Molecular Products and Fundamentally Based Reaction Pathways in the Gas-Phase Pyrolysis of the Lignin Model Compound p-Coumaryl Alcohol

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Supporting Information

ABSTRACT: The fractional pyrolysis of lignin model compound para-coumaryl alcohol (p-CMA) containing a propanoid side chain and a phenolic OH group was studied using the System for Thermal Diagnostic Studies at temperatures from 200 to 900 °C, in order to gain mechanistic insight into the role of large substituents in high-lignin feedstocks pyrolysis. Phenol and its simple derivatives p-cresol, ethyl-, propenyl-, and propyl-phenols were found to be the major products predominantly formed at low pyrolysis temperatures (<500 °C). A cryogenic trapping technique was employed combined with EPR spectroscopy to identify the open-shell intermediates registered at pyrolysis temperatures above 500 °C. These were characterized as radical mixtures primarily consisting of oxygen-linked conjugated radicals. A comprehensive potential energy surface analysis of p-CMA and p-CMA + H atom systems was performed using various DFT protocols to examine the possible role of concerted molecular eliminations and free-radical mechanisms in the formation of major products. Other significant unimolecular concerted reactions along with formation and decomposition of primary radicals are also described and evaluated. The calculations suggest that a set of the chemically activated secondary radical channels is relevant to the low temperature product formation under fractional pyrolysis conditions.

1. INTRODUCTION

Lignin is the Nature’s dominant aromatic polymer—the second most abundant biomass component after cellulose, and accounts for ca. 30% of the organic carbon in the biosphere.1−3 It is an important resource of renewable fuels and products, as well as high-value chemicals,4−12 however, the hydrophobic nature of lignin, its insolubility in aqueous systems, structural diversity, and heterogeneity pose challenges to controlled deconstruction of biomass and production of the feedstock materials, and therefore, lignin is typically regarded as a waste material and burned during the pulp and paper production to generate heat and steam.1−8 Lignin is a three-dimensional, highly cross-linked macromolecule generated via radical-driven polymerization of three 4-hydroxy phenylpropanoid monomers (lignols): p-coumaryl alcohol (p-CMA), coniferyl alcohol, and sinapyl alcohol, which are phenolic derivatives of cinnamyl alcohol (CnA) additionally involving none, one, and two methoxy groups, respectively, attached to the benzene ring.1,13,16 The monomeric phenylpropane units are linked in a complex network through different types of ether, ester, and carbon−carbon bonds. Depolymerization and upgrading of lignin includes thermochemical treatment1,4,6,9,10,12,17,20 and homogeneous and heterogeneous catalysis.2,4,7,8,14 Other more intricate approaches have also been applied, such as the immobilized enzyme-based catalysis developed, particularly, by Ruckenstein and co-workers, in the early 1990s.15 The pyrolysis, whether separately or combined with catalysis, is a key approach in lignin valorization, and a large number of studies have been devoted to the thermal conversions of lignin and molecular characterization of its pyrolysis;1,4,6,9,10,12,17,20,21 however, due to the complexity and variability of lignin macromolecules, the mechanistic understanding of elementary reactions still remains limited.18,19 Lignin depolymerization is particularly challenging because of the broad distribution of bond strengths in the various C−O and C−C linkages, as well as the recondensation tendency, which often forms undesirable low-molecular-weight species possessing diverse functionalities.1 An improved understanding of underlying processes could provide insight into process control strategies and regulation of the byproduct formation. The alkylphenols represent a substantial portion of the lignin-derived biofuel stocks,22 and the mechanism of their formation remains under investigation.23
formation is of practical importance. During the pyrolysis at low and medium temperatures, lignin is mainly converted to the oligomers and monophenols, along with the char, water, and gases,
however, the yield of monophenols is typically low. The increased content of alkylated phenols is seen when the temperature increased, being explained through reactivity of the side groups.30 The side groups and substituents also play decisive roles in the product distribution of the pyrolysis of the other biomaterials. They constitute a considerable portion of lignans1 and the lighter fractions from lignite (brown coal) pyrolysis.

The study of elementary step models is essential to obtain a better understanding of kinetics and conversion pathways and to determine the stability of intermediate compounds formed during the lignin pyrolysis. The most extensive and impressive results have been obtained for reactivity of model dimers containing β-O-4 and α-O-4 aryl ether linkages typical for lignin macromolecules.34–37 The pyrolysis of substituted dimers and monolignols bearing a typical C3-side chain terminated with an aliphatic OH group (Figure 1) has been studied to a lesser degree, with most of the product-formation mechanisms being tentative.38–49 A more detailed analysis of the pyrolysis products has been performed for a series of phenylpropanoid and phenylpropanol models.46,47 In our previous studies, we also reported some mechanistic analysis of the CnA and p-CMA lignins’ pyrolys.

In spite of the significant advances in this area, the knowledge of detailed elementary reaction pathways remains limited and often elusive, and fundamentally based mechanistic studies are therefore a vital step in progressing development of the novel elementary reaction pathways and kinetic schemes.

A number of comprehensive and fundamental theory-based mechanistic and kinetic studies have been performed for the pyrolysis of contracted lignin models, such as anisole, o-quinone methide (α-QM), catechol, hydroquinone, chroman, phenol, and arylmuran, which are believed to be the key intermediates in lignin thermolysis and char formation.34,36,50 The H-abstraction of the phenolic hydroxyl groups, for instance, is believed to initiate formation of the ortho-quinone methide (α-QM) intermediate involving a methoxy group,50 whereas the chroman formation is explained via ring closure processes.50,51 The dimerization of p-coumaryl alcohol has been linked to the formation of a para-QM intermediate.50

The retro-en pericyclic and Maccoll pathways are the two most popular in literature concerted mechanisms to explain decomposition of lignin dimers containing β-O-4, α-O-4, and β-5 linkages.25,27–33 It is common to consider the cleavage of β-O-4 linkage to follow the molecular pathways, whereas the breakage of α-O-4 to occur via a homolytic dissociation of C–O bonds to form radicals as an initiating pyrolysis step.33 A detailed kinetic analysis of the pyrolysis of 2-phenethyl phenyl ether model by Jarvis et al.27 particularly suggested that the concerted retro-ene and Maccoll reactions are dominant at low temperatures (below 1000 °C), whereas the contribution of the C6H5C2H4–O–C6H5 homolytic bond scission reaction increases at higher temperatures (above 1000 °C).

Recently, we reported on registration of the intermediate radicals associated with gas-phase pyrolysis of lignin and its model compounds.23,48,49 We particularly detected the mixtures of radicals from the pyrolysis of CnA48 and p-CMA49 at low to moderate (400–700 °C) and high (700–1000 °C) temperatures, respectively, using a low temperature matrix isolation trapping technique interfaced with electron paramagnetic resonance spectroscopy (LTMI-EPR). On the basis of a concomitant theoretical analysis of the g-factors for model radicals, along with the reaction pathway analysis, it has been suggested that the mixtures predominantly consist of the highly conjugated O-centered and O-linked radicals. Furthermore, the PES studies revealed the main pathways to the formation of major products in CnA pyrolysis: cinnamaldehyde, indene, styrene, benzaldehyde, 1-propynyl benzene, and 2-propenylnitro.

Herein, we continue the examination of the thermolysis mechanisms in simple lignols with a focus on p-coumaryl alcohol (p-CMA), which is the simplest lignin model containing both a phenolic hydroxyl group and the propanoid side chain of the cinnamyl alcohol bearing the γ-OH group (Figure 1). The reactivity of side groups often constitutes a bottleneck in upgrading recondensed molecules possessing diverse functionalities.1 The CnA end group, for instance, has been shown to be responsible for propenylnaphthol and cinnamyl compound (dihydrocinnamyl alcohol, cinnamaldehydes, and CnA) formation during lignin pyrolysis.39

To our knowledge, the only detailed analysis of the p-CMA pyrolysis has been recently performed by Akazawa et al. at temperatures of 400–600 °C.47 The pyrolysis of a solid reagent in a heated pyrolyser chamber (hereafter called conventional pyrolysis) at 600 °C for 0.2 min yielded phenol, p-cresol, 4-vinylphenol, (E)-4-(1-propenyl) phenol, and dihydro-p-coumaryl alcohol, as the major identified products. The basic reaction mechanisms have also been postulated on the basis of the homolytic bond cleavages and reactions of H and OH radicals.

In the present work, a detailed fractional pyrolysis of the p-coumaryl alcohol is studied experimentally at low (<500 °C) and relatively high (500–900 °C) temperatures using a modified System for Thermal Diagnostic Studies (STDS) method for products analysis27 (sections 2.2 and 3.1) and LTMI_EPR for detection and identification of intermediate radicals55–57 (sections 2.3 and 3.2). A comprehensive density functional theory (DFT) analysis of the potential energy surfaces (PES) is performed (section 4) to develop a fundamentally based elementary reaction network operating during the pyrolysis of p-CMA, and to identify the most plausible pathways leading to the formation of major low-temperature products—simple phenolics.

Figure 1. Chemical structure of p-coumaryl alcohol.
2. MATERIALS AND METHODS

2.1. Reagent. Para-Coumaryl alcohol (p-CMA), also called 4-[(E)-3-hydroxy-1-propenyl] phenol (Figure 1), was provided by BIONE (Ryan Scientific Inc.) and used as is without further purification.

2.2. System for Thermal Diagnostic Studies: STDS. The fractional pyrolysis was performed using the previously employed System for Thermal Diagnostic Studies instrumental interface,21,86 STDS, with a modified reaction chamber, Figure 2. The present instrumental setup consists of a vertical movable sample holder with a basket at the end, a quartz pyrolysis reactor of dimensions of 7 mm internal diameter and 110 mm long (the isothermal part is 20 mm long). The reactor can be heated from 200 to 900 °C with a furnace mounted within a GC oven compartment. The pyrolysis reactor with furnace and part of transfer line were heated to 300 °C (dashed square, Figure 2). The furnace temperature was regulated by three thermocouples at three locations of the quartz tubular reactor in which the sample resided during pyrolysis. In a typical experiment, about 10 mg of p-coumaryl was loaded in a quartz basket. The sample in the basket was purged for 3 min at room temperature using nitrogen carrier gas (in cold zone, outside of the GC compartment) and then inserted quickly into the preheated reactor at a certain temperature and pyrolyzed for 3 min (heated zone). A continuous flow of ultrahigh purity nitrogen (99.99%) was maintained to provide an inert atmosphere and also to sweep directly the pyrolysis products at a residence time of 0.2 s. The products from the pyrolysis reactor passed through a heated transfer line at 300 °C and then entered a GC/MS injection port where they were collected and condensed at the head of the column at −60 °C. After each run, the solid residue was moved to the cold zone and cooled to room temperature at flowing of N2 gas. The fractional mass loss of the p-CMA sample was determined by weighing the sample after each pyrolysis temperature using a balance with accuracy to ±10^-4 mg. The evolved volatiles were analyzed by the MSD (Agilent S973N), where the injector temperature was kept at 300 °C. The chromatographic separation was performed with a 5% diphenyl/95% dimethyl polysiloxane fused-silica capillary column (Agilent J&W DB-5 ms Ultra Inert GC Column, 30 m × 0.25 mm × 0.25 μm). The oven temperature was programmed from −60 °C (3 min) to 180 °C (1 min) at 4 °C/min heating rate and then to 300 °C (5 min) with 10 °C/min heating rate. The mass spectra were operated in EI mode at 70 eV and scanned from 10 to 650 (m/z). The chromatographic peaks were identified according to NIST 2005 and Wiley Libraries.

2.3. EPR Measurements. Low Temperature Matrix Isolation - Electron Paramagnetic Resonance (LTMI-EPR) spectroscopy65−67 has been employed for the gas-phase pyrolysis of p-CMA to detect intermediate radicals at 77 K, Figure S1 (Supporting Information). Briefly, ca. 10 mg of p-CMA was loaded into a Pyrex container and vaporized in a carbon dioxide carrier gas at a constant temperature of 65 °C in an electrically heated preheater. The addition of carbon dioxide as a supporting matrix has been demonstrated to improve the resolution of EPR spectra. Using a rotary pump, the reactants were delivered at a pressure of ≤0.01 Torr through the electrically heated pyrolysis reactor (i.d. = 19 mm, length = 76 mm) operating at a temperature range of 400–1000 °C. Upon exiting the reactor, the pyrolysis products were condensed onto the coldfinger of the Dewar placed in the EPR cavity cooled by liquid nitrogen (77 K). The linear accumulation of the radical yields vs time was maintained up to 12 min.

Figure 2. Experimental setup of the modified System for Thermal Diagnostic Studies.

Figure 3. (a) Profile of fractional pyrolysis of p-coumaryl alcohol, blue line, and pyrolysate as a sum of detected oxygenated products, red line. (b) Temperature dependence of the recovered amount of p-CMA (identified by GC-MS from the gas phase).
The spectra of gas-phase radicals captured by the cold finger were recorded on a Bruker EMX-20/2.7 EPR spectrometer with dual cavities, X-band, 100 kHz, with microwave frequency in the range 9.458–9.474 GHz. The EPR registration parameters for temperature-dependent studies were as follows: sweep width, 200 G; microwave power, 2.0 mW; modulation amplitude, 4.0 G (or less); time constant, 10.24 ms; sweep time, 167.77 s; and number of scans, 3. Comprehensive window-based PC software, WINEPR, was used to control the EPR spectrometer, perform automation routines, and retrieve EPR spectra.

2.4. Computational Details. Various decomposition pathways of p-CMA and relevant intermediates were computed using nonlocal Kohn–Sham density functional theory based on the generalized gradient approximation. Bond dissociation patterns (electronic energies corrected with zero point vibration energies) are computed at the M06-2X/6-31G(d,p) level of theory using the Q-Chem 4.3 quantum chemistry package. The B3PW91 hybrid functional in conjunction with the moderate Pople-type basis set 6-31G(2d,p) augmented with diffuse and polarization functions is employed for detailed PES analysis, using Gaussian 03 software. These methods are well tested in the literature, and have also been evaluated in our previous studies on various open-shell systems.

Transition states are characterized as having only one negative eigenvalue of Hessian (force constant) matrices. The absence of imaginary frequencies verifies that structures are true minima at their respective levels of theory. Intrinsic reaction coordinate (IRC) calculations were performed at the B3PW91/6-31+G(2d,p) level to ensure the connectivity of stationary points. In addition, the final point geometries at both sides of TS were reoptimized to verify minima.

3. RESULTS AND DISCUSSION

3.1. Weight Loss and Product Analysis. A typical mass loss from p-CMA fractional pyrolysis is presented in Figure 3. The decomposition profile is similar to that observed earlier for the pyrolysis of lignin under analogous conditions (horizontal reactor) with the high content of the residue ~30%. About 50 pyrolysis products and unreacted p-CMA were experimentally identified. The majority of products reach maxima in the temperature range from 350 to 500 °C, Figure 4. The characteristic GC-MS chromatograms of all released products and molecular structures of some major compounds are provided in the Supporting Information (Figure S2 and Table S1, respectively).

The integrated peak values are illustrated in Figures 4 and 5 in the decomposition range 200–900 °C, and the yields of products (larger than 0.5% based on GC-MS peak area count) are listed in Table 1 (at 425 °C) and Table S2 (at 350 °C), respectively.
para-CMA pyrolysis yielded phenolic compounds as the major products detectable by GC-MS, in accord with earlier pyrolysis experiments.47

Remarkably, only a few simple phenolics account for a large part of the total product yields. The sum of contributions at 350 and 425 °C for cresol (31% vs 32%), phenol (19% vs 10.5%), ethyl phenol (10.5% vs 11.8%), and 4-propenylphenol (10% at 350 °C) vs 2,4-dimethyl phenol (8% at 425 °C), constitutes about 70.5% at 350 °C and 62.5% at 425 °C, based on the total product budget provided in Table S2 and Table 1, respectively.

The product analysis suggests a predominant reactivity of the propenoid side chain (Figure 1) during the pyrolysis of p-CMA, up to the complete removal of the C3-fragment and generation of the unsubstituted phenol. This is believed to be substantial addition to the results on lignin model dimers that mostly bring out the superior role of the phenoxy-type radicals in lignin pyrolysis.25−37 The major products formed at low temperature pyrolysis and identified in this paper mostly preserve their phenolic moieties.

It should also be emphasized that almost all oxygen containing products (including benzaldehydes and benzofurans, Figure 4b) are formed within a low temperature window 350−450 °C, Figures 4 and S, which matches well with the maximum conversion rate of p-CMA, shown in Figure 3a.

The bond energy of the aromatic hydroxyl group could serve as an upper energy limit at corresponding temperatures if the simple bond homolysis was to control the product formation. However, the product formation occurs via complex radical and molecular (concerted or stepwise) pathways (see section 4).

The temperature dependence data shows (Figure 4a) that the phenol, cresol, and ethylphenol products are initially formed and disappear in a low temperature range of 300−500 °C and then reappear as the temperature is increased, with a maximum rate at 600 °C. As will be justified in the theoretical section 4.2.2, this is likely due to the switch to a distinct reaction mechanism, which involves higher activation higher energy levels but also higher pre-exponential factors.

A comparison of Figure 4a and d suggests that the 3-(p-hydroxyphenyl)-1-propanol (p-HPP), which in fact is a dihydrogenated counterpart of the p-CMA (most abundant product of the conventional pyrolysis), is generated at remarkably low temperatures (ca. 250 °C), reaches the maximum at 350−375 °C, and effectively decomposes at 400−450 °C (the relative yield is 6.24% at 350 °C, Table S1), where the p-cresol, phenol, and ethylphenol are formed, perhaps at the expense of p-HPP (viz., dihydro-p-CMA) as well.

Note that significant amounts of benzaldehyde (Table 1) and its 4-methyl derivative are also produced at lower temperatures with maximum rates at 450 °C (Figure 4b), whereas the benzofuran derivatives are generated at somewhat lower temperatures with maxima at 350 and 450 °C, respectively, depending on the species structure. Perhaps the dihydrobenzofuran formed at 350 °C serves as a source of the methylbenzofuran formation at 450 °C, when the dihydro derivative is disappeared.

Considerable (11−17%) amounts of branched products (C10−C17 species) of the radical origin, such as the bis-phenols, biphenyl, 4-butylphenol, and multisubstituted phenols, are also formed at low temperatures, clearly indicating the intricacy of reactions at low temperatures (Table 1 and Table S1). Therefore, both alternative unimolecular (concerted and stepwise) and free-radical mechanisms should be considered to explain the fractional pyrolysis of p-CMA (see section 4).

At higher temperatures, BTX products (benzene, toluene, xylene) as well as styrene and alkyl-benzenes are formed starting from 500 °C, when the lower-temperature products are decomposed (cf. Figures 4 and S).

3.2. Radicals from Lower Temperature Pyrolysis of p-CMA. Recently, we have reported on registration of the intermediate radical mixtures from pyrolysis of p-CMA at high temperatures (700−1000 °C). Earlier, such radical mixtures have been detected during the pyrolysis of cinnamyl alcohol at significantly lower temperatures (400−500 °C).48 Therefore, we reexamined the radical formation at low and moderate temperature pyrolysis of p-CMA.
The intermediate radicals were trapped from the gas phase pyrolysis of p-CMA in the temperature range 400−900 °C using the LTMI_EPR technique by matrix isolation at liquid N2 temperature (see section 2.3 and Figure S1 in the Supporting Information). An unresolved EPR spectrum was registered at 500 °C, whereas only traces of free radicals (close to the detection limits of EPR ∼1010−1011 paramagnetic centers) were detected at lower temperatures (400−450 °C). The radicals detected at higher temperatures showed similar to each other anisotropic EPR signals (Figure 6, blue spectra). The signal intensity was increased with increasing pyrolysis temperature, as exhibited in Figure S3.

All EPR signals showed high g-values (>2.0080) that also considerably increased with temperature. We note that similar anisotropic EPR signals, detected earlier from the pyrolysis of cinnamyl alcohol, are included in Figure 6, for comparison (green lines). Apparently, the same types of radicals are operating during the pyrolysis of both p-CMA and CnA compounds, despite the presence of the phenolic hydroxyl group in p-CMA, perhaps originating from the interplay between the propanoid carbon backbone and the aliphatic OH group. On the basis of the theoretical calculations of g-factors for model radicals and PES analysis, such signals have been previously identified by us as typical radical mixtures dominantly containing conjugated oxygen-centered and O-linked radicals.

The absence of the detectable amounts of radicals in p-CMA pyrolysis at temperatures below 500 °C (Figure S3) immediately suggests a nonradical mechanism to govern low-temperature thermolysis; however, this phenomenon does not necessarily rule out the formation and operation of the "non-detectable" by our cryogenic technique open-shell systems (vide infra), as well as the role of interface and condensed-phase reactions, which could well contribute to the product balance of the fractional pyrolysis.

The lack of detectable amounts of radicals for p-CMA, and their presence in CnA at even lower temperatures, cannot be merely explained by the presence of the phenolic OH group in p-CMA. BDE comparisons, indeed, showed insignificant differences in generation of primary radicals in two compounds.

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Table 1. Products Formed from p-Coumaryl Alcohol Fractional Pyrolysis at 425 °C

<table>
<thead>
<tr>
<th>compound no.</th>
<th>retention time (min)</th>
<th>name</th>
<th>chemical formula</th>
<th>area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.9</td>
<td>phenol</td>
<td>C6H6O</td>
<td>10.5</td>
</tr>
<tr>
<td>2</td>
<td>25.2</td>
<td>phenol, 2-methyl + phenol, 4-methyl</td>
<td>C6H6O</td>
<td>32.1</td>
</tr>
<tr>
<td>3</td>
<td>26.7</td>
<td>phenol, 2-ethyl</td>
<td>C6H6O</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>27.4</td>
<td>phenol, 2,4-dimethyl</td>
<td>C6H6O</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>28.3</td>
<td>phenol, 4-ethyl</td>
<td>C6H6O</td>
<td>11.8</td>
</tr>
<tr>
<td>6</td>
<td>29.5</td>
<td>2-propenal, 2-methyl-3-phenyl</td>
<td>C6H6O</td>
<td>0.8</td>
</tr>
<tr>
<td>7</td>
<td>30.0</td>
<td>benzaldehyde, 4-methyl + phenol, 2-(1-methylethyl)</td>
<td>C6H6O + C6H5O</td>
<td>4.9</td>
</tr>
<tr>
<td>8</td>
<td>30.5</td>
<td>phenol, 2-ethyl-6-methyl</td>
<td>C6H6O</td>
<td>3.4</td>
</tr>
<tr>
<td>9</td>
<td>31.2</td>
<td>phenol, 4-propyl</td>
<td>C6H6O</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td>32.2</td>
<td>2-allylphenol</td>
<td>C6H6O</td>
<td>1.0</td>
</tr>
<tr>
<td>11</td>
<td>32.8</td>
<td>benzene, 1-methoxy-4-(1-methylethyl)</td>
<td>C6H6O</td>
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</tr>
<tr>
<td>12</td>
<td>32.9</td>
<td>phenol, 4-(2-propenyl)</td>
<td>C6H6O</td>
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<tr>
<td>13</td>
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<td>benzene, 1-methoxy-4-propyl</td>
<td>C6H6O</td>
<td>1.2</td>
</tr>
<tr>
<td>14</td>
<td>34.4</td>
<td>phenol, 4-butyl</td>
<td>C6H6O</td>
<td>0.8</td>
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<tr>
<td>15</td>
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<td>benzaldehyde, 4-hydroxy</td>
<td>C6H6O</td>
<td>0.9</td>
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<tr>
<td>16</td>
<td>35.6</td>
<td>phenol, 4-(1,1-dimethylpropyl)</td>
<td>C6H6O</td>
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<tr>
<td>17</td>
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<td>C6H6O</td>
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</tr>
<tr>
<td>18</td>
<td>37.0</td>
<td>ethanone, 1-(2,5-dimethylphenyl)</td>
<td>C6H6O</td>
<td>0.7</td>
</tr>
<tr>
<td>19</td>
<td>37.6</td>
<td>2H1-benzopyran, 3,4-dihydro-2,2-dimethyl + 2-butanoate, 4-(4-hydroxyphenyl)</td>
<td>C6H5O + C6H5O2</td>
<td>1.2</td>
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<td>20</td>
<td>40.4</td>
<td>3-(p-hydroxyphenyl)-1-propanol</td>
<td>C6H5O2</td>
<td>0.5</td>
</tr>
<tr>
<td>21</td>
<td>45.1</td>
<td>p-hydroxybiphenyl + [1,1'-biphenyl]-3-ol</td>
<td>C6H5O2</td>
<td>1.7</td>
</tr>
<tr>
<td>22</td>
<td>50.6</td>
<td>phenol, 2,2-(4-hydroxyphenyl)methyl + phenol, 2,2'-methylenebis</td>
<td>C6H5O2</td>
<td>1.7</td>
</tr>
<tr>
<td>23</td>
<td>52.6</td>
<td>ethanone, 2-(2-hydroxyphenyl)-1-(3-methylphenyl)</td>
<td>C6H5O2</td>
<td>3.6</td>
</tr>
<tr>
<td>24</td>
<td>53.9</td>
<td>1,3-bis(p-hydroxyphenyl) propane</td>
<td>C6H5O2</td>
<td>1.7</td>
</tr>
<tr>
<td>25</td>
<td>55.6</td>
<td>phenol, 2-butyln</td>
<td>C6H5O2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

This table provides the maximum percentage area (% ≥0.5) of the major phenols formed during the p-CMA pyrolysis.
Figure 7. Concerted unimolecular decomposition of p-CMA involving transfer of hydrogen atoms to different centers indicated at arrows along with the corresponding barrier heights in kcal/mol.

Probably, the success of the cryogenic trapping of CnA-derived radicals below 500 °C is due to the saturated vapor pressure of CnA (0.012 Torr at 25 °C, liquid state), which is higher than that for solid state p-CMA (not reported in the literature, however, expected to be much less than 0.01 Torr, detected in our experiments at room temperature).

In addition, some intermediate radicals such as the phenol precursor p-HO-C6H4*, discussed above, may not simply be trapped at liquid nitrogen temperature (77 K) employed in our cryogenic experiments, similar to that for phenyl (C6H5*)39 and benzyl (C6H5CH2*) radicals, which are known to be successfully trapped only at liquid helium temperature (4 K) and annihilated quantitatively when the matrix was heated from 4 to 77 K.89,90

It should be emphasized that three different types of pyrolysis experiments are discussed in this paper that operate at different experimental conditions: (a) fractional pyrolysis of p-CMA (performed in this work), (b) conventional pyrolysis of CnA reported earlier,47 similar to that employed by Akazawa et al.,47 and (c) pure “gas-phase” pyrolysis employed in cryogenic experiments for EPR registration of radicals for both CnA and p-CMA models. Indeed, the experimental procedure employed in this work (a continuously present solid-state reagent or its residue from a previous step, section 2.2), fundamentally differs from the “pure” gas-phase procedure utilized in cryogenic experiments, when the reagent is fully vaporized (section 2.3). Accordingly, a complex set of secondary processes can be expected to occur during the fractional pyrolysis, both in the gas phase and at the interface of the condensed-phase materials and reactor walls. Moreover, due to the thermal prepyrolysis, the solid phase residues can contain various intermediates, such as the char components, and undesorbed species, which can alter the chemistry of low-temperature pyrolysis (for instance, by providing hydrogen donors). A detailed investigation of the intermediate solid-state residues from the reaction zone is underway in order to gain further insight into the role of the condensed-phase radical processes.

Thus, the secondary, primarily radical processes can well occur to control the formation of final products at low temperatures, and hence both molecular and free-radical pathways should be explored in detail to elucidate the low-T products formation during pyrolysis of p-CMA.

4. DFT ANALYSIS OF THE ELEMENTARY REACTION MECHANISMS

As discussed in the Introduction, there are two general mechanisms commonly employed in the pyrolysis of lignin and its model compounds: (i) concerted reactions (called also synergy processes38), involving decomposition of molecules via intramolecular rearrangements, and (ii) free radical processes stemming from homolytic cleavage of the weakest bonds in the parent molecules and intermediates, followed by the free-radical chain reactions. These mechanisms variably dominate depending on the reagents and pyrolysis conditions. DFT theory has been largely invoked to explore the thermolysis of dimeric models through PES analysis and homolysis patterns of parent molecules.35–33,36

Our earlier results on the pyrolysis of simple models CnA,48 p-CMA,49 catechol,58,59 and hydroquinone59,66 also support such a diversity of underlying mechanisms. We have also proposed the key role of the oxygen-centered and oxygen-linked radicals in moderate and high temperature lignin thermolysis.

In this section, various unimolecular rearrangement and homolytic bond fission channels of the p-CMA are further explored. The emphasis is on the theoretical analysis of the most plausible elementary reaction pathways relevant to the low temperature (<500 °C) pyrolysis, where the major products—phenolic compounds—are formed.

A possible role of the unimolecular rearrangement pathways and concerted mechanisms is discussed in section 4.1, whereas the formation and unimolecular decomposition of primary radicals is explored in section 4.2. The relevance of the secondary reaction channels triggered by H atom addition to the double bond of the p-CMA is analyzed in section 4.3. The most plausible pathways relevant to the phenolics formation are summarized in section 4.4.

4.1. Unimolecular Decomposition of p-CMA: Concerted Mechanisms. Reactions 4.1.1–4.1.5 represent five unimolecular direct (concerted) decomposition mechanisms for the p-CMA reagent illustrated in Figure 7. The degradation
channels involving initial isomerization of the p-CMA are not accentuated here, since they are less competitive compared to their fragmentation counterparts, which encounter barriers of similar magnitude but largely benefit from the entropy gain. The lowest energy isomerization barrier that could be identified is about 60 kcal/mol, which combined with the low predicted pre-exponential factor makes this pathway unlikely to occur at low temperatures.

Since the major products listed in Table 1 preserve their aromatic hydroxyl groups, the possible reactivity of the phenolic OH groups is merely considered in the context of radical reactions, discussed in section 4.2, stemmed from the low BDE for the phenolic O–H bond (section 4.2.1).

The five hitherto identified concerted decomposition mechanisms (eqs 4.1.1–4.1.5) involve a straightforward dehydrogenation, formaldehyde elimination, as well as three dehydration processes triggered by various H-migration processes in p-CMA (Figure 7). The migration of the Hγ atom of the terminal γ-OH group to the C8 skeletal atom of the side chain directly produces 4-hydroxy styrene (4-vinylphenol, HO–C6H4–CH=CH2) appears to be one of the two major products, alongside the most abundant hydrogenated-p-CMA. As a side note, the abundance of the latter product clearly suggests that a plausible hydrogenation mechanism exists at low temperatures (see section 4), which certainly cannot involve a direct hydrogenation by Hγ, which is a costly process (see, e.g., ref 76). At elevated temperatures, the indenol has also been observed in ref 47.

It is important also to note that a significant amount of unsubstituted styrene is produced during the fractional pyrolysis of p-CMA at higher temperatures (Figure 5b and Figure S2), which is likely related to the degradation of the 4-hydroxy-styrene, promoted by the phenolic hydroxyl group (vide supra).

Due to the significant activation barriers, all identified concerted processes can be considered noncompetitive at low temperatures, and thus irrelevant to form simple phenolics. This conclusion is in accord with our previous results on pyrolysis of CnA.48 The most noticeable difference between the pyrolysis products of CnA and p-CMA is the lack of p-CMAld in the latter case (Table 1), in full accordence with data from Akazawa et al.47 This phenomenon could be well ascribed to the higher barrier of the concerted dehydrogenation of p-CMA (77.5 kcal/mol), compared to that for other concerted reactions presented in Figure 7; however, almost the same magnitude barrier has been found earlier for the direct dehydrogenation of CnA, which has the highest yields of CnAld.48 A rapid unimolecular decomposition of p-CMAld at low temperatures can also be ruled out, since the calculated concerted decarbonylation barrier to form 4-vinylphenol, postulated in some tentative mechanisms,46,47 is too high (ca. 75.6 kcal/mol) to be relevant at low temperatures. The homolysis of the carbonyl C=H and phenolic O–H bonds also requires high energies of 79 and 89 kcal/mol, respectively. Therefore, both aldehydes can be expected to be formed through bimolecular radical reactions (section 4.3).
be assumed that the rapid degradation of p-CMAld promoted by the reactive phenolic OH group is much faster than that for CnAld. This issue needs further clarification.

The lowest energy unimolecular pathway that could be identified for p-CMA was the one involving formation of the 6-indenole (Figure 7) with a calculated barrier of ca. 65 kcal/mol height, the traces of which have been observed only at 600 °C during the conventional pyrolysis.47 Since similar barriers exist for 4-vinylphenol and 4-cyclopropenylphenol formation, the similarly small yields would be expected for these products as well. Even less yields are anticipated for 4-allenylphenol and p-CMAld, which are facing even higher barriers, never being identified experimentally. Apparently, the unimolecular concerted mechanism cannot account for formation of the 4-vinylphenol, which is the dominant product in conventional pyrolysis even at low temperatures.43 As shown in section 4.3, indeed, there are other, more competitive pathways to form such a product under mild conditions.

All of the materials described above combined together lead to a more general conclusion that p-CMA would be unlikely to have much unimolecular chemistry at low temperatures, and the radical processes would be prevalent.

4.2. Formation and Degradation of Primary Radicals.

The homolytic bond dissociation of p-CMA reagent generates primary radicals and small particles—pool radicals, to initiate further radical reactions. The unimolecular dissociation of primary radicals, in turn, can dissociate to products of interest when low energy pathways are available. Provided below (section 4.2.1), analysis of the bond dissociation energies (BDEs, Figure 8) indicates the two most dynamic hydrogen atoms of the parent molecule being H9 and H4 atoms belonging to the skeletal C9-center and phenolic OH group, respectively (see Figure 1 for atom numerations), and hence their reactivity will be of primary interest in subsequent analysis of the unimolecular decomposition pathways (section 4.2.2).

4.2.1. Homolytic Bond Cleavage and Generation of Primary Radicals. The simple bond dissociation channels and corresponding energies (electronic energies corrected by ZPE) are calculated at the M06-2X/6-31G(d,p) level, and presented in Figure 8 (see also ref 78).

The homolytic cleavage of the skeletal C9−H and phenoxy O−H bonds constitutes the most favored pathways with BDEs equal to 70.7 and 81.1 kcal/mol, respectively.

The aromatic O−H bond fission of the parent compound is much easier than that for its aliphatic counterpart with BDE = 96.59 kcal/mol owing to the formation of the resonantly stabilized phenoxy-type (semiquinoidal) radical denoted as R(O4) in Figure 9, with a typical phenoxy-type radical distribution of spin densities (see, e.g., ref 48). Instead, the conjugation in alkoxy radical R(O9) is intermitted by the saturated CH3 group of the hydroxymethyl moiety. For the same reason, the dissociation energies of the Oγ−H bonds in p-CMA and calculated previously nonphenolic CnA48,79 are close to each other. Thus, the effective termination of the conjugation between the benzene ring and γ-methyl group leads to the passive electronic role of the phenolic hydroxyl group in unimolecular processes involving aliphatic-OH, and hence not discussed further in detail.

The C9−H bond scission is the lowest energy channel with BDE = 70.7 kcal/mol. It forms thermodynamically most favored conjugated radical denoted as R(C9), Figure 9, which involves an allylic side chain with an unpaired electron localized on the C7 and C9 atoms (ρ = 0.60e and 0.45e, respectively), and partially delocalized over the ring (ρ = 0.18e for Cipso and two Cmeta positions). The spin density in another favored, phenoxy type radical R(O4) is also delocalized over the whole molecule: ca. 20% in average on each of the para and ortho carbon atoms of the benzene ring, as well as O4 and C8 exocyclic atoms, thus forming a p-QM derivative of the semiquinoidal structure (Figure 8).

The calculated entropy gain for the favorite radical R(C9) to generate an atomic hydrogen is significant (ΔS = +38 cal/K.mol), and hence this process is well favored kinetically at respective temperatures.

The elimination of the γ-OH group (C9−OH bond fission with BDE = 90.51 kcal/mol, Figure 8) generates another highly

**Figure 8.** Primary bond dissociation channels (homolytic bond cleavage patterns) for para-coumaryl alcohol. Electronic energies including ZPE are at the M06-2X/6-31G(d,p) level.
conjugated 4-hydroxyphenyl-1-(3-allyl) radical, denoted as R(HPA). It is basically the same type of radical as R(C9) involving a common allyl radical fragment attached to the benzene ring, only with no OH group at the side chain terminus. The geometrical and electronic characteristics of R(HPA) calculated in the current paper are close to those computed by Sebree et al. for a smaller homologue.82

Apparently, under proper conditions, such as the ones provided by the fractional pyrolysis procedure (section 2.2), the reactions at interfaces with condensed phase materials and the reactor surfaces (see, e.g., ref 91) can more feasibly generate the primary radicals, also in a bimolecular manner via H-abstraction or dehydration (see sections 4.3.1 and 4.3.2), following the same order of stabilities provided by simple bond fissions (Figure 8). Again, the R(C9) and R(O4) would be the most favored radicals to justify the focus of our further mechanistic analysis on these two species, along with the sterically active aliphatic O-centered radical R(O9).

4.2.2. Unimolecular Decomposition of Primary Radicals. Figure 9 illustrates the identified pathways for direct dissociation (concerted and bond homolysis) and isomerization of the thermodynamically favored primary radicals R(C9), R(O4), as well as a key alkoxy radical R(O9). The lowest energy pathway highlighted in green involves a rapid isomerization

Figure 9. Predicted by theory unimolecular decomposition pathways for key primary radicals R(C9), R(O4), and R(O9). Hydrogen and oxygen atoms of the parent molecule are specified by proximal C-centers. Hy represents the terminal OH group. Calculated barrier heights (electronic energies + ZPE corrections) or bond fission asymptotes for simple dissociation reactions (in parentheses) are in kcal/mol and indicated on arrows. The O-linked radical is encircled (see text). The lowest energy pathway is highlighted in green, whereas the pool radicals and their precursors are in red.
ization of the R(C9) radical (eq 4.2.1a), which is exothermic by ca. 4 kcal/mol and feasibly forms an O-linked intermediate radical HOC₆H₄CH═(CHCHO). The O-linked intermediate decomposes further (eq 4.2.1b) to give acrolein and p-hydroxyphenyl radical via a loose, “late-type” transition state (enlarged ring-tail bond length is ca. 2.7 Å).

\[
R(C9) \rightarrow HOCC₆H₄CH═(CHCHO)⁺
\]

\[
(\Delta E^g = 27.8 \text{ kcal/mol})
\]

(eq 4.2.1a)

\[
HOCC₆H₄CH═(CHCHO)⁺ \rightarrow p-HOCC₆H₄⁺ + CH₃═CHCHO
\]

\[
(\Delta E^g = 47.1 \text{ kcal/mol})
\]

(eq 4.2.1b)

Notably, the second reaction step requires a considerably higher conversion to 47.1 kcal/mol, which could explain the higher stability of the transported from the reaction zone and registered by EPR spectroscopy O-linked radical intermediate, in case of the moderate and high temperature pyrolyses (section 3.2).

The newly generated p-HOCC₆H₄⁺ radical can be stabilized to form a major product phenol adding an H atom from the pool or abstracting it from an H-donor. Note that the barrier for the reverse reaction (4.2.1b) is only of 3.0 kcal/mol height, which would not affect the reaction yields in the gas-phase processes due to the departing products, whereas a possible “cage effect” in the condensed phase processes could provide more diversity.

To conclude, this attractive channel can likely occur at relatively higher temperatures due to the significant barrier of the rate-limiting step (\( \Delta E^g = 47.1 \text{ kcal/mol} \)). Such a scenario could be well attributed to the second higher energy mechanism of the phenol formation suggested by the second peak in the experimental data on temperature dependent product yields (Figure 4a). Such a relatively high-temperature mechanism explains the significant amounts of phenol produced at 500–700 °C temperatures, consonant with our EPR results discussed above on generation of the O-linked radicals registered at the same temperatures.

The radical R(C9) can isomerize at elevated temperatures to form R(O9) via a barrier of ca. 47.7 kcal/mol; however, the process is endothermic by ca. 21 kcal/mol and not supported entropically, when compared with its decomposition counterparts such as that described by eq 4.2.1b. Note that the oxygen-centered radical R(O9) is an alternative source of the phenol precursor radicals p-HO-C₆H₄⁺ due to its feasible defragmentation (eq 4.2.2a) and acetylene elimination (eq 4.2.2b).

\[
R(O9) \rightarrow p-HOCC₆H₄CH═CH⁺ + CH₃O
\]

\[
(\Delta E^g = 24.5 \text{ kcal/mol})
\]

(eq 4.2.2a)

\[
p-HOCC₆H₄CH═CH⁺ \rightarrow p-HOCC₆H₄⁺ + C₂H₂
\]

\[
(\Delta E^g = 44.0 \text{ kcal/mol})
\]

(eq 4.2.2b)

The stepwise pathway through two consecutive barriers of 24.5 and 44.0 heights, respectively, is preferred energetically over the direct process, which encounters a significant barrier of 68.6 kcal/mol height.

The p-hydroxy phenyl radical can also serve as a source of the other phenolics via its further reactions with alkyl and other radicals. The reactivity of the p-HO-C₆H₄⁺ is stemmed from its feasible transformation to the classical C₆H₅O⁺ isomer radical, as shown by da Silva and co-workers.\(^{50}\)

At lower temperatures, the intermediate 4-hydroxyphenyl-vinyl radical can also be stabilized to form 4-vinylphenol product. Intriguingly, only unsubstituted styrene was observed in our experiments (Figure 5b, Figure S2), whereas the 4-vinylphenol has been well detected by Akazawa\(^{47}\) during the conventional pyrolysis. This issue will be discussed later on in section 4.3.3.

There is also a possibility for R(C9) to lose a H atom of the phenoxyl group to form a closed-shell quinoidal product. However, the corresponding BDE is much higher at 57.8 kcal/mol. Besides, the expected highly conjugated product was not observed either, among the gas-phase products.

The radical R(C9) can also undergo other transformations. A competitive path is an entropically favored H-removal from R(C9) with BDE = 40.8 kcal/mol to form p-coumaryl-aldehyde (p-CMAld), HO-C₆H₄—CH═CH—CHO, which, as noted above, has been observed neither in our fractional nor in our conventional\(^{47}\) pyrolysis experiments. The calculations also suggest another feasible path to p-CMAld formation involving the loss of H9 atom of the alkoxyl primary radical R(O9) through a remarkably low barrier of 12.9 kcal/mol (Figure 9).

Perhaps, more competitive (bimolecular, surface mediated) processes, involving a phenolic OH group, could become effective to eliminate p-CMAld, since its rapid unimolecular decomposition is not a straightforward process (see section 4.1). Further clarifications are certainly needed here. Note only that the bimolecular H-Abstraction from the HCO group is much easier (\( \Delta E^g = 0.2 \text{ kcal/mol} \)) than that for either of the OH groups (section 4.3.1).

The primary radical R(O4) predominantly produces the highly conjugated quinoidal structures (Figure 9) owing to the conjugation between the ring and side chain double bond. They are mostly of the quinone methide (QM)-type structures containing a cyclohexadiene with a carbonyl and an exocyclic methylene group. Such structures can well contribute to the char formation and undergo further reactions during fractional pyrolysis, since none of these structures were identified experimentally at studied temperatures (up to 900 °C). According to the literature (see, e.g., refs 56 and 57), the QM and likely its derivatives are key intermediates in lignin pyrolysis. They can be easily hydrogenated to form cresol and other alkyl-phenolics. The unsubstituted p-QM can be formed from decomposition of an oxirane (epoxide) intermediate. We have identified two pathways for substituted oxirane formation involving the H atom removal from R(O9) and R(O4) primary radicals with BDEs equal to 52.0 and 70.7 kcal/mol, respectively (Figure 9).

To summarize, the unimolecular conversions of primary radicals are generally high energy demanding processes similar to their molecular counterparts discussed in the previous section, and, again, are unlikely to account for the low-T formation of phenolics listed in Table 1. However, they could well explain some high energy processes. The most favored pathway, highlighted in green in Figure 9, could explain the experimentally observed phenol formation during the second temperature window (second peak in Figure 4a). Moreover, it involves a low-energy dissociation of the R(O9) radical via an O-linked intermediate (encircled in Figure 9), which rationalizes our cryogenic results, suggesting it to be a major constituent of the radical mixtures registered at the same temperatures by EPR spectroscopy (section 3.2).

4.3. Secondary Radicals as a Plausible Low-Temperature Source of Phenolics. The possible rapid reactions of
the continuously present reagent p-CMA and its residues with intermediate and pool radicals (primarily H and OH radicals) are the most straightforward secondary processes during the fractional pyrolysis. We considered three possible outcomes of such reactions: (a) H-abstraction, (b) dehydration, and (c) radical addition to the double bond of the p-CMA, either at C7 (Cα) or C8 (Cβ) positions. The addition of radicals to the benzene ring, which can alter the ring structure, is not considered, since the major products preserve their phenolic moieties. H-addition to the ipso-ring position also can occur.

4.3.1. H-Abstraction Reactions. The H-abstraction of aromatic and aliphatic hydroxyl groups is the most plausible bimolecular process to generate the primary radicals R(O9) or R(O4), the unimolecular degradation of which was detailed above. As expected from the BDE analysis (Figure 8), the phenolic hydrogen atom of the p-CMA is somewhat more reactive than that of the terminal (alkyl) hydroxy group. The calculated barriers for corresponding H-abstraction reactions mediated by an external H atom are 4.4 and 5.7 kcal/mol, respectively.

The OH-radicals, particularly, regenerated during the secondary processes (vide infra), can also be involved in the H-abstraction processes to produce water molecules and primary radicals.

4.3.2. Dehydration Reactions. The attack of an external H atom to hydroxyl groups leads to the dehydration of p-CMA. This is a plausible way to generate the radical R(HPA), other than the direct elimination of the γ-OH group with BDE = 90.5 kcal/mol (section 4.2). This process encounters a somewhat larger barrier than that for the H-abstraction reactions discussed above. The formation of R(HPA) requires 12.1 kcal/mol activation energy, whereas the barrier for dehydration involving the stronger phenolic OH group (BDE = 111.2 kcal/mol, Figure 8) is significantly higher at 27.3 kcal/mol.

4.3.3. H Atom Addition to the Double Bond of the Side Chain. As noted above, the hydrogenated p-CMA is the most abundant low-temperature product of the conventional pyrolysis, substantially produced also under our low-T fractional pyrolysis conditions (6.2% at 350 °C). This phenomenon clearly suggests that the hydrogenation of p-CMA at low temperatures is a straightforward process. Since direct hydrogenation of a double bond by dihydrogen (when available) is a costly process (see, e.g., ref 76), the radical processes may become potentially relevant.

To generate the major pyrolysis products p-cresol, ethyl-, propyl-, propenyl-, and dimethyl phenols, one, indeed, needs to add up hydrogen atoms to the “hydrogen-lean” side chain of the p-CMA containing an unsaturated bond. The addition of an
external H atom (pool radical) to the well available reagent is a straightforward hydrogenation process. The H atoms required to initiate such a process can be likely produced from cleavage of the weakest C9−H bond of the parent molecule with a fairly low BDE of 70.7 kcal/mol (Figure 8).

The potential energy diagrams presented in Figures 10 and 11 illustrate a variety of chemically activated reactions triggered by H-addition to both Cα and Cβ unsaturated carbon atoms of the propenoid side chain (for p-CMA notations, see Figure 1) (the Cartesian coordinates for stationary points on the PES are provided in the Supporting Information, Table S3 and Table S4). H-addition to the β-carbon atom (C8) forms the thermodynamically most stable RB1 adduct, HOC6H4CH\textbullet\text{CH2CH2OH}, with a large well-depth of −45.1 kcal/mol (Figure 11), whereas the H-addition to C7 (Cα) forms an RA1 intermediate, HOC6H4CH2\textbullet\text{CH2OH}, with a much shallower well-depth of −33.2 kcal/mol (Figure 10).

RB1 formation is also preferred kinetically; H-addition to Cβ encounters a barrier of 1.2 kcal/mol height, which is somewhat lower than that for RA1 formation with ΔE° = 2.5 kcal/mol. The energetic preference of the RB1 adduct by as much as 11.9 kcal/mol is due to the partial delocalization of the spin density over the ring: ρ(C7) = 0.80e, ρ(Cortho) ≈ ρ(Cmeta) ≈ ρ(Cpara) = 0.25e. For comparison, the spin density in RA1 is predominantly located on the β-carbon atom, ρ(C8) = 1.05e. Qualitatively, the more spin is located in a reaction center, the less it is delocalized over the molecule, and hence the less stable the radical is (some spin density−stability−reactivity relationships also are discussed in refs 16, 48, and 92).

All pathways provided in Figures 10 and 11 represent chemically activated reactions of adducts, and hence they can well occur at low-temperature pyrolysis. The most common mechanisms for decomposition of the “energized” adducts are 1,3- and 1,4-H-shifts, and β-scission. A remarkable exception is the energetically most favored pathway (highly highlighted in green in Figure 10) involving a sequence of transition states TSa4 and TSa5 (eqs 4.3.1−4.3.2), which employs a pivotal low-energy OH-migration mechanism for the RA1 → RA3 transition. The OH-migration mechanism has been identified for the first time by Green and co-workers, \cite{84} and independently characterized by us as a key mechanism in atmospheric processes \cite{85} (later it has also been applied to the combustion of iso-octane \cite{86}).

The RA3 intermediate readily undergoes β-scission (ΔE° = 20.1 kcal/mol) to eliminate vinyl alcohol and to form a para-hydroxybenzyl radical (eq 4.3.1b).

Finally, the p-hydroxybenzyl radical stabilizes either by H-abstraction from a donor or recombines rapidly with a pool...
HOC₆H₄CH₂CH₂ radicals (eq 4.3.2) to form the most abundant low-T product p-cresol (31–32% relative yields, Table 1).

\[ \text{RAI} \rightarrow \text{RA3} \quad (\Delta E^\# = 25.0 \text{ kcal/mol}) \quad (4.3.1a) \]

\[ \text{RA3} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_2^* + \text{CH}_2==\text{CHOH} \quad (\Delta E^\# = 20.1 \text{ kcal/mol}) \quad (4.3.1b) \]

\[ \text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_2^* + \text{H}^*(\text{RH}) \rightarrow \text{HOC}_6\text{H}_4\text{CH}_3(\rightarrow +\text{R}^*) \quad (4.3.2) \]

Two entropically favored, formally β-scission processes also can well occur to form phenolics. The one described by eq 4.3.3 includes a straightforward formation of the 4-(2-propenyl)phenol via an exothermic by 4.8 kcal/mol (relative to the entrance level) decomposition of RAI adduct (10.10% relative yield at 350 °C and 2.4% at 450 °C, Table 1).

\[ \text{RAI} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_2==\text{CH}_2 + \text{CH}_2==\text{CHOH} \quad (\text{BDE} = 28.4 \text{ kcal/mol}) \quad (4.3.3) \]

No OH-elimination barrier was identified for this reaction, which can be justified with the barrierless reverse reaction of the OH-addition to the double bond of the side chain. This is in accord with similar conclusions on OH-addition to olefins with negative activation energy in the high pressure limit.²⁷

It should be emphasized that reaction 4.3.3 is an important chain propagation process in pyrolysis of p-CMA, since it generates OH active radicals to promote the chain reactions.

Another simple dissociation involves cleavage of the O–H bond with BDE = 44.5 kcal/mol to regenerate the H atoms and to form a closed-shell benzoxirane (Figure 10). In spite of the high BDE, the barrier for this process is located only at ca. 11.3 kcal/mol above the entrance channel.

Furthermore, the phenol (more precisely, its precursor 4-hydroxyphenyl radical) can be directly formed via TsaI, which is located above the entrance level by ca. 6.5 kcal/mol (eq 4.3.4).

\[ \text{RAI} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_2==\text{CH}_2 + \text{OH} \quad (\Delta E^\# = 39.8 \text{ kcal/mol}) \quad (4.3.4) \]

Figure 11 provides reaction pathways to form 4-hydroxyphenyl ethyl radical, HOC₆H₄CH₃CH₂*, which is a precursor of another abundant product ethylphenol with 47.0% observed relative yields at 350 °C and 11.8% at 450 °C (Table 1). The HOC₆H₄CH₃CH₂* radical can be particularly formed via the most preferred sequence of TSB3 and TSB4 transition states (\(\Delta E^\# = 26.6 \text{ and } 14.5 \text{ kcal/mol, respectively} \)) highlighted in green (eqs 4.3.5a and 4.3.5b).

\[ \text{RB1} \rightarrow \text{RB2} \quad (\Delta E^\# = 26.6 \text{ kcal/mol}) \quad (4.3.5a) \]

\[ \text{RB2} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_3\text{CH}_2^* + \text{CH}_2\text{O} \quad (\Delta E^\# = 14.5 \text{ kcal/mol}) \quad (4.3.5b) \]

An alternative pathway passes through relatively higher energy transition states TSB5 and TSB6 (\(\Delta E^\# = 41.3 \text{ and } 20.1 \text{ kcal/mol, respectively} \)), yet the energy barriers remain below the entrance channel (Figure 11).

As seen from Figure 10, the same p-hydroxyphenyl radical can be formed via even faster conversion of the RAI adduct to RA2 radical, HOC₆H₄CH₃CH₂CH₂O*, and then to HOC₆H₄CH₂CH₂* via elimination of formaldehyde (corresponding barriers via Tsa2 and Tsa3 are 29.0 and 14.5 kcal/mol, respectively) (eqs 4.3.6a and 4.3.6b).

\[ \text{RAI} \rightarrow \text{RA2} \quad (\Delta E^\# = 29.0 \text{ kcal/mol}) \quad (4.3.6a) \]

\[ \text{RA2} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_3\text{CH}_2^* + \text{CH}_2\text{O} \quad (\Delta E^\# = 14.5 \text{ kcal/mol}) \quad (4.3.6b) \]

\[ \text{HOC}_6\text{H}_4\text{CH}_3\text{CH}_2^* + \text{H}^*(\text{RH}) \rightarrow \text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_3(\rightarrow +\text{R}^*) \quad (4.3.7) \]

The radical intermediate is further stabilized to form 4-ethylphenol (eq 4.3.7).

Both processes are producing formaldehyde and 4-hydroxyphenylethyl radical as coproducts. The formaldehyde is an abundant product in the lignin pyrolysis.⁹⁻²¹ Moreover, recent experiments even suggested its critical role in lignin degradation.⁸⁸

The two radical-adducts RB1 and RA1 also can interconvert via a TSB1 barrier of 43.1 kcal/mol height (2.0 kcal/mol higher than the entrance level in Figure 11). Considering the chemically activated nature of the RB1 intermediate, the interconversion is expected to occur easily under pyrolysis conditions; however, the newly formed RA1 will be thermalized, chemically deactivated. Thus, the only activated portion of the RA1 radicals formed from direct H-addition (“energized” ones) would have options to overcome the remaining barriers in Figure 10 under mild conditions.

Notably, the PES in Figure 10 provides also some other pathways, such as the formation of the 2-(4-hydroxyphenyl)-acetalddehyde via Tsa8. Some other possible products can be formed via stabilization of the intermediate radicals; however, such processes involve a multitude of intermediate steps, and can likely account for formation of the minor or high energy products.

The pathway RA1 to RB3 (C9–C8 1,2-H-shift) is also an attractive option being exothermic by 4.2 kcal/mol, as follows from Figures 10 and 11. However, the process requires a high activation energy, which puts the TS above the entrance channel in Figure 10 by as much as 10 kcal/mol relative to the RA1 with \(\Delta E = -33.2 \text{ kcal/mol} \) (not shown for clarity), and thus it is significantly less favored kinetically than alternative pathways provided in Figure 10.

As discussed in section 4.2, the C9–H bond is the weakest one (BDE = 70.7 kcal/mol) to form the R(C9) primary radical and to generate H atoms needed to develop a radical-chain process.

For regeneration of H atoms, we identified three relevant channels. The one via a pathway involving TSB2 is depicted in Figure 11 (eqs 4.3.8a and 4.3.8b).

\[ \text{RB1} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_3==\text{CH}_2 + \text{C}^*\text{H}_2\text{OH} \quad (\Delta E^\# = 32.3 \text{ kcal/mol}) \quad (4.3.8a) \]

\[ \text{C}^*\text{H}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}^* \quad (\text{BDE} = 31.2 \text{ kcal/mol}) \quad (4.3.8b) \]

This pathway forms C*H₂OH radical (source of H atoms through decomposition to CH₂O+H with BDE 31.2 kcal/mol) and 4-vinylphenol (4-hydroxystyrene), which is the most abundant product of the conventional pyrolysis.⁴⁷ Not observed during the fractional pyrolysis. Assuming that 4-hydroxystyrene...
is similarly formed in both processes, its rapid degradation can be anticipated in the last case.

A bimolecular reaction, perhaps, remains as an option for its degradation. At medium temperatures (500–700 °C), we indeed observed appreciable amounts of unsubstituted styrene (Table S1), which can be traced back to the 4-vinylphenol through the elimination of the reactive aromatic OH group.

**RA1** radical can easily give away an H atom at C7 to form enol HO—Ph—CH2—CH==CHOH. This is an almost thermoneutral reaction starting from initial reagents (Figure 10). A direct loss of the phenolic hydrogen atom of the radical-adduct **RB1** to form a quinoidal product (Figure 11) also is a possible source of the H atoms. However, it is exothermic by 9.1 kcal/mol compared to the entrance level.

Formation of the OH-radical and cyclopropylenol is even more plausible. Notably, the cyclopropylenol was not observed in our experiments, being likely unstable due to the energetically strained three-member ring. The hydroxyl radicals can also be generated from direct decomposition of **RA1** (eq 4.3.9) and well contribute to the regeneration of H atoms, as shown by our preliminary calculations. This issue needs further explorations.

Apparently, the pool radicals can interact also with other intermediates, given that the reactions are sufficiently fast during pyrolysis. H atom addition to one of the resonance structures of the 3-(4-hydroxyphenyl)allyl intermediate radical, R(HPA) (see section 4.2), for instance, can form 4-(2-propenyl)phenol observed in our experiments (Table 1) via eq 4.3.9; the stabilization energies are indicated at arrows.

![Diagram](Image)

Either the 4-(2-propenyl)phenol or its 4-(1-propenyl)phenol isomer can be formed on the basis of this theory with the proportion of produced isomers being controlled by thermochemistry (data at arrows), which in turn correlate with spin distributions on alternative reaction centers: ρ(C7) = 0.60e, ρ(C9) = 0.57e. Thus, if this mechanism was to occur alone, both isomers would be formed in comparable proportions, as is seen in conventional pyrolysis experiments (0.89:2.02), performed at 600 °C temperatures. However, only 4-(2-propenyl)-phenol is overwhelmingly formed in our fractional pyrolysis experiments (10.10% at 350 °C and 2.4% at 450 °C), likely to suggest an alternative mechanism for its formation.

**4.3.4. H Atom Addition to the ipso-Position of the Ring.**

The ipso addition—elimination pathway also is an attractive pathway to form products, as it particularly follows from our previous studies. However, the H-addition to p-CMA to form ipso-radical requires ca. 8 kcal/mol activation energy, which is significantly higher than that for H-addition to the double bond (1.2–2.5 kcal/mol, Figures 10 and 11). Moreover, the decomposition of the newly generated ipso-radical to form phenol requires 27.3 kcal/mol energy; i.e., the second barrier is again located significantly above the entrance channel (by about 9 kcal/mol). Even though this pathway is less favored compared to the chemically activated pathways triggered by H-addition to the double bond described in Figures 10 and 11, it can well operate at somewhat higher temperatures to generate phenol.

**4.4. Summary of Mechanisms Relevant to the Major Product Formation.**

On the basis of the described above theoretical results, selected mechanisms operating under different pyrolysis conditions can be attributed to the formation of the most abundant products.

**para-Cresol** is the most abundant product predominantly formed at low temperatures (ca. 31% both at 425 and 350 °C, Table 1 and Table S1, respectively). The T-dependence of the product yields provided in section 3.1 (Figure 4a) shows two peaks, correspondingly, at lower (300–500 °C) and higher (500–700 °C) temperature regions, suggesting that at least two different mechanisms operate to produce p-cresol, depending on the pyrolysis conditions. A similar phenomenon is seen for phenol and ethylphenol formation, which also constitute the major products of the fractional pyrolysis.

To account for low energy p-cresol formation during the lower temperature window, the calculations suggested eqs 4.3.1a and 4.3.1b, involving TSa4 (Figure 10). The process starts from isomerization of the **RA1** adduct-radical to form **RA3** intermediate via a small 1,2-OH-migration barrier of activation (eq 4.3.1a); then, **RA3** radical is decomposed to form vinyl alcohol and p-hydroxybenzyl radical (eq 4.3.1b), which is a precursor of the p-cresol.

**RA1** → **RA3** (ΔE° = 25.0 kcal/mol) (4.3.1a)

**RA3** → HOCH2H2CH2• + CH2==CHOH

(ΔE° = 20.1 kcal/mol) (4.3.1b)

HOC6H4CH2• + H*(RH) → HOCH6H4CH2 (+R•) (4.3.2)

A potentially relevant higher energy unimolecular stepwise process (eqs 4.1.6a and 4.1.6b) involves an initial isomerization of the p-CMA to form p-hydroxybenzyl-oxirane, which is further decomposed to form ketene and HOCH2H2CH2• radical. This is likely to explain the origin of the second (smaller intensity) peak of the p-cresol formation at higher temperatures in Figure 4a.

p-CMA → p-Hydroxybenzyl-Oxirane

(ΔE° = 63.0 kcal/mol) (4.1.6a)

p-Hydroxybenzyl-Oxirane → HOCH6H4CH2• + CO

(ΔE° = 30.5 kcal/mol) (4.1.6b)

The generated hydroxybenzyl radical HOCH6H4CH2• can further add-up a hydrogen atom to form p-cresol. Note also that direct decomposition of the hydroxybenzyl radical HOCH6H4CH2• feasibly forms para-quinoine methide (p-QM) and regenerates an H atom (NB! this important propagation channel is brought to our attention by one of the reviewers). The process is endothermic only by ca. 25 kcal/mol. These two channels, viz., an entropically favored but somewhat energy demanding unimolecular dissociation and entropically unfavored but barrierless bimolecular addition reaction, will compete depending on temperature and pressure. H-abstraction from an H-donor by hydroxybenzyl radical to form p-cresol also is a viable option to be considered. A future kinetic analysis based on the PES results provided here could clarify the branching ratios.

**Phenol** is the second abundant low-T product (ca. 10.5% at 425 °C and 19% at 350 °C, Table 1 and Table S1, respectively).
A small increase in temperature considerably reduces its yield. In analogy with p-cresol, two distinct mechanisms can be operating at low and higher energy regions, respectively. However, as opposed to the p-cresol, the second peak in Figure 4a is fairly large, which suggests a higher rate reaction to form phenol at corresponding temperatures.

We have identified several channels to plausibly form p-hydroxyphenyl radical HO\textsubscript{C}H\textsubscript{4}—the precursor of phenol. A plausible channel for lower temperature phenol formation involves decomposition of the chemically activated adduct-radical RA\textsubscript{1} via a TS\textsubscript{A1} barrier, followed by the elimination of the 1-propenol fragment (eq 4.3.4).

\[
\text{RA\textsubscript{1} \rightarrow HOCH\textsubscript{2}CH\textsubscript{2}OH (} \Delta E^\ddagger = 39.8 \text{ kcal/mol) (4.3.4)}
\]

This chemically activated process encounters an overall barrier only somewhat exceeding the energy of the entrance channel (Figure 10). As a simple defragmentation reaction, it is also favored entropically.

A higher energy mechanism involves decomposition of the R(C\textsubscript{9}) primary radical via a small barrier of 27.8 kcal/mol to form an O-linked radical (eq 4.2.1a), followed by the more energy demanding decomposition to vinyl alcohol and p-hydroxynaphthalenoidal (eq 4.2.1b). This pathway is highlighted in green in Figure 9.

\[
\text{R(C\textsubscript{9}) \rightarrow HOCH\textsubscript{2}CH\textsubscript{2}(CHCHO)* (} \Delta E^\ddagger = 27.8 \text{ kcal/mol) (4.2.1a)}
\]

Even though a direct formation of R(C\textsubscript{9}) radical via homolytic cleavage of the weakest in R(C\textsubscript{9})—H skeletal bond has BDE = 70.7 kcal/mol (Figure 8), it can effectively be formed through secondary reactions.

The formation of an O-linked radical is supported by our cryogenic trapping experiments combined with theoretical analysis of the g-factors for model radicals \textsuperscript{15,49} (section 3.2). To be registered in our experimental conditions, the O-linked intermediate radical is expected to be relatively stable. The calculations, indeed, showed that further dissociation of the HOCH\textsubscript{2}CH\textsubscript{2}(CHCHO)* radical faces a considerably higher barrier of activation (\Delta E^\ddagger = 44.1 kcal/mol, Figure 9). Such a rate-determining step in the overall process could perfectly also explain the origin of the second peak in T-dependent phenol formation in Figure 4a at a relatively higher temperature range of 500–700 °C.

An alternative pathway (eqs 4.2.2a and 4.2.2b). A somewhat similar decomposition of the R(O\textsubscript{9}) radical occurs via generation of HO—PhCH\textsubscript{2}CH\textsubscript{2}CH\textsuperscript{*} (Figure 9), with a somewhat lower barrier of activation for the first step.

\[
\text{R(O\textsubscript{9}) \rightarrow p-HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsuperscript{*} + CH\textsubscript{2}OH (} \Delta E^\ddagger = 24.5 \text{ kcal/mol) (4.2.2a)}
\]

\[
p-HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsuperscript{*} \rightarrow p-HOCH\textsubscript{2}H\textsubscript{4} + C\textsubscript{2}H\textsubscript{2} (} \Delta E^\ddagger = 44.0 \text{ kcal/mol) (4.2.2b)}
\]

Again, the second step decomposition (now for the carbon-centered intermediate HO—PhCH\textsubscript{2}CH\textsuperscript{*}) faces almost the same magnitude barrier as above (44.0 kcal/mol), to justify its relevance at higher temperatures.

4-Ethylphenol is also a major product with somewhat increasing yields with temperature (10.5% at 350 °C and 11.8 at 450 °C). It can be formed from both RB\textsubscript{1} and RA\textsubscript{1} radical-adducts via two low temperature pathways (eqs 4.3.5a and 4.3.5b) and (eqs 4.3.6a and 4.3.6b), involving a common intermediate RA\textsubscript{2} \equiv RB\textsubscript{2}, and sequence of the transition states TS\textsubscript{B3}–TS\textsubscript{B4} and TS\textsubscript{A2}–TS\textsubscript{A3}, respectively (Figures 10 and 11). The radical intermediate is further stabilized to form 4-ethylphenol (eq 4.3.7).

\[
\text{RB\textsubscript{1} \rightarrow RB\textsubscript{2} (} \Delta E^\ddagger = 26.6 \text{ kcal/mol) (4.3.5a)}
\]

\[
\text{RB\textsubscript{2} \rightarrow HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} + CH\textsubscript{2}O (} \Delta E^\ddagger = 14.5 \text{ kcal/mol) (4.3.5b)}
\]

\[
\text{RA\textsubscript{1} \rightarrow RA\textsubscript{2} (} \Delta E^\ddagger = 29.0 \text{ kcal/mol) (4.3.6a)}
\]

\[
\text{RA\textsubscript{2} \rightarrow HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} + CH\textsubscript{2}O (} \Delta E^\ddagger = 14.5 \text{ kcal/mol) (4.3.6b)}
\]

\[
\text{HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} + H* (RH) \rightarrow HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} (+R* (4.3.7))}
\]

4-Vinylphenol (aka, 4-hydroxystyrene, HO—C\textsubscript{9}H\textsubscript{4}—CH═CH\textsubscript{2}) is a potential product that is not detected in our fractional pyrolysis experiments (see section 3.1). Instead, at medium temperatures (500–700 °C, Figure 5b), we observed the formation of significant amounts of unsubstituted styrene (the results at 900 °C are provided in Figure S2, Supporting Information). On the other hand, the 4-vinylphenol constitutes one of the most abundant products of the conventional pyrolysis even at lower temperatures (400 °C),\textsuperscript{47} little less than that for the predominantly formed hydrogenated p-CMA.

Notably, a significant amount of hydrogenated p-CMA was also observed in our fractional pyrolysis conditions (6.2% at 350 °C, Table S2), which implies operation of a plausible hydrogenation channel at low temperatures (see section 4.3).

The theoretical calculations suggested at least two pathways for 4-vinylphenol formation under mild conditions. A direct pathway described in Figure 11 (eq 4.3.8a) passes through decomposition barrier TS\textsubscript{B2}, and generates hydroxymethyl radical, C\textsubscript{9}H\textsubscript{4}OH, which further decomposes to form a H atom, to continue the chain reactions (eq 4.3.8b).

\[
\text{RB\textsubscript{1} \rightarrow HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} + C\textsubscript{9}H\textsubscript{4}OH (} \Delta E^\ddagger = 32.3 \text{ kcal/mol) (4.3.8a)}
\]

\[
\text{C\textsubscript{9}H\textsubscript{4}OH \rightarrow CH\textsubscript{2}O + H* (BDE = 31.2 kcal/mol} (4.3.8b)
\]

The second plausible pathway described above (eq 4.2.2a) involves formation of the p-hydroxyphenyvinyl intermediate via unimolecular decomposition of R(O\textsubscript{9}) primary radical.

A significantly higher energy concerted decomposition of p-CMA reagent (Figure 7) can also contribute to the product balance of the 4-vinylphenol at high temperatures.

\[
p-CMA \rightarrow HOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} + CH\textsubscript{2}O (} \Delta E^\ddagger = 65.3 \text{ kcal/mol) (4.1.1)}
\]
4-(2-Propenyl)phenol (HOC₆H₄CH₂CH═CH₂), frequently known as 4-allylphenol, is a natural phenylpropene called *chavicol*, observed in significant amounts in our experiments: 10.10% at 350 °C and 2.4% at 450 °C. Figure 10 provides a feasible concerted pathway for its formation (eq 4.3.3). Importantly, this pathway generates a OH-radical through a plausible decomposition of RA1 radical-adduct.

\[
\text{RA1} \rightarrow \text{HOC}_6\text{H}_4\text{CH}_2\text{CH}═\text{CH}_2 + \cdot\text{OH} \\
(\Delta E^\ddagger = 28.4 \text{ kcal/mol}) \tag{4.3.3}
\]

### 5. CONCLUSIONS

*para*-Coumaryl alcohol (p-CMA) is the simplest lignin precursor and structural model of the lignin end groups containing a propanoid side chain and phenolic OH group, and its thermal decomposition can shed light onto the thermolysis mechanisms of the intricate lignin macromolecules, particularly the alkylation of monophenols produced during lignin pyrolysis.

The System for Thermal Diagnostic Studies along with DFT analysis of the potential energy surfaces demonstrated that the pyrolysis of p-CMA has a rich low and moderate temperature chemistry involving a variety of elementary reactions identified in this work. The simple phenolics, p-cresol, phenol, ethyl-, propyl-, propenyl-, and dimethyl phenols, are the major products of the *fractional* pyrolysis of p-CMA, predominantly formed at low temperatures (<500 °C), and can constitute over 70% of the total balance of the gas-phase products. A significant amount of benzaldehydes and benzofurans as well as a quantity of more branched molecules are also formed to demonstrate the possibility of the free-radical reactions at low temperatures. However, the radical mixtures, predominantly consisting of O-centered and O-linked radicals, were only detected at temperatures above 500 °C using the LTMI-EPR cryogenic trapping technique.

Various interface and condensed-phase processes could well initiate the low temperature radical reactions during the *fractional* pyrolysis since a solid reagent continuously present in the reaction zone, unlike the LTMI-EPR experiments that utilize a vaporized p-CMA reagent.

To pave a theoretical background, a comprehensive PES analysis is performed. Three types of mechanisms are considered to contribute to the low-temperature products formation: (a) concerted (or stepwise) unimolecular decomposition of p-CMA reagent, (b) bond homolysis in p-CMA to form primary radicals, and their further unimolecular (concerted or homolytic) decomposition, and (c) rapid secondary processes involving open-shell intermediates and radical-chain reactions.

A number of relevant pathways are identified on the PES of the p-CMA molecule and its primary (formed from bond homolysis) and secondary (H-addition adduct) radicals. The secondary radical processes are suggested to be responsible for the low-temperature formation of the major phenolics, which contain saturated (“hydrogen-rich”) side chains, as opposed to the “hydrogen-leak” reagent containing an unsaturated bond in the side chain. Formation of the chemically activated H-addition radical-adducts, and their unimolecular decomposition, is suggested to be the main source of the major products p-cresol, phenol, ethylphenol, propylphenol, 4-allylphenol, as well as 4-vinylphenol, which has also been abundantly observed during conventional pyrolysis by Akazawa et al.⁴⁷

PES analysis suggested that the concerted molecular and radical pathways are likely to occur only at higher temperatures. The most competitive unimolecular decomposition channel leads to the phenol formation via the most favored primary radical R(C9) formed from homolysis of the weakest C(γ)−H bond in the p-CMA. A low-energy first step generates an O-linked radical intermediate, followed by its decomposition through a considerably higher energy barrier. This scenario perfectly explains the phenol formation observed in this work during a second temperature window (500−700 °C)—second peak in T-dependent product yields. The first low-temperature window (300−500 °C) is assigned to the chemically activated reactions. Operation of the second mechanism and formation of the relatively stable O-linked radical intermediate (allowing its EPR detection in cryogenic conditions) are consonant with our current and previous interpretation of the radical mixtures trapped during pyrolysis of the p-CMA and CmA (section 3.2).

A (pressure, temperature)-dependent kinetic analysis on the system with comparison to experimental results will provide more quantitative insight into the reaction mechanisms, and hence, development of the fundamentally based detailed kinetic models based on the identified in this paper reaction network is essential.

Since the yields of a small set of phenolics in low temperature *fractional* pyrolysis constitute as high as 70% of the total gas-phase products, the experimental approach employed in this paper can also have a certain practical importance. A detailed investigation of the intermediate solid-state residues separated from the reaction zone is needed to comprehend the role of solid surfaces and condensed-phase radical processes.

Finally, an identified plethora of the radical reactions of the simplest lignin precursor p-CMA (one of the three main lignins) can shed light onto the radical-polymerization processes responsible for the formation and whole structural diversity of the lignin feedstocks in Nature.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b01656.

Figures and tables showing the system for gas-phase pyrolysis, GC/MS species analysis, molecular structures of major compounds, products formed from p-coumaryl alcohol fractional pyrolysis, and geometries of stationary points on PES and the full citation for ref 75 (PDF)

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