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Radicals from the gas-phase pyrolysis of a lignin model compound: *p*-coumaryl alcohol[†]

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Abstract

The intermediate radicals produced in the gas-phase pyrolysis of one of the main building blocks of lignin – *p*-coumaryl alcohol (*p*-CMA) – were investigated using the low temperature matrix isolation technique interfaced with electron paramagnetic resonance spectroscopy (LTMI-EPR). An anisotropic EPR spectrum characterized by a high *g*-value (>2.0080) and a relatively low saturation coefficient (~1.40) throughout the high pyrolytic temperature region (700 to 1000 °C) was observed. Theoretical calculations revealed plausible decomposition pathways for *p*-CMA comprising highly delocalized aromatic radicals. The results provide evidence for a dominant role of oxygen-centered radicals during the pyrolysis of *p*-CMA.

1. Introduction

Lignin is a complex natural polymer biosynthesized *via* oxidative coupling of three phenyl propane monomers: *p*-coumaryl alcohol, coniferyl alcohol and synapyl alcohol.^{1,2} As the most abundant aromatic hydrocarbon in nature, lignin is regarded as a promising renewable alternative to petroleum for the production of high-value added materials, fuels and chemicals.^{3–5}

Although the study of lignin pyrolysis dates back to 1965,⁶ the detailed mechanisms of this process still remain unclear, largely due to the complex structure and random composition of lignin.^{2,7,8} Both concerted molecular and radical-chain mechanisms, along with an ionic mechanism in the liquid phase, have been debated in the literature.^{9,10} There is new evidence that the thermal degradation of lignin and its precursors may occur *via* free-radical reaction pathways.^{9,11–15}

Free radicals have been detected in various conditions during the pyrolysis of lignin and its model compounds in the gas phase,^{11,12} bio-oil^{13,14} and biochar media.¹⁶ Kibet *et al.* have identified phenoxy and substituted phenoxy radicals in the gas phase from lignin pyrolysis at 450 °C¹¹ using a well-suited technique of low temperature matrix isolation in conjunction

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with electron paramagnetic resonance spectroscopy (LTMI-EPR).¹⁷ The disproportionation of semiquinone radicals to form quinone and hydroquinone species has been identified by Bährle *et al.* from lignin pyrolysis at 550 °C using EPR spectroscopy.¹² Custodis *et al.* detected phenyl, phenoxy, cyclopentadienyl (CPD) and propargyl radicals generated from diphenylether pyrolysis and *o*-hydroxyphenoxy and hydroxycyclopenta-dienyl radicals generated from guaiacol pyrolysis in the temperature ranges of 650 to 900 °C and 550 to 850 °C, respectively, using the technique of imaging photoelectron photoion coincidence (iPEPICO) with vacuum ultraviolet synchrotron radiation.¹⁵

Due to the complexity, irregularity and unavoidable modification of the lignin structure, investigations of model compounds, especially those representing the building blocks of lignin, have proven to be significant in providing detailed mechanistic insights into the thermal decomposition of lignin.^{9,15,18} Whereas moderate efforts have been made to elucidate the free radical mechanisms of lignin pyrolysis using β -O-4 or α -O-4 model compounds, few studies have been performed on species that bear the cinnamyl alcohol group ($-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$),^{19,20} which is well represented in some synthetic and natural lignin structures.^{21–23}

Recently, we reported a detailed analysis of the decomposition pathways for cinnamyl alcohol (CnA) pyrolysis, which is the simplest precursor and structural model of the lignin end-groups.¹⁸ A radical mechanism combined with molecular pathways has been suggested based on the analysis of the products and the intermediate radical species detected by EPR spectroscopy using the low-temperature matrix isolation and spin-trapping techniques. Density function theory (DFT)-analysis of the isotropic *g*-values of model radicals with high *g*-values detected experimentally support the fact that the observed open-shell species dominantly contain oxygen-centered and/or oxygen-linked radicals. The experimental data in conjunction with the theoretical analysis of the possible decomposition pathways of CnA provided a combined radical-molecular mechanism for primary product formation during the pyrolysis of CnA.

Research on the pyrolysis of *p*-coumaryl alcohol (*p*-CMA), a 4-(3-hydroxy-1-propenyl) phenol (Fig. 1) that contains the cinnamyl alcohol group, is scarce. The majority of publications focus on the biological implications of *p*-CMA, particularly, microbiological formation,²⁴ oxidizing peroxidases,²⁵ biodegradation by *Aspergillus flavus*,²⁶ enzymic dehydrogenation or dehydrogenative polymerization,²⁷ *etc.* It was also suggested that the primary aliphatic hydroxyl group in the allylic side chain of the coniferyl alcohol is a site of transferable hydrogen, and the terminal oxygen-centered radical is suggested to be one of the four radicals that are formed during the thermolysis of coniferyl alcohol.¹⁹ As *p*-CMA has the same allylic side chain as coniferyl alcohol, it is reasonable to believe that a terminal oxygen-centered radical may also form during the gas-phase pyrolysis of *p*-CMA (Fig. 1, structure (e)). In support of this conclusion, a recent theoretical analysis demonstrated that the terminal hydrogen atom is oriented back to the vinyl π -cloud to minimize the interactions between the oxygen lone pairs and the π electrons.²⁸ Note that the dehydrogenation of the end groups in the structure of lignin is a general pathway during the pyrolysis of biomass and lignin²⁹ as well as the gas-phase¹⁸ and catalytic degradation of cinnamyl alcohol.³⁰

Accordingly, the main objective of this study is to detect and identify the intermediate free radicals produced from the gas-phase pyrolysis of *p*-CMA by employing the LTMI-EPR technique and DFT analysis, and to also gain insight into the pyrolysis mechanism of the larger lignin derivatives.

2. Experimental section

2.1. Experimental setup

The system for the gas-phase pyrolysis of *p*-CMA interfaced with LTMI-EPR is depicted in Fig. S1 (ESI†). Briefly, ~10 mg of *p*-CMA (Ryan Scientific Inc.) was loaded into a Pyrex container and vaporized in carbon dioxide carrier gas at a constant temperature of 65 °C in an electrically heated pre-heater. The addition of carbon dioxide as a supporting matrix has been demonstrated to improve the resolution of EPR spectra.¹⁷ The reactant was delivered using a rotary pump at a pressure of 0.01 torr through an electrically heated tubular flow quartz reactor (i.d. = 19 mm, length = 76 mm) operating at a temperature range of 700 to 1000 °C. Upon exiting the reactor, the pyrolysis products were condensed onto the cold finger of a Dewar flask placed in the EPR cavity and cooled by liquid nitrogen (77 K). The linear accumulation of the radical yields vs. time was maintained up to 12 min.

The spectra of the 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 of 9.458 to 9.474 GHz. The EPR registration parameters for the 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. During the microwave power-dependent saturation investigations, the microwave power was changed from 0.50 to 64 mW. A comprehensive Windows-based PC software program, WINEPR, was used to control the EPR spectrometer, perform automation routines and retrieve the EPR spectra.³¹

2.2. EPR measurements

The most important characteristic parameter of an EPR spectrum is the “*g*-value”, often expressed as the baseline crossing of a first derivative of the EPR spectrum. This is an index of difference between the magnetic environment of the unpaired electron and a free, gas-phase electron ($g = 2.0023$). As a rule of thumb for organic radicals, the *g*-value of an oxygen-centered radical ($g = 2.004$) is greater than that of a carbon-centred radical ($g = 2.003$) based on the fact that the closer the unpaired electron to the oxygen atom, the greater the *g*-value.¹⁷ Another important characteristic parameter of an EPR spectrum is the spectral width, often defined as the peak-to-peak distance of a first derivative of the EPR spectrum, H_{p-p} . Variation of the *g*-value and H_{p-p} is indicative of either the existence of different types of radicals or of a significant disturbance in the matrix environment.³² The signal intensity of a trapped radical is also an important characteristic parameter; it is calculated as the double integrated normalized intensity (DI/N) in WINEPR. This accounts for a number

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of variables, such as the conversion time, receiver gain and sweep width. In this study, the DI/N has been normalized by 2,2-diphenyl-1-picrylhydrazyl (DPPH) in each experiment (termed as “DI/N/DPPH”) to minimize additional systematic errors (*e.g.* variations of the surrounding room temperature and humidity) during the EPR experiments.

To conclusively assign the structural information of trapped radicals, judicious variations of the experimental conditions, *e.g.*, pyrolysis temperature, annealing time and microwave power, are needed. Hence, the annealing technique, *i.e.*, gradual warming of the Dewar flask by removing liquid nitrogen, was applied in some experiments to produce cleaner and sharper spectra by selective annihilation of more reactive radicals.^{17,32–38}

2.3. Computational details

Theoretical calculations were performed to obtain the energies for the decomposition of *p*-CMA to form the intermediate radicals. The electronic energies and zero point vibration energies were computed at the M06-2X/6-31G(d,p) level of theory based on initial ground state geometries optimized at the B3LYP/6-31G(d,p) level^{39,40} using the QChem 4.3 quantum chemistry package.⁴¹ The optimal equilibrium geometries have been verified by vibration mode analysis. To identify the radical species registered in the experiments, several theoretical models were constructed for the key intermediates, and the corresponding *g*-tensors were calculated based on Neese's coupled-perturbed DFT methodology.⁴² The lowest energy pathways were considered to generate the dominant radicals, theoretically characterized by their isotropic *g*-factors. Calculations of *g*-factors were performed using unrestricted Hartree-Fock theory, as well as the B3LYP DFT functional in conjunction with the moderate Pople-type basis set, 6-31+G(2d,p), augmented with diffuse and polarization functions.⁴³ These methods are well tested in the literature and have also been evaluated in our previous studies on various open-shell systems.^{18,44}

3. Results and discussion

3.1. Temperature dependence

EPR spectra of the radicals generated during the low-pressure pyrolysis of *p*-CMA in the temperature range of 700 to 1000 °C are depicted in Fig. 2. A partially resolved anisotropic spectrum (with the relative assignments of “Shoulder” and “Central Line” for simplicity purposes) was observed throughout the whole temperature region.

The spectra recorded at higher pyrolytic temperatures tend to have increased complexity due to the additional emerging peaks (*cf.* the spectrum registered at 700 °C, Fig. 2). The same trend was observed earlier in the gas-phase pyrolysis of hydro-quinone (HQ) at 550 to 750 °C and that of catechol (CT) at 600 to 750 °C, indicating the compositional changes of radicals at different temperatures.^{45,46}

Fig. 3A illustrates the temperature dependence of the signal intensity of the trapped radicals from the pyrolysis of *p*-CMA. It can be seen that the intensity of the shoulder remains nearly proportional to that of the central line throughout the temperature range, indicating the relatively stable composition of the major radical(s) in the trapped effluent. Proportionality

does not occur to a certain degree at 950 °C, where the maximum signal intensity is achieved; it coincides with drastic changes in the g -values and H_{p-p} (Fig. 3B).

This implies that a significant change in the radical composition occurs at this temperature.

Overall, the cryogenically trapped radicals exhibit very high g - and H_{p-p} values, ranging from 2.0088 to 2.0101 and from 14.7 to 15.3 G, respectively. This could be a good indication of the prevalence of oxygen-centered radical(s) in the effluent from the pyrolysis of p -CMA.

3.2. Annealing effect

It has been demonstrated in our early publications that by employing the technique of annealing, the spectra of radicals from the gas-phase pyrolysis of HQ,³² CT³⁷ and phenol³⁴ has been greatly improved, such that individual radicals in the mixture could be discerned. The effect of annealing time on the spectra of radicals from the pyrolysis of p -CMA at 1000 °C is presented in Fig. 4.

No apparent changes in the profile occurred up to an annealing time of 180 s, corresponding to a 65% intensity loss compared with the initial profile. Even when the intensity of the spectrum decreases by more than one order of magnitude at an annealing time of 220 s, no drastic change is seen. This indicates that one or more similar types of radicals dominate in the cryogenically trapped mixture. Indeed, during the annealing process, the g -value undergoes large changes from 2.0101 (initial value) to 2.0077 at 220 s (Fig. 4B), illustrating that either a substantial change in the matrix environment or the annihilation of highly volatile radicals has caused a change in the average g value of the EPR spectra.

3.3. Microwave power dependence

Fig. 5 shows the power dependence of the EPR spectra of radicals from the pyrolysis of p -CMA at 850 °C and 1000 °C.

It is notable that as the microwave power decreases, peak A slowly disappears, whereas peaks B, C and D appear and gradually increase. Although we do not have direct evidence here of the existence of one of the favored phenoxy (or substituted phenoxy) radicals, the phenoxy and o -hydroxyphenoxy radicals from diphenylether and guaiacol pyrolysis, respectively, have recently been directly detected by Custodis *et al.*¹⁵ As we will show below, our theoretical calculations also support the formation of phenoxy type radicals (Fig. 1, structure (b)).

The peaks B, C and D (especially at high temperatures, *e.g.*, 1000 °C) can be readily assigned to trace amounts of CPD with decreasing microwave power. It has been experimentally shown in a previous publication⁴⁷ that CPD radicals are easily detected in the high microwave power region (from 0.5 to 64 mW). Note that the characteristic peak D at $g = 1.9932$ (Fig. 5) as well as additional lines appearing on the EPR spectra with increasing pyrolysis temperature (Fig. 2, denoted by asterisks at $g = 1.9932$) are typical for CPD radicals and are validated in the ESI (Fig. S2[†]).

Fig. S3 (ESI†) also shows the EPR spectra differences at pyrolytic temperatures of 850 °C and 1000 °C. It can be seen that for both temperatures, higher microwave power leads to a reduced number of peaks in the central line area. Therefore, the rather complicated power dependence of the EPR spectra in this study strongly indicates the existence of multiple radicals, probably coexisting in trace amounts in the effluent of *p*-CMA pyrolysis.

3.4. Saturation coefficient

Fig. 6 shows a comparison of the power dependence of the shoulder and central lines of the EPR spectra from *p*-CMA pyrolysis at some critical temperatures (a detailed description is provided in Fig. S4 and S5 in the ESI†). It can be seen that the power dependencies of the shoulder and central lines behave similarly at different temperatures. Only slight differences are observed at 950 °C and 1000 °C. This is consistent with the previously observed trends for the corresponding *g*-values, H_{p-p} and signal intensities, which confirms the relatively stable character of the radicals in the effluent.

In order to quantitatively determine the magnetic susceptibility of the trapped radicals, the saturation coefficient (*S*) at a certain microwave power was introduced and defined as the ratio of the extrapolated signal intensity from linear fitting at lower microwave power (1.0 mW) to that of the exponential fitting in the entire range of microwave power, with both curves passing through the origin of the coordinates.⁴⁸ For instance, at a microwave power of 30 mW, the linearly extrapolated signal intensity of the central line at a pyrolytic temperature of 950 °C is 2.43, while the exponentially extrapolated value is 1.63 (Fig. 6), resulting in an *S* of 1.49. Following the same procedure, we calculated the *S* of the central line at a microwave power of 30 mW for other temperatures; it was found to be in the range of 1.31 to 1.49.

The minimum theoretical value of *S* is 1.00, meaning that the radical is invulnerable to saturation and that its intensity is directly proportional to the microwave power. The higher the *S*, the higher the vulnerability of the radical to saturation. Fig. 6 indicates that *S* increases with microwave power. However, at a fixed microwave power, the *S* for a certain radical is unique and can serve as an index to distinguish it from other types of radicals. For instance, the *S* value for CPD radicals based on our previous published data is 1.03,⁴⁷ showing the resistance of CPD radicals to saturation, while phenoxy radicals are easily saturated, *i.e.*, *S* = 2.95.³⁴ The *S* values of the radicals captured in this study, *i.e.*, 1.31 to 1.49, fall between those of the CPD and phenoxy radicals, indicating that they are barely saturated with increasing microwave power.

Another radical that is resistant to saturation and has a high *g* value is the alkylperoxy radical, RO₂, with *S* = 1.09 as calculated from literature data.⁴⁹ These radicals may arise in the presence of traces of oxygen in the vacuum system.⁵⁰ However, they cannot be the dominant species in the radical mixture detected here at high temperatures, *i.e.*, 700 to 1000 °C.⁵¹ Additional evidence of the insignificance of RO₂ radicals during the high temperature pyrolysis of CnA using the spin trapping method in conjunction with EPR is discussed in our recent presentation.¹⁸

4. Degradation pathways for *p*-CMA

4.1. Formation of highly delocalized carbon centred radicals

The structures of radicals potentially formed from simple bond scission in *p*-CMA are depicted in Fig. 1 (a–e). More detailed decomposition pathways for *p*-CMA to form the primary intermediate radicals are reported elsewhere.⁵²

The bond dissociation energies (BDE) and calculated g values are listed in Table 1. As expected, the calculated g_{iso} values for highly delocalized carbon centered radicals, such as the species (a), (c) and (d), are close to that of the free electron, 2.0023. The lowest energy decomposition pathway *via* C(9)-H bond fission (BDE = 70.71 kcal mol⁻¹) forms a conjugated carbon-centered radical (a), Scheme 1. The spin density is mostly localized on the terminal allylic group. This radical can be in equilibrium with the resonance structure (a').

Analogous to the interconversions in CnA reported earlier,¹⁸ a feasible internal H atom transfer can be expected from the terminal OH group to the C7 atom (see also^{28,53}). Thus, the radical (a'') with a high calculated g_{iso} value = 2.0070 (not presented in Table 1) is formed.

4.2. Formation of highly delocalized oxygen centred radicals

An O-centered highly delocalized phenoxy type radical (b) can be plausibly formed by scission of the phenolic hydroxyl group with BDE = 81.11 kcal mol⁻¹ (Table 1). The formal mesomer structures are depicted in Scheme 2.

Long-range delocalization of the unpaired electron enables its interaction with the distal oxygen center; as a result, a low g_{iso} of 2.0031 was calculated (the spin density at oxygen is 0.36). The g value calculated for the un-substituted phenoxy O-centered radical is substantially higher (2.0062, Table 1) at BDE = 89.00 kcal mol⁻¹,⁵⁴ with the spin density at the oxygen atom being equal to 0.42.

It is important to note that the phenoxy type of radical (b) (Fig. 1, Scheme 3) can be easily degraded by the elimination of CH₃OH (*via* H-migration to the CH₂ group) or dehydration (*via* H-migration to the terminal OH group) and transformed into the acetylenyl phenoxy and allenyl phenoxy radicals with high calculated g values of 2.0059 and 2.0055, respectively. The g values are closer to the g_{iso} for the phenoxy radical (2.0062, Table 1) than to that of the delocalized radical (b) with g = 2.0031.

4.3. Formation of highly localized oxygen centred radicals

A localized structure, radical (e) (ref. Fig. 1), may be formed by scission of the terminal OH group with BDE = 96.5 kcal mol⁻¹, Table 1. The spin density localized on the terminal oxygen atom is as high as 0.89; as a consequence, the g value is also high (2.0338, Table 1).

Thus, the DFT calculations supported the existence of high g -value radicals detected experimentally from *p*-CMA pyrolysis in the high temperature region of 700 to 1000 °C. Different mixtures of radicals with different proportions can be formed with increasing

pyrolysis temperature, such as carbon centered (structure (a), $g = 2.0022$), delocalized phenoxy type (structure (b), $g = 2.0031$), degraded phenoxy type O-centered (acetylenyl phenoxy, $g = 2.0059$ and allenyl phenoxy, $g = 2.0055$), oxygen linked (structure (a''), $g = 2.0070$), and localized oxygen centered (structure (e), $g = 2.0338$) species. This may explain the fact that an average experimental value of $g_{\text{iso}} = 2.0092$ is registered at temperatures below 900 °C, whereas $g_{\text{iso}} = 2.0100$ is detected at 1000 °C (Fig. 3B). Based on the above results, it can be concluded that the oxygen-centered radicals dominate in the radical mixtures, especially at high temperatures.

5. Conclusions

The gas-phase pyrolysis of *p*-CMA in the high temperature region (700 to 1000 °C) produces radicals that exhibit anisotropic character, high g -values, broad line width and relatively low saturation coefficients. These features are persistent regardless of changes in the pyrolytic conditions. On the basis of the experimental findings together with DFT calculations, the dominant formation of O-centred radicals from the pyrolytic decomposition of *p*-CMA was established.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Molecular structures of *p*-CMA and five favorable radicals produced from simple bond scissions (assigned **a–e**) discussed in this work.

Fig. 2. Temperature dependence of the EPR spectra of radicals from the pyrolysis of *p*-CMA. The peak marked by an asterisk is at $g = 1.9932$.

Fig. 3. Temperature dependence of the signal intensity (A), g -value and H_{p-p} (B) of radicals from the pyrolysis of *p*-CMA accumulated and detected at 77 K on a cold finger.

Fig. 4. Effect of annealing time on the spectra (A), g -value and signal intensity (B) of radicals from the pyrolysis of *p*-CMA at 1000 °C accumulated and detected at 77 K on a cold finger.

Fig. 5. Microwave power dependence of the EPR spectra of radicals from the pyrolysis of *p*-CMA at 850 °C (left) and 1000 °C (right). The peak D is at $g = 1.9932$.

Fig. 6. Microwave power dependence of radicals from the pyrolysis of *p*-CMA; the green and blue symbols indicate the signal intensities of the shoulder and central lines, respectively.

Scheme 1.
Conjugated carbon centered (**a** and **a'**) and oxygen-linked (**a''**) radicals.

Scheme 2.

Highly delocalized phenoxy type *p*-CMA radical (b) in equilibrium with formal mesomers. Numbers are electron spin densities (negative spins are omitted).

Scheme 3.

Formation of phenoxy type radicals (allenyl phenoxy, $g_{\text{iso}} = 2.0055$ and acetylenyl phenoxy, $g_{\text{iso}} = 2.0059$) from the highly delocalized *p*-CMA radical (structure (b), $g_{\text{iso}} = 2.0031$).

Table 1

BDE and g values calculated for the radicals presented in Fig. 1 (a–e) and for PhO•

Radical ^a	a	b	c	d	e	PhO•
BDE, kcal mol ⁻¹	70.71	81.11	90.51	95.04	96.59	89.00 ^b
g value	2.0022	2.0031	2.0028	2.0023	2.0338	2.0062

^a All g values calculated at the HF/6-31G** level.

^b From ref. 54.