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A computational study of pyrolysis reactions of lignin model compounds

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Abstract

Enthalpies of reaction for the initial steps in the pyrolysis of lignin have been evaluated at the CBS-4m level of theory using fully substituted β-O-4 dilignols. Values for competing unimolecular decomposition reactions are consistent with results previously published for phenethyl phenyl ether models, but with lowered selectivity. Chain propagating reactions of free radicals with a closed-shell dilignol are dominated by structures in which extensive electron delocalization occurs.

Keywords: bond dissociation enthalpy; CBS-4m; free radicals; lignin model compounds; pyrolysis.

Introduction

During the recent past there has been an intense renewal of interest in the use of lignocellulosic biomass as an alternative to fossil-based energy resources. Biochemical conversions for the production of ethanol, direct combustion or thermal degradation methods such as gasification or pyrolysis are the most promising approaches. The advantage of the latter two is that although the products can obviously be used as fuels, they might also be further processed into value-added products such as commodity or specialty chemicals. The current paper will focus on the chemistry of lignin reported to occur under elevated temperatures, providing information that could allow for control of the product slate or optimization of thermal processes for specific uses.

Two decades ago, Brežný et al. (1983, 1984) and Evans et al. (1986) published experimental results on the pyrolysis of lignin and lignin model compounds. More recently, the authors Nakamura et al. (2007), Kawamoto and Saka (2007), Kawamoto et al. (2007a,b, 2008a,b), and Watanabe et al. (2009) reported on the effect of substitution on the products and proposed mechanisms of the thermal conversion of dimeric lignin models.

An extensive body of both experimental and computational research has been concerned with the pyrolysis reactions of phenethyl phenyl ethers, representing the β-ether group, ubiquitous in the lignin polymer. Mechanistic studies by Klein and Virk (1983) proposed that the first step is a homolytic cleavage reaction, yielding phenoxyl and phenethyl radicals. More recently, detailed mechanistic schemes have been proposed based on experimental results on the pyrolysis of lignin and its model compounds (Britt et al. 2000, 2007) and computational results (Beste et al. 2007, 2008; Beste and Buchanan 2009). These authors have proposed mechanisms based on the homolysis of phenethyl phenyl ethers and evaluated the effect of substitution on the reactions. In the most recent contribution from this group, Beste and Buchanan (2009) report computational results for the enthalpy of reaction at 298°K of a number of substituted phenethyl phenyl ethers based on the M06-2X functional method. In other current research, enthalpies of reaction at elevated temperatures have been calculated (Wang et al. 2009) for 1-(4-hydroxyphenyl)-2-phenoxy-propane-1,3-diol by the application of density functional methods and large basis sets (B3LYP/6-31++G(2df,p).

Lignin is the polymerization product of coniferyl, sinapyl and *p*-coumaryl alcohol. Thus, the polymer consists of phenylpropane units, with varying degrees of methoxylation on the aromatic rings. The objective of the current paper is to evaluate both the initial homolytic cleavage reactions and subsequent chain propagating steps during thermal degradation of fully substituted dilignols based on computational methods. The study includes reactions of the free radicals generated in the first step and the fate of the original closed-shell dilignols. The results of this study will be compared with those of previous literature describing related compounds.

Materials and methods

Computational methods: G3MP2 (Curtiss et al. 1999) and CBS-4m (Montgomery et al. 2000). These are both compound techniques based on several calculations of increasing intensity in series, resulting in highly accurate enthalpies of reaction. G3MP2 is a variant of the G3 method, relying on second-order Møller-Plesset basis set extensions. The method was found to be very accurate and results in a considerable savings in central processing unit (CPU) time compared to the G3 method (Curtiss et al. 1999). CBS-4m is a modification of the CBS-4 method, from which Mulliken artifacts have been eliminated, resulting in the correction of previously reported errors (Montgomery et al. 2000).

These methods have been specifically designed to provide highly accurate energies for equilibrium geometries (Foresman and Frisch 1996), as documented by Curtiss et al. (1999) and Montgomery et al. (2000). Although very accurate in this regard, the limitations of such methods for the determination of transition states has recently been reported by Wheeler et al. (2008), and overestimation of bond lengths has been shown by Tang et al. (2009). Given these limitations, the current paper will restrict its comments to the energetics of the reactions in question at equilibrium geometries.

All calculations were performed using Gaussian 09, revision A.01 (Frisch et al. 2009), as implemented on an SGI Altix administered by the Alabama Supercomputer Authority.

To verify consistency of results, calculations were performed at these levels of theory on anisole and the *ortho*-substituted phenethyl phenyl ether (PPE-oCH_3) for which results have been reported (Beste and Buchanan 2009).

The initial unimolecular decomposition reactions to be addressed in this study are shown in Figure 1. The β-carbon-oxygen and α-β carbon homolysis reactions have the lowest enthalpies of reaction according to Beste and Buchanan (2009) and Wang et al. (2009). The structures for dilignol models 1 and 2 are based on crystal structures from the literature (Stomberg and Lundquist 1994; Langer et al. 2002), whereas compound 3 is based on the crystal structure of compound 1, after removal of the methoxyl groups.

The chain propagating steps of the free radicals generated by the reactions in Figure 1 with compound 1 are presented in Figures 2 and 3. These reactions, involving the abstraction of a hydrogen atom from the phenolic and α-positions correspond to those proposed by Watanabe et al. (2009).

Results and discussion

For comparison purposes, the enthalpies of reaction for anisole and PPE-oOCH_3 were determined using both the G3MP2 and CBS-4m levels of theory, the results of which are listed in Table 1.

The homolysis of anisole has been extensively studied and at the G3MP2 level is reported to be 66.7 kcal mol^{-1} (Johnson et al. 2003), compared to an average experimental value of 65.3 kcal mol^{-1} (Mulder et al. 2005). The results from the current G3MP2 calculations are in agreement with data from the literature. The same is true for the CBS-4m value which also compares rather favorably with other data. Both values are not dissimilar to the M0-2X results. For the PPE-oOCH_3 model, the G3MP2 and CBS-4m results are slightly higher than the M0-2X values, but are internally somewhat consistent.

Furthermore, in the process of performing the G3MP2 calculations for the PPE-oOCH3 model it was found that the time requirements were relatively intense, requiring in excess of 2300 h of CPU. This is in comparison to approximately

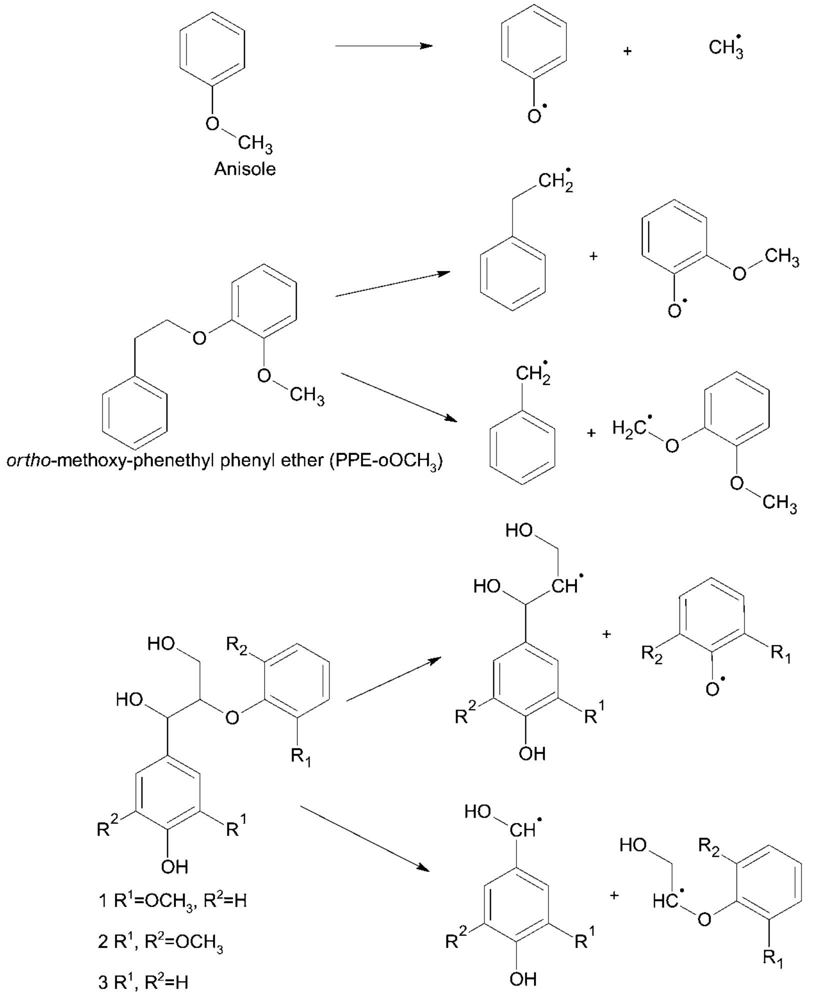

Figure 1 Model compounds investigated in the present paper and their possible homolytic bond cleavages.

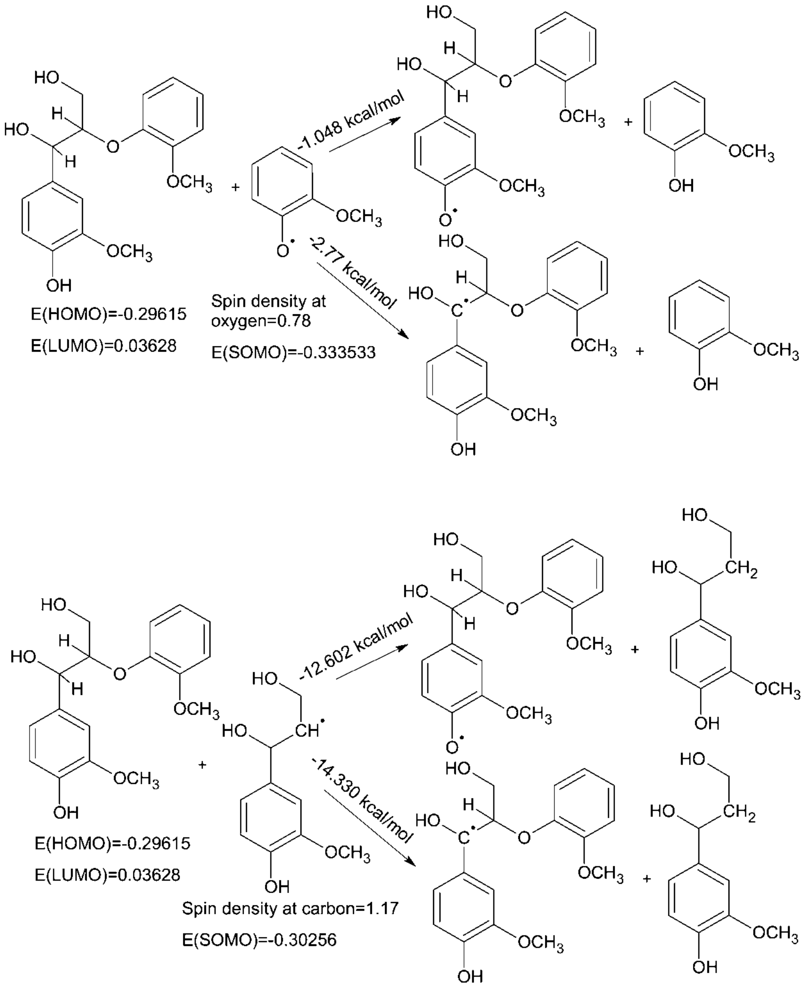

Figure 2 Reactions of free radicals from β-O cleavage with model compound 3 (see Figure 1).

36.5 h of CPU time for the same calculation at the CBS-4m level. Although the first step of a CBS-4m calculation is a geometry optimization only at the HF/3-21G* level, given the agreement with the more intense methods and the massive time savings, the calculations of lignin models 1–3 were done at the CBS-4m level.

The bond dissociation enthalpies for the homolytic cleavage reactions (Figure 1) of the lignin models are presented in Table 2. These calculations were done at 298°K, and although pyrolysis reactions occur at much higher temperatures, 298°K is defined as standard state for enthalpy calculations. Indeed, even enthalpies of combustion of hydrocarbons, which occur at elevated temperatures, are reported at 298°K (Sontag and Van Wylen 1971). Furthermore, this allows for direct comparison with the results of Beste and Buchanan (2009). Similarly, for comparison purposes the calculations of Wang et al. (2009), for compound 3, performed at 800°K and 101 kPa were repeated under these conditions at the CBS-4m level, the results of which are also presented in Table 2.

All calculations show, as would be expected, that the bond dissociation enthalpy (BDE) of the α-β reaction is greater than the β-O cleavage. A comparison of the CBS-4m results for the current models to the PPE-oOCH$_3$ structure shows that β-O homolysis is consistently higher for the former, whereas the α-β results are variable. It can also be seen that the difference in BDE between these two pathways is greater for PPE-oOCH$_3$ than the more heavily substituted dilignols, indicating less selectivity for such models over the phenethyl phenyl ethers.

This behavior should not be unexpected owing to differential substitution and linkages and was indeed predicted by Beste and Buchanan (2009). Furthermore, the quoted authors found that BDE consistently decreased with increasing methoxyl content, and this finding was particularly true for the β-O reaction. This pattern is not reflected in the current study, in which the model 3 without methoxyl groups and model 2 with four methoxyl groups have around the same enthalpy of reaction, whereas model 1 with two methoxyl groups had the lowest enthalpy of reaction. Wang et al. (2009) performed density functional calculations (DFTs) and found that the results at 800°K are at considerable variance with the values reported in the literature. In preliminary research for the current paper, density functional theory

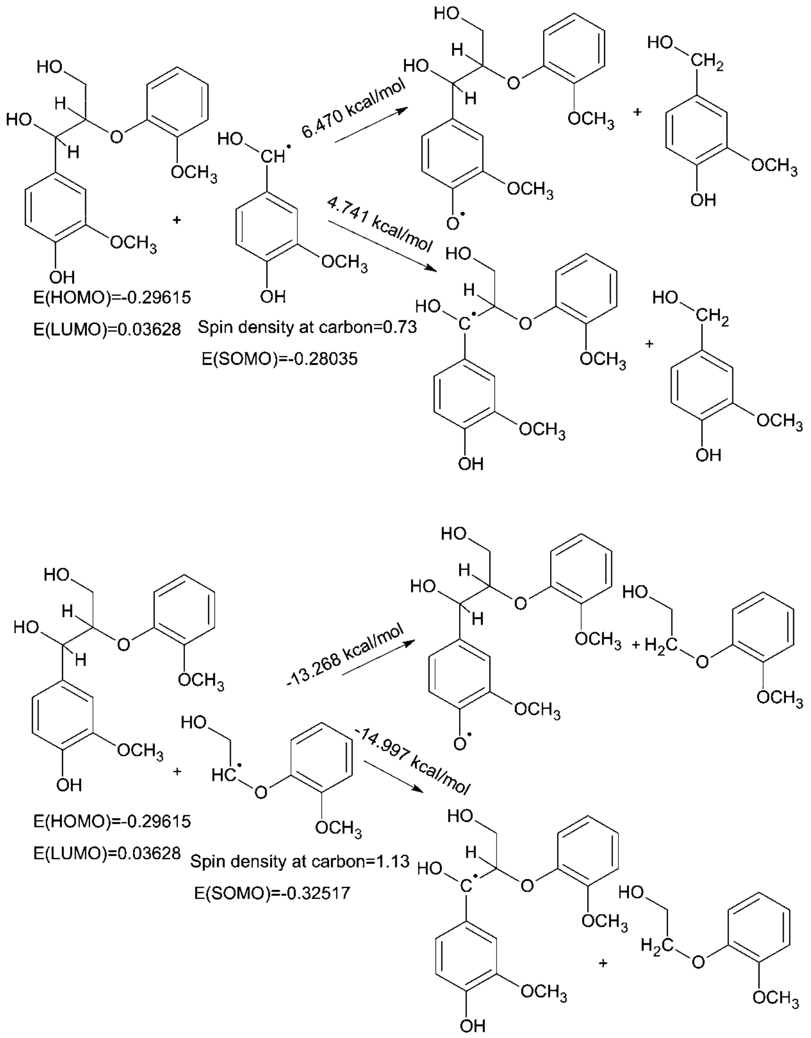

Figure 3 Reactions of free radicals from α-β cleavage with model compound 3 (see Figure 1).

calculations were performed and results similar to those of Wang et al. (2009) were found. The differences between these calculations and the previous study on phenethyl phenyl ethers leads to the conclusion that DFT is not appropriate for these reactions, and that computational methods in which electron correlation is explicitly addressed are needed.

Figures 2 and 3 show results from the isodesmic reactions of model 1 with free radicals generated from β-O and α-β cleavage, respectively. Several general observations can be derived from these calculations. The abstraction of hydrogen from the α-carbon is a less energetic reaction than from the phenolic position. The energy difference between the singly occupied molecular orbital (SOMO) of the radicals and the highest occupied molecular orbital (HOMO) of model 1 is much smaller than with the lowest unoccupied molecular orbital (LUMO), such that orbital interactions would be predicted to occur between the HOMO and SOMO. Such orbital interactions should not be surprising in this case, owing to

Table 1 Enthalpies of reaction at 298°K for anisole and PPE-oOCH$_3$ as determined by different methods (see Figure 1).

Compound/ linkage	Enthalpy obtained with M0-2X[a] (kcal mol^{-1})	G3MP2 (kcal mol^{-1})	CBS-4m (kcal mol^{-1})
Anisole	67.5	66.7	67.0
PPE-oOCH$_3$/β-O	64.4	66.6	68.3
PPE-oOCH$_3$/α-β	77.0	79.8	79.6

[a]According to Beste and Buchanan (2009).

Table 2 Enthalpies of two linkages in lignin model compounds presented in Figure 1 (bottom).

Compound	Temp. (°K)	Enthalpy for linkages β-O (kcal mol^{-1})	α-β (kcal mol^{-1})
1	298	72.3	81.1
2	298	73.7	79.2
3	298	73.6	75.3
3	800	73.6	74.6
3[a]	800	54.5	57.6

[a]According to Wang et al. (2009).

the inherent softness of free radicals. Furthermore, based on these observations, the electron density in the HOMO for the α- and phenolic-hydrogen was calculated, resulting in values of 0.0088 and 0.0003, respectively, supporting the preferential reaction at the α-position. Finally, both of the product dilignol radicals have considerable and similar opportunities for electron delocalization, and with an energy difference of less than 2 kcal mol^{-1} are energetically somewhat similar.

Figure 2 shows the reactions of the free radicals resulting from the unimolecular decomposition of the β-O bond, generating a phenoxyl and 1-phenyl-2-propyl radical. The former structure exhibits a much lower unpaired spin density at the oxygen, owing to a greater degree of delocalization throughout the aromatic system, and is therefore more stable. Based on these results, it is interesting that the reaction of the 1-phenyl-2-propyl radical is more exothermic than that of the phenoxyl radical. This can be accounted for by the relative stability of the radicals. As indicated, the phenoxyl structure, owing to its electron delocalization is more stable, such that the energy difference associated with the addition of the abstracted hydrogen is lower. Conversely, hydrogen addition to the 1-phenyl-2-propyl radical results in a large net decrease in energy owing to its relatively high energy.

Similarly, Figure 3, illustrating the reactions of radicals from α-β cleavage, indicates that the hydroxybenzyl radical has a lower unpaired spin density at the α-position than the β-phenoxyethanol radical has at the β-position. It can also be seen that the reaction of the former is actually endothermic, whereas the latter is relatively exothermic. As previously discussed, this difference is as a result of the stability of the hydroxybenzyl radical such that the addition of the hydrogen atom, to give the closed-shell product, results in a relatively small energy difference.

Although perhaps initially surprising, these results are consistent with those reported in a computational study by Beste et al. (2007) in which abstraction of the α-hydrogen from phenethyl phenyl ether by a phenoxyl radical is reported to be an endothermic reaction, whereas the reaction of a benzyl radical is slightly exothermic. These radical species, which have extensive electron delocalization are analogous to the phenoxyl and hydroxybenzyl radicals in the current study. It is furthermore proposed (Beste et al. 2007) that an alternative and more highly exothermic reaction involving a phenethyl radical makes only a minor contribution to the overall chain reaction.

These results can be accounted for by the relative stability of the radicals. In the case of the phenoxyl and hydroxybenzyl radicals a large degree of delocalization, and therefore stability, is exhibited. The products are stable closed-shell systems and stable radicals with a large amount of delocalization. As the reaction proceeds from stable reactants to stable products, there is only a slight change in the overall energetics of the system. In contrast, in the 1-phenyl-2-propyl and β-phenoxyethanol radicals the unpaired electron is somewhat localized such that these reactants are less stable than the phenoxyl and hydroxybenzyl radicals. The products, as before are stable closed-shell structures and stable radicals. The observed exothermicity is explained by the combination of relatively unstable reactants yielding stable products. Based on these results from the literature and the current study, it would appear that initial chain propagating reactions of lignin with free radicals are controlled by the stability of the radical, as evidenced by electron delocalization, rather than the net energy associated with hydrogen abstraction.

Conclusions

In summary, the current study reports on the application of compound quantum chemical calculations to fully substituted β-O-4 linked dilignols. Preliminary work indicated that the G3MP2 and CBS-4m methods were consistent with data obtained by experimental research and M0-2X density functional calculations as reported in the literature. Furthermore, it was found that the CBS-4m calculations were much faster to perform and they yield accurate results.

Calculations of the BDE of phenethyl phenyl ethers showed a marked difference, in excess of 10 kcal mol^{-1}, between the β-O and α-β cleavage reactions. In contrast, CBS-4m calculations on the dilignols (compounds 1–3) exhibited a smaller range of 1.7–8.8 kcal mol^{-1}. As such, the initial homolysis reaction of the dilignols will be less selective than the phenethyl phenyl ethers, resulting in a more uniform product distribution, potentially altering the course of subsequent reactions. This would indicate that the products of α-β decomposition would be of more importance than predicted from the phenethyl phenyl ether results, particularly for the syringyl and *p*-coumaryl based models.

Turning to the second step, the reactions of the homolytically generated free radicals with the original closed-shell dilignol, the radical reactants were found to differ substantially with regard to delocalization of the unpaired electron and therefore stability. Interestingly, the reactions of the radicals with the most extensive delocalization are those which exhibit the least net stabilization upon hydrogen abstraction from the dilignol. Indeed, one of these reactions is found to be endothermic. These results, which are consistent with previous literature reports (Beste et al. 2007), are due to the relative stability of the radicals. Those which exhibit greater delocalization are stable to the point that hydrogen addition results in only small reductions in energy. Finally, the 1-phenyl-2-propyl and β-phenoxyethanol radicals result in reactants for which delocalization is minimal, and unpaired spin density is concentrated at the reactive center. Consequently these radicals are severely limited with regard to the sites that are capable of abstracting a hydrogen from the dilignol. In addition, these radicals would result in intermediates that would be sterically hindered, further limiting their participation in the chain propagating reactions.

In conclusion, reactant stability is more important than energetics in controlling the chain propagating steps of lignin pyrolysis. Furthermore, although it was found that the selectivity of the initial unimolecular decomposition was lower than previously reported, only those free radicals for which unpaired electron delocalization is extensive will have a significant role in the subsequent pyrolysis reactions.

Based on these results, subsequent research has been initiated examining reaction coordinates and transition state calculations, along with the assessment of additional secondary pyrolysis reactions.

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