

Simple approach for predicting the heats of formation of high nitrogen content materials



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ABSTRACT

Heat of formation is an important thermochemical parameter, which determines the combustion and detonation performances of energetic materials and nitrogen-rich compounds can be considered as high-performance energetic materials. A novel method is introduced to predict the heats of formation of high-nitrogen content materials ($N > 50\%$) including different derivatives of triazole, tetrazole, triazine, tetrazine, furazan, and some of organic nitrogen-containing chains. It is based on elemental composition and some of the molecular moieties, such as azido, azo, azoxy, guanidino, carbonyl, hydroxide and amino groups. High reliability of the new model has been proved in comparison with two recent quantitative structure-property relationships (QSPR) and group additivity methods as well as different quantum mechanical approaches. For 96 high nitrogen content compounds, the values of standard deviation (SD) are 61.6, 131.1 and 110.1 kJ/mol for the new method, QSPR method and group additivity method. The values of SD are 92.8 and 103.3 kJ/mol for the new and quantum mechanical methods, respectively, where the calculated data of different quantum mechanical approaches were available.

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1. Introduction

Common organic explosives contain nitro groups and have heat of formation (HOF) of approximately zero. Thus, the energy released during their detonation process is mainly derived from the oxidation reaction between oxygen atom of nitro group and fuel atoms to water and oxides of carbon [1]. Due to the negative oxygen balance in common high explosives, significant amounts of solid carbon and unoxidized organic species produced during their detonation. Nitrogen-rich compounds, on the other hand, liberate their energy content due to their high positive HOFs rather than oxidation of the carbon backbone [2]. Their high HOFs stem from the presence of N–N, N–C, and N=C bonds. Nitrogen atoms in N–N and N=C bonds have non-bonding electrons in their p-orbitals which creates electrostatic repulsion between adjacent atoms, while in N=C, non-bonding electrons are tied up in stable pi bonds [3]. Since the average energies of N–N (160 kJ/mol) and N=C (418 kJ/mol) bonds are very lower than N=C (954 kJ/mol), such transformations are accompanied by enormous energy release [4,5]. The main detonation product of high nitrogen content

materials is N_2 gas and the limited amounts of C and H atoms convert to methane, especially in lack of oxygen atoms. Thus, detonation products are generally low-molecular weight gases and detonation process is clean [1,6,7]. Higher densities and good oxygen balance are further advantages of high-N materials because they have low values of carbon and hydrogen [2,8].

Nitrogen content of common high explosives is up to 38% (in RDX, HMX, and CI-20), while some derivatives of triazole, tetrazole, triazine, tetrazine, furazan, and organic nitrogen-containing chains have up to 88% nitrogen in their structure. Klapötke [9] has defined high-N materials as those with more than 50% W/W nitrogen in their molecular structure. These materials are suitable candidates for insensitive high explosives [4], gun propellants [10–12], and clean gas generators in vehicle airbags [6,13].

Since HOF involves the interactions between valence electrons and the nuclei [14], it defines the energy content of a molecule [15]. HOF has also been used in affording data for the study of chemical characteristics and performance of energetic materials such as heat of detonation, detonation temperature, velocity of detonation, detonation pressure, and the strength of energetic materials [16–18]. Calorimetry is used to determine the experimental HOF values of energetic compounds. It is an exacting but time-consuming and destructive technique. Moreover, in order to obtain reliable results, it is essential to provide extremely pure

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List of symbols

<i>a</i>	the number of carbon atoms
<i>b</i>	the number of hydrogen atoms
<i>c</i>	the number of nitrogen atoms
<i>d</i>	the number of oxygen atoms
<i>IF</i>	increasing factor
<i>DF</i>	decreasing factor
ΣIF	sum of the increasing factors in each molecule
ΣDF	sum of the decreasing factors in each molecule
$\Delta_f H^\circ$ (or HOF)	the condensed phase heat of formation (kJ/mol)
AARD%	average absolute relative deviation
AD	average deviation (kJ/mol)
AD _{max}	absolute maximum deviation
R ²	coefficient of determinations
SD	standard deviation of model (kJ/mol)
sd	standard deviation of each individual coefficient (in different units)

samples in large quantities. So the difficulty of purification of unstable, unknown, and hazardous samples is a further limitation [19,20].

Different computational methods have been used to predict HOF of energetic compounds in gas or condensed phase. Due to the presence of different molecular interactions, molecular packing, and polymorphism in some solid compounds, prediction of the condensed phase HOF is more difficult than gas phase HOF [21]. However, the condensed phase HOF of common CHNO energetic materials has been determined by several group additivity [21–23], quantum mechanics [24–26], and quantitative structure-property relationships (QSPR) [27,28] methods. Since quantum mechanical calculations need intensive computations, they can only be used for relatively small molecules [29,30]. Additivity schemes have been developed on the basis of a large number of compounds for the desired property. Unlike quantum methods, group additivity methods do not need computational costs but they cannot be used for the compounds containing unusual chemical structures [31]. For example, Argoub et al. [21] recently used a relatively complete database (contains 1222 experimental values) for constructing the group additivity model of the prediction of condensed phase HOF of organic compounds but still there is no group value for azoxy group.

QSPR models relate the desired physical, chemical, and analytical properties of molecules to their structures through different molecular descriptors [32]. Descriptors may be experimental properties or computed parameters on the basis of molecular

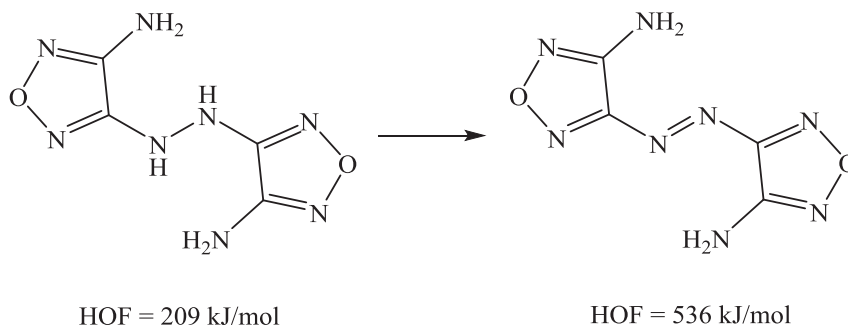
structure [33]. Multiple linear regression (MLR), non-linear regression (NLR), partial least squares (PLS), artificial neural network (ANN), genetic algorithm (GA), support vector machine (SVM) are some examples of multivariate statistical tools used to derive mathematical equations or algorithms between property and descriptors [32,34]. It was shown that molecular fragments can also be used to predict the heats of formation of different classes of energetic materials [28].

The purpose of this work is to introduce a new model for predicting HOF of high-nitrogen content energetic materials, *i.e.* triazoles, tetrazoles, triazines, tetrazines, furazans, and some organic chains with more than 50% nitrogen. The present model is based on the number of C, H, N, and O atoms and two correcting factors, which affect the energy content of molecule. It will be shown that application of the new correlation for different complex high nitrogen molecules is straightforward and very simple. For several CHNO high-N energetic compounds, the predicted results will be compared with the calculated results of two new simple models. Further assessment of the new model will be done by comparing its results with different complex quantum mechanical methods.

2. Development of the new model

The contribution of the number of carbon, hydrogen, nitrogen, and oxygen atoms is important in predicting different properties of energetic materials such as detonation velocity [35,36], detonation pressure [37], strength of energetic materials [31], heats of formation [28], heats of sublimation [38], and entropy of melting [39]. Moreover, some molecular fragments have significant effects on the condensed phase HOFs of different molecules. For example, Yang et al. [40] have shown that $-\text{NH}_2$, $-\text{NO}_2$ groups decrease the HOF of N, N'-azobis(1, 2, 4-triazole) derivatives but $-\text{N}_3$ group increase it. Haiges et al. [41] have also mentioned that the $-\text{N}_3$ group adds 292 kJ/mol to the energy content of molecules. Furthermore, Zhu et al. [42] have been proved that $-\text{N}_3$ group and azo bridge ($-\text{N}=\text{N}-$) increase the HOF of di-tetrazole derivatives. The effect of azo bridge on HOF of molecules has been displayed in Scheme 1, where the HOF of 4,4'-hydrazobis-(1,2,5-oxadiazol-3-amine) is 209 kJ/mol and the HOF of 4,4'-azobis(1,2,5-oxadiazol-3-amine) is 536 kJ/mol. Thus, an increase of 327 kJ/mol in the HOF has been occurred due to substituting the $-\text{NH}-\text{NH}-$ fragment with $-\text{N}=\text{N}-$ group. Xiao-hong et al. [43] have investigated HOF and the detonation properties of furazan-based energetic materials through quantum mechanical methods and showed that azo and azoxy groups ($-\text{N}=\text{N}^+\text{O}^-$) can increase their HOF.

Most high-N energetic materials are derivatives of five or six membered cyclic or nitrogen-containing chains. They have a variety of molecular fragments, *e.g.* $-\text{NH}_2$, $-\text{NO}_2$, $-\text{N}_3$, $-\text{C}\equiv\text{N}$, $\text{N}=\text{N}-$, $-\text{C}=\text{N}-$, $-\text{N}=\text{N}^+\text{O}^-$, *etc.* The study of experimental values of HOF



Scheme 1. Increasing the HOF by introducing the azo group [44].

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