



A reliable method for prediction of enthalpy of fusion in energetic materials using their molecular structures

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ABSTRACT

A new method is introduced to predict the enthalpy of fusion of energetic materials, which can undergo very rapid and highly exothermic reactions. It can be applied for different classes of energetic compounds including polynitro arenes, polynitro heteroarenes, acyclic and cyclic nitramines, nitrate esters, nitro-aliphatics, cyclic and acyclic peroxides as well as nitrogen rich compounds. This model is based on linear combination of elemental composition as additive part and two correcting functions as non-additive contributions, which depend on intermolecular interactions. It can be easily applied for energetic compounds containing complex molecular structure. For 194 different energetic compounds (corresponding to 233 measured values), the predicted results of this simple model, on the basis of additive contribution and correcting functions, give more reliable results as compared to two of the best available predictive methods.

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1. Introduction

Due to non-ideal behaviors of energetic materials and unavailability of experimental thermophysical data for many of energetic materials, it is important to develop reliable predictive methods to eliminate poor candidates from further consideration. However, suitable predictive methods are essential before expensive and often hazardous synthesis and testing processes of new high energy materials. For safe handling, storage and process design of a new energetic material, it is essential to have thermochemical properties. Different methods have been developed to predict thermodynamic and physical properties of energetic compounds as well as their sensitivity with respect to different stimuli [1–7].

Thermal analysis of energetic compounds reveals that they can start to decompose at certain temperature. Their exothermic chemical reaction overcomes the ability of the explosive charge to dissipate the applied heat [8]. Decomposition initiates usually above or during the melting process. However, energetic materials

with higher melting points have high thermal stability. For example, the introduction of the amino groups in nitroaromatics can raise their melting points and thermal stabilities [9,10]. For polynitroaromatics, large molecular masses and better molecular symmetries are also responsible for high melting point and favorable thermal stability [10]. Furthermore, it was found that decomposition of polynitroaromatics is more rapid in molten phase [11].

Enthalpy of fusion ($\Delta_{fus}H$), which is defined as the enthalpy change in the transition from the most stable form of solid to liquid state of high energy compounds. It can be related to the entropy of fusion ($\Delta_{fus}S$) and the fusion temperature (T_{fus}), i.e. $\Delta_{fus}H = T_{fus}\Delta_{fus}S$. Zeman and coworkers [12–15] were stabilized some relationships between $\Delta_{fus}H$ and impact sensitivity as well as electric spark sensitivity of nitramines and polynitro compounds. Differential scanning calorimetry (DSC) can be used for measuring $\Delta_{fus}H$ of explosive materials [16]. For some of the explosives, which can be decomposed in solid phase, $\Delta_{fus}H$ should be predicted. Moreover, prediction of $\Delta_{fus}H$ creates a better insight about the intermolecular interactions and sensitivity of energetic molecules, which have not been synthesized yet.

Quantitative structure–property relationships (QSPR) [17], quantum mechanics [18], group contribution method [19,20],

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List of symbols

$\Delta_{fus}H$	Enthalpy of fusion (kJ mol^{-1})
$(\Delta_{fus}H)_{add}$	Additive contribution of the enthalpy of fusion (kJ mol^{-1})
$(\Delta_{fus}H)_{non-add}^{inc}$	Non-additive contribution of the increasing parameters in enthalpy of fusion (kJ mol^{-1})
$(\Delta_{fus}H)_{non-add}^{dec}$	Non-additive contribution of the decreasing parameters in enthalpy of fusion (kJ mol^{-1})
$\Delta_{fus}S$	Entropy of fusion (kJ mol^{-1})
T_{fus}	Fusion temperature (K)
n_C	Number of carbon atoms
n_H	Number of hydrogen atoms
n_N	Number of nitrogen atoms
$n_{O(S)}$	Number of oxygen (or sulfur) atoms
n_{hal}	Number of halogen atoms

artificial neural network [21] and simple correlations on the basis of molecular structures [22–27] are suitable methods for predicting $\Delta_{fus}H$. QSPR methods require special computer codes and their training set should contain large number of compounds with different molecular structures to obtain suitable results for the compounds with similar molecular structure in test set. Moreover, they are based on complex molecular descriptors, which are difficult to understand and interpret their effects. They were often used to predict thermodynamic properties of particular chemical families of compounds [28]. The group contribution methods have also been developed to predict the values of $\Delta_{fus}H$ for different types of organic compounds [29–33]. They may give large deviations in $\Delta_{fus}H$ for some organic energetic compounds [17,34]. For several energetic compounds, quantum mechanical methods have been used to study their phase change properties [18,35,36]. These methods require high speed computers and specific computer codes. Some simple methods have also been developed on the basis of molecular structures for prediction of the values of $\Delta_{fus}H$ for some classes of energetic compounds [22–26]. Since these correlations are restricted to certain classes of energetic compounds, application of certain correlation belong to one class of energetic compounds to the other classes may lead to large deviations. The purpose of this work is to improve previous correlations [22–26] in order to introduce a general and simple approach for prediction of the values of $\Delta_{fus}H$ in large classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester, nitroaliphatic, cyclic and acyclic peroxides as well as nitrogen rich compounds. It will be shown that the new method is based on elemental composition and two correcting functions as increasing and decreasing contribution terms. The values of correcting functions depend on attractions and repulsions resulting from different molecular moieties. This method can also be applied to halogenated energetic materials as well as energetic materials containing complex molecular structures.

2. Materials and method

2.1. Additive contribution of elements

There are a large variety of steric, inter- and intra-molecular interactions due to the contribution of dipole moment, polarizability, hydrogen bond donor and acceptors. There are some additive and non-additive constitutive properties for T_{fus} [37–41] and $\Delta_{fus}S$ [42] of energetic compounds. For some classes of the energetic

compounds with the general formula $C_aH_bN_c(O \text{ or } S)_d(\text{halogen})_e$, it was shown that the elemental composition can be used as an essential parameter for prediction of their $\Delta_{fus}H$ [22,27]. The study of $\Delta_{fus}H$ for the other classes of energetic compounds, including cyclic and acyclic peroxides and nitrogen rich compounds as well as energetic compounds containing complex molecular structures and simultaneously multiple different energetic bonds such as N–NO₂ and C–NO₂, has shown that the contribution of elemental composition is also important for these compounds. However, previous model has been extended for large classes of energetic compounds where their experimental data for 194 energetic compounds (corresponding to 233 experimental data) are given in Table 1. Molecular structures of these compounds are also given in Table S.1 as supporting information. The additive contribution of elemental composition in $\Delta_{fus}H$ can be derived on the basis of experimental data using multiple linear regression as:

$$(\Delta_{fus}H)_{add} = 0.6047 n_C + 0.6211 n_H + 2.750 n_N + 1.424 n_{O(S)} + 3.048 n_{hal} \quad (1)$$

where $(\Delta_{fus}H)_{add}$ is the additive contribution of elemental composition in kJ mol^{-1} ; n_C , n_H , n_N , $n_{O(S)}$ and n_{hal} are the number of carbon, hydrogen, nitrogen, oxygen (or sulfur) and halogen atoms, respectively. As indicated in Eq. (1), all coefficients of elemental composition have positive sign, which confirms positive contribution of elemental composition.

2.2. Non-additive contribution

With respect to the existence of some specific polar groups and molecular fragments, some non-additive corrections can be used to adjust the predicted $(\Delta_{fus}H)_{add}$. Based on additive and non-additive contributions, using multiple linear regression, the optimized correlation is given as Eq. (2):

$$\Delta_{fus}H = 0.9781 (\Delta_{fus}H)_{add} + 7.567 (\Delta_{fus}H)_{Non-add}^{Inc} - 8.784 (\Delta_{fus}H)_{Non-add}^{Dec} \quad (2)$$

where $(\Delta_{fus}H)_{Non-add}^{Inc}$ and $(\Delta_{fus}H)_{Non-add}^{Dec}$ are non-additive contributions for increasing and decreasing effects of specific groups on $\Delta_{fus}H$.

3. Results and discussion

The values of $\Delta_{fus}H$ are affected by intermolecular interactions, for example, the values of $\Delta_{fus}H$ of benzene, aniline, and phenol are 9.87, 10.54, 11.51 kJ mol^{-1} , respectively [43] which means that adding the polar groups to a molecule, increase its $\Delta_{fus}H$. As another example, the values of $\Delta_{fus}H$ of 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline are 16.11, 23.68, 21.09 kJ mol^{-1} , respectively [43] which shows that intramolecular hydrogen bonding in 2-nitroaniline is responsible of its lower $\Delta_{fus}H$. As a general rule, intermolecular attractions of a molecule with its neighboring molecules will be increased by the presence of polar groups. In contrast, intramolecular attractions will be decreased in the presence of intramolecular hydrogen bonding. However, the existence of polar groups, such as –OH, –COOH, –NH₂, and intramolecular attractions in $\Delta_{fus}H$ can be contributed as non-additive terms. Table 2 contains some functional groups and molecular fragments, which can be used to determine the values of $(\Delta_{fus}H)_{Non-add}^{Inc}$ and $(\Delta_{fus}H)_{Non-add}^{Dec}$.

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