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Prediction of heats of sublimation of nitroaromatic compounds via their molecular structure

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Abstract

This work presents a new approach to predict heats of sublimation of nitroaromatic compounds derived from their molecular structure information. The number of carbon, hydrogen and nitrogen atoms as well as the contribution of some specific groups attached to aromatic ring would be needed in the new method. Predicted heats of sublimation for 40 nitroaromatic compounds are compared with experimental data. Calculated results for some nitroaromatic compounds are also compared with complicated quantum mechanical computations of Rice et al. [B. M. Rice, S. V. Pai, J. Hare, Combust. Flame 118 (1999) 445] where computed outputs were available. The root mean square deviation (rms) from experiment for the predicted heats of sublimation of 40 compounds by new method is 7.78 kJ/mol with a maximum deviation of 18.52 kJ/mol. The rms deviations of new procedure and reported quantum mechanical method for six nitroaromatic compounds are 9.19 and 10.18 kJ/mol, respectively.

Keywords: Heats of sublimation; Nitroaromatic compounds; Correlation; Structural parameters

1. Introduction

In an effort to predict various properties of a notional energetic material with the best use of limited resources and to minimize the waste ensuing from experimental measurements, different theoretical approaches have been developed to aid in the formulation of propellants and explosives [1,2]. A long-sought-after goal within the energetic materials community has been to develop capabilities for predicting performance, sensitivity, physical and thermodynamic properties of a new energetic compound before expending resources in its synthesis. Furthermore, different theoretical models can allow experimental researches to expend resources only on those molecules that show promise of enhanced performance, reduced sensitivity or reduced environmental hazard, good physical and thermodynamic properties. For example, sensitivity [3–7], melting point [8,9] and heat of detonation [10–12] of selected class of energetic compounds can be determined by some new methods.

Condensed phase heat of formation is usually the desired quantity for assessment of the energetic material of interest. It can be determined by using the gas phase heat of formation and heat of phase transition (either sublimation or vaporization) according to Hess' law of constant heat summation [13]:

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub} \quad (1)$$

$$\Delta H_f(l) = \Delta H_f(g) - \Delta H_{vap} \quad (2)$$

Since condensed phase for most energetic compounds is solid, Eq. (1) can be used to evaluate their solid phase heats of formation. Quantum mechanical computations can be used to predict heats of sublimation of energetic compounds [14–16]. Heat of sublimation is best obtained from solid vapor pressure data by using Clausius-Clapeyron equation [17]. Since the sublimation pressure at the melting point is known with accuracy for only a few cases, it can be calculated from a liquid vapor pressure correlation by extrapolating to melting point [17]. Goodman et al. [18] have recently found that a group-contribution method can be used to estimate heat of sublimation at triple point for organic solids. The purpose of this work is to present a new simple scheme to predict heats of sublimation of nitroaromatic compounds as an important class of energetic compounds. This work assumes that heat of sublimation of a nitoaromatic energetic compound with composition $C_aH_bN_cO_d$ can be determined from the elemental composition

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and some structural parameters. The results will be compared with experimental data and some of reported results of complicated quantum mechanical method [15]. It will be shown that results predicted by this simple method are comparable with outputs from complicated quantum mechanical computations and the accuracy is not necessarily enhanced by greater complexity.

2. Theory

2.1. Gas phase heat of formation

To evaluate solid phase heat of formation from Eq. (1) using theoretical prediction alone, different methods can be used. Quantum mechanical and group-contribution methods are two usual procedures for calculating gas phase heats of formation of various compounds. The semi-empirical molecular orbital methods such as PM3, MNDO, MNDO/3, AM1 and molecular mechanics MM2 can be used to estimate gas phase heat of formation for different energetic compounds. For example, Akutsu et al. [19] combined heats of vaporization and sublimation by additivity rule with gas phase heat of formation from PM3 and MM2 to estimate solid and liquid phase heat of formation of nitramines and alkyl nitrate. A group-contribution method, such as Benson, Yoneda and Joback methods, assumes that properties of molecules can be derived from properties of atoms or functional groups from which they are made [17]. Meanwhile, root mean square (rms) deviation of quantum mechanical computations are less than group-contribution methods but they have special complexity and take much time for the optimization of large molecule system. Two new correlations were recently introduced for desk calculations of gas phase heats of formation of selected class of energetic compounds so that they can provide reliable simple pathways as compared to complex quantum mechanical methods [20,21].

2.2. Heat of sublimation

In contrast to the other methods for prediction of gas phase heat of formation, few methods were used to determine heat of sublimation of energetic compounds. Politzer et al. [14] have established that correlations exist between the electrostatic potential of a molecule and heats of sublimation. The predicted heat of sublimation can be represented by:

$$\Delta H_{\text{sub}} = a(\text{SA})^2 + b\sqrt{\sigma_{\text{Tot}}^2 \nu} + c \tag{3}$$

where SA is the surface area of the 0.001 electron/bohr^3 isosurface of the electron density of the molecule, σ_{Tot}^2 is a measure of the variability of electronic potential on the surface and ν is the degree of balance between the positive and negative charges on the isosurface. The constants a, b and c in Eq. (3) are determined from least-squares fitting to experimental values for the heats of sublimation. They applied this procedure to predict heats of sublimation of 34 organic compounds [14]. Rice et al. [15] applied a procedure proposed by Politzer et al. [14] to calculate heats of sublimation of energetic materials. They used the Gaussian 98 suite of quantum chemistry codes [22] with the 6-31G* basis set [23] and the hybrid B3LYP [24,25] density functional to determine heats of formation and detonation of energetic compounds. Byrd and Rice [16] have also improved an earlier effort of Rice et al. through the use of a larger basis set and the application of group equivalents. They have modified the work of Rice et al. [15] in the prediction of gas, liquid, and solid heat of formation by using quantum mechanical data through the incorporation of group additivity and the use of the more complicated 6-311++G(2df, 2p) basis set. Zeman and Krupka [26] have also found some relationships between heats of sublimation of some polynitro compounds and lattice energies.

3. Results and discussion

Thermo-physical properties of polyfunctional compounds are influenced by different molecular interactions. Magnitude, number, distances and orientation of group dipoles within a molecule are directly connected with the size of a molecule, its conformation, symmetry and with the quantity of the constituents present [27].

The study of heats of sublimation for various nitroaromatic compounds has shown that it is possible to find a new correlation for predicting heats of sublimation. To establish a new correlation, experimental data of various nitroaromatic compounds were taken from literature. For $C_aH_bN_cO_d$ nitroaromatic compounds, it was found that elemental composition and the contribution of some specific groups can influence the values of heats of sublimation. The collected data are listed in Tables 1 and 2

. The study shows that the following general equation with some adjustable coefficients is suitable for this purpose:

$$\Delta H_{\text{sub}}\,(\text{kJ/mol}) = x_1 + x_2 a + x_3 b + x_4 c + x_5 C_{\text{SG}} \tag{4}$$

where x_1 to x_5 are adjustable parameters; a, b, c are the number of carbon, hydrogen and nitrogen atoms, respectively; C_{SG} is the contribution of specific polar groups attached to aromatic ring. Experimental data given in Table 1 were used to optimize the values of x_1–x_5. Multiple linear regression method [28] was used to find adjustable parameters. The left-division method for solving linear equations uses the least-squares method because the equation set is overdetermined [28]. The results give the following optimized correlation:

$$\Delta H_{\text{sub}}\,(\text{kJ/mol}) = 64.51 + 4.555a - 2.763b + 10.32c + 16.51C_{\text{SG}} \tag{5}$$

Different values of C_{SG} for various polar groups attached to nitroaromatic ring were studied and optimized with experimental data. As seen in Eq. (5), coefficient of C_{SG} has a positive sign. This confirms that the existence of some specific polar groups can influence the values of heat of sublimation. Moreover, it was found that the effects of carboxylic acid functional group or two hydroxyl groups on predicted heats of sublimation are higher than the other specific groups. The value of C_{SG} can be determined as follows: