Computational and Theoretical Chemistry 1011 (2013) 30–36

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Reliable approach for prediction of heats of formation of polycyclic saturated hydrocarbons using recently developed density functionals

Mohammad Hossein Keshavarz [a,*], Mehdi Zamani [b], Fariborz Atabaki [a], Khadijeh Hosseini Monjezi [a]

[a] *Department of Chemistry, Malek-ashtar University of Technology, Shahin-shahr, P.O. Box 83145/115, Islamic Republic of Iran*
[b] *Department of Chemistry, Isfahan University of Technology, Isfahan, P.O. Box 84156-83111, Islamic Republic of Iran*

ARTICLE INFO

Article history:
Received 10 January 2013
Received in revised form 30 January 2013
Accepted 30 January 2013
Available online 17 February 2013

Keywords:
Heat of formation
Homodesmotic reaction
DFT
MP2

ABSTRACT

The efficiency of recently developed ωB97X-D and M06-2X density functionals was investigated for estimating the gas phase and the condensed phase heats of formation of 27 polycyclic saturated hydrocarbon $C_nH_{n'}$ ($5 \leqslant n \leqslant 12$). The homodesmotic reaction of $C_nH_{n'} + m(C_2H_6) \rightarrow x(C_3H_8) + y(C_4H_{10}) + z(C_5H_{12})$ was used where the experimental reference data are available in the literature. The reliability of predicted results through these density functionals were also compared to the corresponding values calculated by B3LYP and MP2 computational approaches. The maximum absolute (MAX), mean absolute (MAE) and root mean squared (RMS) errors are decreased in moving from B3LYP to ωB97X-D and M06-2X. The performance of ωB97X-D and M06-2X methods is also good with respect to MP2. All three M06-2X, ωB97X-D and MP2 methods show excellent linear relationship with the experimental data. The second order perturbation theory does not reduce the MAX, MAE and RMS errors more than that for ωB97X-D and M06-2X methods.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The condensed phase heat of formation ($\Delta_f H^\circ$ (c)) of an organic compound is a measure of its energy content, which can be used to investigate its characteristics and thermochemical stability. It enters as input in different computer codes such as CHEETAH [1] and NASA-CEC-71 [2] in order to investigate detonation characteristics of explosives and evaluation of the performance of propellants. For solid and liquid organic compounds at 298.15 K, it can be obtained from combining the gas phase heats of formation ($\Delta_f H^\circ$ (g)) with the heats of sublimation (ΔH°_{sub}) and vaporization (ΔH°_{vap}), respectively.

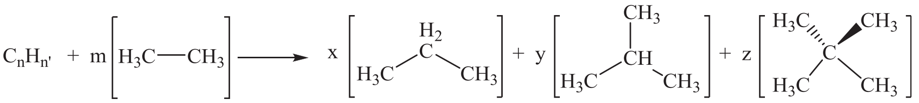
Different approaches were developed to predict $\Delta_f H^\circ$ (g) for some classes of organic compounds, e.g. molecular mechanic methods, semi-empirical quantum mechanical methods (SEQMs), quantitative structure–property relationship (QSPR) theory, group additivity methods, empirical procedures on the basis of molecular structures and the heat of combustion as well as studying the isodesmic, homodesmotic and atomization reactions by quantum chemical methods [3,4]. Group additivity methods can be used to estimate the ideal gas phase heats of formation [5]. They can be applied to calculate $\Delta_f H^\circ$ (c) for some specific classes of explosives, e.g. prediction of the standard heats of formation of aliphatic and alicyclic poly nitro compounds [6]. There are also some older AM1, PM3, MNDO, and the new developed semi-empirical methods such as PDDG/PM3, RM1, and PM6, which can be employed to approximate $\Delta_f H^\circ$ (g) of various energetic compounds [3,4]. To determine the solid and liquid phase heats of formation using predicted ΔH°_{vap} and ΔH°_{sub}, the Hess's law can be used [7]. Yoshiaki et al. [8] have combined ΔH°_{vap} and ΔH°_{sub} using additivity rule with $\Delta_f H^\circ$ (g) data obtained by semi-empirical and molecular mechanic methods to calculate $\Delta_f H^\circ$ (c) of nitro compounds. Some empirical methods have also been developed for predicting $\Delta_f H^\circ$ (c) and $\Delta_f H^\circ$ (g) of organic compounds containing C–NO_2, Ar–NO_2, N–NO_2 and O–NO_2 groups via their molecular structures [9–16]. Shi et al. [17] have used the SEQM and QSPR methods for calculation of $\Delta_f H^\circ$ (g) of strained cyclic organic molecules. In order to compute $\Delta_f H^\circ$ (c), they have applied the calculated values of ΔH°_{vap} and ΔH°_{sub} using the electrostatic potential method developed by Politzer et al. [18–22]. In this method, ΔH°_{vap} and ΔH°_{sub} of organic compounds can be estimated on the basis of molecular surface properties including the molecular surface area and the positive, negative and total average potentials, variances, average deviation and the electrostatic balance parameter on the molecular surface. This method can be utilized for estimating the phase transformation properties of various nitrogen containing energetic materials [23–27]. It was recently indicated that the electrostatic potential method can be used for calculation of ΔH°_{vap} and ΔH°_{sub} of 45 polycyclic saturated hydrocarbon [28].

---

* Corresponding author. Tel.: +98 312 522 5071; fax: +98 312 522 5068.
E-mail addresses: keshavarz7@gmail.com, hkeshavarz@mut-es.ac.ir (M.H. Keshavarz).

2210-271X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.comptc.2013.01.015

If the calculated $\Delta_f H^\circ$ can be obtained within about of ±3 kcal/mol, using model has good accuracy. When errors are less than 2 kcal/mol, the $\Delta_f H^\circ$ is quite accurate [29]. The density functional theory (DFT) includes electron correlation effects in an approximate approach, so the energies are more accurate than Hartree–Fock (HF) level of theory. However DFT methods, in comparison to higher-order ab initio calculations, are unable to describe correlation effects and dispersion forces [30–33]. These forces are so important in thermochemistry, reaction barrier heights and packing of molecules into solids [30–33]. Therefore, the higher-order perturbation theory, coupled-cluster and composite methods produce more reliable values for $\Delta_f H^\circ$ of molecules. For example, Politzer et al. [21] have used the B3PW91 density functional method to compute $\Delta_f H^\circ$ (g) of 107 organic compounds from their elements. They have found that the average absolute deviation from experiment is 11.9 kcal/mol, with the largest being 38.3 kcal/mol [21]. These poor values were further improved to 2.6 kcal/mol by additive correction terms [21]. Hudzik et al. [34], and Zehe and Jaffe [35] have reported the values of −20.3, −19.5 and −18.5 kcal/mol for $\Delta_f H^\circ$ (g) of exo-tetrahydrodicyclopentadiene (JP-10) via DFT, CBS-QB3/G3MP2B3 and the average of G3MP2, G3MP2//B3LYP and CBS-QB3 methods, respectively, where the experimental value is −17.7 kcal/mol [36].



$$C_nH_{n'} + m[H_3C{-}CH_3] \longrightarrow x[H_3C{-}CH_2{-}CH_3] + y[(H_3C)_2CH{-}CH_3] + z[C(CH_3)_4] \quad (1)$$

Since the composite computational methods are time-consuming and limited to small molecules, some independent research groups have tried to modify the density functional methods in recent years by empirical dispersion corrections or developed a new hybrid exchange–correlation functional with improved long-range properties [30–33,37–39]. The dispersion is an electron correlation effect, because it operates also intramolecularly, i.e. between atoms or functional groups that are not directly bonded to each other [33]. This situation contributes to the internal energy of molecules and improves the thermochemical properties [33]. The ωB97X-D functional is a long-range and dispersion corrected hybrid density functional that provides more accurate prediction in thermochemistry, kinetic and noncovalent interactions as compared with common hybrid density functionals [37,38]. The M06-2X functional is also a high-nonlocality meta hybrid density functional, which is recommended for applications involving main-group thermochemistry, kinetic and noncovalent interactions [39].

For liquid propellants, the accurate estimation of $\Delta_f H^\circ$ (c) is one of the key factors in calculation of their performance [2]. Synthetic hydrocarbon fuels containing favorable $\Delta_f H^\circ$ (c) and physical properties can be used as desirable jet fuels. Polycyclic saturated hydrocarbons are attractive candidates as liquid fuels in liquid bipropellants; because they contain suitable $\Delta_f H^\circ$ (c) for increasing their performance. For example, JP-10 with molecular formula of $C_{10}H_{16}$ is used as suitable synthetic jet fuel [34,35]. The purpose of this work is to introduce a reliable method for estimating the heat of formation of polycyclic saturated hydrocarbons. Here we examine the performance of ωB97X-D and M06-2X new density functionals for estimating $\Delta_f H^\circ$ (g) and $\Delta_f H^\circ$ (c) of 27 polycyclic saturated hydrocarbon $C_nH_{n'}$ $(5 \leqslant n \leqslant 12)$ (Fig. 1) where their experimental reference data are available in the literature. Moreover, we applied the present method for predicting the $\Delta_f H^\circ$ (c) of 9 well-known isomers of the JP-10 jet fuel with molecular formulas of $C_{10}H_{16}$ in which the experimental values are unavailable.

2. Computational details

Geometry optimization and frequency calculations of compounds 1–36 were performed at B3LYP, ωB97X-D and M06-2X levels of theory along with the 6-311++G** basis set. The MP2/6-311G** frequency calculations were done on the optimized B3LYP/6-311++G** geometries (MP2/6-311G**//B3LYP/6-311++G**).

The values of $\Delta_f H^\circ$ (g) of compounds 1–36 were calculated by the following homodesmotic reaction, i.e. Eq. (1), using the B3LYP, ωB97X-D, M06-2X and MP2 level of theory. In this reaction, every equivalent group in the cyclic molecules of 1–36 is matched with an equivalent group in a short acyclic molecule in the product. To determine the $\Delta_f H^\circ$ (g), first the standard enthalpy of reaction ($\Delta_{rxn} H^\circ$ (g)) were calculated (Table 1); then these values along with the experimental $\Delta_f H^\circ$ (g) of C_2H_6 (−20.1 kcal/mol), C_3H_8 (−25.0 kcal/mol), C_4H_{10} (−32.1 kcal/mol), and C_5H_{12} (−40.1 kcal/mol) were used for estimating $\Delta_f H^\circ$ (g) of polycyclic saturated hydrocarbon $C_nH_{n'}$ $(5 \leqslant n \leqslant 12)$.

The experimental values of $\Delta_f H^\circ$, ΔH°_{vap} and ΔH°_{sub} for compounds 1–36 were taken from National Institute of Standards and Technology (NIST) [40]. Theoretical values of ΔH°_{vap} and ΔH°_{sub} are calculated by following equations (Table 2):

$$\Delta H^\circ_{vap} = \alpha_1 (A_S)^{0.5} + \alpha_2 \left(\upsilon \sigma^2_{tot}\right)^{0.5} + \alpha_3 \quad (2)$$

$$\Delta H^\circ_{sub} = \beta_1 (A_S)^2 + \beta_2 \left(\upsilon \sigma^2_{tot}\right)^{0.5} + \beta_3 \quad (3)$$

where A_S is the molecular surface area, υ is electrostatic balance parameter and σ^2_{tot} is total variance of electrostatic potential on the molecular surface. The α_{1-3} and β_{1-3} parameters are determined from least-squares fitting to reliable values of the enthalpies of phase change. Details of these calculations were described elsewhere [28].

The condensed phase heat of formation ($\Delta_f H^\circ$ (c)) of compounds 1–36 were calculated by Eq. (4) and given in Table 3. All calculations of this work were performed using Gaussian-09 software package [41].

$$\Delta_f H^\circ(c) = \Delta_f H^\circ(g) - \Delta H^\circ{}_{vap(sub)} \quad (4)$$

3. Results and discussion

Table 1 gives the calculated standard enthalpy of reaction ($\Delta_{rxn} H^\circ$ (g)) for homodesmotic reaction of $C_nH_{n'} + m(C_2H_6) \rightarrow x(C_3H_8) + y(C_4H_{10}) + z(C_5H_{12})$, where $C_nH_{n'}$ is representative to the polycyclic saturated hydrocarbons 1–36 (Fig. 1). The visual comparison between the calculated values via various B3LYP, M06-2X, ωB97X-D and MP2 levels of theory is shown in Fig. 2. As seen, the $\Delta_{rxn} H^\circ$ (g) of many of compounds 1–36 is improved in moving from B3LYP to M06-2X, ωB97X-D and then MP2.

Table 3 summarizes the calculated values of $\Delta_f H^\circ$ (g) and $\Delta_f H^\circ$ (c) of polycyclic saturated hydrocarbons 1–36 via B3LYP, M06-2X, ωB97X-D and MP2 methods in comparison to the experimental

Download English Version:

https://daneshyari.com/en/article/5394219

Download Persian Version:

https://daneshyari.com/article/5394219

Daneshyari.com