



The heats of formation in a series of nitroester energetic compounds: A theoretical study

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ABSTRACT

Quantum chemical calculations are used to compute the heats of formation (HOFs) for 24 nitroester (NE) energetic compounds in which only 5 nitroester energetic compounds have the available experimental heats of formation. The heats of formation of the five compounds are calculated from isodesmic reactions by employing the hybrid density functional theory (DFT) (B3LYP, B3PW91, and B3P86) methods with 6-31G** and 6-311G** basis sets. It is demonstrated that B3PW91/6-31G** method can yield reliable HOFs, which has the mean absolute deviation of 1.1 kcal/mol. The HOFs of other 19 nitroester energetic compounds are calculated by using B3PW91/6-31G** method. Through the analysis of the calculated result, it is found that the computed heat of formation decreases when the number of methylene (CH₂) group increases for normal chain nitroester compounds. The further study shows that our results about gas-phase heats of formation of nitroester compounds are better than the results of Muthurajan et al. [H. Muthurajan, R. Sivabalan, M.B. Talwar, M. Anniyappan, S. Venugopalan, Prediction of heat of formation and related parameters of high energy materials, *J. Hazard. Mater.* A133 (2006) 30–45], and Byrd Edward and Rice Betsy [F.C. Byrd Edward, M. Rice Betsy, Improved prediction of heats of formation of energetic materials using quantum mechanical calculations, *J. Phys. Chem. A* 110 (2006) 1005–1013]. In addition, the condensed phase heat of formation of the nitroester compounds are computed through the same method of Byrd Edward and Rice Betsy.

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1. Introduction

One of the fundamental goals in the field of energetic materials is to develop methods for predicting performance, sensitivity, physical and thermodynamic properties before synthesis. Various simple theoretical and empirical methods can help the chemists to develop systematic and scientific formulations of appropriate futuristic target molecules with desired performance, sensitivity and thermochemical properties.

A key property of an energetic material that is used to assess its potential performance in a gun or warhead is its heat of formation (ΔH_f^0). For notional compounds, significant resources could be expended in synthesizing the material, only to discover upon measuring its ΔH_f^0 that it is an unsuitable candidate for use. Therefore, efforts have been made to develop computational tools that will predict this important property a priori [1–8].

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Nitrate esters impart high energy to explosive/propellant formulations because of their better oxygen balance as compared to aromatic nitro compounds. At the same time, these compounds possess high sensitivity due to the presence of O–NO₂ bond [9]. Bunte and Sun [10] have performed MO calculations on methyl and ethyl nitrates at various theoretical levels to develop the parameters for organic nitrates in the COMPASS force field. Previous studies [10–13] showed that it is possible to achieve reliable geometries and vibrational frequencies at certain high theoretical level. Gong and Xiao [14] studied the molecular structures, vibrational spectra and thermodynamic properties of small organic nitrates using ab initio method. However, much previous work only focused upon the molecular structures and vibrational frequencies. The accurate theoretical study on the heats of formation of nitroesters (NEs), which has significant practical application to explore reactivity and equilibrium of a chemical reaction, is still unavailable.

Heat of formation is one of the most important thermochemical properties of NEs because it is related directly with detonation parameters. Though some of their heats of formation can be found experimentally, certain nitroester compounds are difficult

to synthesize and some of them are highly unstable. Hence, in the past, several theoretical procedures such as group additive method, molecular mechanics and semi-empirical MO methods have been used to estimate the heat of formation of NEs. But since these are all parameterized method, the produced results are strongly dependent on the parameters used and thus are less reliable. On the other hand, density functional theory (DFT) are independent on the experimental results and parameters, and the computed results of geometry, energy and frequency are quite reliable [15–18]. Therefore they are gaining more and more popularity in chemical researches.

Ab initio methods have been selected to calculate the heat of formation for many years, especially for some high level theories, such as G2, G3, QCISD(T), CCSD(T), MP4DTQ approaches [19–25]. However, the impractical problem is that the sophisticated methods require far too much computational time and disk spaces to treat electron correlation. This limits their applicability to rather small molecules, consisting of up to seven or eight non-hydrogen atoms where computational resources are limited.

Rice et al. [9] proposed methods to predict gas phase heats of formation of energetic materials using quantum mechanical calculations, where methyl nitrate, ethyl nitrate and tetranitrate are included. Byrd Edward and Rice Betsy [26] used atom and group-equivalent method to compute the gas-phase heats of formation for CHNO system, where five nitroester compounds included. Mohammad [27] used an empirical approach to calculate the heats of formation of nitramine, nitrate esters, nitroaliphatics and related energetic compounds. Muthurajan et al. [28] predicted the heat of formation and related parameters of high-energy materials. Obviously, only the heats of formation of several nitroester compound are calculated in Refs. [9,26–28]. To the best of our knowledge, for nitroester compounds, the report on the gas-phase heats of formation is very few.

Generally, predictions for gas-phase heats of formation are based on Hess' Law [29], combined with quantum mechanical and experimental information. The application of the Hess' Law requires building a chemical reaction scheme. The isodesmic reaction, in which numbers of electron pairs and chemical bond types are conserved in the reaction, allows canceling of errors inherent in the approximate treatment of electron correlation in the solutions to quantum mechanic equations. Hence, various reports of the heats of formation of the molecules have been given by various isodesmic reaction schemes [15,30–34]. Ventura et al. [35,36] have pointed out that DFT methods using modest basis sets and isodesmic reactions can produce very accurate thermochemical information, in many cases superior to results from Gaussian-2 (G2) and even the coupled cluster method (CCSD(T)).

In this study, a series of nitroesters explosives were selected, using various DFT methods and basis sets to calculate the heats of formation through the selected isodesmic reactions. The calculated heats of formation were compared with the experimental results. If these kinds of calculation are reliable, then the heat of formation of a compound whose heat of formation cannot be determined by experimental technique can be obtained theoretically. Further analysis is performed by comparing the current result with the results of Muthurajan et al. [28].

2. Theory and computational details

All calculations were carried out with the GAUSSIAN 03 program package [37]. The hybrid density functional used in this study are semi-empirical exchange-correlation functionals B3LYP [38,39], B3P86 [38,40], B3PW91 [38,41]. 6-31G*, 6-31G**, 6-311G*, and 6-311G** basis sets were used. Molecular and fragmental geometries were optimized for each computational method. The optimized

Table 1

The reference compounds and their experimental heats of formation at 298.15 K.

Reference compounds	ΔH_f^0 (kcal/mol)	Ref.
CH ₃ ONO ₂	-29.43	[28]
CH ₄	-17.80	[42]
C ₂ H ₆	-20.05	[42]
CH ₃ NO ₂	-19.3	[42]
CH ₃ OH	-48.11	[43]

structures were characterized as true local energy minima on the potential surface, without imaginary frequencies. The zero-point energies (ZPEs) and the corresponding thermal corrections (HTs) to the enthalpy at 298.15 K were also obtained from frequency calculation and were subsequently added to the electronic energies.

Isodesmic reactions were used to compute the HOF. Various isodesmic reaction schemes were selected for the calculation of the heats of formation of C₂H₅ONO₂, CH₃(CH₂)₂ONO₂, CH₃(CH₂)₃-ONO₂, CH₃(CH₂)₄ONO₂, O₂NO(CH₂)₂ONO₂, O₂NO(CH₂)₃ONO₂, O₂NO(CH₂)₄ONO₂, CH₂OHCH₂ONO₂, CH₂OHCHOHCH₂ONO₂, O₂NCH₂CH₂ONO₂, O₂NOCH₂CHONO₂CH₃, (CH₃)₂CHCH₂ONO₂, O₂NCH₂CHOHCH₂ONO₂, (O₂NCH₂)₄C, O₂NO(CH₂)₂CHONO₂-CH₃, CH₃CHONO₂CH₃, O₂NOCH₂CHONO₂CH₂CH₃, O₂NOCH₂-CHONO₂CH₂ONO₂, CH₂OHCHONO₂CH₂ONO₂, CH₃CHONO₂-(CH₂)₂CH₃, CH₃CHONO₂CHONO₂CH₃, CH₃CHONO₂C₂H₅, HOCH₂-CH(ONO₂)CH₂OH, and (CH₃)₃CONO₂. Choosing suitable references is the key point to make sure that the conjugated bond of NO₂ is not destroyed during the reaction. The reference compounds we selected are listed in Table 1, included in experimental heats of formation.

The HOFs at 298.15 K can be calculated from the following equation:

$$\begin{aligned} \Delta H_{298.15\text{ K}} &= \Delta E_{298.15\text{ K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \\ &= \sum_{\text{product}} \Delta H_f^0 - \sum_{\text{reactant}} \Delta H_f^0 \end{aligned} \quad (1)$$

where ΔE_0 and ΔZPE are the total energy difference and the zero-point energy difference between products and reactants at 0 K, respectively; ΔH_T is the change in thermal correction to enthalpies between products and reactants; $\sum_{\text{product}} \Delta H_f^0$ and $\sum_{\text{reactant}} \Delta H_f^0$ are sums of the heats of formation for products and reactants in gas at 298.15 K, respectively. $\Delta(PV)$ equals ΔnRT for reaction in gas phase. For isodesmic reactions, $\Delta n = 0$.

The average errors of the HOFs for the B3LYP, B3PW91, B3P86 and CBS-Q methods are determined by calculating the average absolute error (ϵ_{aae}), defined as

$$\epsilon_{\text{aae}} = \frac{1}{N} \sum_{i=1}^N |x_i - c_i| \quad (2)$$

where x_i represents the experimental data, c_i denotes the calculated values and N is the number of experimental or calculated data.

3. Results and discussion

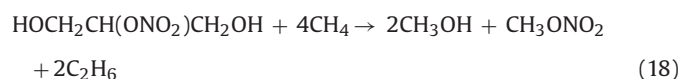
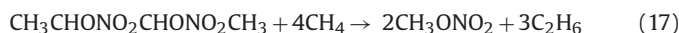
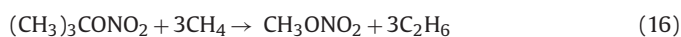
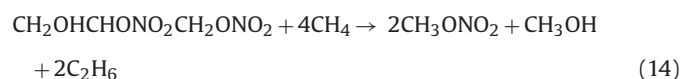
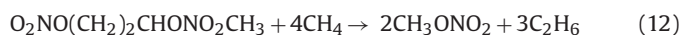
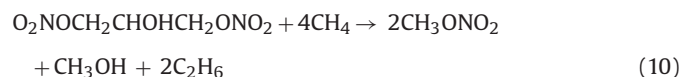
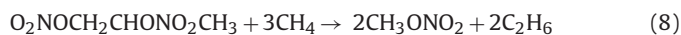
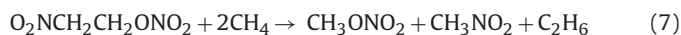
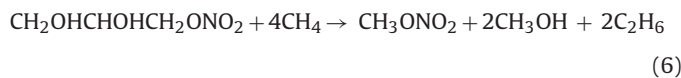
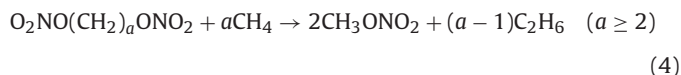
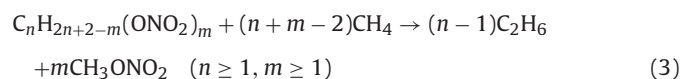
3.1. The selected isodesmic reactions

As indicated by Foresman and Frisch [44], different isodesmic reactions would predict different value of heat of formation for the same molecule. It is necessary to properly select the isodesmic reaction of the studied molecule. The following isodesmic reactions were selected in order to calculate the heats of formation for the

Table 2
The reaction enthalpies (kcal/mol) of Eqs. (3)–(18).

	B3LYP		B3PW91		B3P86	
	6-31G**	6-311G**	6-31G**	6-311G**	6-31G**	6-311G**
C ₂ H ₅ ONO ₂	5.1	5.1	5.0	5.0	5.2	5.2
CH ₃ (CH ₂) ₂ ONO ₂	6.5	6.6	6.5	6.5	6.8	6.8
CH ₃ (CH ₂) ₃ ONO ₂	8.0	8.1	8.0	8.0	8.4	8.4
CH ₃ (CH ₂) ₄ ONO ₂	9.5	9.6	9.5	9.5	10.2	10.2
O ₂ NO(CH ₂) ₂ ONO ₂	4.4	4.9	4.3	4.5	4.5	4.7
O ₂ NO(CH ₂) ₃ ONO ₂	8.3	8.7	8.2	8.4	8.6	8.7
O ₂ NO(CH ₂) ₄ ONO ₂	-2.1	12.0	11.5	11.7	12.1	12.3
CH ₂ OHCH ₂ ONO ₂	8.0	8.6	7.9	8.3	8.2	8.5
CH ₂ OHCHOHCH ₂ ONO ₂	22.2	23.0	22.1	18.7	23.0	19.5
O ₂ NCH ₂ CH ₂ ONO ₂	4.3	4.4	4.2	4.0	4.5	4.4
O ₂ NOCH ₂ CHONO ₂ CH ₃	10.3	10.5	10.1	10.1	10.6	10.8
(CH ₃) ₂ CHCH ₂ ONO ₂	8.9	9.1	8.8	9.0	9.5	9.7
O ₂ NOCH ₂ CHOHCH ₂ ONO ₂	16.1	16.9	15.9	16.3	16.7	17.1
(O ₂ NOCH ₂) ₄ C	23.4	24.2	22.1	22.7	24.8	25.4
O ₂ NO(CH ₂) ₂ CHONO ₂ CH ₃	12.9	13.2	12.7	12.8	13.6	13.7
CH ₃ CHONO ₂ CH ₃	10.0	10.0	9.8	9.7	10.4	10.3
O ₂ NOCH ₂ CHONO ₂ CH ₂ CH ₃	12.3	12.7	12.0	12.1	12.8	13.0
O ₂ NOCH ₂ CHONO ₂ CH ₂ ONO ₂	8.7	10.5	8.4	9.8	9.1	9.5
CH ₂ OHCHONO ₂ CH ₂ ONO ₂	23.1	15.6	22.7	15.0	15.5	15.8
CH ₃ CHONO ₂ (CH ₂) ₂ CH ₃	13.0	13.1	12.8	12.9	13.8	13.8
CH ₃ CHONO ₂ CHONO ₂ CH ₃	15.0	15.5	15.2	15.1	15.8	15.7
CH ₃ CHONO ₂ C ₂ H ₅	11.5	11.6	11.4	11.4	12.2	12.2
HOCH ₂ CH(ONO ₂)CH ₂ OH	18.2	19.0	17.9	18.4	18.8	18.4
(CH ₃) ₃ CONO ₂	11.5	11.5	11.3	11.3	12.4	12.4

nitroester compounds studied here.



3.2. The reaction enthalpies of isodesmic reactions selected

The reaction enthalpies (i.e. the energy differences ($\Delta H_{r,n}$) between the products and reactants) of Eqs. (3)–(18) can be calculated and the results of various DFT methods are presented in Table 2.

It is noted that all the isodesmic reactions have the positive reaction enthalpies, which proves that these reactions are endothermic reactions. CH₃(CH₂)₂ONO₂ and CH₃CHONO₂CH₃ are isomeric compounds and their isodesmic reactions are similar. From Table 2, we can see that the reaction enthalpy of isodesmic reaction of CH₃(CH₂)₂ONO₂ is smaller than that of CH₃CHONO₂CH₃, which proves that the reaction enthalpy is sensitive to the position of -ONO₂ group. The conclusion can also be proved by the reaction enthalpies of Eqs. (12), (13), (17) and isodesmic reaction of O₂NO(CH₂)₄ONO₂. O₂NO(CH₂)₄ONO₂, O₂NO(CH₂)₂CHONO₂CH₃, O₂NOCH₂CHONO₂CH₂CH₃ and CH₃CHONO₂CHONO₂CH₃ are isomeric compounds and the reaction enthalpy of Eq. (17) is much bigger than those of Eqs. (12), (13) and isodesmic reaction of O₂NO(CH₂)₄ONO₂. The reaction enthalpy of isodesmic reaction of O₂NO(CH₂)₄ONO₂ is the smallest among the four equations. CH₃CHONO₂C₂H₅, (CH₃)₃CONO₂, (CH₃)₂CHCH₂ONO₂ and CH₃(CH₂)₃ONO₂ are also isomeric compounds and the reaction enthalpy of isodesmic reaction of CH₃(CH₂)₃ONO₂ are the smallest among the four isodesmic reactions.

Comparing the three series of isomeric compounds, we can see the reaction enthalpy is the smallest for the compound which has the normal chain such as CH₃(CH₂)₂ONO₂, O₂NO(CH₂)₄ONO₂ and CH₃(CH₂)₃ONO₂, while the reaction enthalpy is the bigger for the compound which has the secondary explosives such as (CH₃)₃CONO₂, CH₃CHONO₂CH₃ and CH₃CHONO₂CHONO₂CH₃.

Table 3

Calculated HOFs (kcal/mol) and experimental ones at 298.15 K for nitroester compounds from isodesmic reaction.

	B3LYP		B3PW91		B3P86		HOF _{exp}	HOF _{other}
	6-31G**	6-311G**	6-31G**	6-311G**	6-31G**	6-311G**		
C ₂ H ₅ ONO ₂	-36.8 (0.2)	-36.8 (0.2)	-36.8 (0.2)	-36.7 (0.3)	-36.9 (0.1)	-36.7 (0.3)	-37.04 ^a	-36.9 ^b
CH ₃ (CH ₂) ₂ ONO ₂	-40.4 (1.2)	-40.7 (0.9)	-40.5 (1.1)	-40.4 (1.2)	-40.7 (0.9)	-40.4 (1.2)	-41.6 ^a	-40.3 ^b
O ₂ NO(CH ₂) ₂ ONO ₂	-47.8 (-2.5)	-48.2 (-2.9)	-47.6 (-2.3)	-47.8 (-2.5)	-47.8 (-2.5)	-48.0 (-2.7)	-45.3 ^c	
CH ₃ CHONO ₂ CH ₃	-43.6 (2.1)	-43.4 (2.3)	-44.0 (1.7)	-43.5 (2.2)	-43.3 (2.4)	-43.9 (1.8)	-45.7 ^d	
O ₂ NOCH ₂ CHONO ₂ CH ₂ ONO ₂	-66.8 (-0.1)	-68.6 (-1.9)	-66.8 (-0.1)	-67.8 (-1.1)	-67.2 (-0.5)	-67.6 (-0.9)	-66.7 ^e	
Mean absolute deviation	1.22	1.64	1.1	1.46	1.28	1.38		

All the values in the parenthesis correspond to the theoretical results minus the experimental results.

^a The data are from Ref. [41].^b Theor. (B3LYP/6-31G**), from Ref. [48].^c The data are from Ref. [45].^d The data are from Ref. [46].^e The data are from Ref. [47].

It is noted that the reaction enthalpies increase gradually with the increment of the number of methylene group for the compounds which have the normal chain. The reaction enthalpy of isodesmic reaction of CH₃(CH₂)₄ONO₂ is the biggest among the series of C_nH_{2n+1}ONO₂ compounds studied, while the reaction enthalpy of the isodesmic reaction of C₂H₅ONO₂ is the smallest. The conclusion can be proved by the reaction enthalpy of isodesmic reaction of O₂NO(CH₂)₂ONO₂, O₂NO(CH₂)₃ONO₂, O₂NO(CH₂)₄ONO₂.

HOCH₂CH(ONO₂)CH₂OH and CH₂OHCHOHCH₂ONO₂ are isodesmic compounds, O₂NOCH₂CHOHCH₂ONO₂ and CH₂OHCHONO₂CH₂ONO₂ are also isodesmic compounds. From Table 2, we can see that the four compounds all have two -OH groups or two -ONO₂ groups, but it is noted that the compound with 1,2-OH group (or 1,2-ONO₂ group) has bigger reaction enthalpies, while the compound with 1,3-OH group (or 1,3-ONO₂ group) has smaller reaction enthalpies.

In addition, the compound with secondary -ONO₂ group has smaller reaction enthalpy, which can be proved by comparing HOCH₂CH(ONO₂)CH₂OH and CH₂OHCHOHCH₂ONO₂, O₂NOCH₂CHOHCH₂ONO₂ and CH₂OHCHONO₂CH₂ONO₂.

3.3. Heat of formation from computed isodesmic reaction

From the calculated ΔH_{rxn} and experimental heats of formation at 298.15 K of the selected reference compounds, the HOFs from isodesmic reactions of C₂H₅ONO₂, CH₃(CH₂)₂ONO₂, O₂NO(CH₂)₂ONO₂, CH₃CHONO₂CH₃, O₂NOCH₂CHONO₂CH₂ONO₂ in the gas phase at 298.15 K are predicted using the B3LYP, B3P86, and B3PW91 three-parameter hybrid DFT methods with 6-31G** and 6-311G** basis sets. The results are presented in Table 3. The experimental data taken from Refs. [41,45–47] are also included. In addition, the heats of formation of C₂H₅ONO₂ and CH₃(CH₂)₂ONO₂ computed by Zeng et al. [48] are also listed in Table 1. It is obvious that the results calculated by Zeng are similar to our results calculated by B3LYP/6-31G** method.

From Table 3, we can note that the deviations from the experimental values are all positive for C₂H₅ONO₂, CH₃(CH₂)₂ONO₂, CH₃CHONO₂CH₃ and they are all negative for O₂NO(CH₂)₂ONO₂ and O₂NOCH₂CHONO₂CH₂ONO₂, which shows that the deviation from the experimental value is irrespective of the method of calculation. In addition, it is noted that C₂H₅ONO₂, CH₃(CH₂)₂ONO₂, CH₃CHONO₂CH₃ all have one -ONO₂ group while O₂NO(CH₂)₂ONO₂ and O₂NOCH₂CHONO₂CH₂ONO₂ have the number of -ONO₂ group bigger than one.

It is also noted that the computed HOFs are all closer to the experimental ones and the mean absolute deviations are within 2.0 kcal/mol, which is the desirable precision of order for quan-

tum thermochemical methods [49]. But the heats of formation computed by B3PW91/6-31G** level are the closest to the experimental heats of formation with the mean absolute deviation of 1.1 kcal/mol. Using B3PW91/6-31G** method, we calculated the other 19 nitroester compounds, and the heat of formation calculated are listed in Table 4.

From Tables 3 and 4, it is found that the heats of formation of C₂H₅ONO₂, CH₃(CH₂)₂ONO₂, CH₃(CH₂)₃ONO₂, CH₃(CH₂)₄ONO₂ are -36.8, -40.5, -44.3, and -48.0 kcal/mol, respectively. This shows that the computed heat of formation decreases when the number of methylene (-CH₂) group increases for normal chain nitroester compounds. The conclusion can also be proved by the heats of formation of O₂NO(CH₂)₂ONO₂, O₂NO(CH₂)₃ONO₂, O₂NO(CH₂)₄ONO₂ with the HOFs of -47.6, -53.8, and -59.3 kcal/mol, respectively. Through comparing, we found that the conclusion is the same for the normal chain thiol compounds [50].

It is noteworthy that the HOFs of nitroester isomers with the same number of -ONO₂ group are affected by the position of -ONO₂ group. CH₃CHONO₂C₂H₅, (CH₃)₃CONO₂, (CH₃)₂CHCH₂ONO₂ and CH₃(CH₂)₃ONO₂ are isomeric compounds with a -ONO₂ group and the heat of formation of CH₃(CH₂)₃ONO₂ is the biggest while the heat of formation of CH₃CHONO₂C₂H₅ is the smallest, which is contrary to the change of the reaction enthalpies of their isodesmic reactions. CH₃(CH₂)₂ONO₂ and CH₃CHONO₂CH₃ are isomeric compounds and the heat of formation of CH₃(CH₂)₂ONO₂ is bigger than

Table 4

Calculated HOFs (kcal/mol) of the other 19 nitroester compounds at 298.15 K from isodesmic reaction with B3PW91/6-31G** method.

Compounds	HOF
CH ₃ (CH ₂) ₃ ONO ₂	-44.3
CH ₃ (CH ₂) ₄ ONO ₂	-48.0
O ₂ NO(CH ₂) ₃ ONO ₂	-53.8
O ₂ NO(CH ₂) ₄ ONO ₂	-59.3
CH ₂ OHCH ₂ ONO ₂	-69.9
CH ₂ OHCHOHCH ₂ ONO ₂	-116.6
O ₂ NCH ₂ CH ₂ ONO ₂	-37.4
O ₂ NOCH ₂ CHONO ₂ CH ₃	-55.7
(CH ₃) ₂ CHCH ₂ ONO ₂	-45.7
(CH ₃) ₃ CONO ₂	-47.5
O ₂ NOCH ₂ CHOHCH ₂ ONO ₂	-103.0
(O ₂ NOCH ₂) ₄ C	-98.1
O ₂ NO(CH ₂) ₂ CHONO ₂ CH ₃	-61.5
O ₂ NOCH ₂ CHONO ₂ CH ₂ CH ₃	-49.8
CH ₂ OHCHONO ₂ CH ₂ ONO ₂	-98.6
CH ₃ CHONO ₂ (CH ₂) ₂ CH ₃	-51.4
CH ₃ CHONO ₂ CHONO ₂ CH ₃	-63.0
CH ₃ CHONO ₂ C ₂ H ₅	-47.6
HOCH ₂ CH(ONO ₂)CH ₂ OH	-112.5

Table 5

Comparison of heats of formation predicted by Muthurajan et al., and Byrd Edward and Rice Betsy and our study with experimental results.

	Muthurajan et al. results ^a	Byrd Edward and Rice Betsy results ^b	Current study	Experimental results
C ₂ H ₅ ONO ₂	−35.4 (1.64)	−34.9 (2.14)	−36.8 (0.2)	−37.04 ^c
CH ₃ (CH ₂) ₂ ONO ₂	−40.5 (1.1)	–	−40.5 (1.1)	−41.6 ^c
O ₂ NO(CH ₂) ₂ ONO ₂	−53.92 (8.62)	–	−47.6 (−2.3)	−45.3 ^d
CH ₃ CHONO ₂ CH ₃	−45.65 (0.05)	–	−44.0 (1.7)	−45.7 ^e
O ₂ NO(CH ₂) ₄ ONO ₂	−63.9	–	−59.3	–
(CH ₃) ₃ CONO ₂	–	−38.3	−47.5	–
Mean absolute deviation	2.85	–	1.33	–

All the values in the parenthesis correspond to the theoretical results minus the experimental results.

^a The data are from Ref. [28].^b The data are from Ref. [26].^c The data are from Ref. [41].^d The data are from Ref. [45].^e The data are from Ref. [46].

that of CH₃CHONO₂CH₃. This shows that the HOF of the normal chain compound with a −ONO₂ group at its 1-position is the biggest, while the HOF is the smallest for the normal chain compound with NO₂ group at its 2-position.

The HOFs of CH₂OHCH₂ONO₂, CH₂OHCHOHCH₂ONO₂, CH₂OHCHONO₂CH₂ONO₂ are −69.9, −103.0, and −98.6 kcal/mol, respectively. It is noted that when a H group in CH₂OHCH₂ONO₂ is substituted with a −OH group, the HOF decreases from −69.9 to −103.0 kcal/mol. While an H group in CH₂OHCH₂ONO₂ is substituted with a −ONO₂ group, the HOF decreases from −69.9 to −98.6 kcal/mol. In addition, from the HOFs of CH₂OHCHOHCH₂ONO₂, CH₂OHCHONO₂CH₂ONO₂, it is noted that the more the −OH group, the smaller the HOF. This conclusion can also be proved by CH₂OHCHOHCH₂ONO₂ (−116.6 kcal/mol) and O₂NOCH₂CHOHCH₂ONO₂ (−103.3 kcal/mol).

From Table 4, we also found that the compound with secondary −ONO₂ group has bigger reaction enthalpy. This can be proved by HOCH₂CH(ONO₂)CH₂OH (−112.5 kcal/mol) and CH₂OHCHOHCH₂ONO₂ (−116.6 kcal/mol), O₂NOCH₂CHOHCH₂ONO₂ (−103.3 kcal/mol) and CH₂OHCHONO₂CH₂ONO₂ (−98.6 kcal/mol).

3.4. Comparison with other computational results

Muthurajan et al. have developed [28,51–53] a code which can predict heat of formation at gaseous phase. So a direct comparison of the results of this study to those of Muthurajan is necessary to determine whether our method is reliable to be used in calculating the heats of formation at gaseous phase of the energetic compounds studied. In addition, Byrd Edward and Rice Betsy [26]

Table 6

Heats of formation, heat of sublimation (kcal/mol).

Name	ΔH_f^0							ΔH_{sub}
	Gas			Solid			Theo.	
	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.		
C ₂ H ₅ ONO ₂	−37.04 ^a	−36.8	0.2	–	−50.8	–	14.0	
CH ₃ (CH ₂) ₂ ONO ₂	−41.6 ^a	−40.5	1.1	–	−55.6	–	15.1	
CH ₃ (CH ₂) ₃ ONO ₂	–	−44.3	–	–	−61.2	–	16.9	
CH ₃ (CH ₂) ₄ ONO ₂	–	−48.0	–	–	−66.3	–	18.3	
O ₂ NO(CH ₂) ₂ ONO ₂	−45.3 ^b	−47.6	−2.3	–	−65.7	–	18.1	
O ₂ NO(CH ₂) ₃ ONO ₂	–	−53.8	–	–	−74.3	–	20.5	
O ₂ NO(CH ₂) ₄ ONO ₂	–	−59.3	–	–	−81.8	–	22.5	
CH ₂ OHCH ₂ ONO ₂	–	−69.9	–	–	−84.4	–	14.5	
CH ₂ OHCHOHCH ₂ ONO ₂	–	−116.6	–	–	−133.4	–	16.8	
O ₂ NCH ₂ CH ₂ ONO ₂	–	−37.4	–	–	−54.6	–	17.2	
O ₂ NOCH ₂ CHONO ₂ CH ₃	–	−55.7	–	–	−83.2	–	17.5	
(CH ₃) ₂ CHCH ₂ ONO ₂	–	−45.7	–	–	−57.0	–	11.3	
O ₂ NOCH ₂ CHOHCH ₂ ONO ₂	–	−103.0	–	–	−124.3	–	21.3	
(O ₂ NOCH ₂) ₄ C	–	−98.1	–	−128.7 ^c	−127.2	1.5	29.1	
O ₂ NO(CH ₂) ₂ CHONO ₂ CH ₃	–	−61.5	–	–	−74.7	–	13.2	
CH ₃ CHONO ₂ CH ₃	−45.7 ^d	−44.0	1.7	–	−52.8	–	8.8	
O ₂ NOCH ₂ CHONO ₂ CH ₂ CH ₃	–	−49.8	–	–	−69.1	–	19.3	
O ₂ NOCH ₂ CHONO ₂ CH ₂ ONO ₂	−66.7 ^e	−66.8	0.1	–	−86.4	–	19.6	
CH ₂ OHCHONO ₂ CH ₂ ONO ₂	–	−98.6	–	–	−118.0	–	19.4	
CH ₃ CHONO ₂ (CH ₂) ₂ CH ₃	–	−51.4	–	–	−64.8	–	13.4	
CH ₃ CHONO ₂ CHONO ₂ CH ₃	–	−63.0	–	–	−75.3	–	12.3	
CH ₃ CHONO ₂ C ₂ H ₅	–	−47.6	–	–	−58.5	–	10.9	
HOCH ₂ CH(ONO ₂)CH ₂ OH	–	−112.5	–	–	−125.0	–	12.5	
(CH ₃) ₃ CONO ₂	–	−47.5	–	−54.9 ^e	−57.0	−2.1	9.5	

^a The data are from Ref. [41].^b The data are from Ref. [45].^c The data are from Ref. [26].^d The data are from Ref. [46].^e The data are from Ref. [47].

used B3LYP/6-311++G(2df,2p) and group equivalent to obtain the gas-phase heats of formation for some nitroester compounds. The results of Muthurajan and Byrd et al. are all listed in Table 5.

From Table 5, it is noted that the results of current study are generally better than that of Muthurajan. The mean absolute deviation for our study is 1.33 kcal/mol and the maximum deviation is 2.3 kcal/mol. The mean absolute deviation for the result of Muthurajan is 2.85 kcal/mol and the maximum deviation is 8.62 kcal/mol. In addition, Byrd Edward and Rice Betsy only calculated the gas-phase heats of formation of $C_2H_5ONO_2$ and $(CH_3)_3CONO_2$. The computational results obtained by Byrd Edward and Rice Betsy are bigger than those that we obtained and the absolute deviation for $C_2H_5ONO_2$ is 2.14 kcal/mol.

3.5. The condensed phase heats of formation of nitroester energetic compounds studied

For assessment of the potential performance of the energetic material of interest, the desired quantity is usually the condensed phase ΔH_f^0 . In order to accommodate this need, we compute the condensed phase heat of formation of all mentioned energetic compounds through the same method of Byrd Edward and Rice Betsy. According to Hess's law, the solid phase heat of formation ($\Delta H_{f(s)}^0$) can be obtained by

$$\Delta H_{f(s)}^0 = \Delta H_{f(g)}^0 - \Delta H_{sub} \quad (19)$$

where $\Delta H_{f(s)}^0$ is the predicted gas-phase heats of formation and ΔH_{sub} is the heats of sublimation. The heat of sublimation can be represented as

$$\Delta H_{sub} = a(SA)^2 + b\sqrt{\sigma_{tot}^2} + c \quad (20)$$

where the constants a , b , and c are determined through a least-squares fit of Eq. (20) with experimental values for ΔH_{sub} , where SA is the surface area of the 0.001 electron/bohr³ 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 latter two quantities have been shown by Politzer et al. to be important in treating macroscopic properties that are dependent on noncovalent electrostatic interactions [54–56].

The B3LYP hybrid generalized-gradient approximation (GGA) density functional theory was used with 6-311++G(2df,2p) basis set to optimize geometries and determine the densities for generating the electrostatic potentials (ESPs) and the atom and group equivalents. The optimized structure is assumed to correspond to a local potential energy minimum. The computed condensed phase heats of formation are listed in Table 6. In Table 6, the theoretical gas-phase heats of formation are computed with B3PW91/6-31G** method. B3LYP/6-311++G(2df,2p) method is used to the related computation with the heat of sublimation. For nitroester energetic compounds, there is no experimental heat of sublimation.

From Table 6, it is noted that only two nitroester compounds have the experimental condensed phase heats of formation and the deviation between the computational and experimental result is 1.2 kcal/mol for $(O_2NOCH_2)_4C$, 2.1 kcal/mol for $(CH_3)_3CONO_2$. This shows that our computational results are good agreement with the experimental values.

4. Conclusions

In this paper, the heats of formation for 24 nitroester energetic compounds have been calculated from isodesmic reactions, in which five nitroester energetic compounds with available experimental results have been calculated by three hybrids DFT B3LYP,

B3PW91, B3P86 methods. By comparing all the computed results with the experimental ones, we conclude that B3PW91 method with 6-31G** basis set can yield reliable HOFs, which has the mean absolute deviation of 1.1 kcal/mol. Using this method, we calculated the BDEs of other 19 nitroester energetic compounds. Our results indicate that the computed heat of formation decreases when the number of methylene ($-CH_2$) group increases for normal chain nitroester compounds. The HOF of the normal chain compound with a $-ONO_2$ group at its 1-position is the biggest, while the HOF is the smallest for the normal chain compound with $-ONO_2$ group at its 2-position. It is noted that the compound with secondary $-ONO_2$ group has bigger reaction enthalpy. The more the $-OH$ group, the smaller the HOF. The further study shows that our results about gas-phase heats of formation of nitroester compounds are better than the results of Muthurajan et al. [28], and Byrd Edward and Rice Betsy [26]. In addition, we have computed the condensed phase heat of formation of the nitroester compounds through the same method of Byrd Edward and Rice Betsy. The result shows that our computations are good agreement with the experimental values through comparing with the limited experimental condensed phase heats of formation.

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