

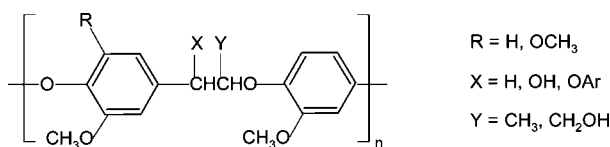
Computational Study of Bond Dissociation Enthalpies for Lignin Model Compounds. Substituent Effects in Phenethyl Phenyl Ethers

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Lignin is an abundant natural resource that is a potential source of valuable chemicals. Improved understanding of the pyrolysis of lignin occurs through the study of model compounds for which phenethyl phenyl ether (PhCH₂CH₂OPh, PPE) is the simplest example representing the dominant β -O-4 ether linkage. The initial step in the thermal decomposition of PPE is the homolytic cleavage of the oxygen-carbon bond. The rate of this key step will depend on the bond dissociation enthalpy, which in turn will depend on the nature and location of relevant substituents. We used modern density functional methods to calculate the oxygen-carbon bond dissociation enthalpies for PPE and several oxygen-substituted derivatives. Since carbon-carbon bond cleavage in PPE could be a competitive initial reaction under high-temperature pyrolysis conditions, we also calculated substituent effects on these bond dissociation enthalpies. We found that the oxygen-carbon bond dissociation enthalpy is substantially lowered by oxygen substituents situated at the phenyl ring adjacent to the ether oxygen. On the other hand, the carbon-carbon bond dissociation enthalpy shows little variation with different substitution patterns on either phenyl ring.

Introduction

Lignin is an underused component of biomass and a potential source of clean fuels and chemicals.¹ Its structure is complex and highly branched, containing a variety of linkages of which the β -O-4 linkage is the most common.^{2,3} Fundamental insights into the pyrolysis of lignin can be obtained through studies of model compounds representing structural features present in lignin. The simplest model for the β -O-4 linkage is phenethyl phenyl ether (PhCH₂CH₂OPh; PPE).⁴⁻⁶ Thermal decomposition

of PPE and several methoxy- and hydroxy-substituted derivatives has been investigated under a range of pyrolysis conditions by Britt et al.⁴⁻⁶ Fast, high-temperature pyrolysis techniques such as flash vacuum pyrolysis (FVP) (500–600 °C, <10⁻⁴ Torr, <0.3 s residence time) highlight primarily unimolecular transformations such as bond scissions and intramolecular rearrangements.⁵ Slow pyrolysis in the liquid phase in sealed tubes at lower temperatures (345–400 °C, several minutes reaction time) allows additional bimolecular and radical chain processes to occur.^{4,6} Under both pyrolysis conditions, the pyrolysis rate and product distribution was found to be substantially influenced by the substituents.^{5,6} Understanding the origin of substituent effects can be vexing, particularly in slow pyrolysis where radical chain reactions occur, since multiple mechanistic steps (e.g., homolytic initiation, competitive hydrogen abstraction, radical rearrangement, radical scission) may be perturbed.⁶ Computational methods offer the advantage of being able to probe the rates of individual reaction steps that would be difficult, if not impossible, to perform experimentally. Recently, we conducted a detailed theoretical analysis of the substituent effects on the selectivity of competitive hydrogen abstraction reactions occurring in the slow pyrolysis of some of these model

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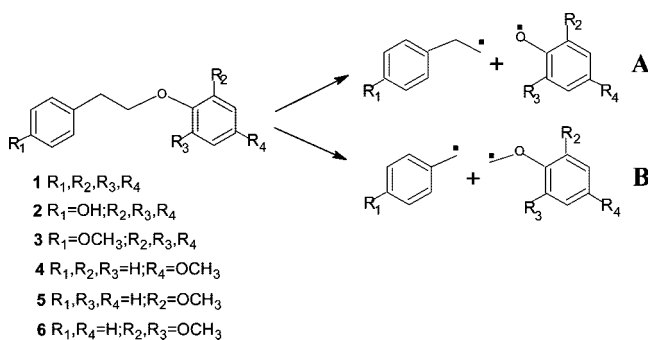
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SCHEME 1. Homolytic Cleavage of the Oxygen–Carbon and the Carbon–Carbon Bond of Substituted PPE


compounds using density functional theory (DFT).^{7,8} The results not only were successful in predicting the influence of substituents on experimentally observed product selectivities but also provided insights into the roles of radical delocalization and electronic polar effects on the hydrogen abstraction reaction rates.

Another critical step in the pyrolysis of PPE and its derivatives under all pyrolysis conditions is the initial homolytic cleavage of the oxygen–carbon bond ($\text{PhCH}_2\text{CH}_2\text{-OPh}$) and carbon–carbon bond ($\text{PhCH}_2\text{-CH}_2\text{OPh}$), whose selectivity should depend primarily on their bond dissociation enthalpies.⁵ The C–O to C–C homolysis selectivity for unsubstituted PPE is estimated to be 37:1 from product analysis in the FVP of PPE at 500 °C, which will likely be sensitive to the pyrolysis temperature and the nature and location of substituents.⁵ For example, it was observed that methoxy substituents on the phenyl ring adjacent to the ether oxygen ($\text{PhCH}_2\text{CH}_2\text{OPh-X}$) enhance the rate of homolysis of the β -O-4 linkage in PPE, apparently as a consequence of an increased rate of C–O homolysis.⁵ However, even under FVP conditions, it is difficult to know with certainty the influence of substituents on the initial homolysis event solely on the basis of products that can be formed from multiple pathways.⁵ Hence, an improved understanding of substituent effects on this key reaction step, which impacts both reaction rates and product selectivities, requires new insights obtainable from computational methods.

In this work, we calculate the bond dissociation enthalpies (BDEs) of the oxygen–carbon and carbon–carbon bonds in substituted PPEs that are not experimentally available. We use DFT, which has been employed successfully to compute the BDEs of a variety of systems^{9–13} including the oxygen–carbon bond in anisole,^{9,11} which is similar to the oxygen–carbon bond in PPE. DFT methods tend to underestimate the BDE,^{11,12} and their accuracy depends on the functional employed.^{10–14} Relative BDEs can generally be calculated more reliably,^{12,13}

TABLE 1. Bond Dissociation Enthalpies (BDEs) of the Oxygen–Carbon and the Carbon–Carbon Bond in Substituted PPEs and Anisole at 298 K^a

	BDE [kcal/mol]	Δ BDE [kcal/mol]	ground state effect [kcal/mol]	radical effect [kcal/mol]
C–O Dissociation; Reaction A in Scheme 1				
anisole	67.5			
PPE [1]	69.5	0.00	0.00	0.00
pHO-PPE [2]	69.6	−0.05	−0.37	−0.42
pCH ₃ O-PPE [3]	69.6	−0.07	−0.25	−0.32
PPE-pOCH ₃ [4]	64.1	5.47	−1.51	3.95
PPE-oOCH ₃ [5]	64.4	5.13	−3.28	1.84
PPE-dioOCH ₃ [6]	60.9	8.61	−6.14	2.47
C–C Dissociation; Reaction B in Scheme 1				
PPE [1]	77.1	0.00	0.00	0.00
pHO-PPE [2]	76.6	0.50	−0.37	0.14
pCH ₃ O-PPE [3]	76.6	0.51	−0.25	0.25
PPE-pOCH ₃ [4]	76.7	0.38	−1.51	−1.13
PPE-oOCH ₃ [5]	77.0	0.10	−3.28	−3.18
PPE-di-oOCH ₃ [6]	78.0	−0.95	−6.14	−7.09

^a Also included are BDE differences (Δ BDEs) relative to PPE for which the ground state and radical effects are listed.

particularly when error cancellation in isodesmic reactions is exploited.¹⁵ We choose to employ the M06-2X functional, which is a newly developed hybrid meta functional by Truhlar and co-workers showing excellent performance for main-group thermochemistry and kinetics.¹⁶ In a recent study, the M06-2X functional was tested for reaction energies involving radicals including the bond dissociation energy of methyl benzyl ether ($\text{CH}_3\text{O-CH}_2\text{Ph}$) and proved to be in good agreement with the G3(MP2)-RAD method.¹⁷

In the following, we report BDEs of aromatic hydroxy- and methoxy-substituted PPEs that are model compounds for β -O-4 linkages in lignin. Furthermore, since we are particularly interested in substituent effects, i.e., differences in BDEs, we are able to exploit error cancellation occurring in isodesmic reactions.

Results and Discussion

The pyrolysis of aromatic oxygen-substituted PPEs under slow and fast pyrolysis conditions begins primarily with the homolytic cleavage of the oxygen–carbon bond, reaction A in Scheme 1.^{4–6} Competitive carbon–carbon cleavage, reaction B in Scheme 1, was found to occur to a much smaller extent.⁵ Table 1 contains the BDEs at 298 K of the oxygen–carbon and the carbon–carbon bonds of the PPE derivatives shown in Scheme 1. Also included in Table 1 is the BDE of the oxygen–carbon bond in anisole ($\text{CH}_3\text{-OPh}$), which serves to calibrate our computational method since literature values are available and the oxygen–carbon bond is similar to the one in our target systems. The BDE for anisole has been measured experimentally by several pyrolysis methods,^{18–20} and an average value of 65.3 ± 0.4 kcal/mol at 298 K is obtained from the four independent measurements reported by Mulder et al.¹⁸

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The BDE of anisole has also been calculated at the G3(MP2) level of theory to be 66.7 kcal/mol⁹ and at the G3 level of theory to be 65.4 kcal/mol.¹⁸ These results compare well with our computed value of 67.5 kcal/mol. From ref 16 we expect the average mean unsigned error for the BDEs to be about 1.7 kcal/mol, which is the value obtained for a thermochemistry database including alkyl bond dissociation energies using the M06-2X functional. The mean absolute deviation of carbon–hydrogen BDEs calculated with the previous generation functional (M05-2X) from experiment was given in ref 13 to be 1.3 kcal/mol. This value decreases to 0.8 kcal/mol for relative BDEs¹³ that are defined by isodesmic reactions. The uncertainties of the experimental values were listed to be 1–2 kcal/mol.¹³ As an additional test for BDE differences, we calculated the oxygen–carbon BDE of ethyl phenyl ether (CH₃CH₂–OPh). At 0 K, the BDE difference of CH₃–OX and CH₃CH₂–OX for X = H was calculated to be 2.5 kcal/mol using the G3-RAD method and 2.8 kcal/mol for X = CH₃.¹⁴ We compute a BDE difference of 2.1 kcal/mol for X = Ph at 0 K. We conclude that the accuracy of the M06-2X functional is sufficient to study the BDEs in substituted PPE. We estimate an error in the BDEs to experiment to be about 2 kcal/mol and an error in the BDE differences to experiment to be smaller than 1 kcal/mol, which is in the same range of error as the experimental values listed in ref 13.

The results in Table 1 show that the carbon–carbon BDE in PPE is 7.6 kcal/mol larger than the oxygen–carbon BDE. This can be used to estimate the ratio of oxygen–carbon and carbon–carbon cleavage contributing to the pyrolysis of PPE at different temperatures. We assume that the Arrhenius pre-factors for the oxygen–carbon and carbon–carbon cleavage are the same and further that the difference in activation energies is equivalent to the difference in BDEs since the energy barriers for the reverse radical recombination is expected to be small. The ratio of oxygen–carbon and carbon–carbon cleavage is then given as $k_{CO}/k_{CC} = e^{\Delta BDE/RT}$. At a typical slow pyrolysis temperature of 375 °C, the ratio is estimated to be 365:1, indicating very little contribution from carbon–carbon cleavage. At higher temperatures typical of fast pyrolysis, the carbon–carbon cleavage gains influence; for example, the ratio is reduced to 80:1 at 600 °C. The influence of the substituents on the homolysis ratio can be substantial, but the difference between the oxygen–carbon and carbon–carbon BDE is too large to allow for a significant contribution of the carbon–carbon homolysis. For example, the slight decrease in ΔBDE of 0.5 kcal/mol for **2** and **3** results in a homolysis ratio of 249:1 at 375 °C and 60:1 at 600 °C. The ΔBDE increases for **4–6** and is largest for **6** with 17.1 kcal/mol. The homolysis ratio for **6** is 588422:1 at 375 °C and 19183:1 at 600 °C. It should be noted that the PPE-type linkages in lignin also contain important substituents on the aliphatic carbons {PhCH(X)CH(Y)OPh}³ that are not the subject of the current investigation but could significantly alter the C–O and C–C BDEs and, hence, the homolysis selectivity.

Our main interest in this study is the effect of the aromatic substituents on the BDEs, i.e., the BDE differences relative to those of PPE ($\Delta BDEs$), which are included in Table 1. Relative BDEs can be calculated to higher accuracy than absolute BDEs,^{12,13} in particular when the calculation is based on an isodesmic reaction.¹⁵ Scheme A in Supporting Information shows that the $\Delta BDEs$ for the oxygen–carbon bond dissociation given in Table 1 are equal to the reaction energies of an

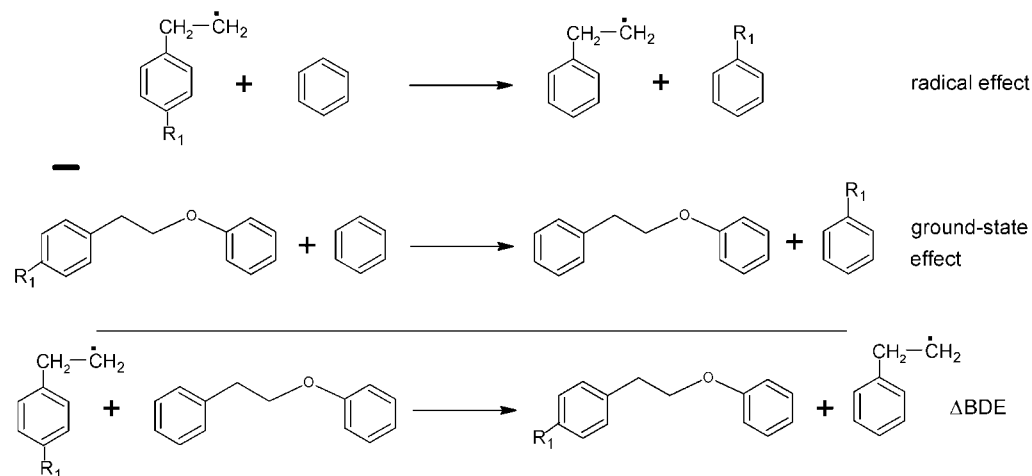
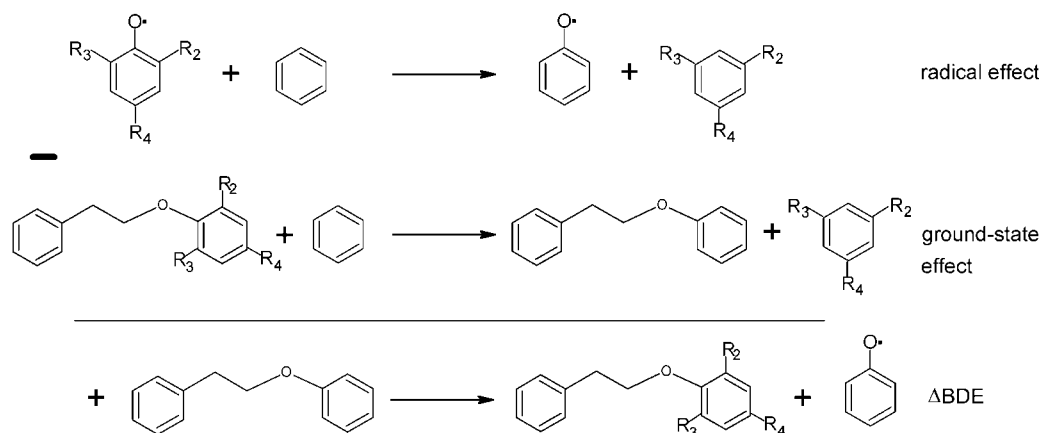
isodesmic reaction, with similar equations for the carbon–carbon dissociation. We observe that the methoxy as well as the hydroxy substituent in the R₁ position (**2**, **3**) have a negligible effect on the oxygen–carbon BDE. If the methoxy substituent is situated on the phenyl ring adjacent to the ether oxygen (**4–6**), the oxygen–carbon BDE is substantially decreased. A methoxy substituent in the ortho position (**5**) reduces the oxygen–carbon BDE by 5.1 kcal/mol to a similar value as when the methoxy substituent is located in the para position (**4**). An additional methoxy substituent in ortho position (**6**) decreases the oxygen–carbon BDE further by 3.5 kcal/mol. Hence, a second *o*-methoxy substituent has a smaller effect on lowering the BDE than the first *o*-methoxy group. These findings are consistent with experimental FVP studies,⁵ which showed that methoxy substituents in the R₂ and/or R₃ position (**5**, **6**) enhance the homolysis of the β -O-4 linkage, but that the second *o*-methoxy group has a smaller influence. Similarly large substituent effects on the oxygen–carbon BDE in anisole have been measured,^{19,20} where based on Arrhenius activation energies the methoxy substituent in ortho position decreases the BDE in anisole by 4.1 kcal/mol and in para position by 3.1 kcal/mol¹⁹ (4.2 and 4.0 kcal/mol in ref 20). Furthermore, in the pyrolysis of benzyl phenyl ether (PhCH₂–OPh),¹⁹ the presence of a *p*-methoxy group (PhCH₂–OPhOCH₃), similar to **4**, resulted in a decrease in the BDE of 5.5 kcal/mol, again based on differences in activation energies. The carbon–carbon BDEs for the substituted PPEs are much less influenced by the substituents in the R₂–R₄ positions (**4–6**) compared to the effects on the corresponding oxygen–carbon BDEs. On the other hand, there is a slight decrease in the carbon–carbon BDEs (compared to no change in the oxygen–carbon BDEs in **2** and **3**) when a hydroxy or methoxy substituent is situated in the R₁ position (**2**, **3**). The apparent anomaly in the data for the substituent effect on the carbon–carbon BDE in **6** is addressed later in the text.

To further analyze the effect of the substituents, we partitioned the total substituent effect into the ground-state and radical contributions, as shown in Scheme 2 for the oxygen–carbon bond dissociation (following the work of Wu and Lai²¹ and references therein). Similar equations can be derived for the carbon–carbon bond dissociation. The computed ground-state and radical effects are included in Table 1. The ground state is destabilized by the substituents. Substituents on the R₁ position (**2**, **3**) have a relatively small effect on the ground state compared to the effect of the substituents on the opposite ring (**4–6**). The ground-state destabilization increases from para to ortho to di-ortho substituents (from **4** to **5** to **6**). The radical effect depends on the radical produced by the dissociation. The phenethyl radical is destabilized by the methoxy and hydroxy substituent to a similar degree. The phenoxy radical is stabilized by *o*-, di-*o*-, and *p*-methoxy substituents in increasing order. Also the benzyl radical is stabilized by the hydroxy and methoxy substituents in para position but to a smaller extent. On the other hand, the phenoxymethyl radical is destabilized by *p*-, *o*-, and di-*o*-methoxy substituents in increasing order. In previous work, electron-donating substituents were found to stabilize the electrophilic phenoxy radical,²¹ whereas both electron-donating and electron-withdrawing groups stabilize benzyl radicals.²² The ground-state and radical effects are additive for the phenoxy and benzyl radicals but cancel for the phenethyl and phenoxymethyl radicals. Even though the ground-state effects are the same

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SCHEME 2. Illustration of Ground-State and Radical Effect for Oxygen–Carbon Bond Dissociation

for $R_2, R_3, R_4 = H$ for $R_1 = H$ 

for the oxygen–carbon and carbon–carbon dissociation, the radical effect opposes the ground-state effect for the oxygen–carbon dissociation when the substituent is located at the R_1 position (**2**, **3**) resulting in a negligible total effect. However, since the radical and ground-state effects are additive for the carbon–carbon dissociation, the total substituent effect for the hydroxy or methoxy substituent at the R_1 position (**2**, **3**) is 0.5 kcal/mol for the carbon–carbon dissociation. It is also interesting that the total effect on the oxygen–carbon BDE of a methoxy substituent in the R_2 and the R_4 position (**4**, **5**) is about the same, but for the para substituent (**4**) the radical effect is dominant whereas for the ortho substituent (**5**) the ground-state effect is larger. The total substituent effect on the carbon–carbon BDEs for substituents in the R_2 – R_4 positions (**4**–**6**) is small because the radical effect opposes the ground-state effect. It is noticeable that the substituent effect in **4**–**6** is positive except for di-*o*-methoxy PPE (**6**), which is -0.95 kcal/mol. This can be explained by steric hindrance in the di-*o*-methoxy phenoxy radical. Figure 1 shows the *p*-, *o*-, and di-*o*-methoxy phenoxy radicals. The substituents in the di-ortho radical prevent the $-\text{OCH}_2^\bullet$ group from rotating into a semi-coplanar position relative to the aromatic ring that allows for interaction of the single electron with the aromatic system. The magnitude of this steric effect can be estimated by the energy difference between the ortho-substituted radicals where the $-\text{OCH}_2^\bullet$ group

is oriented coplanar and perpendicular to the aromatic ring, which is 1.3 kcal/mol. If this is subtracted from the carbon–carbon BDE of **6**, the total substituent effect is estimated to be 0.37 kcal/mol, comparable to the total substituent effect obtained for the other methoxy-substituted PPEs (**4**, **5**).

Another interesting observation can be made by comparing the substituent effect on the oxygen–carbon BDE in **4** to the substituent effect on the carbon–carbon BDE in **3**, the former being about 5 kcal/mol larger. The oxygen–carbon dissociation of **4** leads to the formation of a *p*-methoxy phenoxy radical where oxygen is the radical center, whereas the carbon–carbon dissociation of **3** results in a *p*-methoxy benzyl radical where CH_2 is the radical center. The large difference is mainly due to the difference in the radical effect, which is 3.7 kcal/mol. This can be attributed to a stronger inductive effect of substituents in the electrophilic phenoxy radical compared to that of the less electrophilic benzyl radical.¹⁹ This is demonstrated in Figure 2, which displays the partial charges of the phenoxy and the benzyl radical, showing a large positive charge on the ring carbon next to the radical center in the phenoxy radical. The carbon–oxygen bond length decreases from Ph-OH to Ph-O $^\bullet$ by 0.11 Å and the carbon–carbon bond length shortens from Ph-CH $_3$ to Ph-CH $_2^\bullet$ by 0.10 Å, indicating only little difference in delocalization of the single electron into the ring for the phenoxy and benzyl radical.

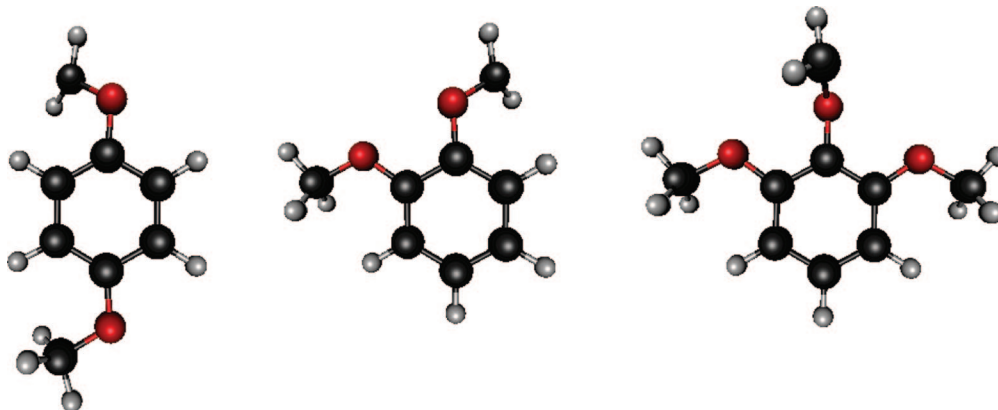


FIGURE 1. Equilibrium geometries of the *p*-, *o*-, and di-*o*-methoxy phenoxymethyl radicals.

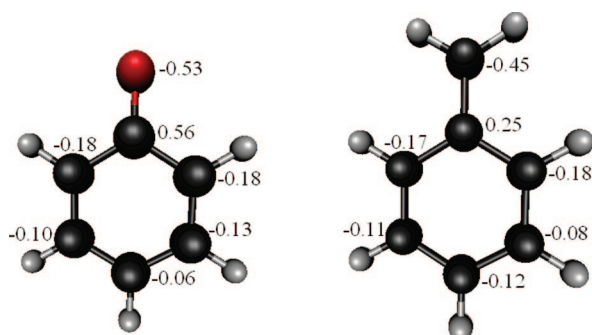


FIGURE 2. Partial charges in electrons for the phenoxy and benzyl radicals.

Conclusion

We have calculated the oxygen–carbon and carbon–carbon bond dissociation enthalpies (BDEs) in several oxygen-substituted phenethyl phenyl ethers (PPEs) that are model compounds for the dominant β -O-4 linkage in lignin, which is a potentially renewable source of fuels and chemicals. The initial reaction in the thermal decomposition of PPE under a range of pyrolysis conditions is the homolytic cleavage of the oxygen–carbon bond and, to a smaller extent, the carbon–carbon bond. The rate of the homolysis depends on the BDE of the oxygen–carbon and the carbon–carbon bonds in PPE, whose selectivity will be influenced by the nature and location of relevant substituents. We have shown that the oxygen–carbon BDE in PPE is 7.6 kcal/mol lower than the carbon–carbon BDE, explaining the low percentage of carbon–carbon cleavage observed experimentally. In this study, we have focused on the impact of hydroxy and methoxy substituents on the aromatic rings. Depending on the substituent, the difference in BDEs increases to up to 17.1 kcal/mol. The oxygen–carbon BDE is substantially lowered, and therefore the initial homolysis step accelerated, by substituents located at the phenyl ring adjacent to the ether oxygen. On the other hand, the carbon–carbon BDE is not significantly influenced by oxygen substituents situated at either phenyl ring. Employing isodesmic reactions, the substituent effects were partitioned into their ground-state and radical contributions, which provides additional fundamental insights into the origin of these effects. PPE-type linkages in lignin also contain important substituents on the aliphatic carbons {PhCH(X)CH(Y)OPh} that

could significantly alter the oxygen–carbon and carbon–carbon BDEs and, hence, the homolysis selectivity. This will be one of the topics of our continued computational investigations into the thermal transformations of lignin model compounds.

Computational Details

All calculations were carried out with the NWChem program package.²³ We used DFT, in particular, the unrestricted M06-2X¹⁶ functional. The conformational space for the reactants was sampled by using different starting structures distinguished by various orientations of the aromatic rings relative to each other and by rotations of the substituents. If more than one minimum structure was found, the calculation of the BDEs was based on the energetic lowest structure. A mixed basis set was used for geometry optimizations and frequency calculations as previously described,⁷ where diffuse functions were added to a 6-31G* basis set at the location of the unpaired electron. The final 0 K energies were obtained by single point calculations employing a 6-311++G** basis set. The total energies were corrected by the zero-point energies, and the thermal contributions at 298.15 K were added. The thermal corrections include electronic, translational, rotational, and vibrational contributions; for the latter the harmonic approximation was applied. The corrected energies were converted into enthalpies, and the BDE was obtained as the difference of the sum of the thermally corrected enthalpies of the dissociation products and the thermally corrected enthalpy of the molecule. The partial atomic charges were calculated by a fitting procedure of the quantum mechanical electrostatic potential on selected grid points.

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Supporting Information Available: Scheme A, Cartesian coordinates, and absolute energies of calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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