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 (CH_2) 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. Talawar, 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].

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–NO_2 bond [9]. Bunte and Sun [10] have preformed 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

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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_3ONO_2	−29.43	[28]
CH_4	−17.80	[42]
C_2H_6	−20.05	[42]
CH_3NO_2	−19.3	[42]
CH_3OH	−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 $C_2H_5ONO_2$, $CH_3(CH_2)_2ONO_2$, $CH_3(CH_2)_3$-ONO_2, $CH_3(CH_2)_4ONO_2$, $O_2NO(CH_2)_2ONO_2$, $O_2NO(CH_2)_3ONO_2$, $O_2NO(CH_2)_4ONO_2$, $CH_2OHCH_2ONO_2$, $CH_2OHCHOHCH_2ONO_2$, $O_2NCH_2CH_2ONO_2$, $O_2NOCH_2CHONO_2CH_3$, $(CH_3)_2CHCH_2ONO_2$, $O_2NOCH_2CHOHCH_2ONO_2$, $(O_2NOCH_2)_4C$, $O_2NO(CH_2)_2CHONO_2$-CH_3, $CH_3CHONO_2CH_3$, $O_2NOCH_2CHONO_2CH_2CH_3$, O_2NOCH_2-$CHONO_2CH_2ONO_2$, $CH_2OHCHONO_2CH_2ONO_2$, CH_3CHONO_2-$(CH_2)_2CH_3$, $CH_3CHONO_2CHONO_2CH_3$, $CH_3CHONO_2C_2H_5$, $HOCH_2$-$CH(ONO_2)CH_2OH$, and $(CH_3)_3CONO_2$. Choosing suitable references is the key point to make sure that the conjugated bond of NO_2 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:

$$\Delta H_{298.15\,K} = \Delta E_{298.15\,K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$$
$$= \sum_{product} \Delta H_f^0 - \sum_{reactant} \Delta H_f^0 \tag{1}$$

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; $\sum_{product} \Delta H_f^0$ and $\sum_{reactant} \Delta H_f^0$ 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

$$\varepsilon_{aae} = \frac{1}{N} \sum_{i=1}^{N} |x_i - c_i| \tag{2}$$

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