

## Performance of an integrated approach for prediction of bond dissociation enthalpies of phenols extracted from ginger and tea

Pham Cam Nam <sup>a,\*</sup>, Asit K. Chandra <sup>b,\*</sup>, Minh Tho Nguyen <sup>c,d</sup>

<sup>a</sup> Department of Chemistry, Danang University of Technology, University of Danang, 54 Nguyen Luong Bang, Lien Chieu, Da Nang, Viet Nam

<sup>b</sup> Department of Chemistry, North-Eastern Hill University, Shillong 793022, India

<sup>c</sup> Department of Chemistry, University of Leuven, B-3001 Leuven, Belgium

<sup>d</sup> Institute for Computational Science and Technology at HoChiMinh City (ICST), Viet Nam

### ARTICLE INFO

#### Article history:

Received 13 August 2012

In final form 26 October 2012

Available online 12 November 2012

### ABSTRACT

Integration of the (RO)B3LYP/6-311++G(2df,2p) with the PM6 method into a two-layer ONIOM is found to produce reasonably accurate BDE(O–H)s of phenolic compounds. The chosen ONIOM model contains only two atoms of the breaking bond as the core zone and is able to provide reliable evaluation for BDE(O–H) for phenols and tocopherol. Deviation of calculated values from experiment is  $\pm(1-2)$  kcal/mol. BDE(O–H) of several curcuminoids and flavanoids extracted from ginger and tea are computed using the proposed model. The BDE(O–H) values of enol curcumin and epigallocatechin gallate are predicted to be  $83.3 \pm 2.0$  and  $76.0 \pm 2.0$  kcal/mol, respectively.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Studies of the structures, properties, activities and also applications of the naturally occurring compounds continue to draw considerable attention of chemists. Many natural organic compounds extracted from leaves, seeds, and other parts of plants are considered as the potential antioxidants [1–7]. The great advantages of these compounds are in their high antioxidant activity, non-toxic effects on human-beings and safety to the environment [8,9].

In nature, we can find many sources of antioxidants such as tea leaves, coffee and curcumin. Tea is known as a good source of phenolic compounds whose beneficial role in the digestive process in humans is well established. Therefore the study of antioxidants extracted from natural substances is a matter of great interest to researchers in different fields. In the domain of antioxidants derived from natural sources, both experimental and theoretical studies are necessary to elucidate and understand their geometric and electronic structures, spectroscopic properties and specially their reactivities.

Theoretical studies have been primarily used to calculate the characteristic bond dissociation energy (BDE) and/or ionization energy (IE) of antioxidant compounds since these two properties are considered as important information to predict the antioxidant capacity [10]. Numerous efforts have already been made to measure or predict the accurate bond dissociation enthalpies of organic compounds. Because the accurate BDE value is one effective

indicator used to evaluate the antioxidant activity or in general reactivity of a natural compound. Besides, we can also easily design new materials with proper functional groups to achieve the required activity.

Density functional theory (DFT) based methods have extensively been used by many authors to determine thermochemical quantities such as BDE and IE of derivatives of phenol, thiophenol, aniline [11–13]. Although quantum chemical study is already well established for accurately predicting these properties, there are still many challenges in treatment of large compounds.

Recently, Nam and coworkers studied the thiophenol, phenylphosphine, toluene and their derivatives [14–16] using DFT with the (RO)B3LYP method to accurately determine the BDE and IE values. This approach consists of the use of the hybrid functional B3LYP, but the open-shell electronic species are treated by a spin-restricted method (RO). However, a major disadvantage of this approach comes when it is applied to the larger molecular systems but the computer resources are limited. In this context we set out to design an economic and efficient but appropriate approach for evaluation of the concerned properties for relatively large natural compounds in maintaining the high accuracy. For this purpose, we here propose an integration of the DFT and semi-empirical calculations into the ONIOM method [17–21], that can be applied to very large systems, and the obtained thermochemical results in such way are of reasonable accuracy. In order to deal with two-layer ONIOM method, we propose to use the DFT restricted open-shell (RO)B3LYP/6-311++G(2df,2p) for a high layer and the semi-empirical PM6 method for the lower layer. To test its performance we apply the approach to determine the BDEs of a series of natural phenolic compounds extracted from ginger

\* Corresponding authors.

E-mail addresses: [camnamp@yahoo.com](mailto:camnamp@yahoo.com) (P.C. Nam), [akchandra@nehu.ac.in](mailto:akchandra@nehu.ac.in) (A.K. Chandra), [minh.nguyen@chem.kuleuven.be](mailto:minh.nguyen@chem.kuleuven.be) (M.T. Nguyen).

and green tea, whose BDEs have been well established. We also complete the study by making predictions for the BDEs of some relevant compounds.

## 2. Computational methods

Quantum chemical calculations were carried out using the Gaussian 09 (version A.02) suite of programs [22]. Geometry optimizations and vibrational frequency calculations were conducted using the semi-empirical PM6 method. Vibrational frequencies obtained at the PM6 level were subsequently scaled by a factor of 1.078 for estimating the zero-point vibrational energies (ZPE) [23]. The enthalpy values at higher level were evaluated from the calculated single-point electronic energy based on PM6 optimized structures.

We thus propose a new ONIOM scheme integrating the (RO)-B3LYP/6-311++G(2df,2p) level with the semi-empirical PM6 method for evaluating the BDE(O–H)'s of all phenolic compounds. The restricted open-shell (RO) formalism was applied in this scheme for the radical species using the same basis set. The use of an RO method improves the energies of the radicals and thereby the BDE values. In Scheme 1, we describe the two ways of choosing the layer in our proposed ONIOM scheme.

In this proposed ONIOM treatment, each molecule is divided into two layers, the atoms in the circle is treated as a high layer; whereas the leftover atoms of the molecule in the rectangle belong to the second layer which is treated as a lower layer. The (RO)-B3LYP/6-311++G(2df,2p) method is thus applied for the atoms in the high layer, whereas the PM6 procedure is applied for the low layer. We consider two different ways of selecting the ONIOM model denoted as **1A** and **3A**. For the **1A**, the model has only one oxygen atom and one hydrogen atom related to the target bond for estimating BDE at the high level (the circle in Scheme 1). The **3A** ONIOM model has three heavy atoms including oxygen and two carbon atoms at the *ipso*- and *ortho*-positions involving hydrogen atoms (as shown in the circle) at the high level. The rest are defined as the low layer.

The homolytic BDE(O–H) value in gas phase at 298.15 K for the phenolic compound (ArOH) was calculated from the expression:

$$\text{BDE(O-H)} = H(\text{ArO}^\cdot) + H(\text{H}^\cdot) - H(\text{ArOH})$$

where  $H$ 's are the enthalpies of different species at 298.15 K. The enthalpies were estimated from the usual expression:  $H(T) = E_0 + \text{ZPE} + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT$ . The  $H_{\text{trans}}$ ,  $H_{\text{rot}}$ , and  $H_{\text{vib}}$  are the translational, rotational, and vibrational contributions to enthalpy, respectively,  $E_0$  is the total energy at 0 K and ZPE is the zero-point vibrational energy. The enthalpy value for the hydrogen atom in the gas phase was taken at its exact energy of  $-0.5$  hartree.

## 3. Results and discussion

### 3.1. Validation of the treatment ONIOM (ROB3LYP/6-311++G(2df,2p):PM6)

Since the two ONIOM models are newly proposed, first it is necessary to check their efficiency in estimating reliable BDE values. If the proposed procedures provide accurate BDE values for model compounds whose BDEs are accurately known from experiment, then it can be applied to unknown target compounds. To this end, we have calibrated our proposed ONIOM methods (**1A** and **3A**) in calculating the BDE(OH) for a series of substituted phenolic compounds. Table 1 presents our calculated BDE(O–H) values of phenolic compounds along with available experimental results.

For the model **1A**, the largest deviation between our calculated BDE(O–H) and experimental values of the corresponding molecules is of  $-2.1$  kcal/mol. For the other substituted compounds of phenol, the calculated BDE(O–H)s are underestimated in a range of 1–2 kcal/mol. The estimated BDE(O–H) of 87.2 kcal/mol for phenol from this work is in quite good agreement to the value of 87.5 kcal/mol obtained by Chandra and Uchamaru [25] using ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p), as well as with the recommended value of  $88.0 \pm 1.5$  kcal/mol [24].

However when we apply the model **3A** with three heavy atoms (one oxygen and two carbons), the difference between our calculated and the experimental BDE(O–H) becomes even larger, ranging between 4 and 6 kcal/mol. The largest deviation of  $-6.4$  kcal/mol is seen for *m*-OH-C<sub>6</sub>H<sub>4</sub>OH.

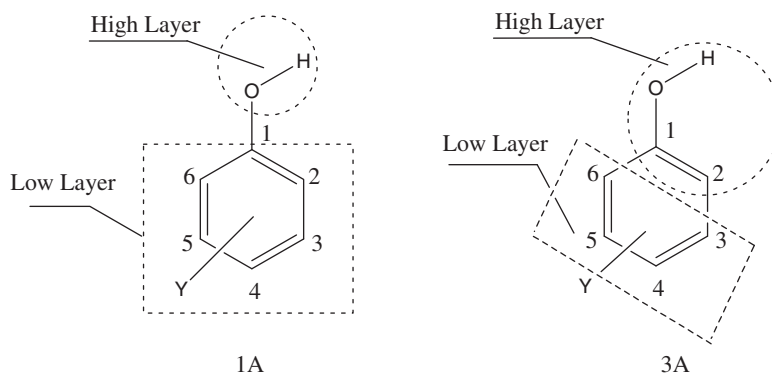
The reference values listed in Table 1 show that the BDE(O–H) values obtained from our model **1A** are reasonably accurate and comparable with the best experimental data. Hence we choose model **1A** as our method of choice for further study. However, the reliability of the model **1A** needs to be checked further for the larger molecules, like tocopherols. The tocopherols exist in *alpha*, *beta*, *gamma* and *delta* forms, in which *alpha*-tocopherol is known as a strong antioxidant.

Figure 1 depicts the optimized structure of tocopherol and the chosen model **1A**. The higher layer is displayed in bond and bond type format and the lower layer is in wire frame format. The calculated BDE(O–H) of tocopherols are given in Table 2. It can be observed that our calculated BDE(O–H) values are in very good agreement with the corresponding experimental values for tocopherols, with the deviation of only  $\pm 1.0$  kcal/mol.

### 3.2. BDE(O–H) of flavanoids extracted from nature

#### 3.2.1. Curcumin

Curcumin is the principal curcuminoid of the popular Indian spice turmeric, which is a member of the ginger family. Curcumin



Scheme 1. Schematic description of two-layer proposed ONIOM models: (a) **1A** and (b) **3A**.

Download English Version:

<https://daneshyari.com/en/article/5382567>

Download Persian Version:

<https://daneshyari.com/article/5382567>

[Daneshyari.com](https://daneshyari.com)