Solution-Sensitivity and Comprehensive Mechanism of Lignin Breakdown during the Phosphoric Acid-Acetone Pretreatment Process

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This work focused on the solution-sensitivity and the comprehensive mechanism of lignin breakdown during the phosphoric acid-acetone pretreatment process using density functional theory calculations. The structures and properties of α-O-4 lignin, β-5-3 lignin, and β-β lignin were detected, which showed that the bond length follows the order: α-O-4 bond < β-5-3 bond < β-β bond, but α-O-4 lignin is more sensitive to solvent molecule thanβ-β lignin and β-5-3 lignin. The decomposition mechanism of α-O-4 lignin, β-5-3 lignin, and β-β lignin in different solutions showed that α-O-4 lignin decomposes much more easily than β-5-3 lignin and β-β lignin, acting as the most accessible and susceptible point of lignin. Further, the selectivity of decomposition of lignin depends markedly on the synergy of solution and position. The physical origin of the structure-selectivity of lignin in different solution can be rationalized in terms of both thermodynamics and kinetics. The reactions investigated in this work constitute a large database for understanding the chemistry of α-O-4 lignin, β-5-3 lignin, and β-β lignin, and their decomposition in different solutions.

Keywords: Lignin; Lignocellulose; Biomass; Pretreatment; DFT

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INTRODUCTION

Biofuel has received increasing attention due to the instability of petroleum prices and the development of government policies in many countries. To enhance biofuel production from biomass, two biological approaches to lignin biosynthetic pathway modification are employed, *i.e.* metabolic perturbation and the fundamental redesign of lignin (Guerriero *et al.* 2013). In addition, the pretreatments are used to reduce cell wall recalcitrance and promote sugar release during enzymatic hydrolysis. The extent and severity of biomass recalcitrance have been mainly attributed to lignin composition and amount. In particular, the S/G ratio affects cell wall deconstruction during pretreatment (Koo *et al.* 2012). Increasing the S/G ratio from 0.56 to 1.06 after phosphoric acid fractionation promotes the enzymatic hydrolysis efficiency (Kang *et al.* 2011). Varanasi concluded that with higher pretreatment times using 1-ethyl-3-methylimidazolium acetate ([C_2mim] [OAc]). (6–12 h), it is easier to remove G-lignin at 120 ^{o}C and to remove S-lignin at 160 ^{o}C (Varanasi *et al.* 2012). The formation of new carbon–carbon bonds during acid-pretreatment leads to the disappearance of the G6 correlation and the obvious shift of G2 correlation due to the steric hindrance of the methoxyl group in the S units (Wang *et al.* 2012). Based on the solubility of cellulose, hemicellulose, and lignin in solvent-phosphoric acid and organic solvent-acetone, concentrated phosphoric acid fractionation is an effective pretreating method leading to the enhancement of enzymatic digestibility (Zhang *et al.* 2006; Zhang *et al.* 2007).

The relative-abundance ranges of the common linkages in monolignol are β–O–4 (45 to 50%), 5–5 (18 to 25%), β–5 (9 to 12%), α-linkages (6 to 8%), and β–β (3%) (Watts *et al.* 2011). Molecular simulation can provide atomistic detail and accurate energies of reactions and processes involving lignin, providing fundamental insight in biomass conversion. (Sangha *et al.* 2012). The density functional theory (DFT) was utilized to evaluate a potential reaction mechanism leading to the formation of coniferyl alcohol α-linkages in lignin (Watts *et al.* 2011).

A formal kinetic model treating the depolymerization and hydrodeoxygenation of wheat straw lignin in ethanol with formic acid as hydrogen source was developed and has been validated in a continuous stirred tank reactor (CSTR) at varying temperatures between 633 K and 673 K (Forchheim *et al.* 2012; Gasson *et al.* 2012). The dispersion-corrected DFT was used to model the interactions of imidazolium chloride ionic liquid anions and cations with cellulose and the lignin polyphenol models, respectively. The results suggested that extended π-systems of benzimidazolium ionic liquids lead to stronger interactions between lignin and the anions and cations of the ionic liquid (Janesko 2011). The C_α–O (C_α–C_β) bond dissociation enthalpies of 40 to 44 (57 to 62) kcal/mol were obtained with DFT calculations (Younker *et al.* 2012). A diverse set of lignin linkages encompassing 65 lignin model compounds were obtained using the DFT approach (Parthasarathi *et al.* 2011). The valence band analysis of cellulose and lignin by DFT provides a powerful basis for a detailed interpretation of spectroscopic data (Haensel *et al.* 2012). However, the detailed physiochemical properties of lignin in phosphoric acid, acetone and water are still unknown. The lignin solubility properties in these different solutions have not been systematically explained yet. These unsolved problems hindered the development and optimization of lignocellulose pretreatment, preventing the selective and efficient conversion of lignin for advantage applications.

Herein, α-O-4 lignin, β-5-3 lignin, and β-β Lignin were chosen as research models to do DFT calculations to investigate the properties of lignin in different solutions (water solution, acetone solution, and 85% w/w phosphoric acid solution) in relation to the phosphoric acid-acetone pretreatment process. In additions, we also detected the decomposition mechanism of these lignins, and the position effect and the different linkage effect on the decomposition of these lignins, in different solutions. This work aimed to reveal a fundamental database for understanding the chemistry of different lignin and the decomposition of such lignins in different solutions. Results will benefit the optimization of lignocellulose phosphoric acid-acetone pretreatment process for suitable applications.

COMPUTATIONAL METHODS

Lignin is formed through nonselective condensation of three phenolic alcohol units (monolignols) (Dorrestijn *et al.* 2000): p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The most dominant linkage in lignin is arylglycerol-β-aryl ether (β-O-4), which is by far the most common linkage and much research has been dedicated to it. Our preliminary work was set to detect the property and breakdown of β-O-4 in different solutions. We herein focus on the other three important linkages in softwood lignin (Karhunen *et al.* 1995): *α*-O-4 lignin, *β*-5-3 lignin, and *β*-*β* lignin. The optimized structure of *α*-O-4 lignin, *β*-5-3 lignin, and *β*-*β* lignin contains two alcohols-coniferyl monomers (Haensel *et al.* 2012), in which the two alcohols (coniferyl monomers) are bonded to each other with the related *α*-O-4 linkage, *β*-5-3 linkage, and *β*-*β* linkage, respectively. Although the stoichiometry of native lignin is not well reflected, we have chosen this constitution in order to keep the system sufficiently small for computational reasons and to have the typical linkage included as that of the simplest model compound for *β*-O-4 linkage for theoretical investigations (Gilbert and Gajewski 1982; Klein and Virk 1983). Then a large molecular structure model containing six alcohols-coniferyl monomers with the five related linkages was built to detect the position effect on the decomposition of *α*-O-4 lignin, *β*-5-3 lignin, and *β*-*β* lignin. Moreover, two optimized structures with two different linkages were built to investigate linkage effects on the decomposition of lignin in different solutions. One contains *α*-O-4 linkage and *β*-5-3 linkage next to each other among three alcohols-coniferyl monomers, and the other contains *β*-5-3 linkage and *β*-*β* linkage next to each other among three alcohols-coniferyl monomers. The lignin models were optimized in different solutions by using a solvation model with the appropriate dielectric constant, ε. Specific interactions between lignin and the solvent molecules were not considered in this study, since the solvent is represented by a polarizable continuum with a particular dielectric constant. The absolute errors in bond lengths with respect to the equilibrium geometrical para-meters were less than 0.1 Å. Values of the solvent dielectric constants ranging from $\varepsilon = 1$ (gas phase) to $\varepsilon = 80.1$ (water) were used, including $\varepsilon = 20$ (acetone) and $\varepsilon = 12.7$ (85% w/w phosphoric acid solution), in reference to the work of Wang and Anderko (2001) and Munson (1964). Then the molar volume for each lignin was computed in solution by making the solvent reaction field self-consistent with the solute electrostatic potential. During geometric optimization, all atoms in these models were allowed to relax freely.

The local-density approximation (LDA) is more accurate than the generalized gradient approximation (GGA) in describing a system with *π*-*π* interactions and other van der Waals systems (Vosko *et al.* 1980; Janotti *et al.* 2001; Qin *et al.* 2010). Thus, all calculations were performed using DFT calculations with LDA for a previously generated exchange-correlation functional and a double-numeric quality basis set with polarization functions (DNP). Brillouin zone integration was performed at the gamma point. Calculations used an energy convergence tolerance at 1×10^{-6} Ha and gradient convergence at 1×10^{-6} Ha Å^{-1}. A new formulation for the linear (LST) and quadratic synchronous transit (QST) methods was used to search the transition states and to investigate lignin fragment decomposition (Govind *et al.* 2003).

RESULTS AND DISCUSSION

Properties of *α*-O-4 Lignin, *β*-5-3 Lignin and *β*-*β* Lignin in Different Solutions

Firstly, the geometric and electronic structures of *α*-O-4 lignin, *β*-5-3 lignin, and *β*-*β* lignin in different solutions are illustrated in Fig. 1. From Fig. 1a, it can be observed that the molar volume for *α*-O-4 lignin in gas phase, aqueous solution, acetone solution, and phosphoric acid solution is 258.482 cm^3/mol, 277.395 cm^3/mol, 274.527 cm^3/mol, and 229.023 cm^3/mol, respectively. The length of the α-O-4 bond in gas phase, aqueous solution, acetone solution, and phosphoric acid solution is 1.469 Å, 1.474 Å, 1.473 Å, and 1.477 Å, respectively, while the bond population is 0.475, 0.459, 0.460, and 0.452, respectively. The bond length has an inverse relationship with the bond population. In comparison with α-O-4 linkage in gas phase, it seems that the interaction between solvent molecule and lignin lengthens the α-O-4 bond length and decreases the bond population on α-O-4. Figure 1a depicts the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) of α-O-4 lignin in different solutions. As can be observed from Fig. 1a, LUMO and HOMO of α-O-4 lignin in gas phase differ greatly from those in solutions. In gas phase, both HOMO and LUMO are mainly attributable to the left part of α-O-4 lignin. However, in the solutions, the left part of α-O-4 lignin contributes to the LUMO and the right part contributes to the HOMO. The energy level of HOMO and LUMO follows the order: gas phase > aqueous solution < acetone solution < phosphoric acid solution. The energy gap (E_{gap}) between HOMO and LUMO for lignin in gas phase, aqueous solution, acetone solution, and phosphoric acid solution is 3.387 eV, 3.262 eV, 3.261 eV, and 3.260 eV, respectively. Results show that these solvent molecules can obviously modify the electronic property of α-O-4 lignin, for which solvent molecules decrease the HOMO, the LUMO, and the E_{gap}, while compared with those of α-O-4 lignin in gas phase. And the interaction between phosphoric acid solution and α-O-4 lignin can greatly change the properties of α-O-4 lignin, especially the molar volume of α-O-4 lignin.

For β-5-3 lignin shown in Fig. 1b, the molar volume in gas phase, aqueous solution, acetone solution, and phosphoric acid solution is 253.074, 265.350, 304.081, and 284.239 cm^3/mol, respectively. The length of β-5-3 bond is 1.565 Å in gas phase compared to 1.546 Å in aqueous solution, acetone solution, and phosphoric acid solution. These results show that the interaction between lignin and solvent molecule lengthens the β-5-3 bond. Also, Fig. 1b illustrates that the bond population on β-5-3 in gas phase is 0.724, whereas the bond population on β-5-3 aqueous solution, acetone solution, and phosphoric acid solution is 0.722. In Fig. 1b, the left part of β-5-3 lignin contributes to the LUMO while the right part contributes to the HOMO. The energy level of HOMO and LUMO follows the order: gas phase < aqueous solution < acetone solution < phosphoric acid solution. The E_{gap} for lignin in gas phase, aqueous solution, acetone solution, and phosphoric acid solution is 3.294 eV, 3.301 eV, 3.300 eV, and 3.300 eV, respectively. Compared with the effect on the structural and electronic properties of α-O-4 lignin by these solvent molecules, the effect on the electronic properties of β-5-3 lignin is smaller, which implies the β-5-3 lignin is more stable in these solutions.

For β-β lignin shown in Fig. 1c, the molar volume in gas phase, aqueous solution, acetone solution, and phosphoric acid solution is 277.341 cm^3/mol, 282.345 cm^3/mol, 258.456 cm^3/mol, and 258.508 cm^3/mol, respectively. The length of β-β bond in aqueous solution, acetone solution, and phosphoric acid solution is the same, namely 1.563 Å, while the bond population in all cases is 0.720. The right part of the β-β lignin fragment contributes to the LUMO while the left part contributes to the HOMO. The HOMO energy of β-β lignin in different solutions follows the order: gas phase > aqueous solution > acetone solution > phosphoric acid solution, while the LUMO energy follows the order: gas phase < aqueous solution < acetone solution < phosphoric acid solution. The solution effect changes the HOMO and LUMO of *β*-*β* lignin in a perverse way. The E_{gap} of *β*-*β* lignin in gas phase, aqueous solution, acetone solution, and phosphoric acid solution is 3.955 eV, 3.933 eV, 3.901 eV, and 3.877 eV, respectively. While comparing the solution effect on the property of *α*-O-4 lignin, *β*-5-3 lignin, and *β*-*β* lignin with each other, it was found that *α*-O-4 lignin is more sensitive to solvent molecule than *β*-*β* lignin and *β*-*β* lignin is more sensitive to solvent molecule than *β*-5-3 lignin.

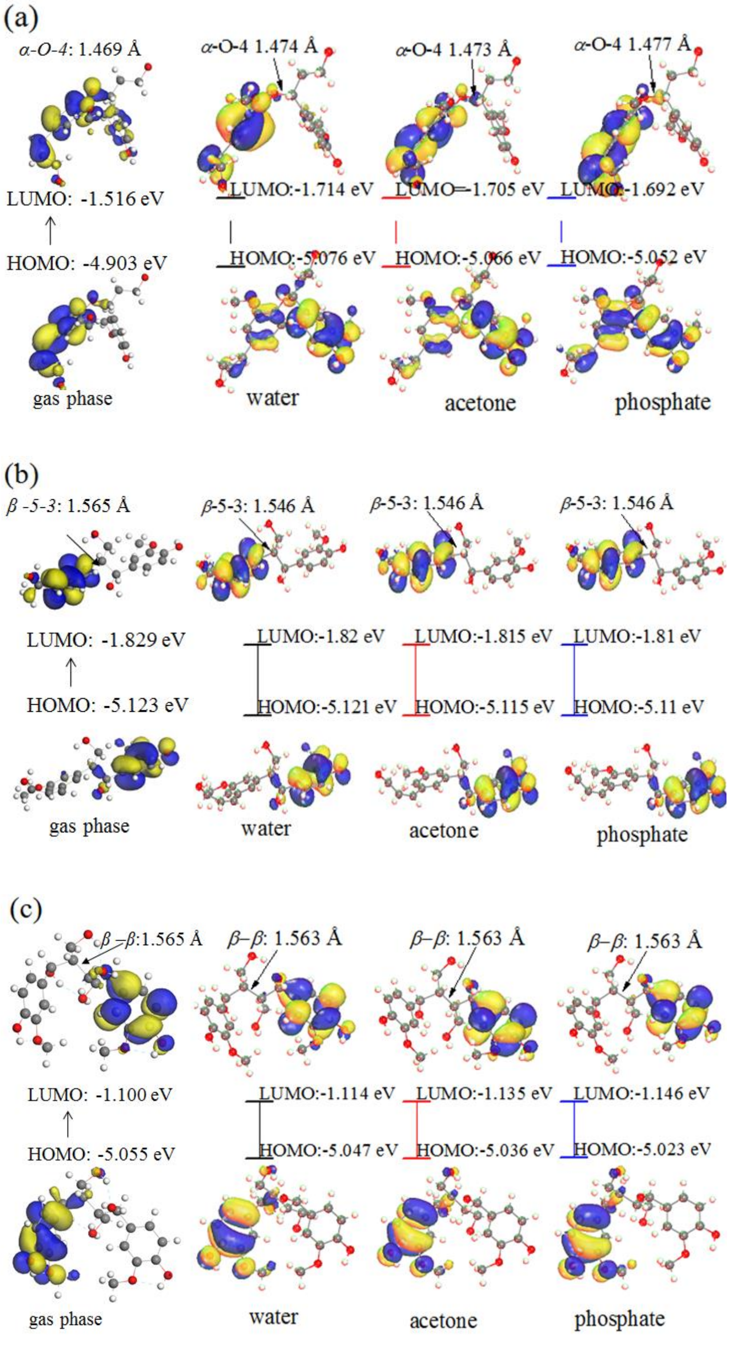

Fig. 1. Stable configurations and the related HOMO and LUMO for *α*-o-4 lignin, *β*-5-3 lignin, and *β*-*β* lignin in different solutions

Decomposition of α-O-4 Lignin, β-5-3 Lignin, and β-β Lignin in Different Solutions

Following the property analysis of α-O-4 lignin, β-5-3 lignin, and β-β lignin in different solutions, the decomposition of these lignin in different solutions was investigated. Figure 2a shows the calculated potential energy profiles for the decomposition of α-O-4 bonds in aqueous solution, acetone solution, and phosphoric acid solution. The reaction initiates from the optimized geometries of α-O-4 lignin. The barrier (E_a) for the α-O-4 lignin decomposition in aqueous solution, acetone solution, and phosphoric acid solution is 1.481 eV, 1.333 eV, and 1.279 eV, respectively, and the related reaction energy (E_r) in those solutions is 1.096 eV, 1.151 eV, and 1.194 eV, respectively. The α-O-4 lignin decomposition in aqueous solution is the most energetically close, while the decomposition in phosphoric acid solution is the easiest, which is inconsistent with the electronic structure (bond length and bond population) of lignin in different solutions. A qualitatively similar one-step reaction mechanism was obtained for α-O-4 decomposing in different solutions. Supposing the reaction rate (r) for lignin decomposition is $r = k\ [C_{\text{lignin}}]^n$ (k is the reaction rate constant, $[C_{\text{lignin}}]$ is the concentration of lignin), and $k = A\exp(-E_a/RT)$, r for the decomposition of α-O-4 lignin in phosphoric acid solution is about 7.893 times as large as that in aqueous solution and 1.992 times as large as that in acetone solution at room temperature (298 K).

Figure 2b shows the same energy profiles as Fig. 2a but for the decomposition of the β-5-3 bond. The one-step reactions initiates from the optimized β-5-3 lignin in aqueous solution, acetone solution, and phosphoric acid solution, respectively. Both the E_a and the E_r for β-5-3 decomposition in aqueous solution, acetone solution, and phosphoric acid solution are 4.999 eV and 4.856 eV, 5.006 eV and 4.874 eV, and 5.014 eV and 4.882 eV, respectively. The E_a follows the increasing order: aqueous solution < acetone solution < phosphoric acid solution, while the E_{gap} follows a decreasing order, which is opposite to the phenomenon found during α-O-4 lignin decomposition process. The value of r for the decomposition of β-5-3 lignin in aqueous solution is about 0.270 times larger than that in acetone solution and 0.585 times larger than that in phosphoric acid solution under room temperature.

Figure 2c shows the same energy profiles as Fig. 2a and b for the decomposition of β-β lignin. The E_a and the E_r for β-β lignin decomposition in these three solutions are 4.277 eV and 3.768 eV, 4.257 eV and 3.770 eV, and 4.195 eV and 3.804 eV, respectively. While the E_a decreases in these solutions, the E_r increases. The value of r for the decomposition of β-β lignin in phosphoric acid solution is about 3.194 times as large as that in aqueous solution and 2.384 times as large as that in acetone solution under room temperature.

Electronic analysis shows that during the decomposition reactions (in Fig. 2a, b, and c), one alcohols-coniferyl monomer in the model α-O-4 lignin, β-5-3 lignin, and β-β lignin contributes to hole transfer at the valence band (related to HOMO), and the other alcohols-coniferyl monomer contributes to the electron transfer at the conduction band (related to LUMO) at initial state and final state. However, both electron and hole transfer occur at the atoms related to the lengthen α-O-4 linkage, β-5-3 linkage, and β-β linkage at the transition state. The active electronic state favors the breakdown of these linkages.

The decomposition of α-O-4 linkage is more accessible than that of β-5-3 linkage and β-β linkage, corresponding to the previous report that the decomposition of α-O-4 linkage needs far lower barrier energy than the decomposition of C–C linkages (*β*-5-3 linkage and *β*-*β* linkage) (Cho and Parthasarathi 2010; Kim *et al.* 2011). Therefore, it is suggested that *α*-O-4 linkage can act as the vulnerable point of lignin. The *r* value for *α*-O-4 lignin decomposition in aqueous solution, acetone solution, and phosphoric acid solution is about 137, 143, and 145 times as large as those for *β*-5-3 lignin decomposition, and is about 108, 114, and 113 times as large as those for *β*-*β* lignin decomposition under room temperature, respectively. The *α*-O-4 bond in lignin breaks more easily than the glucosidic bond in cellulose, while the *β*-5-3 bond and *β*-*β* bond are more stable than the glucosidic bond in aqueous solution, acetone solution, and phosphoric acid solution (Kang *et al.* 2012). According to the value of *r*, solutions have greater effect on *α*-O-4 and *β*-*β* decompositions than on *β*-5-3 decomposition. These results of DFT calculations on lignin model will be accurate enough to predict the bond dissociation energies and reactivity trend, as mentioned previously (Cho 2010).

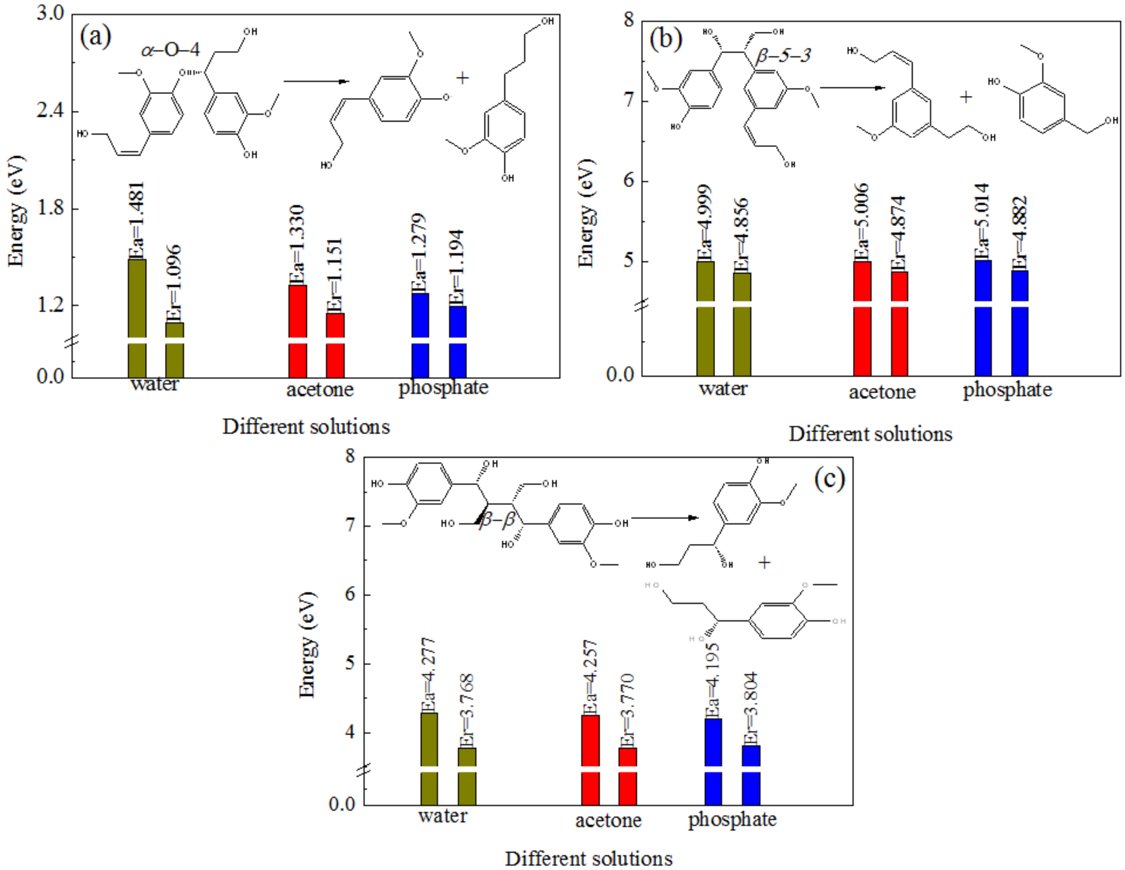

Fig. 2. Calculated potential energy profiles given in eV for the decompositions of (a) *α*-O-4 linkage, (b) *β*-5-3 linkage, and (c) *β*-*β* linkage in water, acetone, and phosphoric acid solution. The symbols E_a and E_r denote the barrier energy and reaction energy, respectively.

Decomposition of *α*-O-4 Lignin, *β*-5-3 Lignin and *β*-*β* Lignin at Different Position in Different Solutions

Two lignin fragments with five *α*-O-4 linkages and five *β*-5-3 linkages were modeled respectively. The break of *α*-O-4(1 or 1′), *α*-O-4(2 or 2′), and *α*-O-4(3), as well as the break of *β*-5-3(1 or 1′), *β*-5-3(2 or 2′), and *β*-5-3(3) were considered. Figure 3 presents the calculated potential energy profiles given in eV for the decomposition of *α*-O-4 (1 or 1′) (the head *α*-O-4 linkage), *α*-O-4(2 or 2′) and *α*-O-4(3) (the center *α*-O-4 linkage), and the decomposition of *β*-5-3(1 or 1′) (the head *β*-5-3 linkage), *β*-5-3(2 or 2′), and *β*-5-3(3) (the center *β*-5-3 linkage) in different solutions. According to E_a and E_r for the decomposition of *α*-O-4(1 or 1′), *α*-O-4(2 or 2′), and *α*-O-4(3), it can be observed that the decomposition of the center *α*-O-4 linkage (*α*-O-4(3)) is more accessible than the decomposition of *α*-O-4(1 or 1′) and *α*-O-4(2 or 2′) in the solutions and especially in the acetone solution. This result implies that *α*-O-4 lignin usually breaks from the center *α*-O-4 linkage. The result will favor the dissolution of lignin into shorter fragments during phosphoric acid treatment process, and the easier decomposition of *α*-O-4 lignin in acetone solution ensures that the temperature is low enough to avoid further breakdown of lignin fragments during acetone treatment.

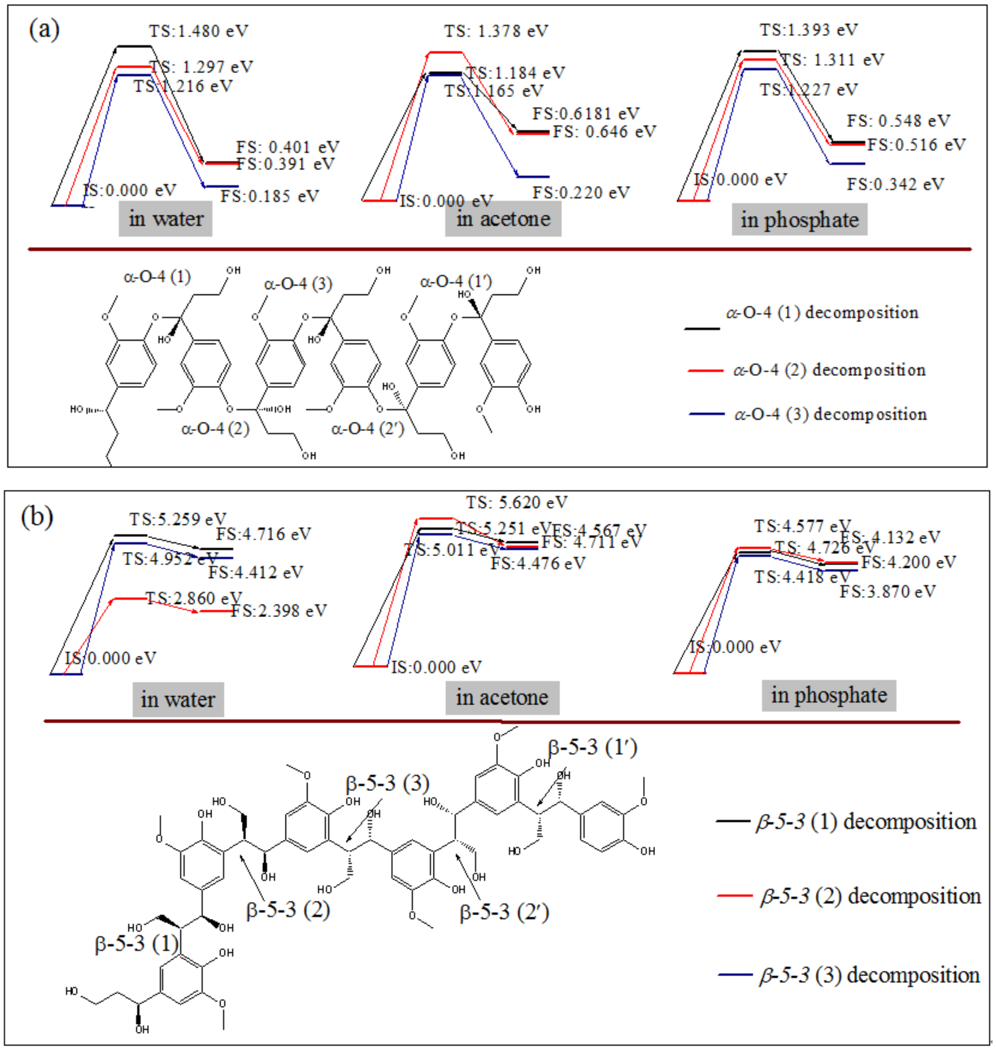

Fig. 3. Calculated potential energy profiles given in eV for (a) the decomposition of *α*-O-4 lignin (including *α*-O-4(1), *α*-O-4(2), and *α*-O-4(3)), and (b) the decomposition of *β*-5-3 (including *β*-5-3(1), *β*-5-3(2), and *β*-5-3(3)) in water, acetone, and phosphoric acid solution. The IS, TS, and FS denote the initial state, transition state, and final state, respectively.

Figure 3b shows that all E_a values for the decomposition of β-5-3(1 or 1′), β-5-3(2 or 2′), and β-5-3(3) in acetone solution and phosphoric acid solution are much larger than those for the decomposition of α-O-4(1 or 1′),α-O-4(2 or 2′), and α-O-4(3), suggesting that β-5-3 lignin is more stable than α-O-4 lignin. However, the position effect together with certain solution effects greatly threatens the stability of β-5-3 lignin, as shown by the fact that the E_a for the decomposition of β-5-3(2) in water is only 2.860 eV, far lower than those for the other cases. On the whole, the independent effect of position on the decomposition of β-5-3 lignin and α-O-4 lignin is relatively small in the same solution system, and the independent effect of solution for the same β-5-3 linkage and α-O-4 linkage decomposition is also small. As far as pretreatment of lignin in solution is concerned, the combination of position effect and solution effect would be an important factor for the dissolution and sedimentation processes.

Different Linkage Effect on the Decomposition of Lignin in Different Solutions

Lignin has been described as a random, three-dimensional network polymer comprised of variously linked phenylpropane units. Different linkages at realistic conditions may be another important factor affecting the pretreatment of lignin. To discuss different linkage effect on the decomposition of lignin in different solutions, we randomly bonded α-O-4 and β-5-3 in one lignin system and bonded β-5-3 and β-β in another lignin system, which is illustrated in Fig. 4.

In the presence of β-5-3, the decomposition of α-O-4 in water, acetone, and phosphoric acid solution requires the overcoming of an barrier energy of 1.743 eV, 1.818 eV, and 1.792 eV, respectively, and these values are higher than those for a single α-O-4 decomposition investigated in Fig. 2a. Conversely, in the presence of α-O-4, the decomposition of β-5-3 in water, acetone, and phosphoric acid solution needs the barrier energies of 4.921 eV, 4.935 eV, and 4.946 eV, respectively, which are lower than those for a single β-5-3 decomposition investigated in Fig. 2b. The β-5-3 linkage favors the stability of α-O-4, since when α-O-4 and β-5-3 are combined next to each other in one lignin system, the α-O-4 bond-length decreases from 1.474 Å to 1.462 Å in water solution, from 1.473 Å to 1.163 Å in acetone solution, and from 1.477 Å to 1.463 Å in phosphoric acid solution, respectively. However, α-O-4 depresses the stability of β-5-3, though β-5-3 bond-length decreases from 1.546 Å to 1.519 Å in the three solution. Differing from the change of E_a in a perverse way for the β-5-3 & α-O-4 lignin system, both β-β and β-5-3 decrease the E_a for each other's decomposition in the β-5-3 & β-β lignin system. β-5-3 in the β-5-3 & β-β system lengthens from 1.590 Å to 1.563 Å, β-5-3 in the β-5-3 & β-β system lengthens from 1.546 Å to 1.555 Å, in water, acetone, and phosphoric acid solution, respectively.

Such a position effect on linkage breakdown can also be analyzed in the previous discussion about bond strength for the diverse set of lignin linkages (Cho 2010) and bond dissociation enthalpies for lignin (Younker *et al* 2011; Younker *et al* 2012). Taking the β-5-3 & α-O-4 lignin system and the β-5-3 & β-β system into consideration, β-5-3 and β-β are also far more stable than α-O-4.

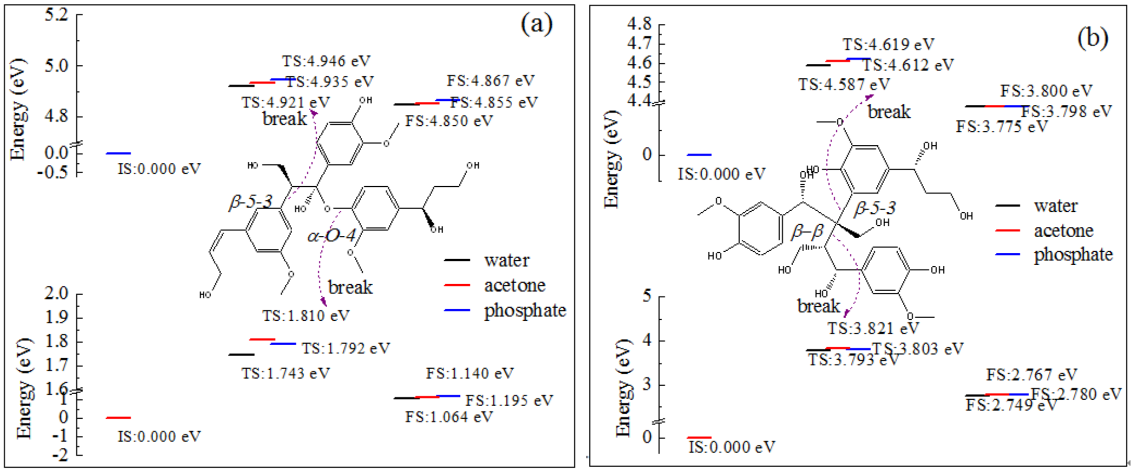

Fig. 4. Calculated potential energy profiles given in eV for the decomposition of lignin linkage under the effect of different linkage in water, acetone, and phosphoric acid solution: (a) decomposition of *α*-O-4 and *β*-5-3; (b) decomposition of *β*-*β* and *β*-5-3. The IS, TS, and FS denote the initial state, transition state, and final state, respectively.

Thermodynamical Factors in Lignin Decomposition

The reactions investigated in this work constitute a large database for understanding the chemistry of different types of lignin and their decomposition in different solutions. For example, the effect of thermodynamics on reaction barriers is able to be examined. The reaction barriers against the reaction energies of the *α*-O-4, *β*-5-3, and *β*-*β* breakage reactions in different solutions are plotted in Fig. 5. Here the reaction energy is defined as the energy difference between the final state and the initial state, which is close to the reaction enthalpy. The barrier *vs.* enthalpy relationship is known traditionally as the Brönsted-Evans-Polanyi (BEP) correlation (Liu and Hu. 2001; Michaelides *et al.* 2003; Bligaard *et al.* 2004). However, for the cleavage of different linkage types of lignin in different solutions, whether the BEP relation holds or not is still unclear.

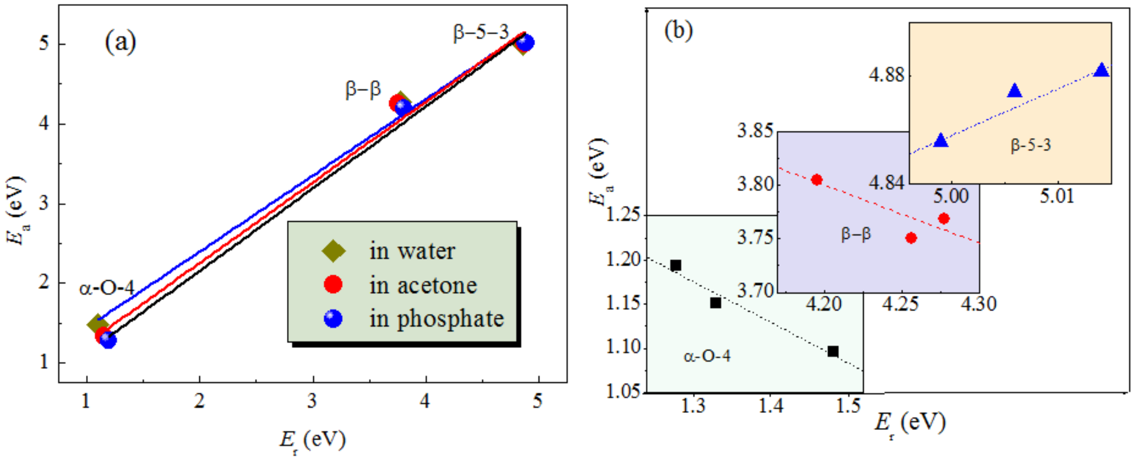

Fig. 5. Plot of E_a against E_r for (a) a different lignin bond (*α*-O-4, *β*-5-3, and *β*-*β*) breaking in the same solution and (b) the same lignin bond breaking in different solutions

As shown in Fig. 5a, a good linear relationship was identified for different linkage (*α*-O-4, *β*-5-3, and *β*-*β*) breakage reactions in the same solution. This striking feature simply reflects the fact that a single BEP relation can be established for these different lignin decomposition paths in the same solution. However, three distinct regions are identified for the same linkage breaking in different solutions, as shown in Fig. 5b, each corresponding to a class of bond-breaking reactions. BEP relation can also be established for α-O-4, β-5-3, and β-β bond breakage. The upper-left region is dominated by the β-5-3 bond breakage, the bottom-right region is mainly about the α-O-4, and the region in-between is for the β-β bond breakage. Inside the upper-left region and the bottom-right region, a positive linear BEP relationship holds for most of the reactions, while the region in-between a negative BEP linear relationship. There is also a minor distinction between reactions in different solutions. As the α-O-4, β-5-3, and β-β bonds are known to possess quite different bond polarities, the figure shows that E_a not only depends on thermodynamics, as represented by the E_r, but also is determined by the intrinsic bond polarity. Under similar thermodynamic conditions, the polar bond α-O-4 breaks first. Except for this, the thermodynamics is often the most important factor that determining the barrier height. The β-5-3 bond breakage is usually a more highly endothermic reaction than the β-β bond breakage. The thermodynamic factor determines that the β-β bond breakage is usually preferred over the β-5-3 bond, although the β-5-3 bond is more polar than the β-β bond. This is what the authors found in lignin decomposition.

CONCLUSION

1. Water, acetone, and phosphoric acid solutions can greatly modify the electronic properties of α-O-4 lignin, for which solvent molecules decrease the HOMO, LUMO, and E_{gap}, compared to those of α-O-4 lignin in the gas phase. The interaction between phosphoric acid solution and α-O-4 lignin can greatly change the properties of α-O-4 lignin, especially the molar volume of α-O-4 lignin. The solution effect changes the HOMO and LUMO of β-β lignin in a perverse way, leading to the decrease of E_{gap} of β-β lignin. However, solvent molecules affect the electronic properties of β-5-3 lignin slightly. The α-O-4 lignin is more sensitive to solvent molecule than β-β lignin while the β-β lignin is more sensitive to solvent molecule than β-5-3 lignin.
2. α-O-4 lignin decomposes much more easily than β-5-3 lignin and β-β lignin. The r value for α-O-4 lignin decomposition in aqueous solution, acetone solution, and phosphoric acid solution is about 137, 143, and 145 times as large as those for β-5-3 lignin, and about 108, 114, and 113 times as large as those for β-β lignin decomposition under room temperature, respectively. Solutions have greater effect on α-O-4 and β-β decomposition than on β-5-3 decomposition.
3. The independent effect of position on the decomposition of β-5-3 lignin and α-O-4 lignin is relatively small in the same solution system, and the independent effect of solution for the same β-5-3 linkage and α-O-4 linkage decomposition is also small. But the position effect together with certain solution effects greatly threatens the stability of β-5-3 lignin.
4. β-5-3 can enhance the stability of α-O-4, while α-O-4 depresses the stability of β-5-3 at the same time. However, β-β and β-5-3 decrease the E_a for each other's decomposition in the β-5-3 and β-β lignin system.

5. A linear BEP relation, a thermodynamic rule, holds clearly for different lignin decomposition reactions in different solutions, which may be used to qualitatively predict the general pattern in lignin dissociation reactions, such as decomposition sites and the reaction precursor.

ACKNOWLEDGEMENTS

The authors thank the financial support for this work provided by National Natural Science Foundation of China (51106051) and National Key Technology R&D Program (2012BAA09B01).

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Article submitted: October 4, 2013; Peer review completed: November 21, 2013; Revised version received and accepted: November 27, 2013; Published: December 4, 2013.