]benzene (DIPSO)		$C_{12}H_4N_6O_{14}S$	0	10.54	8.56	1.98
1,3,7,9-Tetranitro-10H-phenothiazine 5,5-dioxide (TNPTD)		$C_{12}H_5N_5O_{10}S$	0	5.78	7.62	−1.84
1,3,7,9-Tetranitro-10H-phenoxazine (TENPO)		$C_{12}H_5N_5O_9$	0	5.12	6.39	−1.27
1,3,5-Trimethyl-2,4,6-trinitrobenzene (TNMs)		$C_9H_9N_3O_7$	1	8.98	10.95	−1.97
2,4,6-Trinitrobenzene-1,3-diol (TNR)		$C_6H_3N_3O_6$	0	12.3	9.43	2.87
1,8-Dinitronaphthalene (1,8-DNN)		$C_{10}H_6N_2O_4$	0	13.9	13.91	−0.01
5,7-Dinitro-1-(2,4,6-trinitrophenyl)-1H-1,2,3-benzotriazole (BTX)		$C_{12}H_4N_8O_{10}$	0	6.5	6.71	−0.21
2,4,6-Trinitrobenzene-1,3-diamine (DATB)		$C_6H_5N_5O_6$	0	10.97	12.18	−1.21
1,3,5-Trinitro-2-[2-(2,4,6-trinitrophenyl)ethyl]benzene (DPE)		$C_{14}H_8N_6O_{12}$	1	3.89	3.99	−0.10
3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl (BITNT)		$C_{14}H_8N_6O_{12}$	1	4.28	3.99	0.29
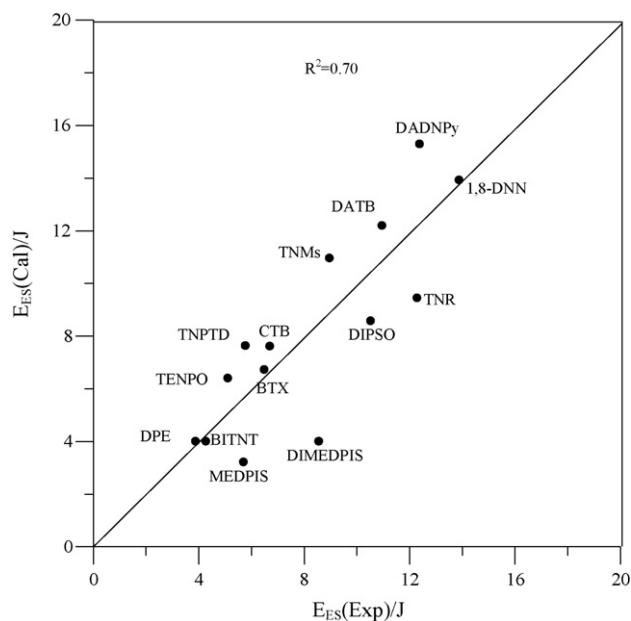
Fig. 2. Calculated electric spark sensitivity of test set versus experimental data for nitroaromatic energetic compounds. Compound names for abbreviations are given in Table 2.

can be used for secondary nitroaromatic explosives only. It should be mentioned that the results from the correlation may not be reliable if the predictions are outside of the energy range of the training set, namely about 4–23 J. Furthermore, since energetic compounds containing just C, H, N and O were used in training set, the results cannot be extrapolated to the other systems, e.g. 1,3,5-trichloro-2,4,6-trinitrobenzene.

4. Conclusions

Since different factors can influence the sensitivity by different stimuli, the main intent in this work was to investigate the likelihood of a generalized method to evaluate electric spark sensitivity of nitroaromatic compounds. A new method for estimating the electrostatic sensitivities of nitroaromatic compounds have been developed so that utilizing the current correlation can be used for reliable estimation of electric spark sensitivity of a new proposed nitroaromatic explosive for which no data exist. However, this may be taken as appropriate validation test of the new method for nitroaromatic compounds.

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