



A theoretical study on bond dissociation enthalpies of coal based model compounds



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HIGHLIGHTS

- The scope of BDE for four typical bond types in coal was presented.
- The relationship between the “weak bond” in coal and the BDE was discussed.
- The effects of radical stability on BDE value were explained.
- The reactions in coal pyrolysis were predicted through our BDE calculation.

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ABSTRACT

The homolytic bond dissociation enthalpies (BDE) of various bonds (C–H, C–C, C–O, and O–H) for coal based model compounds that are representative of the functionalities present in coal were computed by using a double-hybrid method mPW2PLYP. The BDE for C–H, C–C, C–O, O–H cover a range from 111.4 to 81.2 kcal/mol, 114.1 to 62.8 kcal/mol, 107.6 to 52.6 kcal/mol, and 111.2 to 86.6 kcal/mol, respectively. The so-called “weak bond” in coal does not mean a specific bond type, but it is associated with the BDE and highly depends on the stabilization of the fragmented radicals. Our work suggests that the initiation steps of the coal pyrolysis are most probably the cleavage of C–O and C–C bond to form the phenoxy radical or benzyl radicals. With the increase of temperature, the loss of alkyl and hydrogen groups becomes feasible, whereas the phenyl-like radicals are the most difficult to form.

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1. Introduction

Coal is the dominant fossil fuels, and also the main consumption energy in China and some other countries due to its relatively low cost, easy accessibility and huge reserves. Many techniques have been developed to make clean and effective utilization of coal to reduce emissions and alleviate the environmental pollution, yet much remains to be understood about its structure and reactivity. Moreover, it is difficult to characterize coal since many properties of coal, such as elemental composition, reactivity, and rank, vary greatly relying on the origin of the chosen sample [1]. The heteroatoms (oxygen, nitrogen and sulfur) are known to play a very significant role in coal processing [2]. Oxygen in coal is present as phenolic hydroxyl and carboxylic acid groups, aryl–aryl or alkyl–aryl ether bridges, and ring oxygen as furan type structures [3]. Nitrogen and sulfur appear in coal in such forms as pyrrole, pyridine and thiophene rings [4]. In addition, these heteroaromatic

rings have the potential to produce NO_x [5], H₂S, and SO₂ species [6] during thermal processing of coal, which will contribute to acid rain by subsequent reactions [7].

The combustion, gasification, pyrolysis, and liquefaction are the most important processes of coal processing [8,9]. All these processes are directly associated with homolytic bond dissociation of the large organic structures of coal into smaller molecules [10]. Therefore, an understanding of reactivity and thermochemistry of specific bonds within the coal structure is clearly desired as a basis for leading to advances in coal processing. To this end, we are currently investigating the thermochemical properties of the coal based model compounds, since using small molecules as models is effective to understand the overall chemistry of the complex structure of coal, and this approach has been widespread over the past few decades.

Many experimental and theoretical studies on model compounds have been carried out, including aromatic hydrocarbon compounds [11–23], ethers compounds (aromatic ethers [24–31] and ester ethers [32,33]), carboxylic acids [34], and heterocyclic aromatic compounds [35–38], etc. Beste et al. have calculated the

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bond dissociation enthalpies (BDE) of the oxygen–carbon and carbon–carbon bonds in substituted phenethyl phenyl ethers (PPEs) which representing the dominant β -O-4 ether linkage [28], and C_{α} -O and C_{α} - C_{β} BDEs for a series of β -5 arylcoumaran [29]. They also examined the substituent effects on these bond dissociation enthalpies. Barckholtz et al. [4] investigated several computational methods to calculate the BDE of C–H and N–H bonds in monocyclic aromatic molecules, which including six-membered and five-membered rings. They found that the location of heteroatoms in the aromatic ring has greater influence on the C–H bond strengths than the size of the aromatic network. They also proposed that the small aromatic molecules can be used to predict the C–H BDE of the large polycyclic aromatic hydrocarbons (PAHs), in general. Experimental and computational work on the pyrolysis of model compounds also has been done recently by Qi and coworkers, with contributions related to decomposition pathways [39,40] and kinetics [41–43].

Though there are lots of studies have been undertaken on several kinds of coal based model compounds, nevertheless, it is very difficult to compare all the available data in a consistent way due to the varied conditions used in various studies. Herein, our investigation focused on calculating the BDE of several kinds model compounds, which can provide a valuable reference for understanding the coal chemistry. In this work, we present estimations of over 100 BDEs of four bond types (C–H, C–C, C–O, O–H) by using our selected theoretical method. Scheme 1 shows the compounds which were chosen to model the functionalities in coal structures. The BDE of specific bonds as shown are all calculated. Most types of typical coal units have been considered. For example, the pyridine ring is selected to represent the heteroatoms in the aromatic rings. The availability of these data allows us to establish the relationship between the BDE and bond type. Furthermore, the relationship between BDE and the weak bond is also discussed.

2. Theoretical methods

2.1. Computational strategy

BDE is defined as the change in enthalpy of the following reaction in the gas phase:



The BDE values are obtained from the following thermochemical equation [21]:

$$BDE(A-B) = [H_{298}(A') + H_{298}(B')] - H_{298}(A-B) \quad (2)$$

in which the $H_{298}(A')$, $H_{298}(B')$, and $H_{298}(A-B)$ are the enthalpy of the corresponding radical species A, B, and the neutral molecule A–B, respectively.

2.2. Computational method

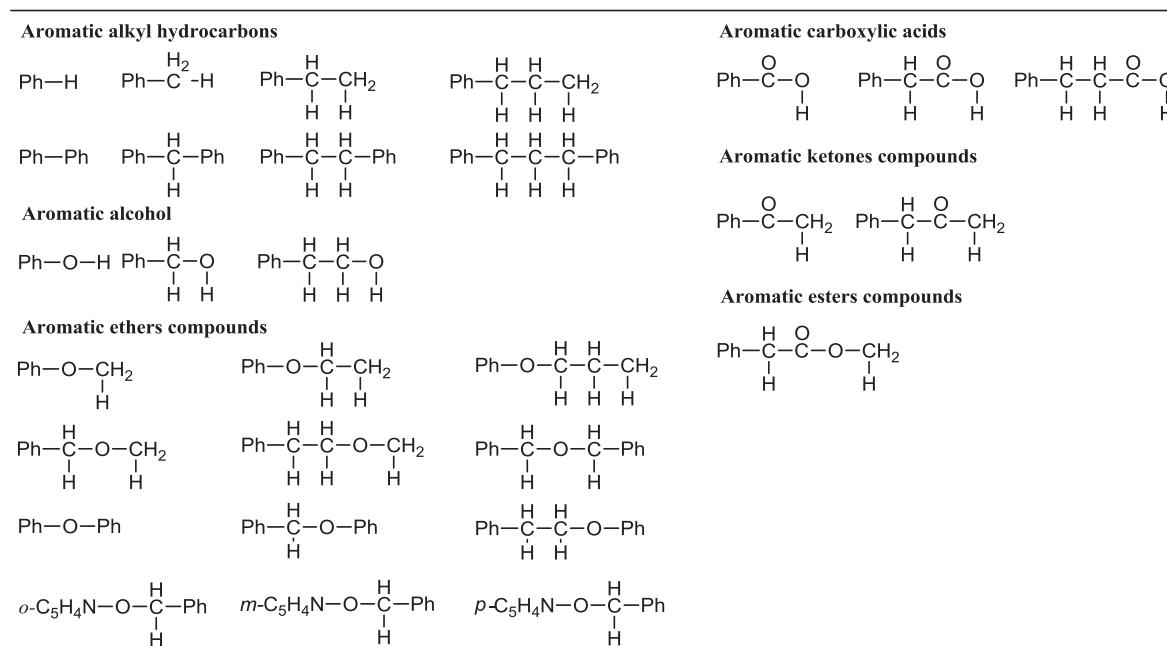
All calculations were carried out with Gaussian 09 program [44]. Double-hybrid method mPW2PLYP [45] which can balance accurate results with computational economy to the greatest extent was selected [46]. The mPW2PLYP/cc-pVDZ [47] was used for all geometry optimizations and vibrational frequency calculations. Single-point energies were calculated at mPW2PLYP/cc-pVTZ [48] level at the optimized geometries. We also compensated for the basis set superposition error (BSSE) [49,50] correction in order to get more precise results.

The enthalpy was calculated using Eq. (3) [34].

$$H(298\text{ K}) = E + ZPE + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT \quad (3)$$

where E is electronic energy; ZPE is the zero point energy; H_{trans} , H_{rot} , and H_{vib} are the thermodynamic corrections calculated with the equilibrium statistical mechanics with harmonic oscillator approximation using unscaled vibrational frequencies under standard temperature.

Several compounds were chosen as the training set (shown in Scheme 2) to verify the accuracy of the selected mPW2PLYP method. The BDE calculated by typical DFT method B3LYP and high level method CCSD(T) are listed for comparison. The results as shown in Table 1 indicate that the mPW2PLYP method can be used to reliably predict the BDEs of various coal based model compounds.



Scheme 1. Studied coal based model compounds under study in this work.

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