Further Revealing Reaction Mechanism on the Oxidation Behavior of the Lignin Model Molecules

Shuqi Dong
Harbin University of Science and Technology

Hui Zhang (✉ hust_zhanghui11@hotmail.com)
Harbin University of Science and Technology

Xia Du
Harbin University of Science and Technology

Tingyu Yao
Harbin University of Science and Technology

Yan Shang
Harbin University of Science and Technology

Liquan Jing
University of Calgary

Jinguang Hu
University of Calgary

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Abstract

It is urgent to further study the mechanism of the oxidation process of biomass energy. Theoretical investigation on the oxidation of p-hydroxybenzyl alcohol (HOL), vanillyl alcohol (VOL) and syringic alcohol (SOL) at the atomic and molecular levels is completed by density function theory (DFT). The oxidative reaction mechanism is further revealed and the oxidation reaction pathway on phenolic hydroxyl group site was identified in detail. The potential energy surface information of fifteen possible reaction channels at B3LYP/6-311 + G(d,p) level was obtained. The influence of substituent effects on the oxidative reaction energy barrier has been estimated. Theoretical calculation results showed that the reactivity of phenolic hydroxyl group is stronger than methoxyl group and hydroxymethyl group. The oxidative reaction energy barrier decreases with increasing of the methoxyl group number. The elucidation of the oxidation mechanism provides a novel perspective for the study of catalytic oxidation in lignin model materials.

1. Introduction

The depletion of fossil fuels has led to increased attention towards biomass energy. Due to its renewable, clean, low-carbon, rich raw materials and other characteristics, lignin has received significant attention in this regard\(^1\)–\(^3\). Lignin model compounds containing active functional groups such as phenolic hydroxyl group, hydroxymethyl group, and methoxyl group on the benzene ring\(^4\)–\(^6\), which can assist in various chemical reactions and synthesizing high value-added products. \(p\)-Hydroxybenzyl alcohol (HOL) is derived from the dried tuber of Gastrodia elata (orchid plant). HOL has been widely used in medicine (Atenolol) and pesticides\(^7\)–\(^8\). HOL can reduce blood lipids, improving cardiovascular function, prevent/treat atherosclerosis caused by hyperlipidemia\(^9\). Vanillyl alcohol (VOL) is widely used in food processing, pharmaceutical industry (anti-oxidation, anti-inflammatory and inhibition of apoptosis), rubber and plastics\(^10\). Syringic alcohol (SOL) displays evident antibacterial effects on pathogenic bacteria (such as staphylococcus and pneumococcus) and has good therapeutic effect on skin infection\(^11\).

The oxidation of lignin has been extensively studied in the recent decades. Selective oxidation can transform lignin into phenolic aldehydes, ketones, and acids and preserve aromatic rings\(^12\). San and co-workers studied the oxidation kinetic of lignosulfonate, and the analysis results of oxidation products showed that aromatic aldehydes (vanillin and syringic aldehyde) had maximum yields\(^13\). Using the density functional theory (DFT)/B3LYP method, Boussetta and co-workers calculated the electronic affinity, electronic chemical potential, frontier molecular orbital and thermodynamic properties of three types, coniferyl alcohol (G), sinapyl alcohol (S) and paracoumaryl alcohol (H). The results showed that the S type compound was the best electron donor while H compound was the best electron acceptor account of Koop-man’s theorem\(^14\),\(^15\). Dashtd and co-workers calculated the ionization potential, electron affinity and recombinant energy of studied molecules by DFT and time-dependent density functional theory (TD-DFT)\(^16\). Lu and co-workers investigate the effects of the substituents, substituent
positions on the geometric and electronic properties of the studied molecules using DFT method\textsuperscript{[17]}. In terms of electronic property, it was found that the lowest unoccupied orbital energy level of molecules may be related to catalytic activity. The electron absorbing group always reduces the energy of the frontier orbitals, while the electron giving group simultaneously increases their energy.

Although there are many reports on the lignin oxidation process and the product yields, there are nearly no researches on the lignin oxidation mechanism in detail at the molecular and atomic level. Therefore, in this work, the DFT \textsuperscript{[18–21]} method is employed to study the oxidation reaction mechanism of HOL, VOL, SOL, and the influence of substituent effects for the oxidation reaction energy barrier. This study is of great significance for further exploring the process optimization of lignin model compounds.

2. Computational Methods

In this paper, the oxidation reaction mechanism of three lignin model compounds was studied using DFT method. The geometry optimizations and frequency calculations of all the stationary points, including the reactants, products and transition states were performed at the B3LYP/6-311 + G(d,p) level. This level was confirmed to be reasonable and suitable for the current study \textsuperscript{[22–23]}. The minimum energy path (MEP) is obtained based on the intrinsic reaction coordinate (IRC) theory with a gradient step size of 0.05 amu\textsuperscript{1/2}bohr. Then, the first and second energy derivatives are obtained to calculate the curvature of the reaction path and the generalized vibration frequencies along the reaction path. The transition states and products are abbreviated to the corresponding TS and P. All the theoretical calculations in this study were performed using the GAUSSIAN09 package.

3. Results and Discussion

3.1. Stationary point geometries

The oxidation reaction mechanism of vanillyl alcohol molecule has been revealed by our previous work. The three oxidation sites of vanillyl alcohol are H on phenolic hydroxyl group, H on hydroxymethyl group and H on methoxyl group. The transition state structures of three oxidation reaction channels and the scheme of the relevant reaction potential energy surface are provided as electronic supplementary material (ESM). The results show that the oxidation is easier on H site of phenolic hydroxyl group. Therefore, the oxidation reaction on H site of phenolic hydroxyl group is selected in this article, and the oxidation mechanism of three lignin model molecules is further revealed at the atomic and molecular level. The scheme of overall reaction process is shown in Fig. 1. The optimized geometry structures of the fifteen transition states at the B3LYP/6-311 + G(d,p) level are presented in Fig. 2. The optimized standard orientation of equilibrium geometries (reactants, transition states and products) of the fifteen reaction channels are listed in the ESM. The equations of fifteen possible reaction channels are listed in Table 1, including the optimized bond lengths of breaking and forming bonds of transition states and corresponding bond lengths in equilibrium reactant and product molecules, and the imaginary frequency values of the transition states are also listed in Table 1.
The oxidation reactions of p-hydroxybenzyl alcohol SOL (HOL or VOL) on H site of phenolic hydroxyl group by O₂ under visible light irradiation forms syringic acid (SCA) via five steps. O₂ attack to the H site of phenolic hydroxyl group and H has been abstracted to form phenoxy radical. The phenoxy radical presented one quinone isomers at the para-position. Then the addition reactions initiated by O₂ at the para-position forming peroxy radical (R¹OO radical), and further oxidize to peroxy acid (R¹OOH) and peroxide products (R¹OOR²). And then undergoes rearrangement to generate related products syringic acid SCA (p-hydroxybenzyl acid HBA or vanillic acid VCL). For reaction channel RTS1-1, a complex CP-1 is located on the product sides, in which the O-H bond distance is 1.734Å, while the other bond lengths are very close to that of the corresponding product P1-1. Similar case is present in RTS2-1 and RTS3-1, O-H bond distances are 1.739 and 1.688Å, respectively. From Table 1, it can be seen that the transition states of hydrogen abstraction reactions TS1-1, TS2-1 and TS3-1 have a common characteristic, the elongation of C-H breaking bond lengths of TS1-1, TS2-1 and TS3-1 are 32.4 18.6 and 41.5% longer than those in the equilibrium state, and the elongation of O-H forming bond lengths are 12.3, 13.9 and 7.1% longer than those in the equilibrium state. The elongation of the breaking bonds is longer than that of the forming bonds, indicating that these structures of the transition state is closer to the corresponding product structure, and these reaction channels are formed by "late" transition states with endothermic reactions, which is consistent with the Hammond hypothesis [24].

### 3.2. Energetics

The reaction Gibbs free energies (ΔG) and the reaction Gibbs potential barrier heights (ΔG⁺) at 298 K of the fifteen reaction channels at the B3LYP/6-311 + G(d,p) level are also listed in Table 1. The schematic diagram of the potential energy surface related to the three oxidation reaction pathways is shown in Fig. 3. And the energies of the reactants are set to be zero as a reference.

Firstly, it can be seen that the Gibbs free energy barriers of SOL oxidation reactions with five steps are the lowest among three oxidation reactions from the overall schematic diagram of the potential energy surface, followed by the oxidation of VOL and the Gibbs free energy barrier of HOL oxidation reactions are the highest. The reaction channels for SOL oxidation are more advantageous than the others. For example, for the first step H-abstraction reaction channel (to see Table 1), the reaction Gibbs barrier of the reaction channel RTS1-1 is 26.42 kcal/mol, which is about 5.70 kcal/mol and 2.09 kcal/mol lower than RTS3-1 and RTS2-1, respectively. Similar cases appear in the other four steps, such as the Gibbs free energy barriers in order of ΔG⁺(TS1-2, 19.53 kcal/mol) < ΔG⁺(TS2-2, 21.38 kcal/mol) < ΔG⁺(TS3-2, 23.15kcal/mol). For reaction channel RTS1-1, a complex CP-1 is located on the product side, while the energy barrier is 2.11 kcal/mol lower than that of product P1-1. The Gibbs free energy barriers of complexes CP-2 and CP-3 are 0.41 kcal/mol and 1.34 kcal/mol lower than those of the correspond products P2-1 and P3-1, respectively.

Secondly, the Gibbs free energy barrier decreases with the increasing of the number of methoxyl group. Such as the reaction Gibbs potential barriers of the third step H-abstraction reaction are in order of ΔG⁺(TS1-3 of SOL with two methoxyl groups, 21.71 kcal/mol) < ΔG⁺(TS2-3 of VOL with one methoxyl
group, 22.46 kcal/mol) < ΔG‡ (TS3-3 of HOL without methoxyl group, 23.88 kcal/mol). Because of the strong electronegativity of oxygen atom on the methoxyl group, there are lone pair electrons on its $p$ orbit, the $p-\pi$ conjugate effect presented between O atom of the methoxyl group and benzene ring. The electron conjugation effect is stronger than that of electron-withdrawing induction effect, and the $p$ electron cloud of the O atom shifts to the benzene ring, which lead to the H-abstraction reaction on the phenolic hydroxyl group site occur easier, so the more methoxyl groups there are, the stronger the reactivity. This is consistent with the experimental results\textsuperscript{[14]}.

Thirdly, the fifth step rearrange reaction channels form syringate acid (SCA), vanillic acid (VCL) and p-Hydroxybenzoic acid (HBA), and release a large amount of heat simultaneously. The results show that the reaction Gibbs free energy of reaction channel RTS1-5 is -92.33 kcal/mol, and reaction channels RTS2-5 and RTS3-5 are − 91.27 and − 88.64 kcal/mol, respectively, which is thermodynamics superior to other reaction channels.

4. Conclusion

In this paper, the oxidation reaction mechanism of three lignin model compounds (SOL, VOL and HOL) under visible light irradiation is studied using DFT method at the B3LYP/6-311 + G $(d,p)$ level. Based on the potential energy surface information, it is concluded that the H-abstraction reaction of lignin model compounds at the phenolic hydroxyl group is more advantageous than the other sites, the Gibbs reaction energy barrier reduces with the increasing of the number of methoxyl groups among three lignin model compound structures. Further revealing of oxidation reaction mechanism of lignin model molecular in more detail through theoretical calculations is helpful to understand the degradation process and provide theoretical support for the design of subsequent catalysts.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Author Contributions
All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Shuqi Dong, Hui Zhang, Xia Du, Tingyu Yao, Yan Shang, Liquan Jing, Jinguang Hu. The first draft of the manuscript was written by Shuqi Dong and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

**Data Availability**

The datasets generated during and analysed during the current study are available from the corresponding author on reasonable request.

**References**

Table 1 is available in the Supplementary Files section.
Figure 1

The scheme of the reaction process on the phenolic hydroxyl sites of three lignin model molecules
Figure 2

The optimized geometric structure of the fifteen transition states at the B3LYP/6-311+G(d,p)
Figure 3

The relevant schematic potential energy surfaces of the three lignin model molecules

Supplementary Files

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- Table1.docx