Radicals and Molecular Products from the Gas-Phase Pyrolysis of Lignin Model Compounds. Cinnamyl Alcohol

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ABSTRACT

The experimental results on detection and identification of intermediate radicals and molecular products from gas-phase pyrolysis of cinnamyl alcohol (CnA), the simplest non-phenolic lignin model compound, over the temperature range of 400-800 °C are reported. The low temperature matrix isolation - electron paramagnetic resonance (LTMI-EPR) experiments along with the theoretical calculations, provided evidences on the generation of the intermediate carbon and oxygen centered as well as oxygen-linked, conjugated radicals. A mechanistic analysis to explain formation of the major products from CnA pyrolysis; cinnamaldehyde, indene, styrene, benzaldehyde, 1-propynyl benzene, and 2-propenyl benzene is performed based on the density functional theory evaluated bond dissociation patterns and unimolecular decomposition pathways involving dehydrogenation, dehydration, 1,3-sigmatropic H-migration, 1,2-hydrogen shift, C-O and C-C bond cleavage processes.

Key words: Renewable fuel, biomass, EPR, spin trapping, theoretical calculations

1. Introduction

The renewable lignocellulosic biomass is a major alternative source of the fuel and chemicals benefitting from its vast abundance, economic efficiency, and CO₂-neutral features.[1-3] One of the main components of biomass, lignin, is an amorphous, three dimensional branched polyphenolic polymer, being synthesized via dehydrogenative polymerization of the three key cinnamyl alcohol-based monomers: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.[1, 4, 5] The pyrolysis of lignin coupled with various analytical and spectroscopic methods have been used over decades to get insight into the mechanism of its thermal decomposition.[2, 6-9] The distribution and chemical composition of the obtained condensed pyrolysates (primarily phenolic monomers and oligomers) have been found to be largely dependent on the reaction temperature, residence time, heating ramp, reactor types and biomass composition.[10-13]

The competing bond-cleavage channels (α - and β - alkyl-aryl ether, C-C, C-O and C-OCH₃ bond scission), and various hydrogenation and hydrogenolysis processes, along with the molecular and free radical decomposition pathways, have been suggested to be the major elementary processes in the thermal decomposition of lignin and formation of functional groups.[2, 14-16] Some of these processes are expected to play also a significant role in bio-oil conversions. However, the nature of lignin, induced by its complex structure, high molecular weight and complex compositional proportions of the cinnamyl alcohol-based monomers, are the main reasons that the intricate pathways of lignin pyrolysis still remain unexplored, in spite of their importance in potential biomass formation and practical applications.[1] Therefore, the investigation on pyrolysis of relevant model compounds is prompted as a constructive approach to disclose the complex nature of the lignin thermal decomposition.

Herein, we studied the pyrolysis of the simplest non-phenolic lignin model compound - cinnamyl alcohol (CnA) (Fig. 1), which provides the main features of the basic lignin precursor monomers: *p*-coumaryl, coniferyl and sinapyl alcohols.

The main focus of this work is the detection and identification of the intermediate radicals generated during the pyrolysis of CnA using the advantages of the low temperature matrix isolation -electron paramagnetic resonance (LTMI-EPR) technique.[17] Furthermore, we provide the experimental results and density functional theory (DFT) analysis of the possible decomposition pathways of CnA to form major molecular products; cinnamaldehyde, indene, styrene, benzaldehyde, 1-propynyl benzene, and 2-propenyl benzene. DFT results discussed in Sect. 3.4, are based on the detailed examination of the various cross-sections of the potential energy surface (PES) of the CnA involving skeletal and peripheral bond dissociation, as well as various isomerization reactions.

2. Materials and Methods

2.1. Materials

The CnA (98% purity) and PBN (N-tert-butyl nitron, minimum 98% GC) were purchased from the Sigma Aldrich, Inc. Ultra-high purity helium (99.99%) was used as a carrier gas. A stock solution of 0.01 M CnA in acetone was used for pyrolysis experiments.

2.2. Experimental Protocol for Pyrolysis

The pyrolysis of CnA was investigated in the temperature range of 400-800 °C, with 100 °C increment using the system for thermal diagnostic studies (STDS), as illustrated in Figure S1.[18, 19] The pyrolysis was conducted in an electrically heated micro-furnace, using a straight tubular, isothermal flow quartz reactor (3.8 mm i.d.; 77.6 mm in length). A temperature controller (CN78000, Omega) was used to adjust the furnace temperature precisely. The micro-furnace was placed inside an Agilent 6890N gas chromatograph (GC) to keep the temperatures of the transfer lines (1 m × 0.53 mm) and connections at 250 °C to avoid condensation of the effluents.[2] The residence time was maintained at 0.2 s by adjusting the gas flow rate to reduce the potential risks of secondary reactions. For each experiment, 5 µL CnA sample (0.01 M in acetone) was injected

into the GC injector port by a syringe. Initially the port was purged with helium for 3 min at 80 °C to sweep the acetone solvent out, and then programmed from 80 °C to 250 °C with the heating ramp of 30 °C/min to ensure the constant concentration of gas-phase sample vaporizing into the reactor. In order to achieve the reproducibility of major products from pyrolysis, all the data were the averaged values of two to three runs. In addition, blank experiments were performed to confirm no residues were detained in the system.

2.3. GC/MS Analysis of Pyrolysis Products

The pyrolysates emerging from the reactor were condensed on the head of the GC capillary column at -60 °C to cryogenically capture the products. The gas chromatography/mass spectroscopy (GC/MS) consisted of an Agilent 6890N gas chromatography coupled with a 5973N mass selective detector (MSD). A DB5-MS capillary column (30 m × 0.25 mm × 0.25 µm) was used to separate and analyze the molecular products. The split mode was used with a ratio of 10:1. The temperature of the oven was programmed from the initial value of -60 °C (5 min hold) followed by a heating rate of 15 °C/min to 130 °C (1 min hold) and then heated at a ramp of 25 °C/min to 300 °C (5 min hold). The temperatures of GC injector and MSD detector were set as 240 and 280 °C, respectively. Total ion current mode (TIC) was used to quantify the products from CnA pyrolysis with a mass range of 15-600 amu. The products were identified based on the NIST library (NIST 98 version 1.6d) and the retention time of the individual compounds.

2.4. EPR Measurements.

A technique referred to in the literature as LTMI-EPR, was used in this study.[20-24] LTMI-EPR allows accumulation and detection of trace quantities of radicals during the gas-phase processes. An electrically heated reactor interfaced to a liquid nitrogen-cooled Dewar located in

the cavity of an EPR spectrometer was used for the pyrolysis of CnA. Reagents were pumped using rotary pumps at a pressure of <0.3 torr through the electrically heated pyrolysis zone. Due to the high boiling point of CnA, the vaporizer was held at room temperature. The carbon dioxide carrier gas was used as a supporting matrix to assist in the freezing of radicals. The details of cryogenic trapping of radicals at low pressures can be found elsewhere.[17]

To further explore the nature of free radicals, a solid phase (*N*-*t*-butyl- α -phenylnitron, PBN) spin trapping technique was used at pyrolysis temperature of 800 °C. [25-27] Approximately 20 mg powdered PBN was placed in the center of an EPR 4 mm quartz tube (hold from both sides by quartz wool) connected to the CnA pyrolysis vacuum line and located at the center of the EPR cavity. The N₂ carrier gas was saturated by CnA vapor, entered into the pyrolysis zone at total pressure ~0.3 torr, and then passed through the tube loaded with solid PBN. The EPR signal was appeared in 5 minutes (*vide infra*, Fig. 4).

The EPR spectra were recorded on a Bruker EMX-20/2.7 EPR spectrometer (Bruker Instruments, Billerica MA) with dual cavities, X-band (100 kHz) and microwave frequency at 9.516 GHz. The typical parameters were: sweep width 200 G, EPR microwave power from 0.5 to 64 mW, modulation amplitude ≤ 4 G, and time constant and sweep time in most cases were 10.24 ms and 167.77s, respectively.

The dimensionless magnetic moment of a radical, g-factor (*a characteristic value which measures how the magnetic environment of unpaired electrons differ from that of a free, gas-phase electron*, $g = 2.0023$) was calculated using Bruker's WINEPR program, which is a comprehensive line of software, allowing control of the EPR spectrometer, data-acquisition, automation routines, tuning and calibration on a Windows-based PC.[28] The exact g-values for key spectra were determined by comparison with a 2, 2-diphenyl-1-picrylhydrazyl (DPPH)

standard. In some experiments, gradual warming of the Dewar was employed to allow annealing of the matrix and annihilation of mobile or reactive radicals. This resulted in cleaner, sharper spectra of single radicals under environmentally isolated conditions.

2.5. Computational Details.

Various decomposition pathways of CnA and relevant intermediates were computed using non-local Kohn-Sham density functional theory based on the generalized gradient approximation. The hybrid B3PW91 functional[29, 30] is employed in conjunction with the moderate Pople-type basis set 6-31+G(2d,p) augmented with diffuse and polarization functions.[31] This method is well tested in literature, and has also been evaluated in our previous studies on open-shell systems.[32, 33] All quantum mechanical calculations are performed using Gaussian 03 software[34] to obtain optimal equilibrium geometries and transition states verified by vibration mode analysis. The energetic diagrams are based on electronic energies corrected with zero-point vibrational energies. Gibbs free energies at different temperatures are also provided, wherever a temperature dependence of the selected reactions is analyzed (see Tables S3 and S4 in Supporting Information).

3. Results and Discussion

The LTMI-EPR is a powerful tool for *in situ* exploration of radical processes.[17] However, the identification of trapped radicals in some cases is challenging when a combination of two or more species are involved. The apparent g-value (the maximum point of the integrated curve), in particular, does not provide a conclusive structural information when the EPR spectrum is a convolution of two or more species. The radical constituents of a mixture can only be

distinguished through a judicious variation of the experimental conditions (temperature, pressure, and annealing parameters, etc.) followed by computer analysis of the digitally stored spectra. Such a procedure as well as an auxiliary – spin trapping experiments were employed here to simplify the interpretation on the EPR spectra of gas-phase radicals trapped from CnA pyrolysis over the wide temperature range.

3.1. Radicals from Pyrolysis of CnA at 400 to 800 °C

A strong anisotropic EPR signal was detected from the gas-phase pyrolysis of CnA during the entire temperature range of 400 to 800 °C, Figs. 2a and 2c.

The anisotropy is generally caused by the superposition of two or more spectra, easily seen in annealing experiments reported elsewhere.[17, 35] However, no drastic changes in EPR spectra have been detected here during the annealing experiments at liquid nitrogen temperature. It is apparent that the radicals detected from high temperature pyrolysis of CnA (at 800 °C, Fig. 2c, d) are more persistent based on the fact that g-value remains unchanged up to 240 s of annealing time, while the radicals collected from the pyrolysis at 500 °C annihilated easily at 180 s, Fig. 2a, b.

The persistent radicals at 800 °C most probably are O-centered which are more resistant to self-recombination than carbon centered radicals [36-38] and hence stable to annihilation (Fig. 2d). Whereas the carbon-centered counterparts are readily annihilated (Fig. 2b) and perhaps dominate at low temperatures of pyrolysis (*vide infra*). The g-value undergoes significant changes during the annealing processes from 2.0085 to 2.0060 at 500°C, and from 2.0096 to 2.0045 at 800 °C, indicating possibly, the existence of the mixture of different radical species.

Another candidate to explain the anisotropy of the observed EPR spectra could serve the alkylperoxy radical (RO₂) readily formed in the presence of trace amounts of oxygen[39] and

described by a high g-value between 2.008 and 2.010.[39, 40] However, the formation of RO₂ traces was ruled out based on the power dependence experiments, Fig. 3. Namely, the EPR signal for radicals from CnA pyrolysis is saturated at low (< 10 mW) microwave power (Fig. 3), whereas RO₂ radicals from gas phase oxidation of simple hydrocarbons are saturated at microwave powers as high as 40 mW.[41] The fact that the saturation behavior of radicals collected at pyrolytic temperatures of 500 °C and 800 °C are somewhat different, Fig. 3, provides an additional evidence on the mixed character of the spectra. The last statement is in full accord with the theoretical results discussed later in the text.

3.2. Spin Trapping Experiments.

The EPR spectrum presented in Fig. 4 obtained from the spin trapping experiments consists of six lines. The hyperfine splitting constants ($\alpha^N = 13.8$ G and $\alpha^H = 2.18$ G) obtained for the PBN-radical adduct were closer to the values reported for the oxygen-centered radicals (RO $\cdot$: $\alpha^N = 13.6$ G, $\alpha^H = 1.56$ G; RO $\cdot$ + ArCO₂ $\cdot$: $\alpha^N = 13.9$ G, $\alpha^H = 2.00$ G), than the carbon-centered radicals (R $\cdot$: $\alpha^N = 15.2$ G, $\alpha^H = 3.85$ G).[42, 43] Note that the EPR spectra presented in Fig. 4 were only detected in oxygen free vacuum system.

A spectrum with 3 broad lines and characteristic peaks of adsorbed oxygen was detected in the presence of traces of oxygen, Figure S2 (Supporting Information). Further pumping down the system to 10⁻³ torr regenerates the signal in Fig. 4, when the oxygen peaks disappeared.

These experimental findings indicate that the anisotropy of the EPR signals detected during the CnA pyrolysis, can clearly be assigned to oxygen-centered radical(s).

3.3. Molecular Product Analysis.

The overall effect of the pyrolysis temperature on the distribution of primary products is illustrated in Fig. 5. The pyrolysis products, mainly aromatic and oxygenated aromatic

hydrocarbons are listed in Table S1 (Supporting Information) and further categorized into two groups: the major products, including cinnamaldehyde, indene, styrene, benzaldehyde, 1-propynyl benzene, 2-propenyl benzene, and minor products, with the proportion less than 1% in total TIC count, i.e., benzene, ethyl benzene, phenylacetylene and methyl benzene.

The dominance of the cinnamaldehyde over other products (more than 50% of total products) was observed at low temperature, 400 °C. A drastic decrease of its proportion of the total products (from 74% to 16%) was observed when the temperature increased from 400 °C to 700 °C. The proportions of cinnamaldehyde and benzaldehyde are initially increased with temperature, achieving the maximum of 10% and 7% at 600 °C, respectively, and then declined with further enhancement of the temperature. Thus, the major low-temperature product is cinnamaldehyde and its content gradually exhausted at 800°C. Except for indene, with traces at 400 °C, all other products are formed at elevated temperatures.

In the category of aromatic hydrocarbons, the benzene, 2-propenyl- and 1-propynyl- benzene, show the variation tendency similar to those observed for cinnamaldehyde and benzaldehyde, and approached the maxima at 600 °C, whereas the indene and styrene exhibited maxima at 700 °C. Further deoxygenation of CnA and newly formed cinnamaldehyde is prevailed at higher temperatures, leading to the formation of the hydrocarbon pyrolysates such as styrene, 2-propenyl benzene, and 1-propynyl benzene. In addition, the indene is formed, perhaps via a dehydration of CnA followed by spontaneous cyclization of adduct, *vide infra*.

3.4. Potential Energy Surface (PES) Analysis

Generally, the pyrolysis of systems similar to those considered in this paper is expected to involve various bond dissociation and unimolecular transformation channels, including

hydrogenation, dehydrogenation and hydrogenolysis of the skeletal C-C and C-O bonds.[16, 44]
 Here, we discuss some relevant pathways to form experimentally observed main products based
 on the calculated potential energy profiles and bond dissociation patterns. Some secondary
 processes are also considered and described during the discussion on the possible pathways to
 primary products.

3.4.1. Molecular Pathways to Primary Products

Theoretically explored unimolecular decomposition and isomerization pathways (selected
 cross-sections of the PES) for CnA to potentially form experimentally identified major products

are illustrated in Fig. 6 and described by

dehydration/cyclization and 1,3-H-migration reactions of CnA, respectively.

No direct single-step pathways are identified to form two other products 2-propenyl benzene
 (2-PBz) and benzaldehyde (BzAld). Instead, two additional transition states are located on the
 respective PES involving 1,3-sigmatropic H- and 1,3-sigmatropic OH-migration processes,
 which generate two isomeric hydroxyl-derivatives of CnA via reactions (4) and (5), respectively.
 Note that these two isomerization processes are entropically less favored compared to the
 defragmentation of CnA via reactions (1) - (3), *vide infra*.

As expected for molecular reactions, all calculated decomposition barriers are fairly high and
 can be afforded only at elevated temperatures. Due to the entropy gain from the fragmentation of

molecules, the unimolecular channels (1) – (3) can principally account for the formation of the experimentally observed primary products, styrene and indene.

However, according to theory, the cinnamaldehyde, which also is the dominant low-temperature pyrolysis product of CnA (Fig. 5), cannot be formed via a straightforward dehydrogenation, since its barrier is significantly higher than those for other products generated at even higher temperatures (*cf.* Fig. 6). The electronic energy barrier is 79.0 kcal/mol, whereas the enthalpy of activation at room temperature is somewhat lower at 78.8 kcal/mol (the enthalpy diagram is provided in Figure S3, Supporting Information). Due to the entropy loss at TS, the Gibbs free energy of activation at the same temperature is 80.1 kcal/mol, and increased to 83.2 kcal/mol at 527 °C (Table 3, Supporting Information). The initially endergonic by 2.91 kcal/mol reaction (1) becomes exergonic (thermodynamically preferred) starting from about 327 °C, as follows from corresponding Gibbs free energies presented in Table S4.

Notably, no typical hydrogenation and hydrogenolysis products of CnA, such as the hydroxy-propyl benzene ($\text{C}_6\text{H}_5\text{-CH}_2\text{CH}_2\text{CH}_2\text{OH}$) and β -methyl styrene ($\text{C}_6\text{H}_5\text{-CH=CH-CH}_3$), respectively, are seen during gas-phase pyrolysis, as opposed to that obtained in Pd/Al₂O₃-catalyzed CnA decomposition processes.[45] This could suggest that dihydrogen product is liberated insignificantly *viz.*, the dehydrogenation of the CnA reactant occurs inefficiently in gas-phase pyrolysis.

Thus, the dominant formation of cinnamaldehyde at low temperature (400 °C), cannot be merely explained by direct dehydrogenation of CnA (reaction 1), but it most likely occurs via secondary processes involving the radical intermediates, as will be advocated in the next section. Formation of some other products, such as styrene, benzaldehyde and ethylene also can be explained via radical reactions, which generally require lower activation energies and can occur

at low and moderate temperatures.

It should be emphasized that the intrinsic barrier from *cis*-CnA is somewhat lower at $\Delta E^\ddagger = 69.0$ kcal/mol, compared to the relative energy of TS1 in regard to the entrance channel indicated in Fig. 6. However, the formation of indene via dehydration (reaction 2) requires an initial isomerization of the cinnamyl alcohol reactant to *cis*-CnA, since it predominantly exists in more stable (by 3.1 kcal/mol) *trans* configuration. Thus, formation of the *cis*-CnA will be accelerated with temperature, and could also contribute in explaining why the indene yield reaches a maximum value at higher temperatures (700 °C, Fig. 5). The Gibbs free energy analysis shows that the temperature enhancement does not affect the free energy barrier ($\Delta G^\ddagger$) for this reaction (2) due to the insignificant entropy loss at TS, as opposed to those seen for other pathways (Table S4). Moreover, this decomposition reaction is exergonic even at room temperature ($\Delta G_{\text{rxn}} = -17.93$ kcal mol⁻¹), whereas the other decomposition reactions become exergonic only at elevated temperatures (*cf.* Table 4).

The unimolecular reaction (3), leading to the elimination of formaldehyde from CnA, could partly explain also the styrene formation at high temperatures ($\Delta E^\ddagger = 67.1$ kcal/mol, Fig. 6). Note that the formaldehyde is one of the major light products in the gas fraction of the lignin pyrolysis.[7] Our preliminary analysis shows that a radical pathway can be involved in the styrene production to explain the higher content of the styrene at 700 °C. The same process may occur with 1-propynyl benzene.

A possible rearrangement of the γ -hydroxy-propenyl benzene (γ -HPBz) formed from 1, 3-sigmatropic H-migration in CnA (reaction 4) via a barrier of 72.3 kcal/mol (see, Fig. 6), can potentially generate 2-propenyl-benzene radical ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{C}(\text{H})^\bullet$). However, dissociation energy of hydroxyl group of γ -HPBz is fairly high at 93.8 kcal/mol. Perhaps, a bimolecular OH-

abstraction reaction could contribute to the further formation of the significant amounts of 2-propenyl-benzene (Fig. 5).

Similarly, dehydration of 3-phenyl-1-propanol ($C_6H_5CH_2CH_2CH_2OH$) could serve as a possible channel to generate the observed 2-propenyl-benzene (2-PrBz). However, the lack of the main hydrogenation adduct 3-phenyl-1-propanol in gas-phase processes (*vide supra*), which is

suggests that the concentration of dihydrogen or a suitable hydrogen donor is marginal, and thus, this pathway also is less likely to occur in gas-phase pyrolysis to generate 2-PrBz.

Reaction (5) describes 1,3-sigmatropic OH-transfer to the C7 center to form α -hydroxy propenyl benzene (α -HPBz, Fig.6). Further H-migration could generate benzaldehyde and ethylene. Benzaldehyde is well presented in pyrolysis products at moderate temperatures (Fig. 5). Activation energy of the unimolecular reaction (5) is well moderate (62.2 kcal/mol), whereas further decomposition of α -HPBz to form benzaldehyde and ethylene via a 1,2-H-transfer (reaction 6), requires higher activation energy of 74.4 kcal/mol.

Due to the small entropy changes between the intermediate and TS, the activation Gibbs free energy remains almost the same as the electronic energy barrier at $\Delta G^\ddagger = 74.43 \text{ kcal mol}^{-1}$. On the other hand, a significant entropy gain occurs during the reaction ($\Delta S_{rxn} = 38 \text{ cal/K.mol}$) to form two product species benzaldehyde and ethylene. Therefore, the temperature enhancement increases the rate of this elementary reaction (6). It should be emphasized that most of the unimolecular decomposition pathways, along with the bond dissociation channels discussed in the next section, generate two product species, and thus are almost equally preferred entropically compared to the isomerization reactions (4) and (5) which are endergonic at reaction operating

temperatures (see Tables S3 and S4).

To summarize, there are a variety of molecular channels to originate primary products, however they are mostly energy demanding and indirect and more feasible pathways should be invoked to explain the low-energy formation of dominant products.

3.4.2. Some Relevant Radical Pathways

The primary radicals during gas phase pyrolysis of CnA can be generated via straightforward bond dissociation channels. Fig. 7 provides the major bond fission channels, involving the C-H, C-O and skeletal C-C bonds, to form CnA-derived primary radicals. The values correspond to electronic energies corrected with zero-point vibrational energies. The corresponding enthalpy and Gibbs free energy diagrams are provided in Figures S5 and S6 in Supporting Information, respectively. Furthermore, these radicals can be generated more feasibly via relevant bimolecular reactions involving available radical pool.

The cleavages of the skeletal C-OH and C(9)-H bonds to form conjugated (*viz.*, stabilized) 1-phenylallyl R(PhA) and hydroxy-phenyl-allyl radicals R(C9), are most favored decomposition processes with bond dissociation energies (BDE) being as low as 66.8 and 69.2 kcal/mol, respectively (Fig. 7). Further transformations of these radicals are *a priori* expected to originate main pathways to the primary products.

Thus, from Fig. 7 clearly follows that the radicals R(PhA) and R(C9) can be dominant species at low temperature pyrolysis of CnA, while the oxygen centered radical R(O•) will prevail at elevated temperatures. The oxygen-centered radicals are known to possess higher g-values, compared to those for carbon-centered ones [17]. The g-value of free electron (2.0023) in such systems is shifted upward by virtue of the heteroatom (in this case, oxygen), which is known to increase the spin-orbit coupling that results in increased g-values.[46, 47].

To distinguish the radical species registered in experiments, some theoretical calculations were performed for g-tensors of key radicals based on the Neese's coupled-perturbed DFT methodology implemented in Gaussian 03 program. [48, 49]

Presented in Table 1 data, indeed, demonstrated that the O-centered CnA-radical R(O•), Fig. 7 generated via cleavage of the C(9)O-H bond, possesses the highest g_{iso} of 2.0159 - 2.0207, depending on the employed method and basis set, whereas isotropic g-values calculated for C-

Table 1. Isotropic g-Values for Intermediate Radicals Calculated at Different DFT Levels

Radical	Notation	g_{iso} ^a				
		B3LYP/ BS-I ^b	B3LYP/ BS-II ^b	B3PW91/ BS-I ^b	B3PW91/ BS-II ^b	B3LYP/ BS-III ^b
$C_6H_5C(H)=C(H)-C(H_2)(O\bullet)$	R(O•)	2.0165	2.0172	2.0159	2.0168	2.0207
C₆H₅CH₂(CHCHO)•	2.0055	2.0056	2.0052	2.0054	2.0063
$C_6H_5C(H)\cdots C(H)\cdots C(H)(OH)$	R(C9)	2.0029	2.0030	2.0029	2.0030	2.0030
$C_6H_5C(H)\cdots C(H)\cdots C(H_2)$	R(PhA)	2.0026	2.0027	2.0026	2.0026	2.0027

^a The g-tensors are calculated as corrections to the free electron value $g_e=2.0023$ ppm using Gaussian 03.³⁰

^b BS-I represents the basis sets 6-31G(d,p); BS-II - 6-311++G(2d,p), and BS-III - the Dunning/ Huzinaga valence double-zeta D 95 basis.³⁰

centered radicals, such as R(C9), is much lower around 2.0029 - 2.0030. The conjugated O-linked radical $C_6H_5CH_2(CHCHO)^\bullet$ possesses an intermediate g-value of *ca.* 2.006. As expected, g-values for highly delocalized C-centered radicals R(C7) and R(C8) are close to the g-value of free electron: 2.0024 and 2.0022, respectively. These data are in accord with conclusions from experimental results discussed above and detailed below.

3.4.3. Dominance of the oxygen-linked radicals at low temperatures

The cryogenic experiments (Figs. 2 and 3) revealed that EPR signals from gas-phase pyrolysis of CnA are characterized by high g-values (>2.008), which indicates the dominance of the oxygen-centered radicals. Direct formation of the most straightforward O-centered radical C_6H_5-

343 CH=CH-CH₂O[•] denoted as R(O[•]), requires higher BDE = 97.5 kcal/mol, as shown in Fig. 7.
 344 Further decomposition of R(O[•]) leads to the low-energy formation of the formaldehyde and
 345 styrene radical ($\Delta E^\ddagger = 25.5$ kcal/mol). This channel could well contribute to the formation of
 346 styrene, but not the one for the low-temperature product cinnamaldehyde.

347 Formation of the dominant product cinnamaldehyde at low-temperature (400 °C), as it occurs
 348 in heterogeneous catalytic reactions (45), cannot be simply explained by direct dehydrogenation
 349 of CnA via reaction (1) due to the high barrier of activation ($\Delta E^\ddagger = 79.0$ kcal/mol, Fig. 6). On the
 350 other hand, the isomerization of the more feasibly formed carbon-centered 3-hydroxy-1-
 351 phenylallyl radical denoted as R(C9) (Fig.7) followed by further H-elimination could provide a
 352 reasonable explanation.

353 Indeed, the PES analysis presented above shows a feasible formation of the R(C9) radical
 354 through a C(9) – H bond scission (BDE = 69.2 kcal/mol). A further rearrangement of this radical,
 355 into an *oxygen-linked* isomeric radical C₆H₅CH₂(CHCHO)[•] (Table 1) via reaction (7) is proven to
 356 be a low energy process illustrated in Fig. 8.

357 Further feasible formation of cinnamaldehyde, as a major low temperature product of
 358 pyrolysis at 400 °C, can either occur via H-atom removal of the generated radical, reaction (8),
 359 with BDE(C7-H) = 37.6 kcal/mol, or via H-abstraction by another radical.

360 The radical C₆H₅CH₂(CHCHO)[•] (referred here as oxygen-linked radical due to a partial
 361 location of the spin density on O-atom) is probably the dominant intermediate in the mixture
 362 registered by EPR at moderate temperatures. DFT calculations demonstrated a $g_{\text{iso}}=2.0051$ -
 363 2.0063 (Table 1) for this radical that combines the terminal oxygen and the proximal (C9) carbon

atoms in one active center, referred to in this paper as O-linked radicals. This resembles the vicinal O-atom effect on g-value of a radical referred in literature as a “carbon centered radical with vicinal oxygen” [47, 50, 51].

In fact, carbon centered radicals (such as R(C9) with calculated $g_{\text{iso}} = 2.0029$, and R(PhA) with calculated $g_{\text{iso}} = 2.0026(7)$) and oxygen-linked $\text{C}_6\text{H}_5\text{CH}_2(\text{CHCHO})^\bullet$ radical with calculated $g_{\text{iso}} = 2.0051 - 2.0063$) are major active species at lower pyrolysis temperatures. Due to the competition of the reactions while increasing of temperature (Fig.7), it is reasonable to expect formation of the mixtures of different radicals (with overlapped, “average” g value) evidencing that the plausible pyrolysis pathways of CnA involve different carbon, oxygen centered as well as oxygen-linked radicals.

Described above dehydrogenation mechanism of CnA can be prevalent phenomenon involving pyrolysis of other natural organic sources. Dehydrogenation of monolignol end groups ($-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$) of the lignin structure, indeed, is known to occur during the pyrolysis of biomass, as well as the pyrolysis of lignin itself [52] and can be explained via the radical-molecular mechanism provided in this work.

Certainly, this mechanism is at variance with the chemical transformation of CnA into cinnamaldehyde, which easily occurs in nature catalyzed by cinnamyl alcohol dehydrogenase (CAD) enzyme,[53, 54] as well as the catalytic conversions of CnA over the typical dehydrogenation catalysts such as $\text{Pd}/\text{Al}_2\text{O}_3$ at moderate temperatures (e.g., 275°C), as particularly shown by Grunwaldt and co-workers. [45]

3.4.4. Other Relevant Radical Pathways to Primary Products.

As indicated above, the straightforward dehydroxylation of CnA to form 1-phenylallyl radical, R(PhA), is the lowest-energy bond dissociation channel ($\text{BDE} = 66.8 \text{ kcal/mol}$) and can

contribute to the formation of the 2-propenyl-benzene (2-PBz). The high delocalization and some reactivity features of this radical have recently been studied by Sebree et al. using DFT-B3LYP and IR-spectroscopy analyses. [55] Intriguingly, it has been suggested to play a potential role in the formation of polyaromatic hydrocarbons (particularly in Titan atmosphere), perhaps due to the ambident nature of its reactivity

The distribution of unpaired electrons in the radicals have long been considered as an index of reactivity to predict the reaction pathways and branching ratios in the homologous series of H-atom abstraction reactions and photochemical processes, as well as for the propagation steps in the radical polymerization processes.[56-60] Similarly, the computed spin densities have been employed to understand the regioselectivity of the radical-radical coupling of the phenoxyl-type radicals by us (37), as well as closely related monolignol radicals by other researchers.[37, 61-66]

The Mulliken population analysis performed in current study, indeed, demonstrated that the two conjugated radical-centers are located at the C7 and C9 atoms of the 1-phenylallyl radical, and thus the radical is stabilized by resonance. Such an ambident radical could further abstract a hydrogen atom via both active C-centers from any H-donor species, such as the well-presented reagent CnA either. A branching can occur to form either 2-propenyl-benzene (also called 3-phenyl-1-propene), or 1-propenyl-benzene (1-phenyl-1-propene) isomers via H-addition to the C7 and C9 active centers, respectively. The higher density of the unpaired electron on C7-center compared to the one on the C9-center (53% vs. 47%) indicates the superior reactivity of the C7-atom of the radical to account for the significant yields of 2-PBz observed in our experiments at 600 °C (Fig. 5).

4. Conclusions

The cinnamyl aldehyde (CnA) constitutes the simplest precursor and structural model of the lignin end-groups and its thermal decomposition can shed a light into the intricate reactions of the biomass formation and pyrolysis. The experimental LTMI-EPR data reported in this paper in conjunction with the DFT-analysis of the possible transformation pathways provided a radical-molecular mechanism for primary product formation during the pyrolysis of CnA. The dominant formation of the cinnamaldehyde at low-temperatures, due to the high barrier of the dehydrogenation reaction in the gas-phase, cannot be explained via straightforward dehydrogenation of CnA, as it feasibly occurs in heterogeneous and biocatalytic reactions. A radical mechanism is invoked based on the analysis of the intermediate radical species detected by EPR spectroscopy using the low-temperature matrix isolation and spin-trapping techniques. The registered open-shell species are suggested to be dominantly containing O-centered radicals, due to the high g-values of the radicals over the range of the studied temperature (400 - 800°C), in full accord with theoretically evaluated isotropic g-values of the respective radicals.

Acknowledgements

This work was funded by National Science Foundation under Grant CBET 1330311. Dr. Lavrent Khachatryan is grateful to Superfund Research Program (#2P42ES013648-03), and Dr. Meng-xia Xu - to RJ Reynolds' Tobacco Company, for partial support. Ruckenstein fund (SUNY Buffalo) is acknowledged by Dr. Rubik Asatryan for continuous support.

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Fig. 1. Molecular structure of cinnamyl alcohol (CnA).

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Fig. 2. Annealing effect on EPR spectra of radicals trapped at 77 K from gas-phase pyrolysis of CnA at 500 °C (a) and 800 °C (c). The g-value and intensity changes at 500 °C (b) and 800 °C (d).

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Fig. 3. Microwave power dependence of the EPR spectra detected at 77 K from CnA pyrolysis at 500 °C and 800 °C.

DI/N value is the double integrated (DI) intensity of the EPR spectrum that has been normalized (N) to account for the conversion time, receiver gain, number of data points, sweep width.

Fig. 4. EPR spectrum of radicals from low pressure gas-phase pyrolysis of CnA at 800 °C trapped by a solid phase spin trapping agent PBN (*N*-*t*-butyl- α -phenylnitrone).

Fig. 5. Product distribution from pyrolysis of CnA at residence time of 0.2s

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Fig. 6. Calculated unimolecular decomposition pathways for CnA. TS notations correspond to the reaction numbering. Total electronic energies (ΔE) are corrected with zero-point vibration energies.

Fig. 7. Calculated bond-dissociation channels for CnA to generate primary radicals. The skeletal radicals are denoted by their core-atom numbers (ref. Fig. 1). R(Sty) and R(PhA) represent the terminal styrene and 1-phenylallyl radicals, respectively.

Fig. 8. Low-energy H-migration profile of R(C9) radical to form a terminal, oxygen-linked $\text{C}_6\text{H}_5\text{CH}_2(\text{CHCHO})^\bullet$ structure (reaction 7).