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LETTER

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Computational Study of Bond Dissociation Enthalpies for a Large Range of Native and Modified Lignins

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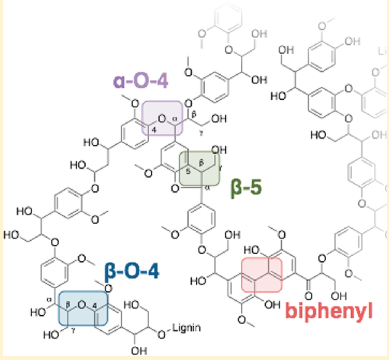
S *Supporting Information*

ABSTRACT: Lignin is a major component of plant cell walls that is typically underutilized in selective conversion strategies for renewable fuels and chemicals. The mechanisms by which thermal and catalytic treatments deconstruct lignin remain elusive, which is where quantum mechanical calculations can offer fundamental insights. Here, we compute homolytic bond dissociation enthalpies (BDEs) for four prevalent linkages in 69 lignin model compounds, including β-O-4, α-O-4, β-5, and biphenyl bonds, with a large range of natural and oxidized substituents. These calculations include ab initio benchmark values extrapolated to the complete basis set limit and full conformational searches for each compound. The results quantify both the relative BDEs among common lignin bonds and the effect of native and oxidized substituents on the functional groups in lignin. These data yield insights into thermal lignin deconstruction for a large range of prevalent linkages and aid in the identification of targets for catalytic cleavage.



SECTION: Macromolecules, Soft Matter

Lignin is an alkylaromatic polymer found in plant cell walls that aids in structure, defense, and water transport. Due to its prevalence in plants, lignin is the most abundant biological material on earth after cellulose, and thus represents a potential feedstock for production of renewable fuels and chemicals.[1] Lignin polymers are comprised of three types of phenylpropanoid monomers: *p*-hydroxyphenylpropane (denoted H), guaiacylpropane (G), and syringylpropane (S), shown in Figure 1.[2] In the plant cell wall, oxidative coupling reactions are responsible for lignin self-assembly, which yields heterogeneous polymers linked by a range of C−O and C−C bonds. There are a number of different lignin linkages, including β-O-4 (the most common, comprising up to 50% of the bonds in lignin), biphenyl (3.5−25%), β-5 (4−10%), and α-O-4 (3−5%) linkages, also shown in Figure 1.[2]

In current selective routes to produce fuels and chemicals from lignocellulosic biomass, residual lignin is typically burned for heat and power.[3,4] To more efficiently utilize lignin, selective strategies, such as catalytic,[1,5−9] enzymatic,[10] and biomimetic[11] routes to deconstruct lignin are under development. Additionally, genetic modifications of lignin synthesis pathways in plants are being investigated to reduce recalcitrance and homogenize feedstocks.[12] Conversely, in high-temperature conversion routes, such as pyrolysis, the products of thermal lignin depolymerization are a major constituent of pyrolysis oil, and the resulting phenolic molecules are often quite reactive, which leads to undesired degradation products.[13,14] Fundamental understanding of lignin chemistry is thus crucial to further develop both the catalytic and thermal routes for effective lignin utilization. To that end, we use density functional theory (DFT) to compute the homolytic bond dissociation enthalpies (BDEs) of 69 dimers representing four common linkages with a range of realistic native and oxidized substituents found in lignin, as shown in Figure 1. This work is complementary to previous studies, which primarily focused on β-O-4 linkages with more limited substituents[15−17] and a recent study wherein all of the native linkages in lignin were examined.[18] In particular, the seminal work of Beste and Buchanan has shown that methoxy substituents close to the β-O-4 linkage are likely responsible for the experimentally observed higher cleavage rates of β-O-4 bonds in substituted phenethyl phenyl ether models.[17] More recent work from Parthasarathi et al. has examined the BDEs of 65 distinct linkages in lignin, which will be useful for developing kinetic models for pyrolysis.[18]

The computational methods are described fully in the Supporting Information. Briefly, all wave function theory (WFT) and

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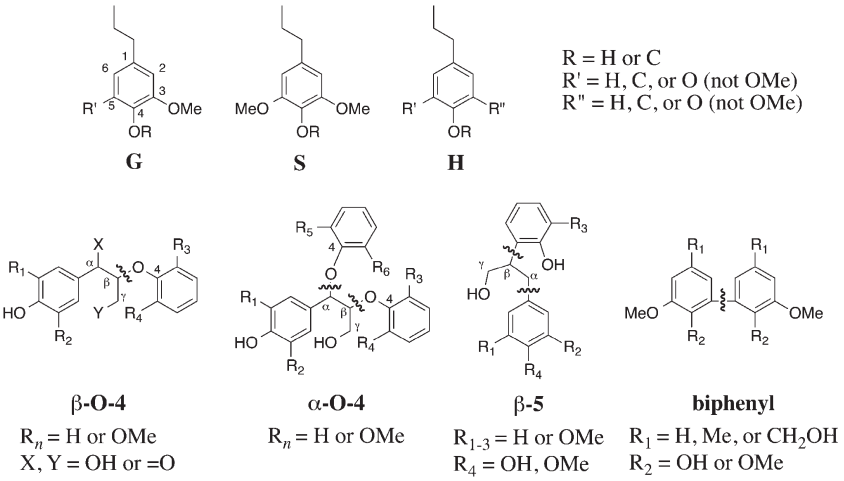

Figure 1. The three types of phenylpropanoid monomers that comprise lignin (top) and the native and modified lignin linkage types investigated here (bottom). We compute the BDE for the full set of 65 model compounds defined here, representing 104 chemical bonds in native and modified lignin. Four additional BDE calculations are described below for benchmark purposes, for a total of 69 lignin model compounds and 108 BDE calculations.

DFT calculations were performed with Gaussian 09.[19] We first benchmarked our methods on smaller model dimers for the β-O-4 linkage (Figure 2) with the composite ab initio CBS-QB3 method,[20] where the correlation energy is extrapolated to the basis set limit, and which has been shown to yield quantitative agreement with BDE experimental measurements on smaller lignin model molecules[14] and an average mean error from the G2 set of molecules of 0.98 kcal/mol.[20] Our results show that the hybrid meta generalized gradient approximation M06-2X functional from Truhlar[21] yields excellent agreement with CBS-QB3, whereas the other three functionals examined here (B3LYP,[22] PBE0,[23] and ωB97XD[24]) produce similar qualitative trends, but are offset from the CBS-QB3 benchmark. The M06-2X functional has also been shown to yield an average mean error from main group thermochemical data from the TC177 database of 1.3 kcal/mol.[25] At the WFT level, Grimme's spin-component-scaled MP2 (scs-MP2[26]) systematically overestimates activation enthalpies. All benchmark models were optimized with a 6-31G(d) basis set, and then single point energies were evaluated with a larger 6-311++G(d,p) basis set at the same level of theory.

For the BDE calculations for all 69 model dimers, we selected four of the most prevalent linkages in lignin, with a large range of substitution patterns on both the aromatic and alkyl moieties. For the β-O-4 linkages, we included an additional set of non-native, chemically modified substitutions on the alkyl chains wherein the alcohol on the α-carbon or on the γ-carbon is oxidized to a ketone or aldehyde, respectively. We chose this substitution because the ketone has been proposed as an intermediate in a catalytic cycle for deconstruction of a β-O-4 model dimer that lacks a γ-methylhydroxy group.[6] By extension, we included a set of compounds wherein the primary alcohol on the γ-carbon has been oxidized to an aldehyde. In addition, for the β-5 linkage, we first cleaved the oxygen bridge in the five-membered ring before computing the BDEs, as this will be the likely first step in deconstruction of this linkage and this is an intermediate in the β-5 linkage formation.[27] For the biphenyl linkage, we include a methoxy group on R_2 to mimic the alkylether linkage to additional lignin branches, and these dimers have also been observed experimentally as degradation products.[28]

Following the benchmarks, for each model compound we performed a 100 step Monte Carlo multiple minimum (MCMM) conformational search,[29] optimizing structures with the semiempirical PM6 Hamiltonian.[30] For each dimer, all low lying conformers within 10 kcal/mol of the global energy minimum were selected, typically yielding between 20 and 30 unique structures, which were subsequently reoptimized at the M06-2X/6-31G(d) level. Single-point energies were then calculated for the lowest energy conformer with the M06-2X functional and the 6-311++G(d,p) basis set, for which the results are presented in Tables 1 and 2 and summarized in

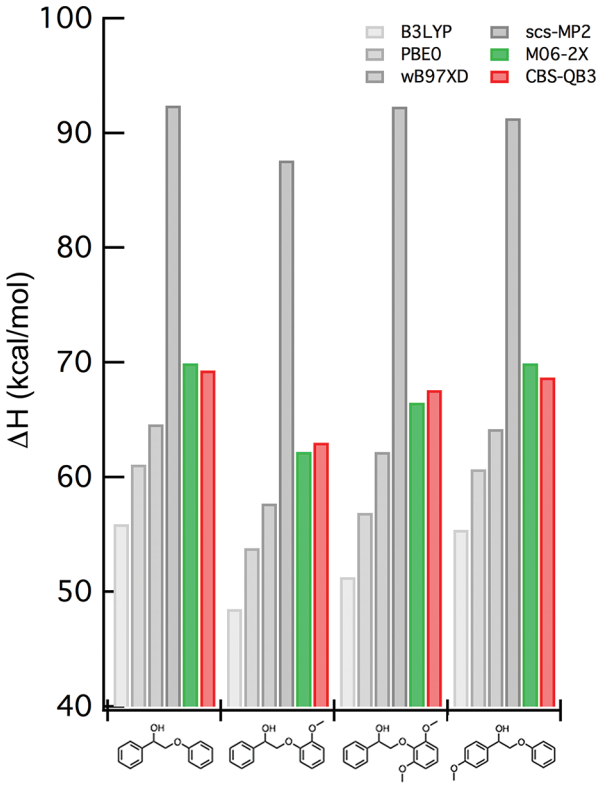

Figure 2. BDE calculations for several functionals used in this study on four model dimers of the β-O-4 linkage benchmarked against the CBS-QB3 method.

Table 1. BDE Results for the α-O-4 and β-O-4 Linkages with the M06-2X Functional and 6-311++G(d,p) Basis Set[a]

								ΔH, kcal·mol^{-1}	
	Compound	R_1	R_6	R_3	R_4	R_5	R_6	C_α–O	C_β–O
	1	H	H	H	H	H	H	58.6	70.9
	2	H	H	H	H	OMe	H	60.4	68.5
	3	H	H	H	H	OMe	OMe	63.4	69.4
	4	H	H	H	OMe	H	H	53.9	68.4
	5	H	H	OMe	H	OMe	H	55.0	65.2
	6	H	H	OMe	H	OMe	OMe	56.0	64.0
	7	H	H	OMe	OMe	H	H	53.1	68.4
α-O-4	**8**	H	H	OMe	OMe	OMe	H	52.1	63.3
	9	H	H	OMe	OMe	OMe	OMe	55.3	64.3
C_α-O: 56.0, 14.1	**10**	OMe	H	H	H	H	H	58.8	71.6
	11	OMe	H	H	H	OMe	H	61.4	70.6
C_β-O: 68.4, 12.1	**12**	OMe	H	H	H	OMe	OMe	63.6	70.4
	13	OMe	H	H	OMe	H	H	54.5	71.6
	14	OMe	H	OMe	H	OMe	H	54.7	68.2
	15	OMe	H	OMe	H	OMe	OMe	55.3	66.3
	16	OMe	H	OMe	OMe	H	H	54.2	69.2
	17	OMe	H	OMe	OMe	OMe	H	52.5	63.8
	18	OMe	H	OMe	OMe	OMe	OMe	54.7	63.6
	19	OMe	OMe	H	H	H	H	66.2	71.0
	20	OMe	OMe	H	H	OMe	H	64.0	71.2
	21	OMe	OMe	H	H	OMe	OMe	64.6	70.0
	22	OMe	OMe	H	OMe	H	H	64.4	72.1
	23	OMe	OMe	OMe	H	OMe	H	56.1	66.2
	24	OMe	OMe	OMe	H	OMe	OMe	58.6	66.8
	25	OMe	OMe	OMe	OMe	H	H	59.6	65.7
	26	OMe	OMe	OMe	OMe	OMe	H	52.9	61.4
	27	OMe	OMe	OMe	OMe	OMe	OMe	53.3	60.0
	Compound	X	Y	R_1	R_2	R_3	R_4	C_β–O	
	28	OH	OH	H	H	H	H	69.5	
native β-O-4	**29**	OH	OH	OMe	H	OMe	H	69.2	
	30	OH	OH	OMe	H	OMe	OMe	68.2	
69.5, 3.6	**31**	OH	OH	OMe	OMe	OMe	H	71.8	
	32	OH	OH	OMe	OMe	OMe	OMe	70.5	
	Compound	X	Y	R_1	R_2	R_3	R_4	C_β–O	
	33	=O	OH	H	H	H	H	60.6	
	34	=O	OH	OMe	H	OMe	H	55.9	
	35	=O	OH	OMe	H	OMe	OMe	56.0	
oxidized β-O-4	**36**	=O	OH	OMe	OMe	OMe	H	57.1	
	37	=O	OH	OMe	OMe	OMe	OMe	56.1	
56.1, 11.4	**38**	OH	=O	H	H	H	H	59.1	
	39	OH	=O	OMe	H	OMe	H	56.7	
	40	OH	=O	OMe	H	OMe	OMe	58.0	
	41	OH	=O	OMe	OMe	OMe	H	59.5	
	42	OH	=O	OMe	OMe	OMe	OMe	59.0	
	43	=O	=O	H	H	H	H	55.6	
	44	=O	=O	OMe	H	OMe	H	51.8	
	45	=O	=O	OMe	H	OMe	OMe	50.7	
	46	=O	=O	OMe	OMe	OMe	H	51.4	
	47	=O	=O	OMe	OMe	OMe	OMe	49.2	

[a] The left column lists the median value and range for each bond type.

Figure 3. We report the median value and the range in the left column with the bond type. Several additional BDE calculations with other functionals are described in the Supporting Information, which support the results in Tables 1 and 2.

In this study, we have only considered the bonds in the aliphatic linkages of native and treated lignin that are likely to be significantly influenced by the substituents on the aromatic rings. Thus, we examined β-O-4, α-O-4, β-5, and biphenyl bond dissociations that result in the formation of phenoxy and phenyl radicals. Breaking the $\alpha-\beta$ bonds in the β-O-4 and α-O-4 linkages requires approximately 76 kcal/mol[14,31] and is not affected by relevant substituents.[31] Scission of the $\alpha-\beta$ bond in the β-5 compounds will be approximately the same as the BDE of diphenylethane, which was determined experimentally to be 65.3 ± 0.7 kcal/mol.[32,33] Relevant substitution will also have little effect on this energy. Because of resonance stabilization of the phenoxy radicals, the C−O bonds shown in Table 1 are significantly weaker than the C−C bonds, which form phenyl radicals when broken.

There are several sets of results to compare in Tables 1 and 2. First, the median BDE values for both sets of C−C bonds in the biphenyl linkages and the β-5 bonds are significantly higher than the BDEs for the C−O bonds. These data align with qualitative evidence from thermal degradation routes for lignin model compounds and biomass-derived lignin wherein nonresonance stabilized C−C bonds are more recalcitrant to cleavage.[1,34] The data in Table 2 show that the C−C bonds in the β-5 linkages (**48**−**59**) also do not display a significant dependence on substituent chemistry for the range examined in this study. However, the biphenyl linkages (**60**−**65**) exhibit an approximately 6 kcal/mol difference depending

Table 2. BDE Results for the β-5 and Biphenyl Linkages with the M06-2X Functional and 6-311++G(d,p) Basis Set[a]

	compound	R_1	R_2	R_3	R_4	ΔH, kcal·mol^{-1} C−C$_\alpha$	C$_\beta$−C
β-5	**48**	OMe	OMe	OMe	OH	102.4	105.1
102.6, 2.0	**49**	OMe	OMe	H	OH	102.8	105.3
105.2, 3.8	**50**	OMe	H	OMe	OH	102.9	105.1
	51	OMe	H	H	OH	102.0	104.0
	52	H	H	OMe	OH	102.4	104.7
	53	H	H	H	OH	103.4	105.5
	54	OMe	OMe	OMe	OMe	101.4	106.4
	55	OMe	OMe	H	OMe	102.9	107.7
	56	OMe	H	OMe	OMe	102.2	105.2
	57	OMe	H	H	OMe	103.2	106.0
	58	H	H	OMe	OMe	102.3	103.9
	59	H	H	H	OMe	103.3	104.7

	Compound	R_1	R_2	C−C
biphenyl	**60**	H	OH	118.1
114.95, 6.3	**61**	CH_3	OH	116.9
	62	CH_2OH	OH	118.5
	63	H	OMe	112.2
	64	CH_3	OMe	113.0
	65	CH_2OH	OMe	112.6

[a] The left column lists the median value and range for each bond type. All BDEs are shown in kcal/mol.

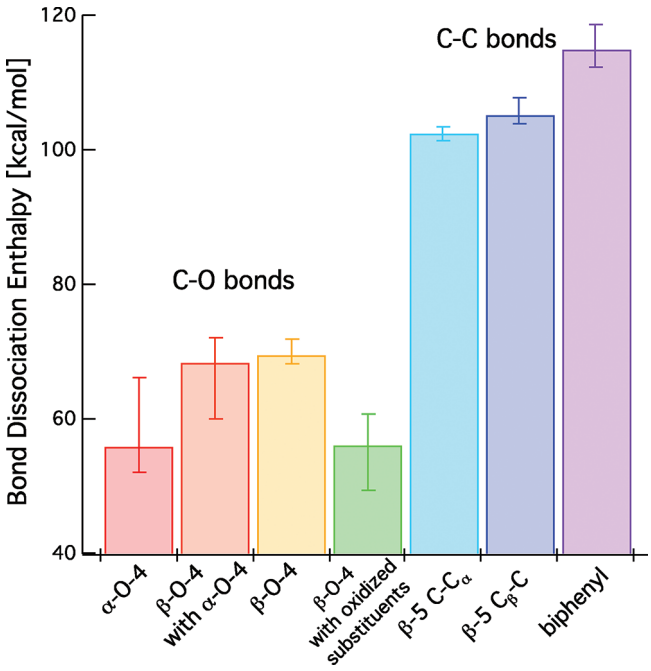

Figure 3. BDEs for the classes of lignin bonds studied here. We report the median and range for each set of compounds listed in Tables 1 and 2. The ranges illustrate the dependencies of substituent chemistry on the BDEs examined in this study.

on whether the R_2 group is hydroxyl or methoxy. To explain the observed differences in BDEs as a function of substituent chemistry, we examined the radical effect by computing radical stabilization energies (RSEs). For our model compounds, RSEs are given by the

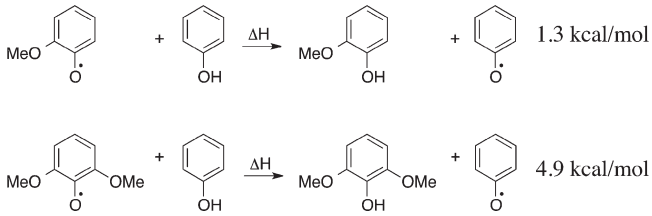

Figure 4. Representative RSE calculation for phenolic radicals. RSEs for the products of the homolytic bond dissociation for compounds **1**−**65** can be found in the Supporting Information.

difference between the O−H BDE in phenol and the O−H BDE in mono- and dimethoxy substituted phenol. This difference is equivalent to the enthalpy change of the isodesmic reactions shown in Figure 4. A positive RSE indicates that the substituted phenolic radicals are stabilized relative to the unsubsituted phenolic radical. The RSE for the biphenyl linkages indicate that the methoxy groups stabilize the radicals by approximately 2.8−3.3 kcal/mol, in reasonable agreement with the BDE differences between compounds **60**−**62** and **63**−**65**.

For the C−O bonds examined here, there are substantial differences in BDEs as a function of substituents on both the aromatic rings and the alkyl chains. For compounds **28**−**32**, which represent β-O-4-linked dimers from native lignin without the α-O-4 linked substituent, the BDEs are approximately 70 kcal/mol. Additionally, the β-O-4 linkages in compounds **28**−**32** display only a minimal effect of substituent chemistry. However, upon oxidation of either the primary or secondary alcohols (the Y or X substituent, respectively, in compounds **33**−**47**) as proposed previously,[6] the average BDEs are reduced. The BDEs for the ketone forms (**33**−**37**) are on average roughly 3 kcal/mol

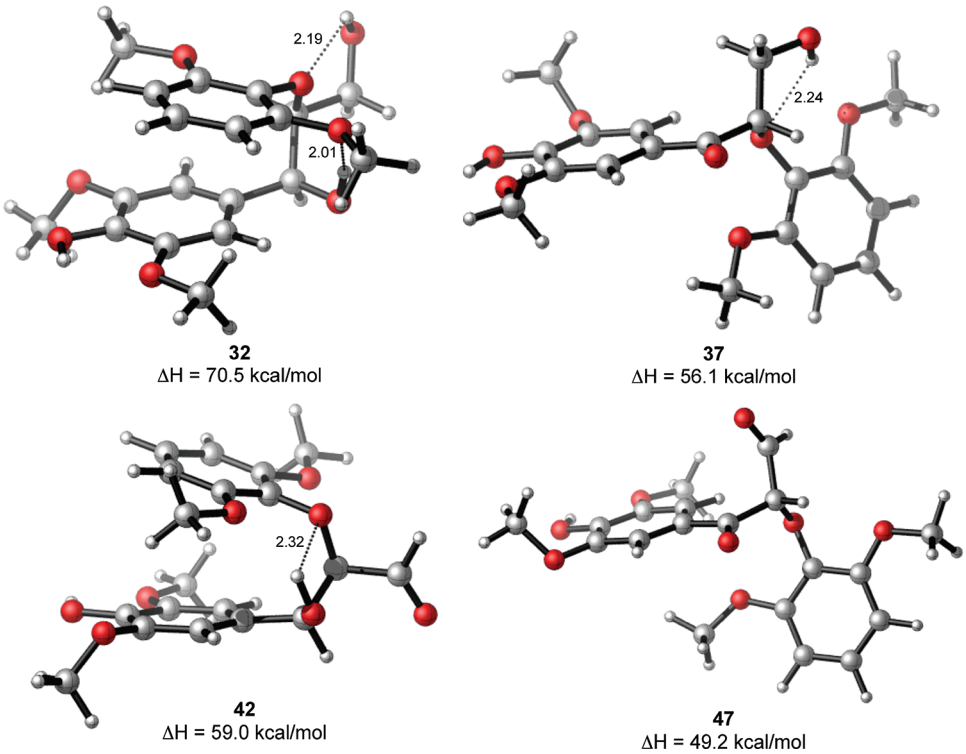

Figure 5. Comparison of native β-O-4 (**32**) and oxidized β-O-4 (**37**, **42**, and **47**) geometries for C−O bond cleavage in the β position. All R groups are OMe. Bond lengths are given in Å.

lower than the aldehyde forms (**38**−**42**), which is partially due to delocalization of the radical into the carbonyl and the aromatic ring for the ketone and only into the carbonyl for the aldehyde. To further explain the BDE differences upon oxidation, Figure 5 illustrates the optimized geometries of the subset of native and oxidized models, **32**, **37**, **42**, and **47**, wherein all of the substituents on the rings are methoxy groups. In compound **32**, both hydroxyl groups are able to form stabilizing hydrogen bonds, whereas in **37** and **42**, the loss of a single hydroxyl group results in only a single hydrogen bond formed. The stability of **42** is further enhanced by a $\pi-\pi$ interaction relative to **37**. In **47**, oxidation of both hydroxyl groups removes the potential for hydrogen bonding completely, and is accompanied by a further reduction in the BDE. This suggests that catalytic dehydrogenation as proposed by Nichols et al.[6] can potentially reduce the bond energy for C−O bond cleavage by oxidizing alcohol groups on either or both the γ or α positions, and that methoxy substituents will potentially reduce the BDE further through radical stabilization, as shown in Figure 4.

For the β-O-4 linkages in the presence of an α-O-4 linked substituent (compounds **1**−**27**), the median BDE is again approximately 70 kcal/mol, but the large additional aromatic group amplifies the substituent effect such that the BDE range is much greater. The R_3 and R_4 methoxy groups on the phenoxy radical offer the most overall stabilization, as shown in Figure 4, with a small additional stabilization observed for the R_1 and R_2 groups as methoxy. For the α-O-4 linkages, the median BDE is approximately 60 kcal/mol with a range of 14 kcal/mol. The compounds with two methoxy groups on the R_5 and R_6 groups exhibit the highest BDE for the α-O-4 linkages in compounds **1**−**15**. Here the stabilization of the radical as shown in Figure 4 is offset via stabilization of the dimer through hydrogen bond formation between the primary alcohol on the γ-carbon and one of the methoxy groups (R_5 or R_6) that is not present when only one substituent, either R_5 or R_6, is a methoxy group. These differences are shown with molecular structures in the Supporting Information. We ensured that this result was not an artifact of the conformational search by recalculating the BDE with the R_6 methoxy converted to hydrogen. Additionally, the R_3 and R_4 groups, as before, affect the stabilization of the resulting radicals via delocalization such that the BDEs are reduced by several kcal/mol in each case, as shown in the Supporting Information. Overall, this shows that the substituent effect on the alkyl chains and aromatic moieties can have significant and opposite effects on the C−O BDE when both delocalization effects and stabilizing hydrogen bonds are accounted for. These results highlight the paramount importance of exhaustive conformational searches required for comparing BDEs in lignin model compounds, especially when the γ-methylhydroxy group is present, which is quite prevalent in native lignin and is thus an important consideration in the use of lignin model compounds.[1]

In summary, we computed BDEs for 69 model lignin dimers in over 100 bonds in native and oxidized lignin model dimers. Our approach was based on a full conformational search for each model compound using semiempirical methods followed by reoptimization of the lowest energy conformers with DFT, and BDE calculations with density functionals validated against benchmark tests extrapolated to the complete basis set limit. Our results quantitatively predict the relative BDEs for carbon−carbon and carbon−oxygen bonds in a substantially expanded range of native lignins over previous efforts and a more realistic set of chemical substituents on both the aromatic and alkyl groups. Additionally, we predict that oxidation of primary and secondary alcohol groups on alkyl chains of ligin will further lower the BDEs for enhanced catalytic conversion rates. This work overall highlights the power of theoretical

approaches to understand lignin deconstruction via thermal or catalytic routes at the molecular level.

■ ASSOCIATED CONTENT

Supporting Information. Complete description of the computational methods employed in this study; full reference 19; BDE results for other density functionals for the α-O-4 and β-O-4 linkages; optimized Cartesian coordinates for all model compounds in Tables 1 and 2 and the four model compounds in the benchmark test; and radical stabilization tests for the full model compound set. This material is available free of charge via the Internet http://pubs.acs.org.

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