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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

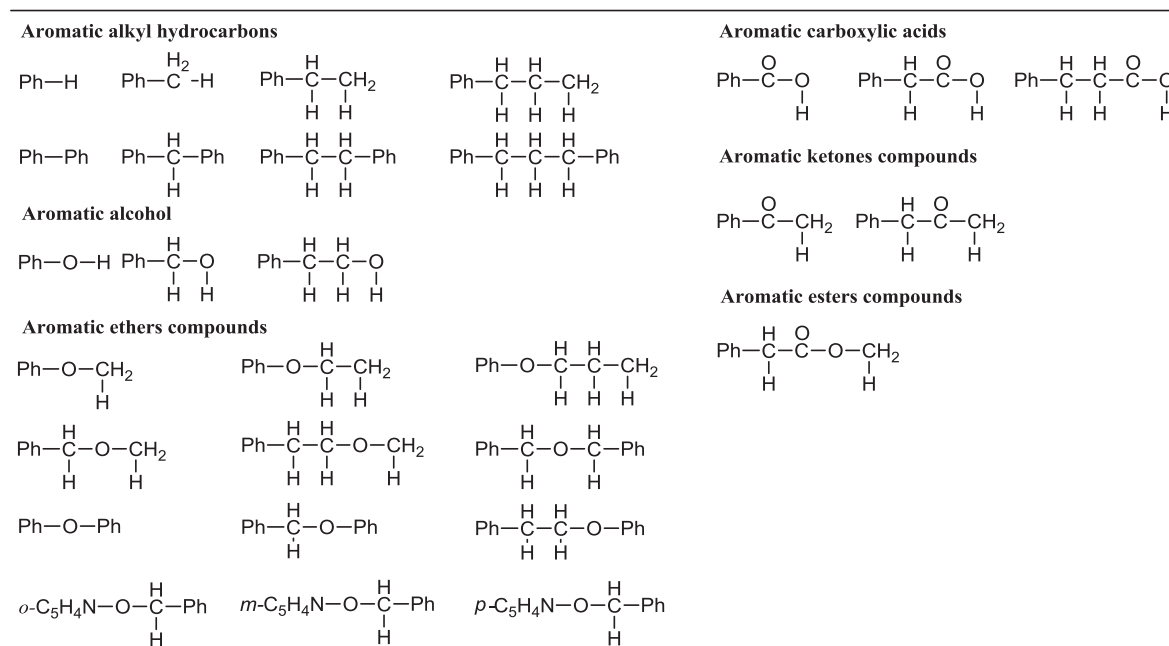
All calculations were carried out with Gaussian 09 program [44]. Double-hybrid method mPW2PLYP [45] which can balance accurate results with computational economy to the greatest extent was selected [46]. The mPW2PLYP/cc-pVDZ [47] was used for all geometry optimizations and vibrational frequency calculations. 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].

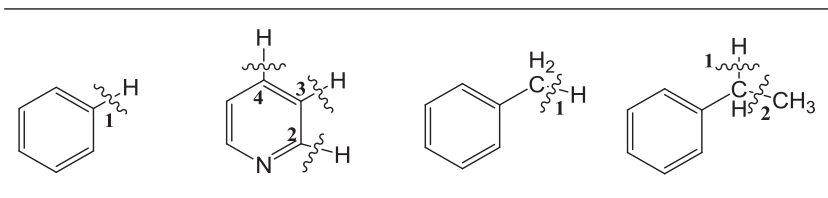
$$H(298\text{ K}) = E + ZPE + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT \quad (3)$$

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.



Scheme 2. The structure of training set and the cleavage site marked with zigzag line.

Table 1

Experimental BDE and calculated BDE by different methods of the compounds in the training set (kcal/mol).

Compound	Site	B3LYP	MPW2PLYP	CCSD(T)	Exp
Benzene	1	110.5	111.4	113.0	112.9 ^a
Pyridine	2	104.7	105.6	107.7	105 ^b
	3	111.9	112.1	113.8	112 ^b
	4	109.6	111.7	112.4	112 ^b
Toluene	1	87.3	89.9	91.0	89.8 ^a
Ethylbenzene	1	83.6	86.7	88.4	86.9 ^c
	2	68.9	74.7	76.6	77.6 ^a
MAD		2.98	0.96	1.22	
MAX		−8.7	−2.9	2.7	

See Scheme 2 for structures and site.

MAD represents mean absolute deviation, while MAX means maximum deviation.

^a Ref. [51].

^b Ref. [4].

^c Ref. [38].

3. Results and discussion

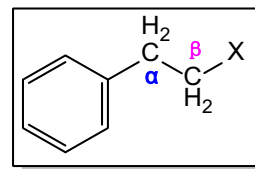
3.1. C–H bonds

The computed C–H BDE results are shown in Table 2. The BDE of C–H bond type ranges from 111.4 to 81.2 kcal/mol. The bond homolysis of Ph–H presents the highest BDE, while the lowest BDE comes from the bond cleavage of PhCH(OH)–H and PhCH(COCH₃)–H. It is found that the energy region of 90–100 kcal/mol covers the C–H bond cleavage for the β-carbon-centered group (see below) and the hydrogen atom loss of the last CH₃ substituent group. The BDE of C–H bond cleavage for the α-carbon-centered group range from 81.2 to 89.9 kcal/mol. The order of C–H BDE values are given in Fig. 1.

Table 2

BDE of C–H bonds (kcal/mol).

Compound	BDE	Compound	BDE	Compound	BDE
<i>Aromatic alkyl hydrocarbons</i>					
Ph–H	111.4	PhCH ₂ –H	89.9	PhCH ₂ CH ₂ –H	98.6
PhCH(CH ₃)–H	85.6	PhCH ₂ CH ₂ CH ₂ –H	98.4	PhCH(CH ₂ CH ₃)–H	85.9
PhCH ₂ CH(CH ₃)–H	95.1	PhCH(Ph)–H	82.5	PhCH(CH ₂ Ph)–H	87.4
PhCH(CH ₂ CH ₂ Ph)–H	87.8	PhCH ₂ CH(CH ₂ Ph)–H	96.8		
<i>Aromatic alcohols</i>					
PhCH(OH)–H	81.2	PhCH(CH ₂ OH)–H	87.8	PhCH ₂ CH(OH)–H	92.4
<i>Aromatic ethers compounds</i>					
PhOCH ₂ –H	95.3	PhOCH(CH ₃)–H	93.4	PhOCH ₂ CH ₂ –H	100.7
PhOCH(CH ₂ CH ₃)–H	93.5	PhOCH ₂ CH(CH ₃)–H	97.2	PhOCH ₂ CH ₂ CH ₂ –H	99.4
PhCH(OCH ₃)–H	81.7	PhCH ₂ OCH ₂ –H	94.3	PhCH(CH ₂ OCH ₃)–H	87.2
PhCH ₂ CH(OCH ₃)–H	91.5	PhCH ₂ CH ₂ OCH ₂ –H	98.8	PhCH(OPh)–H	83.4
PhCH(CH ₂ OPh)–H	87.4	PhCH ₂ CH(OPh)–H	92.4	PhCH(OCH ₂ Ph)–H	82.8
<i>Aromatic carboxylic acids</i>					
PhCH(COOH)–H	83.9	PhCH(CH ₂ COOH)–H	87.3	PhCH ₂ CH(COOH)–H	96.5
<i>Aromatic ketones compounds</i>					
PhCOCH ₂ –H	94.9	PhCH(COCH ₃)–H	81.2	PhCH ₂ COCH ₂ –H	93.7



3.2. C–C bonds

As shown in Table 3, the BDE of various C–C bonds covers a range of 114.1–62.8 kcal/mol. From the order of C–C BDE values shown in Fig. 2, the highest BDE of C–C bonds is 114.1 kcal/mol which comes from the bond homolysis of Ph–Ph, which indicates a much more difficult breakup of the C(ring)–C(ring) bond. The C(linear)–C(linear) bond in the molecule of PhCH₂–CH₂Ph requires the smallest BDE of 62.8 kcal/mol. The BDE of the process which produce phenyl and the other radicals are in the range of 87.1–114.1 kcal/mol. The BDE of PhCH₂–C cleavage and the dissociation of the O=C group with the adjacent carbon-centered group range from 62.8 to 87.1 kcal/mol.

3.3. C–O bonds

As shown in Table 4, the energy region of C–O bonds is from 107.6 to 52.6 kcal/mol, in which the highest BDE is obtained by bond dissociation of Ph–OH, and the bond cleavage of PhCH₂–OPh presents the smallest BDE value. Similar with C–C bonds, the process of C–O homolysis which produce phenyl (or heterocyclic free radical) and the other radicals also require higher energy with the range from 89.2 to 107.6 kcal/mol. The carboxyl group in benzene carboxylic acids is difficult to dissociate to

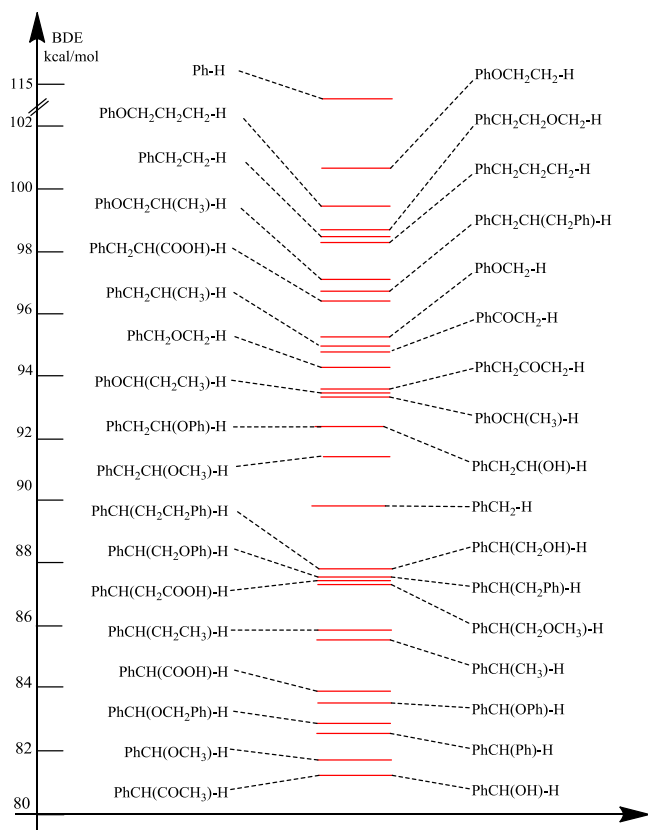


Fig. 1. C–H BDE range from 80 to 115 kcal/mol.

carbonyl group radical and hydroxyl radical, with the cracking energy of $\text{O}=\text{C}-\text{OH}$ bond in benzoic acid, phenylacetic acid, and hydrocinnamic acid of 104.4, 103.8, and 105.5 kcal/mol, respectively. The CH_3 substituent replaces the H of hydroxyl radical, which will make the aromatic carboxylic acids to be aromatic esters compounds and cause the decline of BDE to 90.3 kcal/mol in $\text{PhCH}_2\text{C}(\text{O})-\text{OCH}_3$. The energy region of 50–70 kcal/mol covers

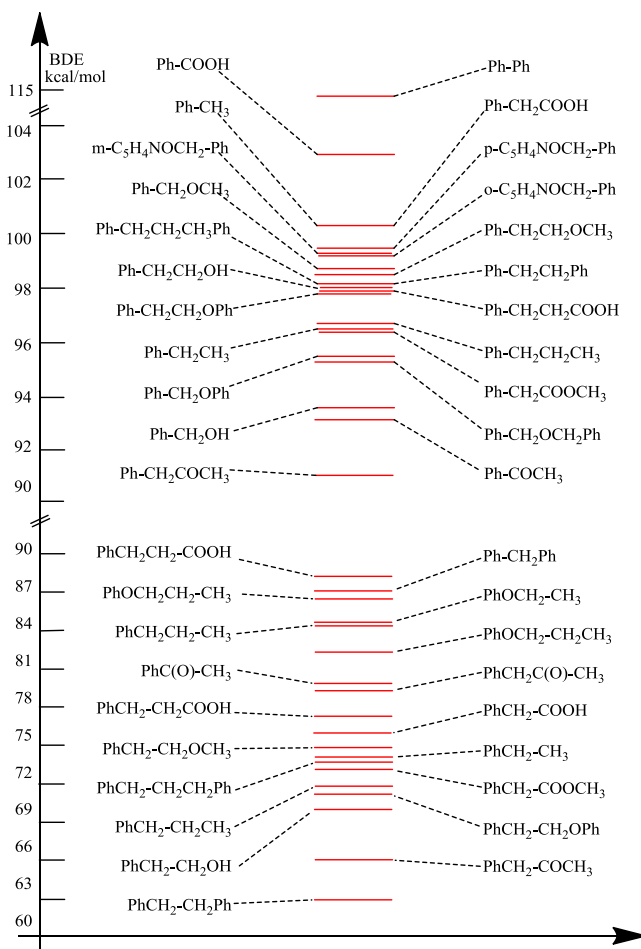


Fig. 2. C–C BDE range from 60 to 115 kcal/mol.

the process of bond dissociation to produce phenoxy radical (regardless of heteroatom) and the bond homolysis of PhCH_2-O . The order of C–O BDE values are given in Fig. 3.

Table 3
BDE of C–C bonds (kcal/mol).

Compound	BDE	Compound	BDE	Compound	BDE
<i>Aromatic alkyl hydrocarbons</i>					
$\text{Ph}-\text{CH}_3$	100.3	$\text{Ph}-\text{CH}_2\text{CH}_3$	96.5	$\text{PhCH}_2-\text{CH}_3$	73.8
$\text{Ph}-\text{CH}_2\text{CH}_2\text{CH}_3$	96.7	$\text{PhCH}_2-\text{CH}_2\text{CH}_3$	71.7	$\text{PhCH}_2\text{CH}_2-\text{CH}_3$	84.2
$\text{Ph}-\text{Ph}$	114.1	$\text{Ph}-\text{CH}_2\text{Ph}$	87.1	$\text{Ph}-\text{CH}_2\text{CH}_2\text{Ph}$	98.1
$\text{PhCH}_2-\text{CH}_2\text{Ph}$	62.8	$\text{Ph}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$	98.1	$\text{PhCH}_2-\text{CH}_2\text{CH}_2\text{Ph}$	73.4
<i>Aromatic alcohols</i>					
$\text{Ph}-\text{CH}_2\text{OH}$	93.6	$\text{Ph}-\text{CH}_2\text{CH}_2\text{OH}$	98.0	$\text{PhCH}_2-\text{CH}_2\text{OH}$	69.9
<i>Aromatic ethers compounds</i>					
$\text{PhOCH}_2-\text{CH}_3$	84.3	$\text{PhOCH}_2-\text{CH}_2\text{CH}_3$	82.1	$\text{PhOCH}_2\text{CH}_2-\text{CH}_3$	86.2
$\text{Ph}-\text{CH}_2\text{OCH}_3$	98.7	$\text{Ph}-\text{CH}_2\text{CH}_2\text{OCH}_3$	98.5	$\text{PhCH}_2-\text{CH}_2\text{OCH}_3$	74.6
$\text{Ph}-\text{CH}_2\text{OPh}$	95.5	$\text{Ph}-\text{CH}_2\text{CH}_2\text{OPh}$	97.8	$\text{PhCH}_2-\text{CH}_2\text{OPh}$	71.0
$\text{Ph}-\text{CH}_2\text{OCH}_2\text{Ph}$	95.3	$o\text{-C}_4\text{H}_4\text{NOCH}_2-\text{Ph}$	99.2	$m\text{-C}_4\text{H}_4\text{NOCH}_2-\text{Ph}$	99.3
$p\text{-C}_4\text{H}_4\text{NOCH}_2-\text{Ph}$	99.5				
<i>Aromatic carboxylic acids</i>					
$\text{Ph}-\text{COOH}$	102.9	$\text{Ph}-\text{CH}_2\text{COOH}$	100.3	$\text{PhCH}_2-\text{COOH}$	75.8
$\text{Ph}-\text{CH}_2\text{CH}_2\text{COOH}$	97.9	$\text{PhCH}_2-\text{CH}_2\text{COOH}$	77.0	$\text{PhCH}_2\text{CH}_2-\text{COOH}$	88.0
<i>Aromatic ketones compounds</i>					
$\text{Ph}-\text{COCH}_3$	93.1	$\text{PhC}(\text{O})-\text{CH}_3$	79.6	$\text{Ph}-\text{CH}_2\text{COCH}_3$	91.1
$\text{PhCH}_2-\text{COCH}_3$	65.9	$\text{PhCH}_2\text{C}(\text{O})-\text{CH}_3$	79.2		
<i>Aromatic esters compounds</i>					
$\text{Ph}-\text{CH}_2\text{COOCH}_3$	96.4	$\text{PhCH}_2-\text{COOCH}_3$	72.9		

Table 4
BDE of C–O bonds (kcal/mol).

Compound	BDE	Compound	BDE	Compound	BDE
<i>Aromatic alcohols</i>					
Ph–OH	107.6	PhCH ₂ –OH	76.7	PhCH ₂ CH ₂ –OH	88.4
<i>Aromatic ethers compounds</i>					
Ph–OCH ₃	97.1	PhO–CH ₃	62.9	Ph–OCH ₂ CH ₃	96.1
PhO–CH ₂ CH ₃	64.0	Ph–OCH ₂ CH ₂ CH ₃	96.0	PhO–CH ₂ CH ₂ CH ₃	64.3
PhCH ₂ –OCH ₃	68.4	PhCH ₂ O–CH ₃	77.1	PhCH ₂ CH ₂ –OCH ₃	79.4
PhCH ₂ CH ₂ O–CH ₃	78.6	Ph–OPh	78.6	PhCH ₂ –OPh	52.6
PhCH ₂ O–Ph	95.7	PhCH ₂ CH ₂ –OPh	63.5	PhCH ₂ CH ₂ O–Ph	101.7
PhCH ₂ –OCH ₂ Ph	67.9	<i>o</i> -C ₅ H ₄ N–OCH ₂ Ph	94.2	<i>o</i> -C ₅ H ₄ NO–CH ₂ Ph	57.8
<i>m</i> -C ₅ H ₄ N–OCH ₂ Ph	89.2	<i>m</i> -C ₅ H ₄ NO–CH ₂ Ph	53.4	<i>p</i> -C ₅ H ₄ N–OCH ₂ Ph	91.8
<i>p</i> -C ₅ H ₄ NO–CH ₂ Ph	59.9				
<i>Aromatic carboxylic acids</i>					
PhC(O)–OH	104.4	PhCH ₂ C(O)–OH	103.8	PhCH ₂ CH ₂ C(O)–OH	105.5
<i>Aromatic esters compounds</i>					
PhCH ₂ C(O)–OCH ₃	90.3	PhCH ₂ COO–CH ₃	79.3		

3.4. O–H bonds

The BDE of O–H bonds are generally higher than other type bonds with the range of 111.2–86.6 kcal/mol, as shown in Table 5. From the order of O–H BDE values in Fig. 4, the homolytic bond dissociation of PhCOO–H shows the highest BDE, while cracking the bond of PhO–H requires the lowest energy. Notably, the smaller BDE of PhO–H, which is comparable to the C–H bonds, is mainly due to the stabilization of phenoxy radical. The O–H bond homolysis in aromatic carboxylic acids is much more difficult than that in aromatic alcohols. The BDE of C–H bonds are in

Table 5
BDE of O–H bonds (kcal/mol).

Compound	BDE	Compound	BDE	Compound	BDE
<i>Aromatic alcohols</i>					
PhO–H	86.6	PhCH ₂ O–H	98.7	PhCH ₂ CH ₂ O–H	101.2
<i>Aromatic carboxylic acids</i>					
PhCOO–H	111.2	PhCH ₂ COO–H	106.0	PhCH ₂ CH ₂ COO–H	109.1

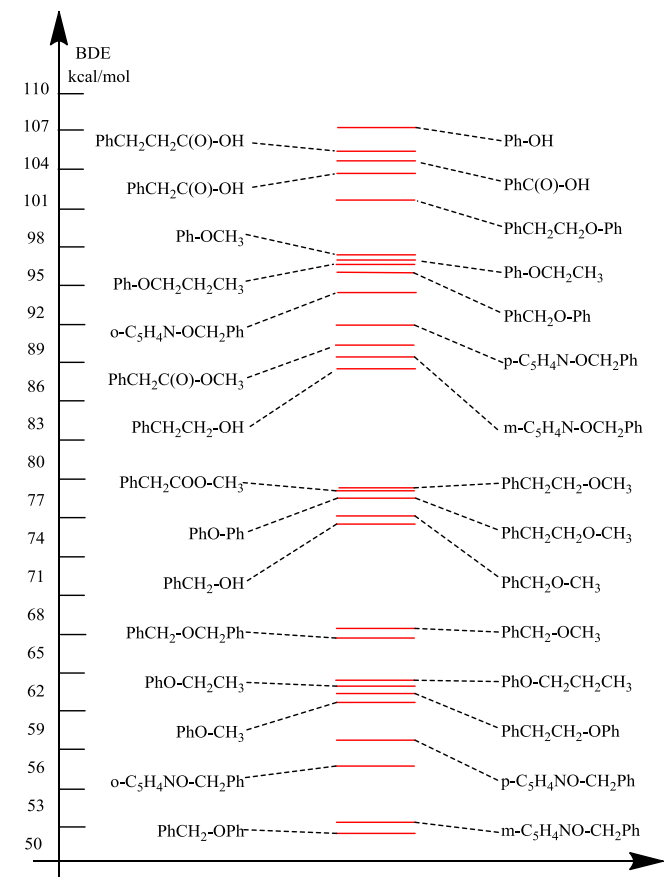


Fig. 3. C–O BDE range from 50 to 110 kcal/mol.

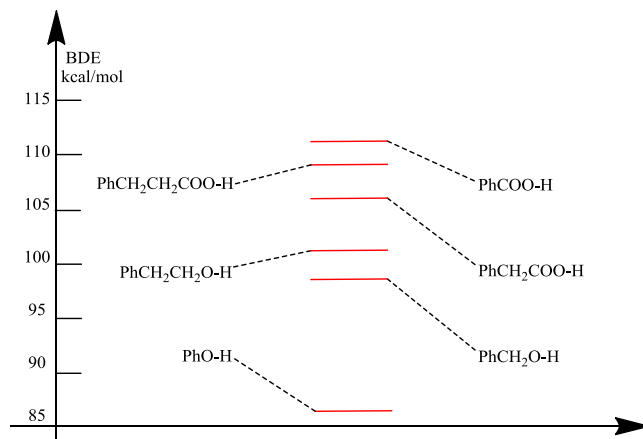


Fig. 4. O–H BDE range from 85 to 115 kcal/mol.

general smaller than O–H bonds, thus the hydrogen radical generated from the pyrolysis of coal more likely come from cracking the C–H bonds rather than O–H bonds, especially at relatively lower temperature.

3.5. BDE analysis of different bond types

The BDE ranges of concerned four bond types are summarized in Fig. 5. The BDE for C–H, C–C, C–O, O–H covers the 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. It is not surprising to find that the minimum BDE of each bond type is in the order O–H > C–H > C–C > C–O. However, the BDE have large ranges for all bond types, and the values overlap with each other. These show that there is not a bond type which always possesses the larger or smaller BDE than other bond types.

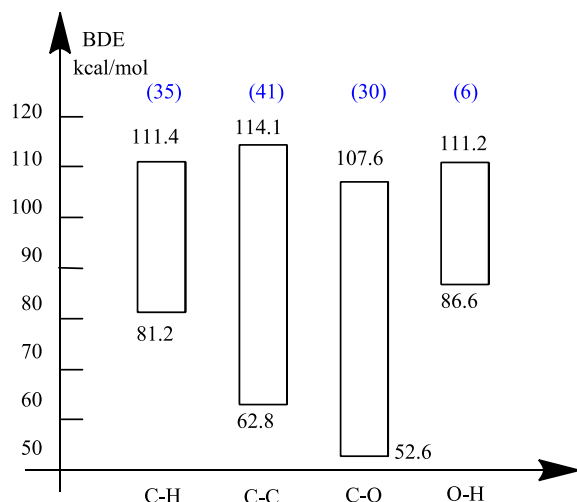


Fig. 5. BDE range of different bond types (the data in parentheses is the number of bond type calculated).

3.6. Relationship between weak bond and BDE

Corresponding to the phenomena observed in our BDE calculation results, it can be found that the weak bond does not necessarily mean the certain bond types. For example, the BDE of C–C bond in $\text{PhCH}_2\text{—CH}_2\text{Ph}$ is 62.8 kcal/mol as shown in Table 2, while the corresponding value in $\text{PhCH}_2\text{CH}_2\text{—CH}_2\text{CH}_2\text{Ph}$ is 82.2 kcal/mol by calculating with the same method. The two C–C bond are almost same in essence, in contrast to the tremendous difference in the corresponding BDEs. Another example is brought up here to further support our point. There are two C–O bonds in $\text{PhCH}_2\text{OCH}_3$,

the BDE of two C–O bonds are 68.4 kcal/mol and 77.1 kcal/mol for $\text{PhCH}_2\text{—OCH}_3$ and $\text{PhCH}_2\text{O—CH}_3$, respectively. It is clear that there is also an energy gap of 8.7 kcal/mol within two C–O bonds in the same parent molecule.

To understand the above phenomenon, we noted that the BDE does not only depend on the bond interaction between A and B in A–B, but also rely on the stability of the radical fragments formed (Eq. (1)). The intrinsic stability of a radical is different from each other [52]. Specifically, benzyl radical is more stable than phenyl radical because in benzyl radical the unpaired electron can delocalize into the phenyl π^* orbital as shown in Fig. 6(1a, 1b). The spin densities (2a, 2b in Fig. 6) are examined to further understand this phenomenon. It can be seen that the phenyl radical localizes its electron density to a great extent at the radical site; correspondingly, the benzyl radical shows more electron density delocalized through the ring and a resultant stabilization. The BDE trends vary with respect to the bond types, while BDE has direct relationship with the stability of radical fragments. Overall, bond homolysis to form a benzyl radical and phenoxy radical are more favorable than other radicals, regardless of heteroatom. The more stable the radical fragments are, the lower the BDE of the parent molecule will be, and vice versa. Therefore there are two conditions for the so called “weak bond”, (1) the type of the bond is not very strong (for example, O–H and C–H are not good candidate compare to C–C and C–O); (2) the fragmented radicals are stable enough.

3.7. Relationship of BDEs between small molecules and complex compounds

It has been shown that the BDE strongly relies on the environment of chemical bond, and each bond can have very different BDE in different molecules. Fortunately, according to the references

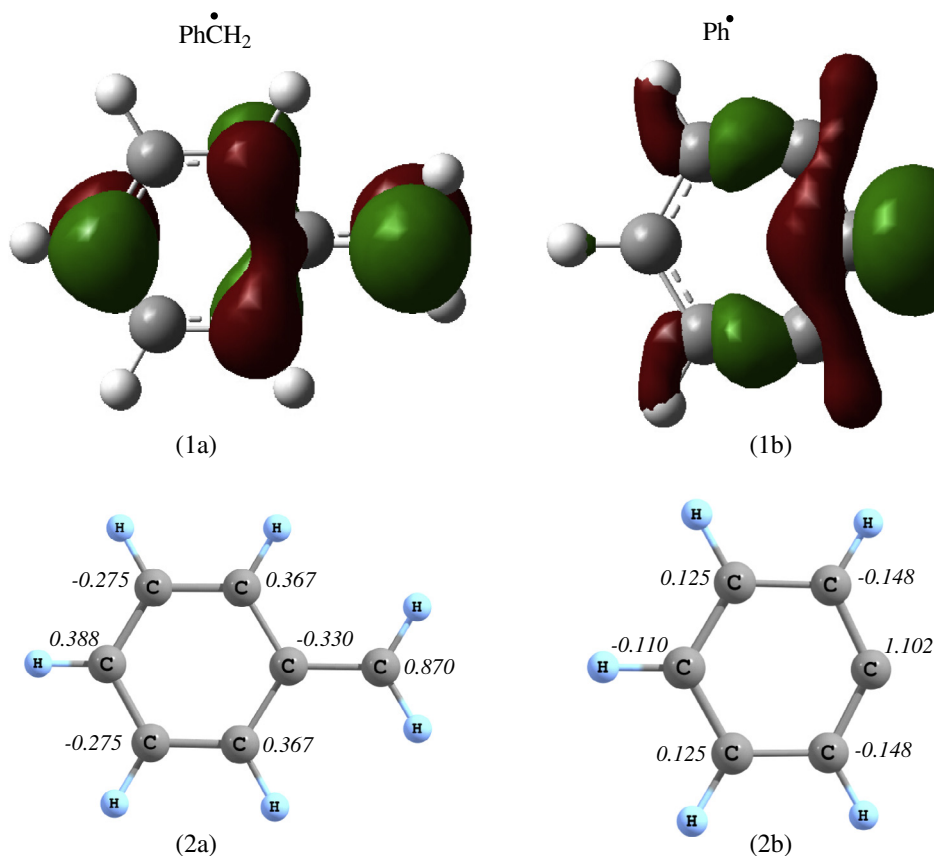


Fig. 6. The singly occupied molecular orbitals and the spin densities (in italic) of PhCH_2 and Ph .

shown below, the BDE mostly relies on the local environment of bond. Therefore the BDE of small molecules could be a good estimation for the BDE of large molecules in coal if the local environments are similar. The evidence to support this argument includes that in Ref. [4], the BDE of C–H for naphthalene, anthracene, pyrene, and coronene vary little (within 1 kcal/mol) from the benzene. This is also true for C–C BDE. Hemelsoet et al. [21] selected representative linear methylated polyaromatics of two, three, four, and five fused benzene rings and investigated the influence of the polyaromatic environment on C–C BDE. The results also show that there is little deviation between the C–C BDE of the methylated polyaromatics and toluene.

Bond homolytic cleavage is the first step in pyrolysis of coal. The BDE of the chemical bonds in coal give the information about how easy or difficult each bond homolytic cleavage is, and therefore are the key issue to understand the pyrolysis of coal. Here we calculated the BDE of the chemical bonds in various coal model compounds. For a specific chemical bond in coal, its BDE can be estimated from the BDE of same bond with the same local environment in our data set.

With respect to predicting the chemistry of larger aromatic constituent systems found in coal, our work suggests that both cracking the C–O bond and C–C bond between two benzene rings to form phenoxy radical or benzyl radical will contribute as the initial step for the coal pyrolysis. Alkyl-group-loss and alkoxy-group-loss reactions will become feasible as the temperature increases. The hydrogen-atom-loss reaction from the substituent α -CH₂ group is much more favorable than other substituent groups such as β -carbon-centered group and COOH group. The dissociation of a hydrogen atom from benzene is the most difficult among these hydrogen-atom-loss reactions. In addition, the bond cleavage to form phenyl-like radical requires higher energies, thus these reactions can only occur at higher temperature.

4. Conclusions

BDEs of different bond types for the selected coal based model compounds were computed using the double-hybrid method mPW2PLYP. Overall, bond homolysis to form a benzyl radical and phenoxy radical are more favorable than other radicals, regardless of heteroatom. The BDE trends vary with respect to the bond types, while BDE has direct relationship with the stability of radical fragments. The BDE of the bond in two molecules with a big gap in size can be comparable if the bond involve extremely analogous chemical environment in two molecules. The more stable the radical fragments are, the lower BDE will be. Bonds cleavage to form phenoxy radical or benzyl radical are most likely to occur at lower temperature, while generating phenyl-like radical requires higher energies, thus these reactions can only occur at higher temperature. The type of the bond and the stabilization of the fragmented radicals are the two necessary criteria to the judgement of weak bond.

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