

A simple procedure for calculating condensed phase heat of formation of nitroaromatic energetic materials

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Abstract

A simple procedure has been introduced for calculating solid and liquid heats of formation of nitroaromatic energetic compounds. This model assumes that the heat of formation of a nitroaromatic compound of composition $C_aH_bN_cO_d$ can be expressed as a new correlation which depends on elemental composition and various structural and special functional group parameters. Condensed phase heats of formation predicted using the method described herein and complicated quantum mechanical computations [B.M. Rice, J. Hare, *Thermochem. Acta* 384 (2002) 377] have a root mean square (rms) deviation of 5.9 and 11.1 kcal/mol for 19 well-known organic nitroaromatic compounds. Predicted heats of formation for 29 polycyclic nitroaromatic energetic compounds have a rms deviation from experiment of 10.6 kcal/mol. The results show that the present method gives comparable prediction respect to the other methods such as complex quantum mechanical computation.

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1. Introduction

The importance of theoretical methods as prediction tools increases with greater relevance for new energetic materials with a given performance, sensitivity and physical properties. High detonation velocity, reduced vulnerability, low shock and impact sensitivities over those in current use are highly desirable for synthesizing of more powerful energetic compounds. The development of theoretical methods would be needed because they help the chemists to improve systematic and scientific formulation of appropriate futuristic target molecules having enhanced performance as well as good thermal stability, impact and friction sensitivity. It can be inferred that high values of detonation pressure and velocity as two important detonation parameters are promoted by the formation of light gaseous detonation products, a high positive heat of formation and increasing initial density of explosive [1,2]. Thus, heat of formation can affect the amount of released energy upon detonation and a higher detonation temperature [3].

The heat of formation is frequently taken to be indicator of the “energy content” of an energetic compound and in some circumstance it is quite appropriate to do so. It is an important factor to consider in designing new energetic materials or evaluating existing ones and to investigate characteristics of energetic compounds. Group additivity and quantum mechanics methods are two usual procedures for calculating heat of formation. Additivity methods assume that properties of molecules can be derived from properties of atoms or functional groups from which they are made [4]. Some additivity methods such as Benson, Yoneda and Joback are commonly used to estimate ideal gas phase heats of formation for many classes of organic compounds [4]. Quantum mechanical methods can develop new algorithms and techniques together with continuing improvement in computer processing to understand molecular problems with much more reliability. Gas phase heat of formation for various energetic compounds can be estimated from the semi-empirical molecular orbital methods like MNDO, MNDO/3, AM1, PM3 and molecular mechanics MM2. Although quantum mechanical methods can be used to predict gas phase heats of formation, it is important to be able to predict the condensed phase heats of formation. Considerable compensation should be considered when these methods are used to evaluate the thermochemistry of all condensed phase reactions. Yoshiaki et al. [5] combined heats of

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vaporization and sublimation by additivity rule with gas phase heat of formation from PM3 and MM2 to calculate condensed phase heat of formation.

Condensed phase heat of formation is usually needed to evaluate performance of an energetic material by a computer code or empirical methods. Thermochemical codes and empirical methods can provide insight to understanding the molecules which are responsible for higher performance and which are not. An equilibrium complicated thermochemical code such as CHEETAH [6] and equations of state for detonation products can be used to estimate detonation parameters of explosives. Some well-known equations of state are Becker–Kistiakosky–Wilson (BKW) [7], the Jacobs–Cowperthwaite–Zwisler (JCZ) [8,9] and Kihara–Hikita–Tanaka (KHT) [10] that can be used for performance evaluation as library in CHEETAH. Various empirical methods complemented the computer output along with structure-sensitivity relationships of selected class energetic compounds have been recently introduced [1–3,11–19] for desk calculations of factors related to detonation parameters, e.g. detonation velocity, Chapman–Jouguet detonation pressure, etc.

The purpose of this work is to present a new approach for obtaining condensed phase heat of formation of an important class of organic energetic material, namely nitroaromatic compounds. Solid and liquid heats of formation of energetic compounds are the essential parameters of somewhat more practical importance to the explosive user. The major goal of present procedure, apart from being developed as predictive tools, is to provide the simplest procedure for estimating condensed phase heats of formation of organic nitroaromatic energetic compounds. To assess potential performance of an energetic material under idealized gun firing conditions or to predict its detonation properties, the present method can be used simply to estimate its heat of formation as fundamental necessary

parameter. The method will be applied to some well-known explosives and compared against result reported using the thermochemical code CHEETAH 2.0 with the JCZS-EOS library and against quantum mechanical calculations as well as experimental values. Additionally, condensed phase heats of formation of some complicated polycyclic molecular structure nitroaromatic compounds will be compared against experimental values. The present method will be appealing because it requires as input only structural formula of nitroaromatic compounds.

2. Development of new method

Sensitivity, density and heat of formation of an energetic molecule are the most important parameters to screen potential explosives. Suitable energetic materials must combine good performance with low vulnerability so that whose high safety is obtained as the expense of the performance. The performance of a new energetic material can be evaluated prior its actual synthesis. Since well-known group additivity and quantum mechanical methods provide gas phase heat of formation, the solid and liquid phase heats of formation for the systems under consideration can be obtained as the difference between gas phase values and sublimation or vaporization enthalpies.

Rice et al. [20] have developed a computational method to predict heats of formation of energetic materials in the gas, liquid and solid state from quantum mechanical calculations of the isolated molecules. They used the 6-31G* basis set [21] and the hybrid density B3LYP [22,23] density functional for computation of heat of formation. Due to time and computer limitations, they did not perform an extensive search of the global minimum energy conformation for each molecule. The heat of detonation defined as the negative of the enthalpy change of detonation reaction. It shows the energy available to do mechanical work and

Table 1
Comparison of the new method for calculations heats of formation (kcal/mol) with experiment [28], CHEETAH 2.0 [24] and quantum mechanical computation by Rice and Hare [24]

Name	Experiment	CHEETAH	DEV ^a	Quantum mechanical	DEV ^a	New method	DEV ^a
2,2',4,4',6,6'-Hexanitrobiphenyl	16.3	16.3	0.0	-16.2	32.5	9.2	7.1
Benzotrifuroxan	144.9	144.4	0.5	143.9	1.0	139.3	5.6
2-Methoxy-1,3,5-trinitrobenzene	-44.75	-37	-7.8	-44	-0.8	-41.4	-3.4
2,2',4,4',6,6'-Hexanitrostilbene	16.2	17	-0.8	-9.5	25.7	8.6	7.6
2,4,6-Trinitroresorcinol	-111.74	-114.5	2.8	-94.4	-17.3	-105.5	-6.2
2,4,6-Trinitro-1,3,5-benzenetriamine	-17.85	-34.7	16.9	-20.8	3.0	-26.6	8.8
1,2-Dinitrobenzene	-0.4	0.7	-1.1	-3.0	2.6	-4.0	3.6
1,3-Dinitrobenzene	-6.5	-3.1	-3.4	-12.0	5.5	-4.0	-2.5
1,4-Dinitrobenzene	-9.2	-9.1	-0.1	-9.2	0.0	-4.0	-5.2
2,4-Dinitrophenol	-56.29	-55.7	-0.6	-54.7	-1.6	-54.2	-2.1
2,6-Dinitrophenol	-50.105	-49.7	-0.4	-47.8	-2.3	-54.2	4.1
1-Methyl-2,4-dinitrobenzene	-15.87	-14.8	-1.1	-20.3	4.4	-12.4	-3.5
2-Methyl-1,3-dinitrobenzene	-13.199	-11.5	-1.7	-15.3	2.1	-12.4	-0.8
1,3,5-Trimethyl-2,4,6-trinitrobenzene	-29.75	-30.6	0.9	-32.4	2.7	-30.4	0.6
1,3,5-trinitrobenzene	-8.9	-13.9	5.0	-16.4	7.5	-5.2	-3.7
2,4,6-Trinitrophenol	-52.075	-52.8	0.7	-54.2	2.1	-55.3	3.3
2,4,6-Trinitroaniline	-17.4	-23.7	6.3	-21.3	3.9	-12.3	-5.1
2,4,6-Trinitrotoluene	-15.1	-15.1	0.0	-20.9	5.8	-13.6	-1.5
N-methyl-N-2,4,6-tetranitroaniline	9.8	1.7	8.1	-1.7	11.5	-6.3	16.1
rms deviation			5.1		11.1		5.9

^a Difference (in kcal/mol) between experimental and mentioned values.

Table 2
Comparison of new method for calculations heats of formation (kcal/mol) with experiment [28]

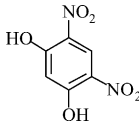
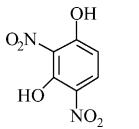
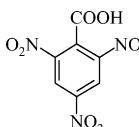
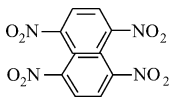
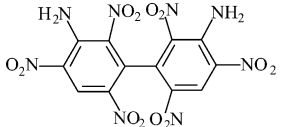
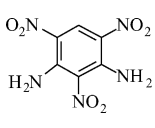
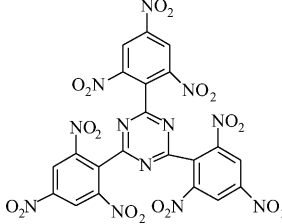
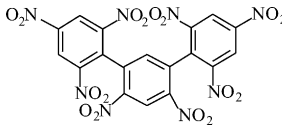
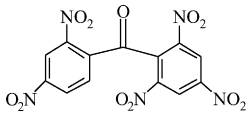
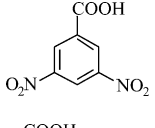
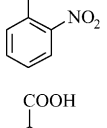
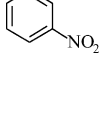
Energetic compound	Experiment	New method	DEV ^a
	-105.98	-104.4	-1.6
	-101	-104.4	3.4
	-97.91	-101.3	3.4
	11.3	12.0	-0.7
	-3.6	-5.2	1.6
	-23.4	-19.5	-3.9
	70.9	91.7	-20.8
	22.6	24.6	-2.0
	-27.4	-9.7	-17.7
	-103.4	-100.1	-3.3
	-95.3	-99.0	3.7
	-98.9	-99.0	0.1

Table 2 (Continued)

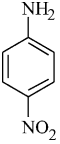
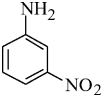

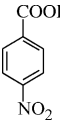
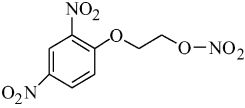
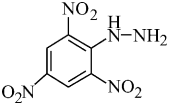
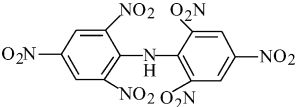
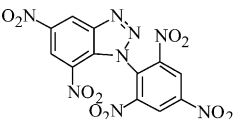
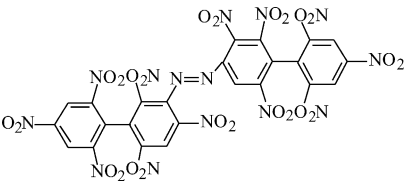
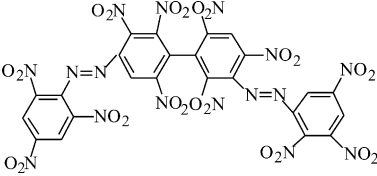
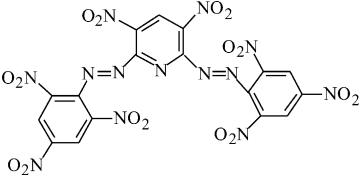
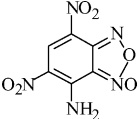
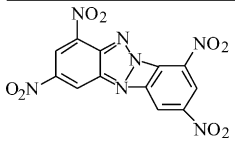
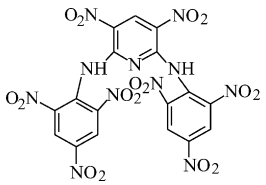
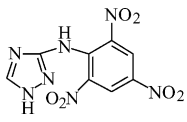
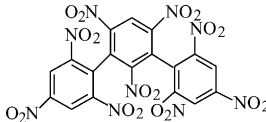
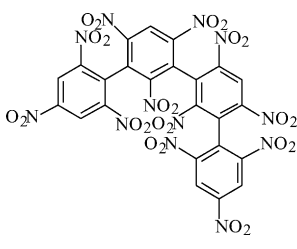
Energetic compound	Experiment	New method	DEV ^a
	-10.9	-10.0	-0.9
	-8.7	-10.0	1.3
	-6.3	-10.0	3.7
	-102.1	-99.0	-3.1
	-71.41	-77.6	6.2
	8.73	11.6	-2.9
	10.65	2.0	8.6
	71.7	68.0	3.7
	114.8	99.9	14.9
	189.2	161.9	27.3
	147.5	165.6	-18.1
	20.63	35.8	-15.2

Table 2 (Continued)

Energetic compound	Experiment	New method	DEV ^a
	110.2	93.8	16.4
	19.2	27.1	-7.9
	36.2	48.0	-11.8
	31.6	23.5	8.1
	59.0	37.8	13.2
rms deviation			10.6

^a Difference (in kcal/mol) between experimental and mentioned values.


has been used to estimate potential damage to surroundings. Rice and Hare [24] have also described the use of quantum mechanical predictions of heat of formation of solid explosives in calculating their heats of detonation. A new correlation has been recently introduced between the corrected heat of detonation of Kamlet's and Jacobs method [25], Q_{corr} , and approximate detonation temperature [26]. This method is complex for user and can be applied for some explosives in the range $Q_{\text{corr}} > 1100$ [26].

The study of condensed phase heats of formation for various nitroaromatic organic compounds show that elemental composition as well as some special structural specifications and functional groups can affect their values. As a first attempt to express condensed phase heat of formation of $C_aH_bN_cO_d$ energetic nitroaromatic compounds as a function of mentioned parameters, the results show that the following general equation with eleven adjustable coefficients is suitable for most nitroaromatic and benzofuroxans energetic compounds:

$$\begin{aligned} \Delta H_f(c) = & x_1a + x_2b + x_3c + x_4d + x_5n_{\text{NO}_2} + x_6n_{\text{Ar-NH}} \\ & + x_7n_{\text{OH}} + x_8n_{\text{COOH}} + x_9(n_{\text{Ar}} - 1) \\ & + x_{10}n_{-\text{N}=\text{N}-} + x_{11}n_{\text{cyclo-N-O-N}} \end{aligned} \quad (1)$$

where n_{NO_2} , n_{OH} and n_{COOH} are the number of specified functional groups, $n_{\text{Ar-NH}}$ the number of NH (or NH_2) functional

groups attached to aromatic rings, $\Delta H_f(c)$ the condensed phase heat of formation, x_1-x_{11} the adjustable parameters, n_{Ar} the number of aromatic rings, $n_{-\text{N}=\text{N}-}$ the number of non-cyclic groups

and $n_{\text{cyclo-N-O-N}}$ is the number of  (in the case of benzofuroxans) groups. The method of Kamlet and Hurwitz [27] were used for determining the parameters of Eq. (1) so that data given in Tables 1 and 2 were used to optimize the values of x_1-x_{11} . The results give the following optimised correlation:

$$\begin{aligned} \Delta H_f(c) \left(\frac{\text{kcal}}{\text{mol}} \right) = & 7.829a - 8.117b + 16.52c - 27.80d \\ & + 29.82n_{\text{NO}_2} - 15.56n_{\text{Ar-NH}} - 22.38n_{\text{OH}} \\ & - 48.34n_{\text{COOH}} + 3.241(n_{\text{Ar}} - 1) \\ & + 29.02n_{-\text{N}=\text{N}-} + 53.34n_{\text{cyclo-N-O-N}} \end{aligned} \quad (2)$$

To demonstrate the present method and test the validity of the correlation, the heat of formation of 47 nitroaromatic energetic compounds are calculated. Predicted condensed phase heats of formation for some of them using the present method and values contained in the CHEETAH library as well as reported quantum mechanical computation by Rice and Hare [24] are given in

Table 1. As indicated in Table 1, the results are in good agreement with values obtained from mentioned methods. The root mean square (rms) deviation of the new method from experiment is 5.9 kcal/mol, but the rms deviation of the values in the CHEETAH reactant library and the quantum mechanical prediction by Rice and Hare [24] from experiment are 5.1 and 11.1 kcal/mol, respectively. Since the CHEETAH values represent commonly accepted values in literature [6], the better agreement of them is not surprising. Table 2 provides a comparison between calculated condensed heat of formation of some polycyclic nitroaromatic compounds and experimental values so that the rms deviation of the new method from experiment is 10.6 kcal/mol. Since in some cases large differences exist between reported values from different sources in Tables 1 and 2, e.g. -111.74 , -103.5 and -129.76 are several different reported experimental data for styphnic acid [28], the latest reported values of the NIST Chemistry Web Book [28] were taken for comparison the mentioned method with experimental data.

The average deviations in Table 1 for CHEETAH, quantum mechanical and new approach are 3.1, 7.0 and 4.8 kcal/mol, respectively. The estimated heat of formation by this new approach is within 5 kcal/mol of the reported values for 11 explosive compounds, within 5–10 kcal/mol for 7 explosive compounds, and more than 10 kcal/mol for remainder 1 explosive compounds. The second series of energetic compounds that are listed in Table 2 consist of 29 nitroaromatic compounds which have the average deviation 7.8 kcal/mol. Of the estimated heats of formation, 55% are within 5 kcal/mol and 14% are within 5–10 kcal/mol of reported heats of formation.

One of the important conclusions regarding the applicability of the new approach to the heats of formation estimation is that the results are very promising. A total 48 mono-, bi- and polycyclic anitroaromatic were considered in the new approach, and 56.2% of the estimated heats of formation were within 5 kcal/mol of the experimental heats of formation, 22.9% were within 5–10 kcal/mol, 16.7% were within 10–20 kcal/mol, 4.2% were more than 20 kcal/mol different from reported heats of formation.

The most challenging immediate problem for explosive chemists is to develop explosives with higher performance than HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine). The compound 2,4,6-trinitro-1,3,5-triazine [29,30], the cyclic trimer nitryl cyanide $(\text{NO}_2\text{CN})_3$, is a high-energy material with high density so that there is no method reported for its synthesis [30]. It is calculated heat of formation by theoretical method [30] is 46 kcal/mol which is close to 45.3 kcal/mol predicted by Eq. (2).

Taking into account geometrical complexities of the polycyclic nitroaromatic energetic compounds, it is found that the overall agreement of the new approach with reported heat of formation is quite good.

3. Conclusions

A new methodology has been developed for simple prediction of heats of formation of nitroaromatic energetic compounds.

Predicted condensed heats of formation for nitroaromatic compounds are comparable with the other complicated procedures. Comparison of calculated results with experimental data listed in Tables 1 and 2 may be taken as appropriate validation of the new procedure for use with nitroaromatic $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$ compounds. The molecular structure of nitroaromatic energetic compounds is only important parameter that would be needed in the novel method. The introduced correlation represents a significant advance in a priori estimation of condensed heats of formation for nitroaromatic energetic compounds. Since the condensed heat of formation of nitroaromatic explosive is readily calculated by a desk calculator of the same reliability as one could expect from a more complex quantum mechanical methods, the results of this work are appealing to chemist. The new approach gives the simplest and easiest pathway for calculation condensed heat of formation of nitroaromatic compounds. This reliable method confirms that the accuracy is not necessarily enhanced by greater complexity.

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