第 16 卷 第 1 期 含 能 材 料 Vol. 16, No. 1
2008 年 2 月 CHINESE JOURNAL OF ENERGETIC MATERIALS February, 2008

文章编号：1006-9941(2008)01-0113-08

Recent Developments in Predicting Impact and Shock Sensitivities of Energetic Materials

Mohammad Hossein Keshavarz*, Arash Shokrolahi, Karim Esmailpoor,
Abbas Zali, Hamid Reza Hafizi, Jamshid Azarniamehraban

(*Department of Chemistry, Malek-ashtar University of Technology, Shahin-shahr P. O. Box* 83145/115, *Islamic Republic of Iran*)

Abstract: Empirical, quantum mechanical and artificial neural network methods are three usual methods in recent years that were used to predict sensitivity of different classes of high explosives. Some recent developments in predicting sensitivity by various methods are reviewed and discussed for various classes of energetic materials.

Key words: explosion mechanics; impact and shock sensitivity; empirical method; quantum mechanical method; artificial neural network method

CLC number: TJ55; O38; O64 **Document code**: A

1 Introduction

Safe handling is one of the most important issues to the scientists and engineers who handle energetic molecules. Some of stimuli can cause detonation including impact, shock, heat, electrostatic charge and friction[1-2]. Of mentioned stimuli, shock and impact are two well-known of many kinds of sensitivity so that the drop-weight impact test is extremely easy to implement. However, one of the important factors in assessing an explosive is its vulnerability to detonation caused by accidental impact or shock. Moreover, impact sensitivity is closely related to many accidents in working places among various aspects of sensitivity. Several properties contribute to explosive response to the stimulus in a sensitivity test, namely the ease with which a detectable relation of any kind and a high-order detonation as well as tendency of a small reaction can be initiated and established in an explosive.

The purpose of this work is to review some recent developments in predicting impact and shock sensitivity for different classes of energetic materials through empirical, quantum mechanical and artificial neural networks.

2 Impact sensitivity

2.1 Different approaches to correlate impact sensitivity

High speed computers allow quantum mechanical calculations of individual molecules so that many macroscopic properties, such as impact sensitivities, of bulk materials can be determined. It should be mentioned that molecular surface of electrostatic potentials of the nitroaromatic molecules have positively charged regions over the C—NO_2 bonds. Some authors have used computed partial atomic charges[3-5], heats of reaction[6-7] and heats of explosion[8] in order to estimate impact sensitivities of some classes of explosives.

Brinck et al[9] introduced a term polarity index (Π), which is a quantitative measure of local polarity and demonstrated its relationship to dielectric constant, an experimentally determined bulk properties of molecules. There is a relationship between Π and impact sensitivities of nitroaromatics.

Xiao and coworkers[10-15] used quantum chemistry calculation to propose the thermodynamic criteria of "the smallest bond order", "the principle of the easiest transition", and the kinetic criterion of "the reaction activation energy of pyrolysis initiation" to judge the impact sensitivity. It should be mentioned that all these are only used to compare the relative magnitude of impact sensitivity qualitatively.

Politzer and coauthors[16-21] have identified a few features of electrostatic potentials using quantum mechanical calculations for $C_aH_bN_cO_d$ explosives that appear to be related to their sensitivity to impact. Owen and coworkers[22] undertook an investigation to address whether the electrostatic potential over the C—NO_2 bonding region reflects a degree of instability in the C—NO_2 bond that would subsequently indicate the sensitivity of the explosive. Murray

Received Date: 2007-08-14; **Revised Date**: 2007-09-17

* **Corresponding author**: mhkeshavarz@mut-es.ac.ir; mhkir@yahoo.com

and coauthors[23] also found a correlation between impact sensitivity measurements and an approximation of the electrostatic potential at the midpoint of C—N bond for 18 nitroaromatics that did not include hydroxynitroaromatic molecules.

Different approaches have been reviewed to determine impact sensitivity of different classes of nitro compounds. Different general methods have some advantages and disadvantages, which can be summarized in Table 1.

Table 1 Summary of generalized impact sensitivity predictions for various classes of nitro compounds

presenters	physical nature	formula	advantages	disadvantages
Rice and Hare[24]	quantum mechanical computations	Eqs. (1) – (5)	application for different classes of nitro compounds	1. Using high speed computer 2. Deviations in some cases are large
Zhang et al[29 – 31]	quantum mechanical computations	–	1. It can be applied for different classes of nitro compounds 2. Determining sensitive explosives 3. Mulliken charge has more availability in almost all nitro compounds	1. Using high speed computer 2. Deviations in some cases may be large
Cho et al[34]	artificial neural network	–	1. Application for different classes of nitro compounds 2. Simple using as compared to DFT computation	1. It needs large number of data as training set 2. Deviations in some cases are large
Keshavarz and Jaafari[35]	artificial neural network	–	1. Application for different classes of nitro compounds 2. Simple using as compared to DFT computation 3. It uses only some structural parameters	1. It needs large number of data as training set 2. Deviations in some cases are large
Kamlet and Adolph[36 – 37,48]	empirical	Eqs. (6a) – (6d)	1. Application for different classes of nitro compounds 2. Much simple to use	deviations in some cases are large
Keshavarz et al[50 – 52]	empirical	Eqs. (7a) – (7c), (8) – (9)	1. Application for different classes of nitro compounds 2. Much simple to use 3. Impact sensitivity of nitroheterocycles can be predicted	deviations in some cases are large

2.1.1 Generalized five quantum mechanical models of Rice and Hare[24]

Rice and Hare[24] used approximations to the electrostatic potential at midpoints, statistical parameters of these surface potentials and the property-structure relation method "generalized interaction property function" (GIPF) or computed heats of detonation to predict impact sensitivity of $C_aH_bN_cO_d$ explosives. Their predictions support the Murray *et al.* observations[25 – 26] that the impact sensitivities of $C_aH_bN_cO_d$ explosives have some dependence on the degree of internal charge imbalance within the molecule. Five introduced models use parameters related to features of the surface electrostatic potentials, which can be summarized as below:

Model Ⅰ: Using the approximate electrostatic potential at the midpoint of each bond:

$$H_{50}(/\mathrm{cm}) = 63.6 + 1.89 \times 10^{3} \times \exp(-8.78 \times 10^{-2}\mathrm{mol/kcal} \times \overline{V}_{\mathrm{mid}}) - 0.368\mathrm{mol/kcal} \times \overline{V}_{\mathrm{mid}} \quad (1)$$

$\overline{V}_{\mathrm{mid}}$ is the approximate electrostatic potential at the midpoint of each bond which is evaluated using the partial charges for all atoms in the molecule rather than only the two atoms of carbon and nitrogen making up the bond C—N in $C—NO_2$ which earlier was described by Murray et al.[25 – 26].

Model Ⅱ: Using the difference between the magnitudes of the averages of the positive and negative values of the electrostatic potential on the isosurface, $|\overline{V}_S^+ - |\overline{V}_S^-||$:

$$H_{50}(/\mathrm{cm}) = 9.2 + 803 \times \exp[-(0.366\mathrm{mol/kcal} \times |\overline{V}_S^+ - |\overline{V}_S^-||)] \quad (2)$$

Model Ⅲ: Using statistical quantity associated with the electrostatic potential of the molecule, the balance parameter ν[23,26]:

$$H_{50}(/\mathrm{cm}) = 29.3 + 1.39 \times 10^{-3} \times \exp(48.8\nu) \quad (3)$$

Model Ⅳ: Using quantum mechanical information about a single molecule can be used to evaluate heats of detonation, Q_{det}:

$$H_{50}(/\mathrm{cm}) = 27.8 + 0.114 \times \exp\{-[11.1\mathrm{g/kcal} \times (Q_{\mathrm{det}} - 1.66\mathrm{kcal/g})]\} \quad (4)$$

Model Ⅴ: Using both the GIPF balance parameter ν and heats of detonation in the following function:

$$H_{50}(/\mathrm{cm}) = 1.34 \times \exp[8.14\nu - 6.79\mathrm{g/kcal} \times (Q_{\mathrm{det}} - 1.47\mathrm{kcal/g})] \quad (5)$$

In nitramines, the rupture of $N—NO_2$ bond is a key step in the process of decomposition initiated by heat, shock and impact, although there may be important competing pathways, which may be predominate in some instances[27]. Edwards and coworkers[28] also used the model Ⅳ of Rice and Hare[24] and an approximate

method for the calculation of heat of detonation of several nitramines using two different levels of PM3 and DFT quantum mechanical theory. They found that there was correlation in exponential decay of the HOMO and LOMO energies versus sensitivity at the DFT level of theory.

2.1.2 Quantum mechanical investigation of Zhang and cowerkers[29-31] on the basis of nitro group charges

Zhang et al[29-31] on the basis of DFT have found some relationships between impact sensitivity and nitro group charges. They used the general gradient approximation (GGA), and the Beck hybrid functional and DNP basis set to calculate Mulliken charges and correlate with impact sensitivity of nitro compounds. They have indicated that the nitro compounds may be sensitive ($H_{50} \leqslant$ 40 cm) when its nitro group has a smaller negative charge than about 0.23. However, the charges on the nitro group can be regarded as a structural parameter to estimate on the bond strength, oxygen balance and molecular electrostatic potential. Thus, the compound with more the Mulliken net charges of the nitro group will be insensitive and gives a large value of H_{50}. Zhang et al method[30] can be applied for nitro compounds when C—NO_2, N—NO_2 or O—NO_2 bond is the weakest in the molecule.

2.1.3 Artificial neural network

The neural network has been recently applied widely to various areas of science and engineering. The neural network of computation has several advantages for solving complicated problems especially in the speed of computation, learning ability and fault tolerance. Theoretical background of neural computing has been given elsewhere[32-33].

Neural networks architectures have been recently used as prediction methodology for impact sensitivity to cover various types of energetic molecules. Cho and coworkers[34] utilized 17 molecular descriptors, which were composed of compositional and topological descriptors in an input layer and 2 hidden neurons in a hidden layer. They showed that subsets composed of compositional and topological descriptors provide better results than those composed of electronic descriptors including LUMO_MOPAC (Lowest Unoccupied Molecular Orbital from MOPAC), HOMO_MOPAC (Highest Occupied Molecular Orbital from MOPAC), Dipole_MOPAC (Dipole moment from MOPAC) and HF_MOPAC (Heat of Formation from MOPAC).

It was recently found that some structural parameters can be used to determine impact sensitivity using an artificial neural network model by choosing only 10 molecular descriptors by Keshavarz and Jaafari[35]. The model was instructed and tested with MATLAB code with a large number of $C_aH_bN_cO_d$ explosives. The final neural structure consists of the three layers input, output, and hidden. The network is composed of fully connected two layers: 10 input nodes, fifteen hidden-layer neurons and a single output neuron corresponding to impact sensitivity of explosive. Ten structural descriptors were used for neural network modeling for any $C_aH_bN_cO_d$ explosive, which include (1) a/MW; (2) b/MW; (3) c/MW; (4) d/MW; indicator variables for (5) aromaticity; (6,7) heteroaromaticity (N and O); (8) N—NO_2; (9) α-hydrogen; (10) salt. If a certain input in the network did not exist in a molecule an input value of zero was assigned to that input. The connection weights of the network were adjusted iteratively by back propagation algorithm. Thus the neural network parameters contain 10 input neurons for ten descriptors as well as 15 hidden-layer neurons plus a bias and one output neuron namely impact sensitivity. The predictive ability of the artificial neural network was checked by training it with only 275 of experimental data after arriving at the best network architecture. The trained networks was then applied to predict impact sensitivity of 14 remaining explosives in the test set, which were not included in the learning data base. The results of the test set were also compared with five quantum mechaical models of Rice and Hare[24]. It was shown that the new simple neural network model for the test data set can give better predictions as compared to quantum mechanical models of Rice and Hare[24].

2.1.4 Simple correlations on the basis of molecular structure

Although quantum mechanical calculations have a stronger theoretical basis for prediction of sensitivity of explosives, simple empirical correlations have the advantages that neither complex quantum chemistry software nor high speed computers needs to be available for tedious computation.

Some simple relationships relate impact sensitivities with measured and predicted molecular properties which

include the oxygen balance of the molecules[36-37], molecular electronegativities[38-39], vibrational states[40-41], molecular masses and detonation gas concentrations[42], parameters related to oxidation numbers[43] and partial atomic charges[44-45].

Zeman and Krupka[2,46-47] have studied the chemical micromechanisms governing the detonation initiation of energetic materials. They found that there is a relationship between the sensitivity and ^{15}N NMR chemical shifts and heat of fusion so that the relationship has different forms for different classes of explosives. Their studies showed that in those energetic materials, which have similar molecular structure, the relationship between the sensitivity and the molecular structure may be easily found and the different relationship forms respond to different molecular structure.

2.1.4.1 Kamlet and Adolph correlations[36-37,48]

Among introduced simple correlations, the oxygen balance method has interested for many authors because its generality for large classes of explosives. Kamlet and Adolph[36-37,48] proposed a method for estimating impact sensitivity based on oxygen balance, which can be defined as $OB_{100} = 100(2c' - b' - 2a' - 2n'_{COO})$ where c', b', a' and n'_{COO} are the number of oxygen, hydrogen, carbon and carboxylate in the molecule divided by molecular weight of explosive. They found reasonable linear correlations between OB_{100} and $\log H_{50}$ for families of high energy molecules with similar decomposition mechanisms, which can be given for selected classes as follows:

a) Nitroaromatic: $\log H_{50} = 1.73 - 0.32OB_{100}$ (6a)

b) Nitroaromatic with α-CH linkage (e.g. TNT): $\log H_{50} = 1.33\text{-}0.26B_{100}$ (6b)

c) Nitroaliphatic: $\log H_{50} = 1.74 - 0.23OB_{100}$ (6c)

d) Nitramine: $\log H_{50} = 1.37 - 0.17B_{100}$ (6d)

Later, Stine[49] introduced a sensitivity index, based on the geometric properties of a regular tetrahedron. A regular tetrahedron has the property that the sum of four distances from any interior point to each of the four sides is a constant, which can arbitrary be taken as unity. Sensitivity index has been shown to correlate with OB_{100} values. Stine has prompted considerable attention to the idea of the key "trigger linkage" in explosives as proposed by Kamlet and Adolph[36-37,48].

It was recently shown that elemental composition and some structural parameters can be used to predict impact sensitivities of large classes of explosives[50-52]. These methods have some advantages such as generality and simplicity, which will be discussed in the following sections.

2.1.4.2 Keshavarz and coworkers approaches[50-52]

2.1.4.2.1 Polynitroaromatics (and benzofuroxans) and polynitroaromatics with α-CH and α-N—CH (e.g. tetryl) and nitramines

It was indicated that application of some empirical correlations to explosives comprised of C, H, N and O have resulted simple relationships between impact sensitivity and elemental composition. The results indicated that the following general equation is suitable for two different categories of $C_aH_bN_cO_d$ explosives, namely polynitroaromatics (and benzofuroxans) and polynitroaromatics with α-CH and α-N—CH (e.g. tetryl) and nitramines:

a) Polynitroaromatics (and benzofuroxans):

$$\log H_{50} = 11.8a' + 61.72b' + 26.9c' + 11.5d' \quad (7a)$$

b) Polynitroaromatics with α-CH and α-N—CH (e.g. tetryl) and nitramines:

$$\log H_{50} = 47.3a' + 23.5b' + 2.36c' - 1.11d' \quad (7b)$$

where a', b', c' and d' are the number of carbon, hydrogen, nitrogen and oxygen for an explosive with general formula $C_aH_bN_cO_d$ divided by molecular weight of explosive. Two sets of coefficients were used for Eqs. (7a) and (7b) because different behaviors of mentioned explosives on impact.

2.1.4.2.2 Nitroaliphatic, nitroaliphatic containing other functional groups and nitrate explosives

For nitroaliphatic, nitroaliphatic containing other functional groups and nitrate explosives, the following correlation can be used to determine impact sensitivity:

$$\log H_{50} = 81.4a' + 16.1b' - 19.1c' + 1.09d' \quad (7c)$$

It was indicated that Eqs. (7a) to (7c) give better predictions for 46 explosives of different classes as compared to Kamlet and Adolph method[36-37,48] as well as five quantum mechanical models of Rice and Hare[24], i.e. Eqs. (1) to (5). Later, it was shown that application of oxygen content and some structural parameters can be used to find reliable correlation for impact sensitivity of nitroaliphatic, nitroaliphatic containing other functional groups and nitrate energetic compounds[51]. The results indicated that the following general equation with some

structural parameters is suitable for mentioned compounds:

$$\log H_{50} = 2.5 + 0.371[100(a' + b'/2 - d')] - 0.485(100c') + 0.185n_{R-C(NO_2)_2-CH_2-} \quad (8)$$

where $a' + b'/2 - d'$ is a parameter that shows distribution of oxygen between carbon and hydrogen to form carbon monoxide and water, $n_{R-C(NO_2)_2-CH_2-}$ is the number of R—C$(NO_2)_2$—CH_2— structural parameters attached to oxygen of carboxylate functional groups where R is alkyl groups. The extra stability was found in some polynitroaliphatics that contain R—C$(NO_2)_2$—CH_2— structural parameters attached to oxygen of carboxylate functional groups. Calculated results of Eq. (8) for 58 different nitroaliphatic, nitroaliphatic containing other functional groups and nitrate explosives have shown a good agreement with experimental values (rms deviation = 27 cm) as compared to Eq. (7c) (rms deviation = 40 cm) and Kamlet and Adolph (rms deviation = 60 cm) method[51].

2.1.4.2.3 Nitroheterocycles

Nitroheterocyclic energetic compounds containing nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines have different behavior on impact. For example, large differences of impact sensitivities between some isomers of nitrohetrocycles, e. g. 1, 2, 3-triazoles and 1, 2, 4-triazoles, are important problem in obtaining desirable correlation. However, large uncertainties associated with some of experimental data also hamper for explosives scientists to find good correlations between some of molecular descriptors and impact sensitivity of nitroheterocycles.

It was indicated that impact sensitivity of nitrohetrocycles can most appropriately be expressed as its elemental composition and some structural parameters[52]. The results indicated that the following general equation can be used for various types of $C_aH_bN_cO_d$ nitroheterocycles including nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines:

$$\log H_{50} = 46.29a' + 35.63b' - 7.700c' + 7.943d' + 44.42n'_{-CNC-} + 102.3n'_{-CNNC-} \quad (9)$$

where n'_{-CNC-} and n'_{-CNNC-} are the number of —CNC— and —CNNC— moieties in aromatic ring divided by molecular weight of explosive.

The new correlation show surprisingly very good agreement with experimental values as compared to complex neural network computation. This may be taken as appropriate validation tests of the new correlation for various nitroheterocycles including nitropyridines, nitroimidazoles, nitropyrazoles, nitrofurazanes, nitrotriazoles and nitropyrimidines.

3 Shock sensitivity

Reliable shock sensitivity tests exist, but the results of impact sensitivity are often not reproducible because factors in the impact experiment that might affect the formation and growth of hot spots could strongly affect the measurements. Zeman[2] has shown that some relationships exist for some groups of nitramines between square of detonation velocities, or heat of explosion and values of the ^{15}N NMR chemical shifts of the nitrogen atoms in nitramino groups, on the other hand.

The gap test data can be used to indicate the shock sensitivity of an explosive. A shock pressure of uniform magnitude is produced by a detonating charge of high explosive which is transmitted to the test explosive through an attenuating inert barrier or gap. Different gap tests have been used to qualitatively measure the shock wave amplitude required to initiate detonation in explosives, e. g. at Naval Surface Warfare Center (NSWC) and Los Alamos National Laboratory (LANL). Two general correlations will be discussed in the following sections for prediction small scale and large scale gap tests.

3.1 Small scale gap test

A standard small scale gap test can be used to measure shock sensitivity. For shock initiated studies, the collection of information has been gathered by NSWC using Navy small scale gap test.

It was recently indicated that a new correlation can be used for reliable estimation shock sensitivity based on small scale gap test as the pressure required for initiating material pressed to 90%, 95% and 98% of theoretical maximum density[53]. Three essential parameters have predominant effects which include distribution of oxygen between carbon and hydrogen to form carbon monoxide and water, the existence of nitramine groups or (—C—H linkage in nitroaromatic compounds and difference of the number of amino and nitro groups in aminoaromatic (Ar—NH_2) energetic compounds. General equation can be given as follows:

$$p_{90\mathrm{TMD}}(\mathrm{kbar}) = 16.8 + 2.26(a + b/2\text{-}d) - 6.31E^0_{\mathrm{NNO_2}} + 17.7(1.93n_{\mathrm{NH_2}} - n_{\mathrm{NO_2}})_{\mathrm{pure}} \quad (10a)$$

$$p_{95\mathrm{TMD}}(\mathrm{kbar}) = 22.0 + 2.48(a + b/2\text{-}d) - 6.37E^0_{\mathrm{NNO_2}} + 32.9(1.93n_{\mathrm{NH_2}} - n_{\mathrm{NO_2}})_{\mathrm{pure}} \quad (10b)$$

$$p_{98\mathrm{TMD}}(\mathrm{kbar}) = 25.4 + 2.21(a + b/2\text{-}d) - 4.16E^0_{\mathrm{NNO_2}} + 46.4(1.93n_{\mathrm{NH_2}} - n_{\mathrm{NO_2}})_{\mathrm{pure}} \quad (10c)$$

where $p_{90\mathrm{TMD}}$, $p_{95\mathrm{TMD}}$ and $p_{98\mathrm{TMD}}$ are the pressure in kbar required to initiate material pressed to 90%, 95% and 98% of theoretical maximum density (TMD, $a + b/2\text{-}d$ is a parameter that shows distribution of oxygen between carbon and hydrogen to form carbon monoxide and water, $E^0_{\alpha\mathrm{CH/NNO_2}}$ is a parameter that shows the existence of α-C—H linkage in nitroaromatic compounds or N—NO_2 functional group, $(1.93n_{\mathrm{NH_2}} - n_{\mathrm{NO_2}})_{\mathrm{pure}}$ is difference of the number of amino and nitro groups in aminoaromatic energetic compounds. It should be mentioned that $E^0_{\alpha\mathrm{CH/NNO_2}}$ is equal to 1 for nitramines or α-C—H linkage in nitroaromatic compounds and has the zero value for energetic compounds in which N—NO_2 functional groups do not exist in their chemical structure. New correlation has shown good agreement with experimental data for $p_{90\%\,\mathrm{TMD}}$, $p_{95\%\,\mathrm{emd}}$ and $p_{98\%\,\mathrm{TMD}}$ of different well-known explosives.

3.2 Large scale gap test

It was shown that large-scale shock sensitivities of various explosives depends on four main essential parameters which include initial density, percent void, distribution of oxygen between carbon and hydrogen as well as structural parameter C—N(NO_2)—C for pure explosives. However, pure explosives containing C—N(NO_2)—C linkage are more sensitive than the other pure explosives containing only C—NO_2 linkage. The results indicate that the following general equation is suitable for various types of $C_aH_bN_cO_d$ pure and mixed explosives[54]:

$$G_{50}(\mathrm{mm}) = 171.5 - 69.1\rho_0 - 2.61(a + b/2 - d) - 0.961\mathrm{Void}_{\mathrm{theo}} + 12.3(\mathrm{C—N(NO_2)—C})_{\mathrm{pure}} \quad (11)$$

where ρ_0 is initial density of explosive, $a + b/2\text{-}d$ is a parameter that shows distribution of oxygen between carbon and hydrogen to form carbon monoxide and water, $\mathrm{Void}_{\mathrm{theo}}$ is theoretical calculated percent void which can be obtained from $\dfrac{(1/\rho_0 - 1/\rho_{\mathrm{TM}})}{1/\rho_0} \times 100$ where ρ_{TM} is theoretical maximum density. The new correlation can be applied for pure and composite mixtures that are prepared under vacuum cast, cast, hot-pressed and pressed conditions. Deviations may be large for creamed, granular and flake situations.

4 Conclusion

Some recent progress in predicting impact and shock sensitivity of $C_aH_bN_cO_d$ explosive were considered in this paper. Empirical, quantum mechanical and neural network methods are the physical nature of different approaches for determination of impact sensitivity. Emiprical methods have some advantages: (a) simplicity; (b) reliable predictions with respect to quantum mechanical and neural network methods. Empirical methods can be applied for calculating impact sensitivities of any $C_aH_bN_cO_d$ explosive and requires only the explosive's composition. Since high percentage errors generally attributed to reported experimental measurements from different sources, the main intent in recent research works was to investigate the likelihood of a generalized method to evaluate impact sensitivity of explosives of practical importance. Results predicted by empirical methods comparable with outputs from complicated quantum mechanical and neural network computations and the accuracy of prediction are not necessarily enhanced by greater complexity.

References:

[1] Sikder A K, Maddala G, Agrawal J P, et al. Important aspects of behavior of organic energetic compounds: A review[J]. *J Hazard Mater A*, 2001, 84: 1 – 26.

[2] Zeman S. New aspects of initiation reactivities of energetic materials demonstrated on nitramines[J]. *J Hazard Mater A*, 2006, 132: 155 – 164.

[3] Delpuech A, J Cherville. Relation entre La structure electronique et la Sensibilité au Choc des Explosifs Secondaires Nitrés. III. Influence de lénvironnement cristallin[J]. *Propellants, Explos, Pyrotech*, 1979, 4: 61 – 65.

[4] Owens F J, Jayasuriya K, Abrahmsen L, et al. Computational analysis of some properties associated with the nitro groups in polynitroaromatic molecules[J]. *Chem Phys Lett*, 1985, 116: 434 – 438.

[5] Murray J S, Lane P, Politzer P, et al. A relationship between impact sensitivity and the electrostatic potentials at the midpoints of C—NO_2 bonds in nitroaromatics[J]. *Chem Phys Lett*, 1990, 168: 135 – 139.

[6] Traver C M, Fried L E, Rigger A J, et al. Energy transfer in solid explosives[C] // 10th Symposium (International) on Detonation, Boston, Massachusetts, 12 – 16 July, 1993.

[7] Vaullerin M, Espagnacq A, Morin-Allory L. Prediction of explosives impact sensitivity[J]. *Propellants, Explos, Pyrotech*, 1998, 23: 237 – 239.

[8] Fukuyama I, Ogawa T, Miyake A. Sensitivity and evaluation of explosive substances[J]. *Propellants, Explos, Pyrotech*, 1986, 11: 140 – 143.

[9] Brinck T, Murray J S, Politzer P. Quantitative determination of the total local polarity (charge separation) in molecules[J]. *Mol Phys*, 1992, 76: 609 – 617.

[10] Xiao H M, Wang Z Y, Yao J M. The theoretical study on sensitivity and stability of polynitro arenes I. nitro derivatives of aminobenzenes [J]. *Acta Chim Sinica*, 1985, 43: 14 – 18.

[11] Fan J, Xiao H. Theoretical study on pyrolysis and sensitivity of energetic compounds. (2) Nitro derivatives of benzene[J]. *J Mol Struct* (*THEOCHEM*), 1996, 365: 225 – 229.

[12] Xiao H M, Fan J F, Gu Z M, et al. Theoretical study on pyrolysis and sensitivity of energetic compounds: (3) Nitro derivatives of aminobenzenes[J]. *Chem Phys*, 1998, 226: 15 – 24.

[13] Fan J, Gu Z, Xiao H, et al. Theoretical study on pyrolysis and sensitivity of energetic compounds. Part 4. Nitro derivatives of phenols[J]. *J Phys Org Chem*, 1998, 11: 177 – 184.

[14] Chen Z X, Xiao M H, Yang S L. Theoretical investigation on the impact sensitivity of tetrazole derivatives and their metal salts[J]. *Chem Phys*, 1999, 250: 243 – 248.

[15] Zhao Xu C, XIao H M. Impact sensitivity and activation energy of pyrolysis for tetrazole compounds[J]. *Int J Quantum Chem*, 2000, 79: 350 – 357.

[16] Politzer P, Murray J S, Lane P, et al. A relationship between impact sensitivity and the electrostatic potentials at the midpoints of C—NO_2 bonds in nitroaromatics[J]. *Chem Phys Lett*, 1991, 181: 78 – 82.

[17] Politzer P, Abrahmsen L, Sjoberg P. Effects of amino and nitro substituents upon the electrostatic potential of an aromatic ring[J]. *J Am Chem Soc*, 1984, 106: 855.

[18] Politzer P, Laurence P R, Abrahmsen L, et al. The aromatic C—NO_2 bond as a site for nucleophilic attack[J]. *Chem Phys Lett*, 1984, 111: 75 – 78.

[19] Politzer P, Murray J S. Relationships between dissociation energies and electrostatic potentials of C—NO_2 bonds: Applications to impact sensitivities[J]. *J Mol Struct*, 1996, 376: 419 – 424.

[20] Politzer P, Lane P. Comparison of density functional calculations of C—NO_2, N—NO_2 and C—NF_2 dissociation energies [J]. *J Mol Struct*, 1996, 388: 51 – 55.

[21] Politzer P, Murray J S. Organic Energetic Compounds[M]. Markinas P L, Ed., Nova Science Publishers: New York, 1996.

[22] Owens F J, Jayasuriya K, Abrahmsen L, et al. Computational analysis of some properties associated with the nitro groups in polynitroaromatic molecules[J]. *Chem Phys Lett*, 1985, 116: 434 – 438.

[23] Murray J S, Lane P, Politzer P, et al. A relationship between impact sensitivity and the electrostatic potentials at the midpoints of C—NO_2 bonds in nitroaromatics[J]. *Chem Phys Lett*, 1990, 168: 135 – 139.

[24] Rice B M, Hare J J. A quantum mechanical investigation of the relation between impact sensitivity and the charge distribution in energetic molecules[J]. *J Phys Chem A*, 2002, 106: 1770 – 1783.

[25] Murray J S, Lane P, Politzer P. Relationships between impact sensitivities and molecular surface electrostatic potentials of nitroaromatic and nitroheterocyclic molecules[J]. *Mol Phys*, 1995, 85: 1 – 8.

[26] Murray J S, Lane P, Politzer P. Effects of strongly electron-attracting components on molecular surface electrostatic potentials: Application to predicting impact sensitivities of energetic molecules [J]. *Mol Phys*, 1998, 93: 187 – 194.

[27] Brill T B, Oyumi Y J. Thermal decomposition of energetic materials. Part 9. A relationship of molecular structure and vibrations to decomposition: Polynitro-3, 3, 7, 7-tetrakis (trifluoromethyl)-2, 4, 6, 8-tetraazabicyclo [3.3.0]octanes[J]. *J Phys Chem*, 1986, 90: 2679 – 2682.

[28] Edwards J, Eybl C, Johnson B. Correlation between sensitivity and approximated heats of detonation of several nitroamines using quantum mechanical methods[J]. *Inter J quantum Chem*, 2004, 100: 713 – 719.

[29] Zhang C, Shu Y, Huang Y, et al. Theoretical investigation of the relationship between impact sensitivity and the charges of the nitro group in nitro compounds[J]. *J Energetic Mat*, 2005, 23: 107 – 119.

[30] Zhang C, Shu Y, Huang Y, et al. Investigation of correlation between impact sensitivities and nitro group charges in nitro compounds[J]. *J Phys Chem B*, 2005, 109: 8978 – 8982.

[31] Zhang C, Shu Y, Wang X, et al. A new method to evaluate the stability of the covalent compound: by the charges on the common atom or group[J]. *J Phys Chem A*, 2005, 109: 6592 – 6596.

[32] Lipmann R P. An introduction to computing with neural nets[J]. *IEEE ASSP Mag*, 1987, 4: 10 – 31.

[33] Widrow B, Lehr M A. 30 years of adaptive neural networks[J]. *Proc IEEE*, 1990, 78: 1415 – 1433.

[34] Cho S G, Tai No K, Goh E M, et al. Optimization of neural networks architecture for impact sensitivity of energetic molecular [J]. *Bull Korean Chem Soc*, 2005, 26: 399 – 408.

[35] Keshavarz M H, Jaafari M. Investigation of the various structure parameters for predicting impact sensitivity of energetic molecules via artificial neural network[J]. *Propellants, Explos, Pyrotechn*, 2006, 31: 216 – 225.

[36] Kamlet M J. Sensitivity relationships[C]// 3th Symposium (International) on Detonation, Princeton, New Jersey, 26 – 28 September, 1960.

[37] Kamlet M J. The relationship of impact sensitivity with structure of organic high explosives: I. polynitroaliphatic explosives[C]// 6th Symposium (International) on Detonation, Coronads, CA, Washington, DC Office of the Chief of Naval Operations, 24 – 27 August, 1976.

[38] Mullay J. A relationship between impact sensitivity and molecular electronegativity[J]. *Propellants, Explos, Pyrotech*, 1987, 12: 60 – 63.

[39] Mullay J. Relationships between impact sensitivity and molecular electronic structure[J]. *Propellants, Explos, Pyrotech*, 1987, 12: 121 – 124.

[40] Fried L E, Ruggiero A J. Energy transfer rates in primary, secondary, and insensitive explosives[J]. *J Phys Chem*, 1994, 98: 9786 – 9791.

[41] McNesby K L, Coffey C S. Spectroscopic determination of impact sensitivities of explosives spectroscopic determination of impact sensitivities of explosives[J]. *J Phys Chem B*, 1997, 101: 3097 – 3104.

[42] Delpuech A, Cherville J. Relation entre La Structure Electronique et la Sensibilité au Choc des Explosifs Secondaires Nitrés. Critère Moléculaire de Sensibilité II. Cas des esters nitriques [J]. *Propellants, Explos, Pyrotech*, 1979, 4: 121 – 128.

[43] Jain S R. Energetics of propellants, fuels and explosives; a chemical valence approach[J]. *Propellants, Explos, Pyrotech*, 1987, 12: 188 – 195.

[44] Kamlet M J, Adolph H G. Some comments regarding the sensitivities,

thermal stabilities, and explosive performance characteristics of fluorodinitromethyl compounds [C] // 7th Symposium (International) on Detonation, Anapolis, Maryland, 16 – 19 June, 1981.

[45] Delpuech A, Cherville J. Relation entre la Structure Electronique et la Sensibilité au Choc des Explosifs Secondaires Nitrés-Critère Moléculaire de Sensibilité. I. Cas des Nitroaromatiques et des Nitramines[J]. *Propellants, Explos, Pyrotech*, 1978, 3: 169 – 175.

[46] Zeman S, Krupka M. New aspects of impact reactivity of polynitro compounds, part III. impact sensitivity as a function of the intermolecular interactions[J]. *Propellants, Explos, Pyrotech*, 2003, 28: 301 – 307.

[47] Zeman S. New aspects of impact reactivity of polynitro compounds, part IV. Allocation of polynitro compounds on the basis of their impact sensitivities[J]. *Propellants, Explos, Pyrotech*, 2003, 28: 308 – 313.

[48] Kamlet M J, Adolph H G. The relationship of impact sensitivity with structure of organic high explosives. part II. polynitroaromatic explosives[J]. *Propellants, Explos, Pyrotech*, 1979, 4: 30 – 34.

[49] Stine J R. On predicting properties of explosives – detonation velocity [J]. *J Energetic Mater*, 1990, 8: 41 – 73.

[50] Keshavarz M H, Pouretedal H R. Simple empirical method for prediction of impact sensitivity of selected class of explosives[J]. *J Hazard Mat A*, 2005, 124: 27 – 33.

[51] Keshavarz M H. Prediction of impact sensitivity of nitroaliphatic, nitroaliphatic containing other functional groups and nitrate explosives [J]. *J Hazard Mat A, in press*.

[52] Keshavarz M H, Pouretedal H R, Semnani A. Novel correlation for predicting impact sensitivity of nitroheterocyclic energetic molecules[J]. *J Hazard Mat A*, 2007, 141: 803 – 807.

[53] Keshavarz M H, Motamedoshariati H, Pouretedal H R, et al. Prediction of shock sensitivity of explosives based on small scale gap test[J]. *J Hazard Mat A*, 2007, 145: 109 – 112.

[54] Keshavarz M H, Pouretedal H R, Kavosh Tehrani M, et al. Predicting of shock sensitivity of energetic compounds[J]. *Asian J Chem, in press*.

(上接 112 页)

[63] 易文斌,蔡春. 甲苯的氟两相硝化反应研究(Ⅱ)[J]. 含能材料, 2006, 14(1): 29 – 31.
YI Wen-bin, CAI Chun. Nitration of toluene with fluorous biphasic system (Ⅱ)[J]. *Chinese Journal of Energetic Materials* (*Hanneng Cailiao*), 2006, 14(1): 29 – 31.

[64] 易文斌,蔡春. 卤代苯的氟两相硝化反应研究[J]. 火炸药学报, 2005, 28(3): 45 – 48.
YI Wen-bin, CAI Chun. Nitration of halobenzens with fluorous biphasic system[J]. *Chin J Explo & Propel*, 2005, 28(3): 45 – 48.

[65] 袁余斌,聂进,王烁今,等. 全氟烷基磺酰亚胺盐催化芳香化合物硝化反应的研究[J]. 有机化学, 2005, 25(4): 394 – 398.
YUAN Yu-bin, NIE Jin, WANG Shuo-jin, et al. Aromatic nitration catalyzed by metal bis[(perfluoroalkyl) sulfonyl]imides[J]. *Chin J Org Chem*, 2005, 25(4): 394 – 398.

[66] Parac-Vogt T N, Binnemans K. Lanthanide(Ⅲ) nosylates as new nitration catalysts[J]. *Tetrahedron Lett*, 2004, 45: 3137 – 3139.

[67] Parac-Vogt T N, Deleersnyder K, Binnemans K J. Lanthanide(Ⅲ) complexes of aromatic sulfonic acids as catalysts for the nitration of toluene alloys and compounds[J]. 2004, 374: 46 – 49.

[68] Laali K K, Gettwert V J. Electrophilic nitration of aromatics in ionic liquid solvents[J]. *J Org Chem*, 2001, 66: 35 – 40.

[69] 马丁·约翰·厄尔,苏哈斯·普拉巴哈卡尔·凯特戴尔. CN1469859A, 2004.

[70] Smith K, Liu S, EL-Hiti G A. Regioselective mononitration of simple aromatic compounds under mild conditions in ionic liquids[J]. *Ind Eng Chem Res*, 2005, 44: 8611 – 8615.

[71] Lancaster N L, Verónica Llopis-Mestre. Aromatic nitrations in ionic liquids: The importance of cation choice[J]. *Chem Commun*, 2003. 2812 – 2813.

[72] Qiao K, Hagiwara H, Yokoyama C. Acidic ionic liquid modified silica gel as novel solid catalysts for esterification and nitration reactions[J]. *J Mol Catal A: Chem*, 2006, 246: 65 – 69.

[73] Rajagopal R, Srinivasan K V. Ultrasound promoted para-selective nitration of phenols in ionic liquid[J]. *Ultrasonics Sonochem*, 2003, 10: 41 – 43.

[74] 方东,施群荣,巩凯,等. 离子液体催化甲苯绿色硝化反应研究[J]. 含能材料, 2007, 15(2): 122 – 124.
FANG Dong, SHI Qun-rong, GONG Kai, et al. Green nitration of toluene in ionic liquids[J]. *Chinese Journal of Energetic Materials* (*Hanneng Cailiao*), 2007, 15(2): 122 – 124.

Research Progress of Clean Nitration of Aromatic Compounds

FANG Dong, SHI Qun-rong, GONG Kai, LIU Zu-liang, Lü Chun-xu

(*School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing* 210094, *China*)

Abstract: Recent advances of clean nitration of aromatic compounds, including liquid-phase nitration with solid acid, nitration in liquid acid/nitrate salt system, vapor-phase nitration with solid acid, liquid-phase nitration with Lewis acid, nitration in ionic liquid system, are reviewed. Their specific features and reaction mechanism are described, and the perspectives of the clean nitration are prospected.

Key words: organic chemistry; aromatic compound; clean nitration; solid acid; Lewis acid; ionic liquid