



# A new approach to predict the condensed phase heat of formation in acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds

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## ABSTRACT

This paper presents a new approach to predict the condensed phase heat of formation in important classes of energetic compounds including acyclic and cyclic nitramines, nitrate esters and nitroaliphatics. The condensed phase heat of formation has been expressed by a combination of a core heat of formation, which is a function of elemental composition of the energetic compound, and correction functions. The correction functions for some energetic compounds can have decreasing or increasing effects on the basis of thermodynamic stability. It has been shown that this model can offer reliable predictions for the above energetic compounds compared to the calculated outputs of the best recent empirical and complex quantum mechanical methods.

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## 1. Introduction

The importance of a reliable prediction method is to get benefit from most of the limited resources and minimize the amount of waste resulting from experimental measurements. Various empirical methods complemented the computer outputs for desk calculations have been developed to help the formulation of advanced propellants and explosives [1,2]. The development of theoretical reliable models allows the suitable screening of hypothetical energetic materials. However, the experimental researchers can expend resources only on those molecules that show promise to provide enhanced performance, reduced sensitivity, or reduced environmental hazards.

In order to assess potential performance of an energetic compound in explosive or propellant cases, the condensed phase heat of formation ( $\Delta H_f^\circ(c)$ ) is considered as an important property. It enters into the calculation of explosive and propellant properties such as detonation pressure, detonation velocity and specific impulse to investigate characteristics of energetic materials. Significant resources could be expended in synthesizing a notional energetic compound only to discover upon measuring its  $\Delta H_f^\circ(c)$ . Suitable predictive methods for  $\Delta H_f^\circ(c)$  can eliminate poor candidates from further consideration. The desired quantity is usually  $\Delta H_f^\circ(c)$  because the standard state of the energetic material of

interest corresponds to the condensed phase. To assess the potential performance of the energetic material of interest, however,  $\Delta H_f^\circ(c)$  should be used in the corresponding computer codes such as CHEETAH [3] and NASA-CEC-71 [4]. Various empirical and theoretical methods can be used to predict heat of formation of different classes of energetic compounds which have been reviewed by some authors [5,6]. In this paper, we will introduce a reliable simple correlation for predicting condensed phase heat of formation for acyclic and cyclic nitramines, nitrate esters and nitroaliphatics considered as some important classes of energetic compounds. The results of this method will be compared with outputs of complex quantum mechanical method [7,8]. The presence of some specific polar groups or molecular fragments in the compounds of interest can increase the thermodynamic stability of energetic compounds which are considered in the correction heat of formation. Additionally, predicted  $\Delta H_f^\circ(c)$  of the new method will be tested against experiment and compared with the calculated results of previously reported work [9] concerning well-known explosives that have complex and different molecular structures.

## 2. Theory

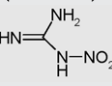
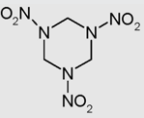
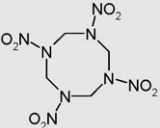
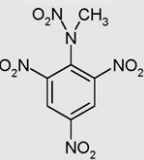
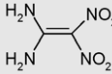
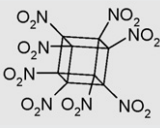
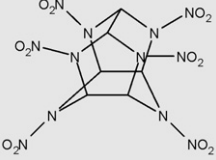
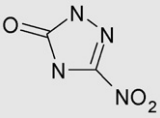
Different quantum mechanical methods can be used to predict gas phase heats of formation of energetic compounds [1]. However, there are also some semi-empirical molecular orbital methods like MNDO, MNDO/3, AM1, PM3 and molecular mechanics MM2 which can be utilized to estimate the gas phase heats of formation for various energetic compounds. To calculate the solid and liquid phase heats of formation using predicted heats of vaporization and

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**Table 1**

Comparison of the predicted heats of formation (kJ/mol) from the present new method, quantum mechanical [7,8] and previous [7] methods with experimental data.

Compound	Experiment	New method	Dev	Quantum mechanical method	Dev	Previous work	Dev
CH <sub>3</sub> NO <sub>2</sub>	-112.5 [23]	-109.9	-2.6	-114.6	2.1	-102.9	-9.6
CH <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	-104.9 [23]	-107.4	2.5	-96.2	-8.7	-108.4	3.5
CH(NO <sub>2</sub> ) <sub>3</sub>	-68.0 [23]	-104.9	36.9	-45.2	-22.8	-113.8	45.8
C(NO <sub>2</sub> ) <sub>4</sub>	38.5 [23]	47.0	-8.5	38.1	0.4	46.4	-7.9
CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	-143.9 [23]	-146.6	2.7	-155.2	11.3	-137.2	-6.7
C(NO <sub>2</sub> ) <sub>3</sub> C(NO <sub>2</sub> ) <sub>3</sub>	108.4 [23]	81.5	26.9	101.7	6.7	92.5	15.9
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub>	-167.4 [23]	-183.3	15.9	-180.3	13.0	-171.1	3.7
CH <sub>3</sub> CH(NO <sub>2</sub> )CH <sub>3</sub>	-180.3 [23]	-183.3	3.0	-189.1	8.8	-171.1	-9.2
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub>	-192.6 [23]	-220.0	27.4	-202.9	10.3	-205.0	12.4
CH <sub>3</sub> CH(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub>	-207.6 [23]	-220.0	12.4	-210.9	3.3	-205.0	-2.6
(CH <sub>3</sub> ) <sub>3</sub> C(NO <sub>2</sub> )	-229.7 [23]	-220.0	-9.7	-225.1	-4.6	-205.0	-24.7
CH <sub>3</sub> CH <sub>2</sub> ONO <sub>2</sub>	-190.4 [23]	-212.7	22.3	-203.3	12.9	-197.5	7.1
CH <sub>2</sub> (ONO <sub>2</sub> )CH(ONO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>	-369.9 [23]	-376.4	6.6	-370.7	0.8	-363.6	-6.3
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ONO <sub>2</sub>	-214.6 [23]	-249.4	34.7	-227.2	12.6	-231.8	17.2
C(CH <sub>2</sub> ONO <sub>2</sub> ) <sub>4</sub>	-538.5 [23]	-513.3	-25.2	-566.1	27.6	-497.5	-41.0
	-86.6 [23]	-107.8	21.2	-31.0	-55.6	-79.9	-6.7
	75.3 [23]	98.8	-23.5	87.0	-11.7	135.6	-60.3
	79.1 [23]	74.1	5.0	107.1	-28.0	101.7	-22.6
	41.0 [8]	39.5	1.5	-7.1	48.1	4.6	36.4
	-133.9 [8]	-168.2	34.3	-82.0	-51.9	-192.7	58.8
	381.2 [8]	374.6	6.6	575.7	-194.6	-60.3	441.5
	377.4 [8]	375.5	1.8	415.1	-37.7	394.2	-16.8
	-129.4 [8]	-135.1	5.7	-66.5	-62.9	-38.3	-91.2
rms deviation			18.8		48.7		97.4

sublimation, Hess's law can be used. Yoshiaki et al. [10] have combined the heats of vaporization and sublimation using additivity rule with gas phase heats of formation data for PM3 and MM2 methods to calculate the condensed phase heats of formation. Politzer et al. [11] and Murray and Politzer [12,13] have shown that correlations could be established between statistically based quantities of electrostatic potentials mapped onto isodensity surfaces of isolated molecules and their heats of sublimation and vaporization. Rice et

al. [7] and Rice and Hare [8] have performed a generalized gradient approximation of density functional theory characterization of all molecules using the 6-31G\* basis set [14] and the hybrid B3LYP [15,16] density functional for converting quantum mechanical energies of molecules into gas phase heats of formation. They also used surface electrostatic potentials of individual molecules for computation of heats of sublimation and vaporization as recommended by Politzer [11] and Murray and Politzer [12,13].

**Table 2**  
Comparison of predicted heats of formation (kJ/mol) of the present and previous [9] methods with experimental data [23] for acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds that have different molecular structures.

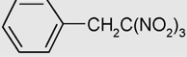
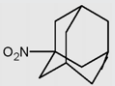
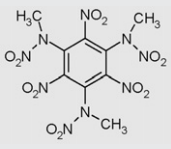
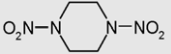
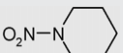
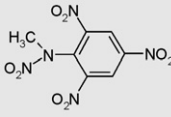
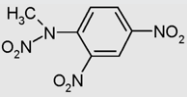
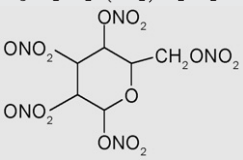
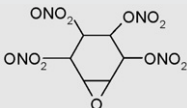
Energetic compound	Experiment	New method	Dev	Previous work	Dev
$\text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)_2$	-163.2	-180.8	17.6	-176.6	13.4
$\text{O}_2\text{NCH}_2\text{CH}_2\text{NO}_2$	-178.7	-144.1	-34.6	-142.7	-36.0
$\text{O}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NO}_2$	-207.1	-180.8	-26.3	-176.6	-30.5
$\text{HOCH}_2\text{C}(\text{NO}_2)(\text{CH}_2\text{OH})\text{CH}_2\text{OH}$	-742.2	-744.5	2.2	-743.9	1.7
$\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NO}_2$	-410.2	-394.8	-15.4	-384.9	-25.3
$\text{C}(\text{NO}_2)_3\text{CH}_2\text{OH}$	-261.1	-262.0	0.9	-327.2	66.1
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{OH})_2\text{NO}_2$	-601.2	-606.3	5.1	-598.3	-2.9
$(\text{HOCH}_2)_2\text{C}(\text{NO}_2)(\text{CH}_3)$	-570.5	-569.7	-0.9	-564.4	-6.1
$\text{C}(\text{NO}_2)_3\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_3$	-402.1	-430.5	28.5	-447.3	45.2
$\text{C}(\text{NO}_2)_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{C}(\text{NO}_2)_3$	-496.2	-467.6	-28.6	-463.2	-33.0
$\text{O}_2\text{NCH}_2\text{CH}_2\text{OH}$	-350.6	-321.5	-29.2	-316.7	-33.9
$(\text{CH}_3)_2\text{C}(\text{NO}_2)_2$	-192.5	-180.8	-11.7	-176.6	-15.9
$\text{O}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-215.5	-256.7	41.2	-239.3	23.8
	-18.4	-58.6	40.1	-97.1	78.7
	-254.3	-212.7	-41.6	-218.4	-35.9
	118.0	88.9	29.1	111.7	6.3
	-53.1	-24.0	-29.2	-0.4	-52.8
	-92.9	-57.4	-35.5	-102.1	9.2
$\text{CH}_3\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_3$	-105.9	-96.5	-9.4	-131.8	25.9
$(\text{CH}_3)_2\text{NNO}_2$	-71.1	-23.1	-48.0	-64.0	-7.1
$\text{CH}_3\text{N}(\text{NO}_2)_2$	1.7	16.1	-14.4	-35.1	36.8
	10.5	2.8	7.6	-29.3	39.8
	16.2	37.0	-20.8	10.0	6.1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{ONO}_2$	-192.5	-233.4	40.9	-265.7	73.2
$\text{CH}_3\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{ONO}_2$	-164.0	-160.0	-4.0	-197.9	33.9
$\text{O}_2\text{NOCH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{ONO}_2$	-257.4	-223.5	-33.9	-263.6	6.2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{ONO}_2$	-206.7	-270.1	63.3	-300.0	93.3
$\text{CH}_3\text{CH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{ONO}_2$	-174.1	-196.7	22.6	-231.8	57.8
	-826.3	-784.4	-41.9	-761.5	-64.8
	-444.3	-464.5	20.2	-494.5	50.2
$\text{O}_2\text{NOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{ONO}_2$	-477.0	-433.3	-43.6	-477.0	0.0
$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{ONO}_2$	-577.0	-599.0	22.1	-590.8	13.8
$\text{O}_2\text{NOCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{CH}_2\text{ONO}_2$	-414.2	-413.1	-1.1	-397.5	-16.7
$\text{O}_2\text{NOCH}_2\text{CH}_2\text{ONO}_2$	-232.6	-276.2	43.6	-263.6	31.0
$\text{O}_2\text{NOCH}_2\text{CH}(\text{ONO}_2)\text{CH}_3$	-297.1	-312.9	15.8	-297.5	0.5
$(\text{O}_2\text{NOCH}_2)_3\text{CCH}_3$	-450.2	-449.8	-0.4	-431.4	-18.8
$\text{O}_2\text{NOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{ONO}_2$	-274.1	-349.6	75.5	-331.4	57.3
$(\text{O}_2\text{NOCH}_2)_3\text{CCH}_2\text{CH}_3$	-479.9	-486.5	6.6	-465.7	-14.2
$\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_3$	-385.8	-386.3	0.5	-365.7	-20.1
$(\text{O}_2\text{NOCH}_2)_2\text{C}(\text{NO}_2)\text{CH}_2\text{CH}_3$	-367.4	-383.7	16.4	-371.1	3.7

Table 2 (Continued)

Energetic compound	Experiment	New method	Dev	Previous work	Dev
	-387.9	-398.4	10.6	-404.2	16.3
CH <sub>3</sub> C(=O)ONO <sub>2</sub>	-331.0	-333.5	2.5	-270.3	-60.7
(O <sub>2</sub> NOCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> OCH <sub>2</sub> C(CH <sub>2</sub> ONO <sub>2</sub> ) <sub>3</sub>	-979.5	-944.2	-35.2	-889.9	-89.6
O <sub>2</sub> NOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> ONO <sub>2</sub>	-656.9	-663.8	6.9	-581.2	-75.7
O <sub>2</sub> NOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> ONO <sub>2</sub>	-451.0	-470.0	19.0	-422.2	-28.8
HOCH <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> OH	-567.8	-599.0	31.3	-590.8	23.0
HOCH <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>	-472.4	-433.3	-39.0	-477.0	4.6
O <sub>2</sub> NOCH <sub>2</sub> CH(ONO <sub>2</sub> )CH(ONO <sub>2</sub> )CH(ONO <sub>2</sub> )CH(ONO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>	-708.8	-677.1	-31.7	-663.2	-45.6
CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>3</sub>	-229.7	-249.4	19.7	-231.8	2.1
	-386.0	-394.2	8.2	-358.6	-27.4
	-298.8	-245.1	-53.7	-248.5	-50.3
O <sub>2</sub> NNHCH <sub>2</sub> CH <sub>2</sub> NHNO <sub>2</sub>	-374.0	-347.0	-27.0	-336.8	-37.2
	-287.7	-296.9	9.2	-342.7	55.0
	-302.5	-304.3	1.8	-367.4	64.9
rms deviation			29.1		41.0

Group additivity methods such as procedures employed by Benson, Yoneda and Joback can be used to estimate the ideal gas phase heats of formation [17]. The heats of formation of condensed phase for some specific classes of explosives can also be calculated by using group additivity methods. For example, Bourasseau [18] has applied group additivity method to predict the standard heats of formation at 298 K for aliphatic and alicyclic polynitro compounds.

Heats of detonation on the basis of Kamlet's method can also be used for predicting solid phase heats of formation of some explosives in the range  $Q_{\text{corr}} > 4602$  kJ/g [19], where  $Q_{\text{corr}}$  is the corrected heats of detonation on the basis of Kamlet's method [20], through approximate detonation temperature,  $T_{\text{ad}}$ . The condensed phase heat of formation of important classes of energetic compounds can also be calculated through simple path [9,21]. For energetic compounds which contain at least one of the functional groups including N-NO<sub>2</sub>, C-ONO<sub>2</sub> or nonaromatic C-NO<sub>2</sub>, the predicted condensed phase heats of formation by this method have a higher root mean square (rms) of deviation from experiment [9]. It will be shown in the next section that a new different approach can be introduced in which the reliability of the predicted values can be improved with respect to previous work [9] and those obtained from quantum mechanical results [7,8].

### 3. Results and discussion

In order to predict reliable condensed phase heats of formation of energetic compounds, it was found that the elemental composition of acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds may be taken as the core correlation ( $\Delta H_{\text{core}}$ ). Two specific structural parameters can decrease or increase the predicted values by core correlation in order to obtain satisfactory results. Some functional groups such as hydroxyl and carboxyl significantly decrease the heat content of energetic

compounds. Meanwhile the presence of one N-NO<sub>2</sub> in molecular structure may increase the predicted values of core correlation under certain conditions. Thus, the suitable relationship of elemental composition as well as positive and negative contributions of some specific functional groups or structural parameters for acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds with general formula  $C_{b_1}H_{b_2}N_{b_3}O_{b_4}$  can be given as:

$$\Delta H_f(c) = \Delta H_{\text{core}} + \Delta H_{\text{corr}} \quad (1a)$$

$$\Delta H_{\text{core}} = \sum_{j=1}^4 y_j b_j \quad (1b)$$

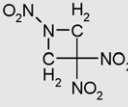
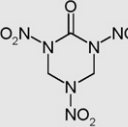
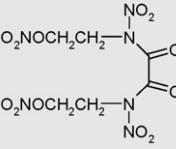
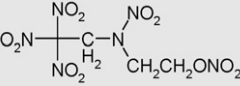
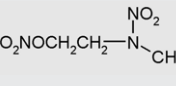
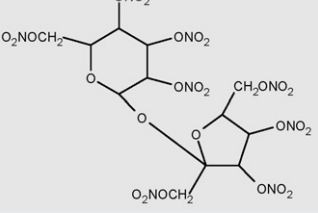
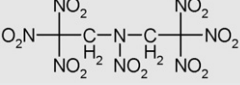
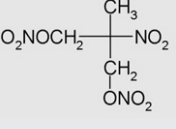
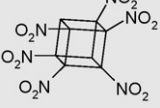
$$\Delta H_{\text{corr}} = y_5 \sum_i n_{i,\text{DE}} + y_6 \sum_i n_{i,\text{IE}} \quad (1c)$$

where  $\Delta H_f(c)$  is the condensed heat of formation;  $\Delta H_{\text{core}}$  is the correcting heat of formation for some energetic compounds that have decreasing or increasing effects (i.e. DE or IE) on the predicted values by the value of  $\Delta H_{\text{core}}$ ;  $n_{\text{DE}}$  and  $n_{\text{IE}}$  are the number of some specific functional groups or structural parameters corresponding to DE or IE, respectively;  $y_1$ – $y_6$  are adjustable parameters which can be found from the experimental data given in Tables 1 and 2. Multiple linear regression method [22] 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 [22]. The optimized adjustable parameters shown in Eq. (1) for condensed heat of formation in terms of kJ/mol can be given as  $y_1 = 9.344$ ,  $y_2 = -9.055$ ,  $y_3 = 23.12$ ,  $y_4 = -15.79$ ,  $y_5 = 51.49$  and  $y_6 = -52.00$ .  $R$ -squared values or the coefficients of determination of Eq. (1) is 0.97 [22]. The values of DE and IE can be described the follows:

**Table 3**  
Comparison of theoretically predicted heats of formation (kJ/mol) of the present and previous [9] methods with experimental data for some well-known energetic compounds.

Energetic compound	Experiment	New method	Dev	Previous work	Dev
	-321.7 [24]	-334.2	12.4	-406.9	85.2
	-405.9 [24]	-413.1	7.2	-397.4	-8.4
	-192.3 [24]	-233.4	41.1	-265.9	73.6
	-305.3 [24]	-341.4	36.1	-209.3	-96.0
	-561.7 [24]	-541.8	-19.9	-409.1	-152.6
	-479.5 [24]	-486.5	7.0	-465.5	-14.0
	-103.7 [24]	-113.4	9.6	4.0	-107.8
	-675.5 [24]	-677.1	1.5	-663.1	-12.4
	22.1 [24]	-16.3	38.3	32.4	-10.3
	-242.7 [24]	-276.2	33.5	-263.5	20.8
	-282.3 [24]	-243.6	-38.7	185.3	-467.5
	-560.4 [24]	-570.2	9.9	-611.0	50.7
$[-\text{CH}_2\text{CH}(\text{ONO}_2)-]_n$	-102.6 [24]	-136.9	34.3	-133.9	31.4
	-229.3 [24]	-249.4	20.0	-231.7	2.3
	-675.8 [24]	-705.1	29.3	-642.4	-33.3

Table 3 (Continued)

Energetic compound	Experiment	New method	Dev	Previous work	Dev
	36.4 [24]	21.0	15.4	-44.9	81.3
	-41.8 [23]	-58.0	16.2	20.8	-62.6
	-536.0 [23]	-541.8	5.8	-409.1	-126.8
$O_2NNHCH_2CH_2NHNO_2$	-100.8 [23]	-113.4	12.6	4.0	-104.9
	-98.3 [23]	-152.4	54.1	-213.9	115.5
	-149.8 [23]	-123.3	-26.5	-255.0	105.2
	-1364.0 [23]	-1408.1	44.1	-1143.8	-220.2
	-28.0 [23]	-81.3	53.3	-164.1	136.0
	-374.0 [23]	-347.0	-27.0	-436.5	62.4
	200.0 [23]	205.1	-5.1	-108.9	308.9
rms deviation			28.4		142.7

(1) Prediction of DE The existence of some specific polar functional groups can reduce the condensed heats of formation through increasing thermodynamic stability of energetic compounds.



- (a) The existence of hydroxyl group: it was found that the ratio of the number of hydroxyl groups to the number of non-aromatic nitro or nitrate groups ( $n_{OH}/n_{NO_2 \text{ or } ONO_2}$ ) is one of the important structural parameters. If  $n_{OH}/n_{NO_2 \text{ or } ONO_2} \geq 1$ , then  $n_{DE} = n_{OH}/n_{NO_2 \text{ or } ONO_2} \times 0.5$  (e.g. for 2-hydroxymethyl-2-nitro-propane-1,3-diol,  $n_{OH}/n_{NO_2 \text{ or } ONO_2} = 3$  and  $n_{DE} = 1.5$ ). For  $n_{OH}/n_{NO_2 \text{ or } ONO_2} < 1$ ,  $n_{DE} = 2.5$  (e.g. for 2,2,2-trinitro-ethanol,  $n_{OH}/n_{NO_2 \text{ or } ONO_2} = 0.33$ ).

(b) The presence of carbonyl group: carbonyl group is another polar functional group which can increase thermodynamic


stability of energetic compounds. For those compounds that contain  $>C=O$  group,  $n_{DE} = >C=O \times 0.6$  (e.g. for 4,4,4-Trinitrobutyric acid 2,2,2-trinitro-ethyl ester,  $n_{DE} = 0.6$ ).

- (c) The existence of cyclic and acyclic ether functional groups: for only six-membered cyclic ether, the value of DE can be considered in such that  $n_{DE} = 0.25$ . If there is ether functional group in the form  $ROCH_2CH_2OR'$ ,  $n_{DE} = 0.5$  (e.g. 1-nitrooxy-2-[2-(2-nitrooxy-ethoxy)-ethoxy]-ethane). The value of  $n_{DE}$  is found to be 0.25 for the other forms of acyclic ethers (e.g. 1-nitrooxy-2-(2-nitrooxy-ethoxy)-ethane).

(d) The existence of some specific molecular structures: For

the presence of molecular fragments ,  and

–NH–NO<sub>2</sub>, the values of  $n_{DE}$  are 1.0, 0.5 and 0.2, respec-

tively. For example, there are two  and one –NH–NO<sub>2</sub> molecular fragments in 1-nitro-3-guanidinourea for which  $\sum_i n_{DE} = 2 + 0.2 = 2.2$ .

## (2) Prediction of IE

The effect of some functional groups in certain situations can decrease the thermodynamic stability of energetic compounds.

(a) For acyclic and cyclic nitramines containing only one C–N(NO<sub>2</sub>)–C fragment, the value of  $n_{IE}$  is found to be 0.3 (e.g. N-ethyl-N-nitro-ethanamine).

(b) The number of nitro groups attached to cubane is another structural parameter in this category for which  $n_{IE} = 0.2$ . As an example,  $\sum_i n_{IE} = 8 \times 0.2 = 1.6$  for octanitrocubane.

(c) For hydrogen free nitroalkanes, the value of  $n_{IE}$  is equal to 1.0 (e.g. tetranitromethane).

It should be noticed that the value of  $\Delta H_{core}$  equals zero if the conditions to assign different values are not met. In order to compare the reliability of the present procedure with the quantum mechanical method, the predicted values of condensed phase heats of formation for some compounds are given in Table 1. The quantum mechanical data given in Table 1 have been taken from the work of Rice et al. [7] and Rice and Hare [8]. The predicted results of previous work are also included in Table 1 which confirms reliability of the present method with respect to a previously reported work [9]. As shown in Table 1, the rms deviation of this new method is lower than that of the other methods. Some further energetic compounds are also given in Table 2 and the predicted results are compared to the previous work [9]. As indicated in Table 2, the reliability of the present method is higher than that of previous work [9]. Since there are different values for the condensed phase heats of formation reported from different sources in Tables 1 and 2, the latest reported values of the NIST Chemistry Web Book [23] were taken to compare the above mentioned method with the experimental data, e.g. 61.5, 66.5 and 79.1 kJ/mol are several different reported experimental data for hexahydro-1,3,5-trinitrotriazine [23]. To examine the application of the present new method for the well-known explosives, the calculated values for some energetic compounds with complex molecular structures are also given in Table 3. However, as before, the rms deviation of this method is less than that of the previous work [9].

It should be noted that the present method can be applied only to selected classes of energetic compounds including acyclic and cyclic nitramines, nitrate esters and nitroaliphatics. Deviations of predicted results from experimental data may be large for the other classes of energetic compounds.

## 4. Conclusions

A new simple method has been introduced which uses only molecular structure information to predict the condensed phase heats of formation in acyclic and cyclic nitramines, nitrate esters and nitroaliphatic energetic compounds. In this method, corrected heat of formation with two variables  $n_{DE}$  and  $n_{IE}$  can correct the

predicted values on the basis of  $\Delta H_{core}$ . Eq. (1) can be used easily without any need to use computer codes or experimental data. As indicated in Tables 1–3, this new method provides reliable results with respect to quantum mechanical method [7,8] and previously reported work [9].

## Acknowledgement

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