

Heats of sublimation of nitramines based on simple parameters

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Abstract

In this work, a simple procedure is introduced to determine heats of sublimation of nitramines as an important class of explosives. Molecular weight and one structural parameter of nitramines would be needed in the new method. Calculated heats of sublimation for well-known explosives such as HMX [1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane], RDX [1,3,5-trinitro-1,3,5-triazacyclohexane] and TETRYL [1-(methylnitramino)-2,4,6-trinitrobenzene] as well as new nitramines CL-20 [2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane] and TNAZ [1,3,3-trinitroazetidene] show good agreement with experimental data. R-squared value or the coefficient of determination of new correlation is 0.945. The root-mean-square deviation (RMS) from experiment for the predicted heats of sublimation by new method is 10.10 kJ/mol.

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1. Introduction

Significant efforts have been directed toward development of empirical and theoretical models that will predict various important properties of an energetic material [1,2]. Different models and computer codes will allow an estimate of potential performance or possible hazard for an explosive. To assess potential performance in a weapon system, detonation velocities and pressures at maximum nominal density [3,4] can be determined by simple methods. Physical and thermochemical properties of some classes of CHNO energetic compounds such as melting point [5,6] and gas phase heat of formation [7,8] can also be predicted through elemental composition and molecular structure. Since condensed phase heat of formation is usually needed to determine assessment of the energetic material of interest by computer codes such as CHEETAH [9], it can be determined using the gas phase heat of formation and heat of phase transition (either sublimation or vaporization) according to Hess' law of constant heat summation [10]. However, heat of sublimation is an important parameter to evaluate solid phase heat of formation so that it can be determined by quantum mechanical computations [11–13].

This work provides a new simple scheme to predict heats of sublimation of nitramines. It will be shown that how heat of sublimation of a nitramine energetic compound can be correlated with the molecular weight and one structural parameter. The results for some well-known nitramine explosives such as RDX and HMX as well as new important explosives such as CL-20 will be compared with experimental data.

2. Theory

It is important to predict the condensed phase heats of formation because for assessment of potential performance of the energetic material of interest, however, it would be the desired quantity. To find the condensed phase heat of formation of energetic compounds, the gas phase heat of formation can be combined with heat of sublimation according to Hess' law of constant heat summation [10]:

$$\Delta H_{f,\text{solid}} = \Delta H_{f,\text{gas}} - \Delta H_{\text{sub}} \quad (1)$$

2.1. Gas phase heat of formation

Gas phase heat of formation can be determined by quantum mechanical computations [1,11–13], group-contribution methods [14] and simple theoretical models [7,8].

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2.1.1. Quantum mechanical computations

The development of new algorithms and techniques together with the continuing improvement in computers processing speed has meant that quantum mechanical technique can be applied to understand molecular problems. The semi-empirical molecular orbital methods such as PM3, MNDO, MNDO/3, AM1 and molecular mechanics MM2 [1] as well as the Gaussian 98 suite of quantum chemistry codes [15] with the 6–31G* basis set [16] or 6–311++G(2df,2p) basis set and the hybrid B3LYP [17,18] can also be used to estimate gas phase heat of formation for different energetic compounds [12,13]. Among the advanced methods developed in semi-empirical quantum mechanical methods for optimizing and determining gas phase heat of formation, the PM3 parameterization scheme has proved particularly effective. For example, Stewart [19] found that the average difference between the calculated and observed gas phase heats of formation were 5.2 and 15.7 kcal/mol for PM3 and AM1, respectively, in some compounds. Moreover, Akutsu et al. [20] showed that PM3 and MM2 methods can estimate gas phase heats of formation for nitro compounds more accurately than AM1 for practical use.

2.1.2. Group contribution methods

Another convenient procedure is group-contribution methods. It assumes that properties of molecules can be derived from properties of atoms or functional groups from which they are made [14]. Benson and Joback methods are two group additivity methods which commonly used to estimate thermochemical quantities of various organic molecules [14]. Joback's method assigns incremental heat of formation values to the ideal gas phase of common functional groups such as $-\text{CH}_3$, $>\text{C}=\text{O}$, OH and so on meanwhile Benson's method incorporate the effects of second-nearest neighbors that produces more reliable values of gas phase heats of formation at the greater complexity. It should be mentioned that root mean square (RMS) of deviation of quantum mechanical computations are less than group-contribution methods.

2.1.3. Simple theoretical methods

Finally, it was recently found that elemental composition and some structural parameters of selected class of energetic compounds can be used to determine gas phase heat of formation [7,8]. Calculated gas phase heats of formation for 85 non-aromatic energetic compounds have shown good agreement with experimental data, where experimental data were available, as compared to semi-empirical quantum mechanical PM3 prediction [7]. Since the new methods provide the simplest procedure for calculation gas phase heat of formation of selected class of energetic compounds which is readily calculated by a desk calculator of the same reliability as one could expect from a more complex quantum mechanical methods, the new correlations are appealing to chemists and engineers.

2.2. Heat of sublimation

In contrast to different methods for calculation of gas phase heat of formation, few methods were used to determine heats of

sublimation of energetic compounds. To calculate solid phase heat of formation of energetic method via predicted gas phase heat of formation, appropriate method would be needed to determine heat of sublimation of energetic compounds. Politzer et al. [11] have found that correlations exist between the electrostatic potential of a molecule and the heats of sublimation. Rice et al. [12] as well as Byrd and Rice [13] have applied a procedure proposed by Politzer et al. [11] to calculate the heats of sublimation of energetic materials. Furthermore, Zeman and Krupka [21] have also found some relationships between heats of sublimation of some polynitro compounds and lattice energies.

Although quantum mechanical computations using the Gaussian code [15] with different basis sets and the hybrid B3LYP [17,18] have shown to give good prediction of gas phase heats of formation, there is larger errors for predicted heats of sublimation in some cases such as hexanitroethane, 1,4-dinitropiperazine and 1-nitro-2-nitrosobenzene [11].

3. Results and discussion

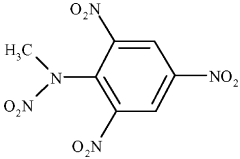
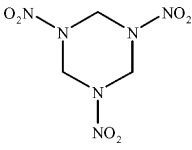
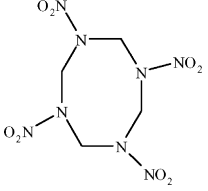
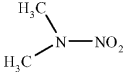
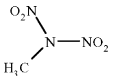
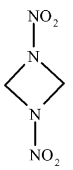
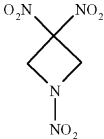
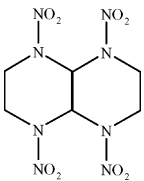
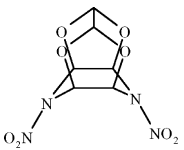
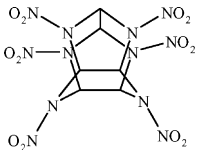
The search for new explosives with a given thermodynamic, performance, sensitivity and physical properties is one of the major challenges to chemists and the chemical industries. Various empirical methods can help chemists for desk calculations of factors related to detonation parameters, crystal density, oxygen balance and heat of formation. For single gas molecule calculations, quantum chemistry methods have advantages over empirical methods. Since the heat of sublimation has a connection with the structures of condensed states, it can be correlated with some specific structural parameters.

Thermochemical properties of energetic compounds such as nitramines are influenced by different molecular interactions. It should be noted that 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 [22]. The study of heats of sublimation for some nitramines, where experimental data were available, has shown that it is possible to find a new correlation for predicting their heats of sublimation. It was found that molecular weight and one structural parameter of cyclic nitramines are sufficient to establish a new correlation. However, the following general equation is suitable for this purpose:

$$\Delta H_{\text{sub}}(\text{kJ/mol}) = y_1 + y_2\text{MW} + y_3n_{\text{O}_2\text{NNCH}_2\text{NNO}_2} \quad (2)$$

where y_1 – y_3 are adjustable parameters; MW is the molecular weight of nitramine; $n_{\text{O}_2\text{NNCH}_2\text{NNO}_2}$ is the number of $-\text{CH}_2-$ groups between two nitramine functional groups in cyclic and non-cyclic nitramines. Multiple linear regression method [23] was used to find adjustable parameters. Since the equation set is overdetermined [23], the left-division method for solving linear equations uses the least squares method. It should be noted that an overdetermined system is a set of equations that has more independent equations than unknowns. In this situation, the matrix inverse method and Cramer's method will not work [23]. However, the left-division method can be used. The left-division method is based on Gauss elimination so that it

Table 1
Comparison of predicted heats of sublimation (kJ/mol) of nitramines with the experimental data

Name	Molecular structure	ΔH_{sub} (exp)	ΔH_{sub} (cal)	Dev.
1-(Methylnitramino)-2,4,6-trinitrobenzene (TETRYL)		133.8 [25]	127.87	5.93
1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)		130.2 [25]	133.52	-3.32
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)		175.3 [25]	172.82	2.48
Methamine		41.4 [24]	50.82	-9.42
Methyldinitramine		52 [24]	62.95	-10.95
1,3-Dinitro-1,3-diazacyclobutane (TETROGEN)		94.2 [25]	94.22	-0.02
1,3,3-Trinitroazetidene (TNAZ)		106.2 [25]	90.71	15.49
<i>trans</i> -1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline (TNAD)		154.2 [25]	141.56	12.64
4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX)		123.4 [25]	118.09	5.31
2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)		168.7 [25]	186.92	-18.22
RMS deviation (kJ/mol)				10.10

Since experimental data of heats of sublimation of nitramines compounds are rare, heat of sublimation can be obtained from the condensed phase heat of formation and gas phase heat of formation using Hess' law of constant heat summation as given in Eq. (1) [10]. Several calculations for some nitramine energetic compounds, where their experimental condensed phase heats of formation were available [24], are also given in Table 2 for comparison with predictions using Eq. (3). Since the measured gas phase heat of formation for mentioned nitramines in Table 2 were not available, PM3 method can be used to calculate gas phase heat of formation because it can predict relatively good results for energetic compounds [19,20]. Moreover, it was indicated that PM3 method can give relatively good prediction of gas phase heat of formation for nitramines and aliphatic nitro compounds as compared to available experimental data [7,26]. To optimize molecular structures of nitramines given in Table 2 by PM3 method, the Polak–Ribiere algorithm was used and the termination was a RMS gradient of 0.42 kJ/mol. As seen in Table 2, Eq. (3) can predict good results with respect to predicted values by this scheme.

4. Conclusions

A new simple theoretical approach is introduced for desk calculation heats of sublimation of nitramines only from molecular structure. As seen in Fig. 1, good agreement is obtained between measured and calculated values. The results of this work are remarkable because the necessary data for this method is only molecular weight and one structural parameter without using any experimental data of nitramines. Since solid heat of formation is an important factor to consider in designing new energetic materials or evaluating existing ones that can enter into the calculation of such key explosive properties as detonation pressure, calculated heat of sublimation can be used to evaluate it. This method confirms that the accuracy is not necessarily enhanced by greater complexity as well as gives the simplest and easiest pathway for calculation heats of sublimation of nitramines.

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References

- [1] A.K. Sikder, G. Maddala, J.P. Agrawal, H. Singh, Important aspects of behaviour of organic energetic compounds: a review, *J. Hazard. Mater. A* 84 (2001) 1–26.
- [2] M.H. Keshavarz, A Simple Theoretical Prediction of Detonation Velocities of Non-Ideal Explosives Only from Elemental Composition, Chapter 8, in: P.B. Wary (Ed.), *New Research on Hazardous Materials*, Nova Science Publishers, Inc., 2006.
- [3] M.H. Keshavarz, Detonation velocity of pure and mixed CHNO explosives at maximum nominal density, *J. Hazard. Mater. A* 141 (2007) 536–539.
- [4] M.H. Keshavarz, Theoretical prediction of detonation pressure of CHNO high energy materials, *Ind. J. Eng. Mater. Sci.* 14 (2007) 77–80.
- [5] M.H. Keshavarz, Approximate prediction of melting point of nitramines, nitrate esters, nitrate salts and nitroaliphatics energetic compounds, *J. Hazard. Mater. A* 138 (2006) 448–451.
- [6] M.H. Keshavarz, H.R. Pouretedal, New approach for predicting melting point of carbocyclic nitroaromatic compounds, *J. Hazard. Mater. A* 148 (2007) 592–598.
- [7] M.H. Keshavarz, M. Kavosh Tehrani, H.R. Pouretedal, A. Semnani, New pathway for quick estimation of gas phase heat of formation of non-aromatic energetic compounds, *Ind. J. Eng. Mater. Sci.* 13 (2006) 542–548.
- [8] M.H. Keshavarz, M. Kavosh Tehrani, A new method for determining gas phase heats of formation of aromatic energetic compounds, *Propellants Explos. Pyrotechnol.* 32 (2007) 155–159.
- [9] L.E. Fried, W.M. Howard, P.C. Souers, CHEETAH 2. 0 User's Manual, Lawrence Livermore National Laboratory, Livermore, CA, 1998.
- [10] P.W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 1982.
- [11] P. Politzer, J.S. Murray, M.E. Grice, M. DeSalvo, E. Miller, Calculation of heats of sublimation and solid phase heats of formation, *Mol. Phys.* 91 (1997) 923–928.
- [12] B.M. Rice, S.V. Pai, J. Hare, Predicting heats of formation of energetic materials using quantum mechanical calculations, *Combust. Flame* 118 (1999) 445–458.
- [13] E.F.C. Byrd, B.M. Rice, Improved prediction of heats of formation of energetic materials using quantum mechanical calculations, *J. Phys. Chem. A* 110 (2006) 1005–1013.
- [14] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, 4th ed, McGraw-Hill, New York, 1987.
- [15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Statmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andrs, M. Head-Gordon, E.S. Replogle, J.A. Pople, *Gaussian 98*, Gaussian Inc., Pittsburgh PA, 1998.
- [16] W.J. Hehre, L. Rdom, P.V.R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986, p. 271, 298.
- [17] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* 98 (1993) 5648–5652.
- [18] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1998) 785–789.
- [19] J.J.P. Stewart, Optimization of parameters for semiempirical methods I. Method, *J. Comput. Chem.* 10 (1989) 209–264.
- [20] Y. Akutsu, S. Tahara, M. Tamura, T. Yoshida, Calculations of heats of formation for nitro compounds by semi-empirical methods and molecular mechanics, *J. Energetic Mater.* 9 (1991) 161–172.
- [21] S. Zeman, M. Krupka, Some predictions of the heats of fusion, heats of sublimation and lattice energies of energetic materials, *HanNeng CaiLiao* 10 (2002) 27–33.
- [22] A. Bondi, *Physical properties of molecular crystals, liquids and glasses*, Wiley, London, 1968.
- [23] W.J. Palm III, *Matlab for Engineering Applications*, WBC/McGraw-Hill, 1999.
- [24] NIST Standard Reference Data Base Number 69, which can be accessed electronically through the NIST Chemistry Web Book (<http://webbook.nist.gov/chemistry/>), references for individual molecules are given therein.
- [25] S. Zeman, M. Krupka, New aspects of impact reactivity of polynitro compounds, part III. impact sensitivity as a function of the intermolecular interactions, *Propellants Explos. Pyrotechnol.* 28 (2003) 301–307.
- [26] P. Duchowicz, E.A. Castro, P. Chen, Improved correlation between theoretical and experimental determination of heat of formation of some aliphatic nitro compounds, *J. Korean Chem. Soc.* 47 (2003) 89–95.