Experimental and Theoretical Studies on the Pyrolysis Mechanism of \( \beta \)-1-Type Lignin Dimer Model Compound

Xiao-Yan Jiang, Qiang Lu,* Xiao-Ning Ye, Bin Hu, and Chang-Qing Dong *

A \( \beta \)-1-type lignin dimer, 1,2-bis(3,5-dimethoxyphenyl)propane-1,3-diol was employed as a model compound in this study. The pyrolysis mechanisms and formation pathways of the pyrolytic products were investigated by using density functional theory (DFT) calculations and analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Four possible initial pyrolysis mechanisms were proposed, including the \( \text{C}_4\text{rC}_\beta \) homolysis mechanism and three concerted decomposition mechanisms (1, 2, and 3). Results indicated that the lignin dimer decomposed via two concerted decomposition mechanisms, forming 3,5-dimethoxybenzaldehyde, 1,3-dimethoxy-5-vinylbenzene, 3-hydroxy-5-methoxybenzaldehyde, and 3-methoxybenzaldehyde. 3,5-Dimethoxybenzaldehyde was the major product, accounting for greater than 50% of all pyrolytic products. In addition to the two concerted decomposition mechanisms, \( \text{C}_4\text{rC}_\beta \) homolysis was a secondary pyrolysis mechanism during the lignin dimer pyrolysis process, and the pyrolytic products included 3,5-dimethoxybenzyl alcohol, 3,5-dimethoxyphenethyl alcohol, 1,3-dimethoxybenzene, and 1,3-dimethoxy-5-methylbenzene. A third concerted decomposition mechanism was judged to be the least likely pathway to occur because of the high activation energy requirement.

**Keywords:** Lignin; \( \beta \)-1 Linkage; Dimer model compound; Pyrolysis mechanism; Py-GC/MS; Density functional theory

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**INTRODUCTION**

The fossil fuel shortage and associated severe environmental pollution problems have raised great attention on the utilization of renewable biomass resources (Azadi et al. 2013; Ioelovich 2015). Among the various biomass conversion technologies, pyrolysis is an efficient way to convert biomass into various valuable chemicals or fuels (Bridgewater 2012). Lignocellulosic biomass mostly consists of cellulose, hemicelluloses, and lignin. Lignin is the most abundant resource of aromatic compounds in nature (Lora and Glasser 2002). The pyrolysis of lignin obtains value-added aromatic compounds (Bai et al. 2014; Zhang et al. 2014); however, the traditional pyrolysis techniques do not take into account the selective production of specific aromatic compounds. Mechanistic studies concerning lignin pyrolysis help to realize the formation pathways of pyrolytic products, and moreover, provide a theoretical basis for exploring efficient selective pyrolysis techniques for target products.

Lignin is biosynthesized from the random polymerization of three monomers (\( \rho \)-coumaryl, coniferyl, and sinapyl alcohols), interconnected by C-O and C-C linkages of varying types, including \( \beta \)-O-4, \( \alpha \)-O-4, 4-O-5, \( \beta \)-1, \( \beta \)-5, etc. The \( \beta \)-O-4 linkage dominates and accounts for approximately half of the total linkages in lignin (Zakzeski et al. 2010;
Azadi et al. (2013). Therefore, most experimental pyrolysis studies have reported on the β-O-4 type lignin dimer model compound pyrolysis characteristics and product distribution. For example, a series of experiments were conducted by Kawamoto et al. (2007a,b; 2008a,b) to investigate the effects of lignin substituents, situated on the aromatic and alkyl groups, on the pyrolysis behavior of β-O-4-linked lignin dimer model compounds. Based on these experimental studies, the formation pathways of pyrolytic products and the whole pyrolysis mechanism could be inferred (Britt et al. 2000; Hu et al. 2013). However, the detailed product formation mechanisms have yet to be discovered.

Density functional theory (DFT) calculations have proved to be an efficient theoretical way to reveal the pyrolysis mechanism of lignin model compounds at the molecular level. Several in-depth studies have been performed to clearly indicate the pyrolysis mechanisms of several lignin monomers and dimers, including guaiacol (Liu et al. 2014), vanillin (Hu et al. 2016), phenethyl phenyl ether (PPE), and PPE derivatives (Beste et al. 2008; Beste and Buchanan III 2010, 2013; Huang et al. 2014; Huang and He 2015). However, limited theoretical research has focused on the pyrolysis mechanism of the C-C-linked lignin dimers. Moreover, current theoretical studies are rarely confirmed via experimental results. Therefore, in this study, to clarify the pyrolysis mechanism of lignin with C-C linkages, a β-1-type lignin dimer model compound (1,2-bis(3,5-dimethoxyphenyl)propane-1,3-diol) was synthesized, since the β-1 linkage is a common lignin linkage accounting for around 7% of all linkages in lignin (Zakzeski et al. 2010). The pyrolysis mechanism and formation pathways of major products were investigated with combined analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments and DFT calculations.

![Figure 1](image_url)

**Fig. 1.** The β-1-type lignin dimer model compound (1,2-bis(3,5-dimethoxyphenyl)propane-1,3-diol)

**EXPERIMENTAL**

**Analytical Pyrolysis-Gas Chromatography/Mass Spectrometry Experiments**

The lignin dimer model compound was provided by the Department of Chemistry at the Peking University (China). Analytical Py-GC/MS experiments were performed on a CDS Pyroprobe 5200HP pyrolyser (CDS Analytical, Oxford, PA, USA) connected to a Perkin Elmer GC/MS (Clarus560S, Waltham, MA, USA). The pyrolysis was carried out at 800 °C, with a heating time of 20 s and a heating rate of 20 °C/ms. The pyrolysis vapors were directly transported into the GC/MS for analysis. The chromatographic separation was performed using an Elite-35MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The oven temperature was programmed from 40 °C (2 min) to 280 °C at a heating rate of 15 °C/min. The temperature of the GC/MS interface was held at 300 °C, and the mass spectrometer was operated in EI mode at 70 eV. The mass spectra were...
obtained from m/z 20 to 400. The chromatographic peaks were identified based on the National Institute of Standards and Technology (NIST) library and the Wiley library.

**Density Functional Theory Methods**

All calculations were carried out using a Gaussian 09 series program (Gaussian Inc., Wallingford, CT) (Frisch et al. 2010). The equilibrium geometries of the reactants, intermediates, transition states, and products were fully optimized by employing the DFT/M06-2X method, with a 6-31+G (d, p) basis set. The M06-2X method has been widely used in the pyrolysis mechanism of lignin model compounds with good accuracy (Beste and Buchanan III 2010; Kim et al. 2011; Parthasarathi et al. 2011), which is suitable for treating main-group thermochemistry, non-covalent interactions, and kinetics with an average mean unsigned error of only 1.3 kcal/mol for the TC177 database (Zhao and Truhlar 2008). Furthermore, the reactants, intermediates, transition states, and products were evaluated by frequency analysis, at the same level as optimization, to verify the stationary points to be minima or first-order saddle points, and to obtain their thermodynamic parameters. Intrinsic reaction coordinate (IRC) calculations were further performed to ensure the correctness of each transition state. Enthalpies were used for the discussion on energetics, under the standard condition of 298.15 K and 1 atm. The activation energy (reaction energy barrier) of the concerted reaction was equal to the relative energy between the transition state and the reactant, including a zero-point energy correction (ZPE). The bond dissociation energy (BDE) of the homolytic cleavage reaction was considered as approximately equal to the activation energy (Huang et al. 2011).

**RESULTS AND DISCUSSION**

**Pyrolysis-Gas Chromatography/Mass Spectrometry Results**

Figure 2 shows the typical ion chromatogram from fast pyrolysis of 1,2-bis(3,5-dimethoxyphenyl)propane-1,3-diol at 800 °C. At this temperature, the lignin dimer model compound would be completely decomposed, and moreover, the primary pyrolytic products would undergo secondary cracking reactions.

![Typical ion chromatogram from fast pyrolysis of the lignin dimer model compound](image)

**Fig. 2.** Typical ion chromatogram from fast pyrolysis of the lignin dimer model compound at 800 °C
Ten pyrolytic products were detected, and their peak area percentages (peak area, %) are given in Table 1. 3,5-Dimethoxybenzaldehyde was the most abundant product, accounting for greater than 50% of the total products. The formation pathways of the pyrolytic products and the overall pyrolysis mechanism of the lignin dimer were analyzed by DFT calculations in the following sections.

Table 1. Identification of Pyrolytic Products and Peak Area (%) Values

<table>
<thead>
<tr>
<th>No.</th>
<th>Retention time (min)</th>
<th>Compounds</th>
<th>Molecular weight</th>
<th>Formula</th>
<th>Peak area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.78</td>
<td>anisole</td>
<td>108</td>
<td>C₇H₆O</td>
<td>1.67</td>
</tr>
<tr>
<td>2</td>
<td>6.30</td>
<td>1,3-dimethoxybenzene</td>
<td>138</td>
<td>C₉H₁₀O₂</td>
<td>14.56</td>
</tr>
<tr>
<td>3</td>
<td>6.66</td>
<td>3-methoxybenzaldehyde</td>
<td>136</td>
<td>C₉H₈O₂</td>
<td>4.87</td>
</tr>
<tr>
<td>4</td>
<td>6.97</td>
<td>3-methoxyphenol</td>
<td>124</td>
<td>C₉H₁₂O₂</td>
<td>3.43</td>
</tr>
<tr>
<td>5</td>
<td>7.23</td>
<td>1,3-dimethoxy-5-methylbenzene</td>
<td>152</td>
<td>C₉H₁₂O₂</td>
<td>0.74</td>
</tr>
<tr>
<td>6</td>
<td>8.89</td>
<td>3,5-dimethoxybenzaldehyde</td>
<td>166</td>
<td>C₁₀H₁₁O₃</td>
<td>50.96</td>
</tr>
<tr>
<td>7</td>
<td>9.03</td>
<td>1,3-dimethoxy-5-vinylbenzene</td>
<td>164</td>
<td>C₁₀H₁₂O₂</td>
<td>4.22</td>
</tr>
<tr>
<td>8</td>
<td>9.81</td>
<td>3,5-dimethoxybenzyl alcohol</td>
<td>168</td>
<td>C₉H₁₂O₃</td>
<td>6.98</td>
</tr>
<tr>
<td>9</td>
<td>9.65</td>
<td>3,5-dimethoxyphenethyl alcohol</td>
<td>182</td>
<td>C₁₀H₁₂O₃</td>
<td>3.67</td>
</tr>
<tr>
<td>10</td>
<td>9.77</td>
<td>3-hydroxy-5-methoxybenzaldehyde</td>
<td>152</td>
<td>C₉H₁₀O₃</td>
<td>8.90</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>total</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

Density Functional Theory Calculations

Initial pyrolysis mechanism of the β-1-type lignin dimer

According to previous studies, both the homolytic cleavage and the concerted decomposition may take place during the preliminary pyrolysis process of lignin (Elder and Beste 2014; Huang et al. 2014; Chen et al. 2015). For all β-1-type lignin dimers, the homolytic cleavage should occur on the Cα-Cβ bond because it has the lowest bond dissociation energy (BDE) value (Parthasarathi et al. 2011). Concerted decomposition may occur via three different modes; therefore, four possible initial pyrolysis mechanisms were considered, and the corresponding reaction energy barriers were calculated (Fig. 3). As shown in Fig. 3, the activation energy of concerted decomposition 1 was lower (113.7 kJ/mol) than concerted decomposition 3, and 76.7 kJ/mol lower than the BDE of the Cα-Cβ bond homolysis. The activation energy of concerted decomposition 2 was slightly higher (5.9 kJ/mol) than concerted decomposition 1. It should be noted that the above results do not completely agree with the calculation results obtained by Huang et al. (2015), who found that the activation energies (or the BDEs) of concerted decompositions 1 and 3, and Cα-Cβ bond homolysis were 209.5 kJ/mol, 224.5 kJ/mol, and 222.4 kJ/mol, respectively. The differences may be attributed to the difference in the two lignin dimers with respect to the methoxyl group placement on the aromatic ring, as well as the different hybrid density functionals employed in the two studies. The functional M06-2X, employed in this study, has been shown to be more accurate than the functional B3LYP selected by Huang et al. (2015) (Kim et al. 2011). Based on the above results, concerted decompositions 1 and 2 were more likely to occur than Cα-Cβ homolysis during the initial pyrolysis process of the lignin dimer. Meanwhile, concerted decomposition 3 hardly took place because of the high activation energy requirement. Subsequent pyrolytic pathways, based on the above three pyrolysis mechanisms, were calculated and analyzed in the sections below.
Fig. 3. Initial pyrolysis mechanism of the lignin dimer model compound

Subsequent pyrolytic pathways based on concerted decomposition 1

The possible subsequent pyrolytic pathways, based on concerted decomposition 1, are shown in Fig. 4. The lignin dimer model compound, M1, underwent a six-membered ring transition state (TS1) to transfer the H radical from the hydroxyl group at the Cα position to the oxygen atom of the hydroxyl group at the Cγ position, breaking the Cα-Cβ and Cγ-OH bonds, simultaneously. The products, M2 (3,5-dimethoxybenzaldehyde), M3 (1,3-dimethoxy-5-vinylbenzene), and water, were formed with an energy barrier of 210.9 kJ/mol.

Fig. 4. Subsequent pyrolytic reaction pathways based on concerted decomposition 1
The product, \( M_2 \), underwent further demethylation and demethoxylation reactions, followed by hydrogenation, to generate the products, \( M_5 \) (3-hydroxy-5-methoxybenzaldehyde) and \( M_7 \) (3-methoxybenzaldehyde), with overall energy barriers of 411.0 kJ/mol and 534.5 kJ/mol, respectively. The product, \( M_5 \), was easier to form than \( M_7 \) due to its much lower energy barrier. According to Table 1, the amount of 3-hydroxy-5-methoxybenzaldehyde (\( M_5 \)) was near 2 times of that of 3-methoxybenzaldehyde (\( M_7 \)), which agreed well with the theoretical calculation results.

**Subsequent pyrolytic pathways based on concerted decomposition 2**

The possible subsequent pyrolytic pathways, based on concerted decomposition 2, are given in Fig. 5. The lignin dimer model compound, \( M_1 \), decomposed directly to generate the product, \( M_2 \), and the intermediate, \( M_8 \), via a six-membered ring transition state (TS2), with an energy barrier of 216.8 kJ/mol, during which the H radical of the hydroxyl group at the C\(_\alpha\) position was transferred to the C\(_2\) position at the aromatic ring (rupturing the C\(_\alpha\)-C\(_\beta\) bond). The product, \( M_2 \), and the intermediate, \( M_8 \), underwent further cracking reactions. The product, \( M_2 \), was transformed into the products, \( M_5 \) and \( M_7 \) (Fig. 4). The intermediate, \( M_8 \), exhibited two possible cracking pathways. In pathway 1, \( M_8 \) underwent an intramolecular dehydration reaction through a six-membered ring transition state (TS3) to form \( M_3 \), with an overall energy barrier of 344.5 kJ/mol. In pathway 2, \( M_8 \) was converted into \( M_9 \) (3,5-dimethoxyphenethyl alcohol) via a four-membered ring transition state (TS4), overcoming an overall energy barrier of 436.1 kJ/mol. The product, \( M_9 \), decomposed into radical \( M_{10} \) and the hydroxymethyl radical, followed by hydrogenation reactions, to form the products, \( M_{11} \) (1,3-dimethoxy-5-methylbenzene) and methanol.

**Fig. 5. Subsequent pyrolytic reaction pathways based on concerted decomposition 2**

**Subsequent pyrolytic pathways based on \( C_\alpha-C_\beta \) homolysis**

The lignin dimer model compound, \( M_1 \), decomposed into the radicals, \( M_{12} \) and \( M_{13} \), through \( C_\alpha-C_\beta \) homolysis, with an energy barrier of 287.6 kJ/mol. Figure 6 shows the possible pyrolytic pathways of \( M_{12} \) and \( M_{13} \).

As shown in Fig. 6(a), \( M_{12} \) was converted into \( M_3 \) through a dehydroxylation reaction, overcoming an overall energy barrier of 447.2 kJ/mol. The radical \( M_{12} \), also
underwent a hydrogenation reaction to form M9, which exhibited five possible subsequent cracking pathways. In pathway 1, M9 could enter the same subsequent reaction pathway as shown in Fig. 5, to generate M11, with an overall energy barrier of 320.3 kJ/mol, which was the lowest among the five cracking pathways. In pathway 2, M9 was converted into the products, M11 and formaldehyde, via a four-membered ring transition state (TS6), with an overall energy barrier of 359.9 kJ/mol. In pathway 3, M9 underwent a complex transition state (TS7) to form the products, M15 (1,3-dimethoxybenzene) and acetaldehyde, with an overall energy barrier of 382.5 kJ/mol. In pathway 4, M9 initially decomposed into the hydroxyethyl radical and the M16 radical, and then M16 underwent a hydrogenation reaction to generate M15, with an overall energy barrier of 430.0 kJ/mol. In pathway 5, M9 was transformed into M15 and vinyl alcohol via a four-membered ring transition state (TS8), with an overall energy barrier of 493.1 kJ/mol.

Fig. 6. Subsequent pyrolytic reaction pathways based on Cα-Cβ homolysis

As shown in Fig. 6(b), radical M13 underwent a dehydrogenation reaction to form M2, with an overall energy barrier of 434.5 kJ/mol. Alternatively, radical M13 underwent hydrogenation to form M14 (3,5-dimethoxybenzyl alcohol), which was subsequently converted to M15 and formaldehyde through a four-membered ring transition state (TS5), with an overall energy barrier of 356.5 kJ/mol. The product, M14, was decomposed into radical M16 and the hydroxymethyl radical, via homolytic cleavage of the C-C bond, and then radical M16 underwent a hydrogenation reaction to generate M15, with an overall energy barrier of 414.5 kJ/mol.

Summary of Pyrolysis Mechanism and Pyrolytic Products of the Lignin

Based on the above results, Fig. 7 shows the overall pyrolysis mechanism of the lignin dimer model compound, M1, and the corresponding energy barriers of the optimal formation pathways of the pyrolytic products.

As shown in Fig. 7, fast pyrolysis of the lignin dimer produced four primary pyrolytic products, including 3,5-dimethoxybenzaldehyde (M2, peak 6 in Fig. 1), 1,3-dimethoxy-5-vinylbenzene (M3, peak 7 in Fig. 1), 3,5-dimethoxybenzyl alcohol (M14, peak 8 in Fig. 1), and 3,5-dimethoxyphenethyl alcohol (M9, peak 9 in Fig. 1). These primary products underwent secondary cracking reactions to form 3-hydroxy-5-methoxybenzaldehyde (M5, peak 10 in Fig. 1), 3-methoxybenzaldehyde (M7, peak 3 in Fig. 1), 1,3-dimethoxybenzene (M15, peak 2 in Fig. 1), and 1,3-dimethoxy-5-methylbenzene (M11, peak 5 in Fig. 1). These eight products were all detected in Py-GC/MS experiments, as shown in Table 1. Two minor pyrolytic products (anisole and 3-methoxyphenol) in Table

Fig. 7. Summarized pyrolytic decomposition mechanism and the products of the lignin dimer model compound

1, are not depicted in Fig. 7. It can be deduced that these products could be derived from 1,3-dimethoxybenzene through a demethylation or demethoxylation reaction, followed by a hydrogenation reaction. According to Fig. 1, 3,5-dimethoxybenzaldehyde (M2) was the most abundant pyrolytic product, since it could be formed via several facile formation pathways with the lowest energy barrier as compared with the other pyrolytic products. The energy barriers of its optimal formation pathways, based on concerted decomposition 1, concerted decomposition 2, and the Cα-Cβ homolysis mechanism, were 210.9 kJ/mol, 216.8 kJ/mol, and 434.5 kJ/mol, respectively. The energy barriers of 1,3-dimethoxy-5-vinylbenzene (M3), based on the above three mechanisms, were 210.9 kJ/mol, 344.5 kJ/mol, and 447.2 kJ/mol, respectively. It was obvious that 3,5-dimethoxybenzaldehyde (M2) and 1,3-dimethoxy-5-vinylbenzene (M3) were mainly derived from concerted decompositions 1 and 2. This concluded that the lignin dimer model compound mainly decomposed through concerted decompositions 1 and 2. Furthermore, it is to note that 1,3-dimethoxy-5-vinylbenzene (M3) was in a much lower yield than that of 3,5-dimethoxybenzaldehyde (M2), although the two products could be produced with similar energy barriers through concerted decomposition 1. The difference between them might be that the formation of M3 via concerted decomposition 2 was more difficult than the formation of M2. Moreover, the M3 contains an unsaturated C= C bond and would be easy to undergo polymerization reactions to form large molecular compounds and chars, resulting in much lower yield of M3 than M2. In addition, the energy barriers of 3,5-dimethoxyphenethyl alcohol (M9), based on concerted decomposition 2 and the Cα-Cβ homolysis mechanism, were 436.1 kJ/mol and 287.6 kJ/mol, respectively, which indicated that this product was easily formed from Cα-Cβ homolysis, rather than concerted decomposition 2. Moreover, 3,5-dimethoxybenzyl alcohol (M14) was derived from Cα-Cβ homolysis. These results illustrated that Cα-Cβ homolysis was a secondary pyrolysis pathway of the lignin dimer model compound. According to Table 1, products from the Cα-Cβ homolysis mechanism were lower than those from the two concerted decomposition mechanisms, which confirmed the theoretical calculation results.

CONCLUSIONS

1. Concerted decompositions 1 and 2 were chiefly responsible for the pyrolysis of the β-1-type lignin dimer model compound (1,2-bis(3,5-dimethoxyphenyl)propane-1,3-diol), while the Cα-Cβ homolysis was a secondary pyrolysis pathway. Concerted decomposition 3 was the least likely pyrolysis pathway.

2. The major pyrolytic products, based on concerted decompositions 1 and 2, included 3,5-dimethoxybenzaldehyde, 1,3-dimethoxy-5-vinylbenzene, 3-hydroxy-5-methoxybenzaldehyde, and 3-methoxybenzaldehyde. Among these products, 3,5-dimethoxybenzaldehyde was the most abundant.

3. The major pyrolytic cleavage of Cα-Cβ included 3,5-dimethoxybenzyl alcohol, 3,5-dimethoxyphenethyl alcohol, 1,3-dimethoxybenzene, and 1,3-dimethoxy-5-methylbenzene.
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