Computational and Theoretical Chemistry 1106 (2017) 28–35

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

Performance of DFT, MP2, and composite ab initio methods for the prediction of enthalpies of formations of CHON compounds using isodesmic reactions

Olga V. Dorofeeva [a,*], Evgeniya L. Osina [b]

[a] Faculty of Chemistry, Lomonosov Moscow State University, 1-3 Leninskie Gory, Moscow 119991, Russia
[b] Joint Institute for High Temperatures, Russian Academy of Sciences, 13-2 Izhorskaya Street, Moscow 125412, Russia

ARTICLE INFO

Article history:
Received 2 October 2016
Received in revised form 6 January 2017
Accepted 3 March 2017
Available online 6 March 2017

Keywords:
Enthalpy of formation
Quantum chemistry
Composite methods
Isodesmic reactions
Hydrazine

ABSTRACT

This paper assesses the performance of quantum chemical models with regard to the calculation of enthalpy of formation of CHON molecules using isodesmic reactions. The high accuracy of prediction of enthalpy of formation of CHON compounds can be achieved by the combination of isodesmic reaction scheme with composite ab initio methods. The best composite methods, such as G4, G4MP2, CBS-QB3, and CBS-APNO, can attain near chemical accuracy or better depending on reaction type. Other composite methods yield the same accuracy only in conjunction with isodesmic or homodesmotic reactions. The DFT and MP2 methods lead to good results if they are used with homodesmotic reactions. For CHO compounds, all composite methods demonstrate the high accuracy not only with isodesmic and homodesmotic reactions, but also with isogyric reactions. Moreover, the DFT and MP2 methods can also yield a high accuracy estimate of the enthalpy of formation when they are used with isodesmic or homodesmotic reactions. Four composite methods (G4, G3, CBS-APNO, and CBS-QB3) employed in conjunction with 45 isogyric reactions yield the enthalpy of formation of hydrazine (97.7 ± 2.0 kJ/mol) in agreement with the best approximating to CCSD(T)/CBS energy, thus calling into question the usually quoted experimental value of 95.5 kJ/mol.

1. Introduction

The standard approach of calculating the enthalpy of formation uses the atomization reactions [1] and requires exceptionally high levels of theory such as complete basis set extrapolations of CCSD(T) method [2,3]. However, to date such calculations are extremely computation demanding and hence, are only applicable to the small molecules. A technique for evaluating the accurate enthalpies of formation ($\Delta_f H^\circ_{298}$) for larger systems is to derive them by using isogyric, isodesmic or other balanced reactions rather than atomization reactions [4,5]. In an isodesmic scheme, owing to better error cancellations, thermochemical predictions of chemical accuracy (~4 kJ/mol) can be obtained using lower level of theory [4–6]. The various types of balanced reactions are used in the computational thermochemistry. The isodesmic concept was extended by introducing the concept of homodesmotic reactions [7]. Recently a new hierarchy of homodesmotic reactions [8,9] and a generalized "connectivity-based hierarchy" [10] were proposed. The methodology of ring conserved isodesmic reactions [11] was used to calculate the enthalpies of formation of aromatic hydrocarbons.

A fairly large number of papers dealing with the use of different reaction type with the various method/basis set combinations has been published, but most of these studies have focused on hydrocarbons [12–18]. However, it should be noted that the enthalpies of formation of hydrocarbons can be calculated with high accuracy from atomization energies using the composite methods such as G4, CBS-APNO, and ccCA [17,19]. There are much less works dealing with the use of isodesmic reactions for oxygen and nitrogen compounds, whereas it was shown that the $\Delta_f H^\circ_{298}$ values calculated for these compounds by composite methods from the atomization energies can have fairly large systematic errors [20–22]. Especially large errors were identified for nitro compounds [23,24], which, however, could not always be found due to the uncertainties in the experimental data used for comparison [25]. Thus the results of using isodesmic reactions for nitrogen containing compounds are of interest for comparison with the experimental data.

---

* Corresponding author.
E-mail address: dorofeeva@phys.chem.msu.ru (O.V. Dorofeeva).

http://dx.doi.org/10.1016/j.comptc.2017.03.006
2210-271X/

Although density functional methods combined with isodesmic reaction energies can yield accurate thermochemistry for large molecules [6], Raghavachari et al. [26] have demonstrated that the combination of bond separation reactions with composite G2 method leads to a dramatic improvement in the accuracy of theoretically evaluated enthalpies of formation. The isodesmic reactions in conjunction with composite ab initio methods such as those of the Gaussian-*n* (G*n*) and complete basis set (CBS) varieties have been used extensively by Bozzelli et al. [27–33] to compute accurate enthalpies of formation of aldehydes, ketones, hydroperoxides, nitro and nitrite compounds, nitrocarbonyls, nitroolefins, and others. It has been shown that the use of isodesmic work reactions with composite ab initio methods (CBS-QB3, CBS-APNO, G3, G3MP2B3, G4) can lead to error reductions from around ±4 kJ/mol to ±2 kJ/mol or less. The DFT methods (B3LYP/6-31G(d,p), B3LYP/6-311G(2d,2p), and M06-2X/6-311+G(2d,d,p)) were also used by Bozzelli et al. in calculating enthalpies of formation [30–33]. In some cases, the authors point out that the results from DFT and ab initio calculations were in excellent agreement [32], whereas more often these methods demonstrate relatively high standard deviations, which were two or more times higher than the composite method calculations.

A variety of isodesmic or homodesmotic reactions, where the bonding environments are similar in products and reagents, has been used in the above mentioned works [27–33]. However, such reactions are not always possible to design for larger molecules with complex structure. Moreover, it becomes often impossible to carry out high level composite ab initio calculations for such molecules. For example, to estimate the enthalpy of formation of polycyclic nitramine CL-20, two not well balanced reactions

$$\begin{aligned}&(CH)_6(NNO_2)_6(CL\text{-}20) + 12\ CH_4 + 6\ NH_3\\&\quad\rightarrow 3\ CH_3CH_3 + 6\ CH_3NHCH_3 + 6\ H_2NNO_2\end{aligned}$$

$$\begin{aligned}&(CH)_6(NNO_2)_6(CL\text{-}20) + 24\ CH_3NH_2\\&\quad\rightarrow 3\ CH_3CH_3 + 6\ CH_3N(NO_2)CH_3 + 12\ NH_2CH_2NH_2\end{aligned}$$

were used in conjunction with the B3LYP/6-31G(d,p) model [34–37]. In our later study [38], it was shown that this approach overestimates the enthalpy of formation of CL-20 by 160–200 kJ/mol. Therefore, it is important to know the errors associated with the type of reactions and quantum chemical methods used in calculation of enthalpies of formation of molecules of different size and composition.

In the present work, we show that the isodesmic and other error canceling reactions can offer significant benefit and increased accuracy when composite ab initio methods are used to calculate the reaction enthalpies. Our conclusion is based on a large number of calculations for different CHON compounds by composite G4 method applied to both atomization and isodesmic reactions [21–24,38–42]. In these works, it was shown that the G4 method combined with atomization reaction is highly accurate for the prediction of enthalpies of formation CHO compounds [21,42], while its accuracy is decreased for nitrogen containing compounds, especially for nitro compounds [23,24]. In the present work, it will be shown that the atomic composition of the target molecule is also important when the isodesmic reactions are used. To clearly show this, we chose two molecules, CH_3ONO_2 and CH_3OCH_3, with reliable experimental $\Delta_f H^\circ_{298}$ values and used them to examine the performance of DFT, MP2, and composite ab initio models in the calculation of enthalpies of formation using isodesmic and other balanced reactions.

2. Computational details

Three DFT functionals (B3LYP, B3PW91, and M06-2X), MP2 method, and seven composite ab initio models (G4, G4MP2, G3, G3MP2B3, G2, CBS-QB3, and CBS-APNO) were assessed for the evaluation of enthalpies of formation of CH_3ONO_2 and CH_3OCH_3. Two relatively large basis sets, 6-311+G(3df,2p) and cc-pVTZ, were considered initially to derive the total energies for the different DFT techniques and MP2 method. In terms of mean absolute deviation (MAD) from experiment, the DFT models with 6-311+G(3df,2p) provide more accurate results than the use of cc-pVTZ basis set. Conversely, the MP2 method gives significantly better results with cc-pVTZ basis set. For this reason, only the results obtained at DFT/6-311+G(3df,2p) and MP2/cc-pVTZ levels are given finally in Tables 1 and 2 and discussed further in next section. All quantum chemical calculations were performed using the Gaussian 03 package of programs [43].

Thirteen reactions of different type (isogyric, isodesmic, and homodesmotic) were constructed for each molecule (Tables 1 and 2). These reactions contain radicals, inorganic, and organic reference species. The accurate values of enthalpies of formation recommended in Active Thermochemical Tables (ATcT) [44] were accepted for most reference species, with the exception of ethers ($C_2H_5OC_2H_5$, $CH_3OC_3H_7$, $(CH_3)_2CHOCH_3$, and $C_6H_5OCH_3$), nitrates ($CH_3CH_2ONO_2$, $C_3H_7ONO_2$, and $(CH_3)_2CHONO_2$), and nitro compounds (CH_3NO_2, $C_2H_5NO_2$, CH_3NHNO_2, and $CH_3N(NO_2)CH_3$). For anisole, the accurate enthalpy of formation determined recently by Simões et al. [45] was used in this work. The $\Delta_f H^\circ_{298}$ values for aliphatic ethers and nitrates were taken from the thermochemical archive by Pedley [46]; these values give consistent results for reactions 11–13 (Tables 1 and 2), thus confirming their accuracy. The enthalpies of formation of four nitro compounds are those recommended in Ref. [23].

The resulting enthalpy of formation was calculated combining the calculated enthalpy of reaction with the experimental enthalpies of formation of reference molecules. The scale factors for DFT and MP2 frequencies needed to calculate the zero-point energies and thermal corrections were taken from Ref. [47]. For comparison, the $\Delta_f H^\circ_{298}$ values calculated using atomization reaction were also included in Tables 1 and 2.

3. Results and discussion

The enthalpies of formation of CH_3ONO_2 and CH_3OCH_3 calculated from thirteen work reactions using different quantum chemical models are given in Tables 1 and 2. These tables also include the error statistics for each method: the mean absolute deviation (MAD), the root-mean-square deviation (RMSD), maximum negative and maximum positive deviation from the corresponding experimental value. The value of $\Delta_f H^\circ_{298}$ (CH_3ONO_2, g) = -122.2 ± 1.3 kJ/mol was determined by Ray and Ogg [48] from calorimetric investigation of the gas phase enthalpy of the reaction between N_2O_5 and CH_3ONO to form an equilibrium mixture of NO_2 and N_2O_4 plus CH_3ONO_2. This value is cited in the NIST Chemistry WebBook [49] and recommended by Pedley [46]. However, this value becomes somewhat more positive when the more recent enthalpies of formation of reaction components are used. The value of -119.4 kJ/mol was obtained in the present work using the enthalpies of formation of nitrogen oxides represented in ATcT [44] and experimental enthalpy of formation of CH_3ONO recommended on the basis of quantum chemical calculations [29]. Another value of $\Delta_f H^\circ_{298}$ (CH_3ONO_2, g) = -123.0 ± 3.3 kJ/mol was found by combining the available value of the enthalpy of formation of liquid CH_3ONO_2 with the enthalpy of vaporization [48]. Thus, the values of -119.4 kJ/mol and -123.0 kJ/mol can be