



Prediction of the condensed phase heat of formation of energetic compounds

Mohammad Hossein Keshavarz*

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

ARTICLE INFO

Article history:

Received 27 November 2010
Received in revised form 1 January 2011
Accepted 14 March 2011
Available online 21 March 2011

Keywords:

Heat of formation
Condensed phase
Energetic compound
Molecular structure
Safety

ABSTRACT

A new reliable simple model is presented for estimating the condensed phase heat of formation of important classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds. For CHNO energetic compounds, elemental compositions as well as increasing and decreasing energy content parameters are used in the new method. The novel correlation is tested for 192 organic compounds containing complex molecular structures with at least one nitro, nitramine or nitrate energetic functional groups. This work improves the predictive ability of previous empirical correlations for a wide range of energetic compounds. For those energetic compounds where group additivity method can be applied and outputs of quantum mechanical computations were available, it is shown that the root mean square (rms) deviation of the new method is lower.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The condensed phase heat of formation of an energetic compound can be used to investigate its characteristics and thermochemical stability. It enters into the calculation of explosive and propellant properties such as detonation pressure, detonation pressure, detonation temperature, heat of detonation and specific impulse through computer codes or empirical methods [1–3].

Quantum mechanical methods, quantitative structure–property relationship (QSPR) theory, group additivity methods, empirical procedures on the basis of molecular structures, the heat of combustion are suitable methods for predicting the heat of formation of energetic compounds [2,4,5]. Applications of some of these methods in energetic materials have been reviewed elsewhere [2,5]. The condensed phase heats of formation of solid and liquid energetic compounds at 298.15 K can be obtained by combining the gas phase heats of formation with heats of sublimation and vaporization, respectively. Rice et al. [6,7] have used the 6–31G* basis set [8] and the hybrid B3LYP [9,10] density functional for converting quantum mechanical energies of molecules into gas phase heats of formation. They used surface electrostatic potentials of individual molecules for computation of heats of sublimation and vaporization as recommended by Politzer and co-workers [11,12]. Salmon and Dalmazzone [13] developed a suitable group contribution method that can be applied for large classes of CHNO energetic compounds in the solid state (at 298.15 K). Applications of their method have

some restrictions for complex molecular structures such as the definition of many group additivity values, ring strain corrections and the non-nearest neighbor interactions. For some classes of energetic compounds, several simple correlations between different structural parameters have also been developed [14–18]. As an example, it was found that heats of detonation on the basis of Kamlet's method [19] can also be used for predicting solid phase heats of formation of some explosives in the range $Q_{\text{corr}} > 4602$ kJ/g [14], where Q_{corr} is the corrected heats of detonation on the basis of Kamlet's method [19].

It is important to have a reliable simple method for predicting the condensed phase heat of formation of a wide range of organic energetic compounds that contain at least one of the functional groups including $-\text{NO}_2$, $-\text{O}-\text{NO}_2$ or $\text{N}-\text{NO}_2$. The purpose of this work is to improve predictive ability of previous models [14–18], which have been used for certain classes of energetic compounds. The reliability of the new method will be tested for important classes of energetic compounds including polynitro arene, polynitro heteroarene, acyclic and cyclic nitramine, nitrate ester and nitroaliphatic compounds. The estimated results of this method will be compared with the calculated values of group additivity method of Salmon and Dalmazzone [13] as well as outputs of complex quantum mechanical method [6,7].

2. Results and discussion

Since the existence of the variety of different molecular interactions in the condensed phase of energetic compounds, predicting the heat of formation may be difficult. A high density energetic material with a high positive heat of formation may be a good

* Tel.: +98 0312 522 5071; fax: +98 0312 522 5068.

E-mail addresses: mhkesavarz@mut.ac.ir, keshavarz7@gmail.com

Table 1

Comparison of the predicted heats of formation (kJ/mol) of the present and Salmon–Dalmazzone (S–D) [13] methods with experimental data for polynitro arene, polynitro heteroarene, acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds that have complex and different molecular structures.

No.	Energetic compound	Experiment	New method	Dev	S–D method	Dev
1		–443.4 [27]	(460.8)	17.4	(416.8)	(26.6)
2		(422.6 [27])	(460.8)	38.3	(416.8)	(5.8)
3		(409.7 [27])	(424.3)	14.7	(466.4)	56.7
4		47.3 [27]	55.7	(8.4)	47.8	(0.5)
5		(15.1 [27])	6.3	(21.3)	(9.5)	(5.6)
6		(97.9 [27])	(73.8)	(24.1)	(110.3)	12.4
7		296.6 [27]	296.0	0.6	322.6	(26.0)
8		94.6 [27]	125.6	(31.1)	126.0	(31.4)
9		(114.6 [27])	(135.3)	20.6	(114.3)	(0.3)
10		(432.6 [27])	(428.5)	(4.1)	(455.5)	22.9
11		(398.7 [27])	(432.7)	34.0	(408.1)	9.4
12		(413.8 [27])	(432.7)	18.9	(427.9)	14.1

Download English Version:

<https://daneshyari.com/en/article/578868>

Download Persian Version:

<https://daneshyari.com/article/578868>

[Daneshyari.com](https://daneshyari.com)