

Investigation of the Gas-Phase Pyrolysis of Lignin Model Compounds by Molecular Beam Mass Spectrometry

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Improvements in the thermochemical processing of biomass for production of fuels and chemicals depend on an understanding of the complex pathways and underlying mechanisms. Unfortunately, the reaction pathways that lead to the complex array of products are still not resolved, and there is little insight into controlling product selectivity. To gain fundamental mechanistic insight into the pyrolysis of lignin, a major component of biomass, our research has focused on the pyrolysis of model compounds that contain key structural elements found in native lignins. In this presentation, the gas-phase pyrolysis of lignin model compounds containing the β -O-4 linkage was investigated by molecular beam mass spectrometry to study the reaction pathways that lead to product formation under fast pyrolysis conditions. Specifically, the pyrolysis of hydroxy- and methoxy-substituted phenethyl phenyl ethers (PhCH₂CH₂OPh) was investigated at 500 to 650 °C and residence times of 0.3 and 0.6 s. These results will be compared to those found from the solution phase pyrolysis and the flash vacuum pyrolysis of lignin model compounds.

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INVESTIGATION OF THE GAS-PHASE PYROLYSIS OF LIGNIN MODEL COMPOUNDS BY MOLECULAR BEAM MASS SPECTROMETRY

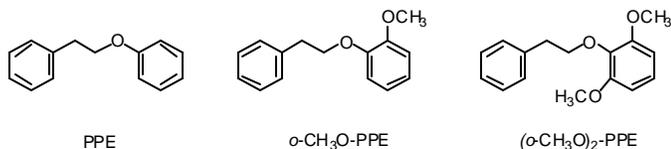
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Introduction

The production of fuels and chemicals from the thermochemical processing of biomass depends on an understanding of the complex pathways and underlying mechanisms.¹ Unfortunately, the reaction pathways that lead to the complex array of products are still not resolved, and there is little insight into controlling product selectivity. To gain fundamental mechanistic insight into the pyrolysis of lignin, a major component of biomass,² our research has focused on the pyrolysis of model compounds that contain key structural elements found in native lignins.³⁻⁵ The flash vacuum pyrolysis of lignin model compounds containing the β -O-4 linkage, which is the dominant linkage in lignin, has been reported.^{4,5} These studies provided insight into the primary gas-phase reaction that occurs at 500 °C under low concentration conditions that favor unimolecular reactions. The reaction pathways were significantly more complex than expected, and the dominant reaction was C-O homolysis followed by intramolecular hydrogen abstraction, 1,2-phenyl shift, and/or β -scission of subsequent radicals to form stable products. In this study, the fast pyrolysis of lignin model compounds was investigated at atmospheric pressure in a stream of helium with real time sampling of the products by mass spectrometry. Under these reaction conditions, bimolecular reactions can compete with the unimolecular reactions for the formation of products. In this investigation, the pyrolysis of phenethyl phenyl ether (PPE) and its methoxy derivatives, *o*-CH₃O-PPE and (*o*-CH₃O)₂-PPE, was studied at 500 – 650 °C with residence times of 0.3 and 0.6 s.



Experimental

The synthesis of the model compounds has been previously described.^{3,5}

The study of pyrolysis by MBMS has been described previously.^{6,7} All reactions were carried out at atmospheric pressure in a quartz tube reactor from 500 °C to 650 °C. A schematic diagram of reactor coupled to a molecular-beam mass spectrometer sampling system is shown in Figure 1. The quartz reactor consisted of inner and outer tubes, with pyrolysis occurring in the inner tube and the outer tube providing additional helium flow to satisfy the demands of the MBMS. The length of the inner tube from the sample to the end was 37 cm while the length of the mixing regime was 13 cm. A reactor with a spiral reaction section was used, so longer length and higher gas linear velocities could be achieved, which improved the flow characteristics. A fraction of the sweep gas (He) was introduced into the reactor through a side port where samples were inserted to facilitate sample introduction.

A sample (1-10 mg) contained in a quartz holder, or "boat", was inserted into flowing, preheated helium carrier gas. The carrier gas was introduced through the ends of inner and outer tubes and vapors exiting from the pyrolysis reactor (inner tube) were diluted with neat carrier gas in the outer tube. The hot gases exiting the reactor are expanded through an orifice on the apex of a sampling cone into the stage one vacuum at 40 mtorr. The pressure difference is sufficient for free-jet expansion, which quenches the products and allows the full range of products, including light gases, high-molecular-weight

compounds, and reactive products, to be simultaneously sampled and analyzed. A molecular beam, collimated through a second expansion, enters an ion source, where approximately 17 eV electron impact ionization is used to form ions. The ionization voltage was adjusted to minimize fragmentation of the lignin model compounds while maintaining good sensitivity. The gas phase residence time is defined as the time in the pyrolysis (inner) tube and in the mixing region of the outer tube. The flow rate of carrier gas in the inner tube was varied from 500 mL/min to 2000 mL/min, keeping total flow rate (inner and outer flow) constant at 10,000 mL/min. This varied the residence time from 0.3 s to 0.6 s.

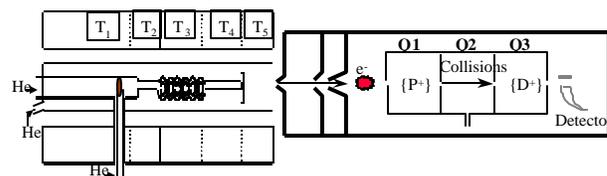
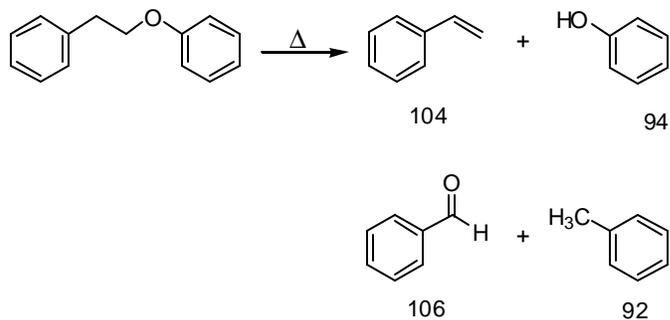


Figure 1. Tubular gas phase pyrolysis reactor coupled to a molecular beam mass spectrometer sampling system.

Results and Discussion

The liquid and gas phase pyrolysis of PPE has been studied at low temperatures (330 – 425 °C).³ Decomposition proceeds by a free radical chain pathway to produce two sets of products: styrene plus phenol and benzaldehyde plus toluene, in a ratio of 3:1, respectively, at 375 °C. In the FVP of PPE at 500 °C (ca. 0.3 s residence time, 0.9% conversion), the dominant reaction was C-O homolysis, which produced styrene and phenol (which accounted for 97% of the products).⁵ Homolysis of the C-C bond, to produce toluene and benzaldehyde, was a minor reaction.



The pyrolysis MBMS of PPE was run at 500, 550, 600 and 650 °C with residence times of 0.3 and 0.6 s. As the temperature and residence time increased, the dominant products that appeared in the mass spectrum were styrene (m/z 104) and phenol (m/z 94) with very small amounts of toluene (m/z 92) and benzaldehyde (m/z 106). This product slate is very similar to that found in the FVP experiments. The mass spectrum of the reaction mixture at 600 °C and a residence time of 0.6 s is shown in Figure 2. Benzene (m/z 78) can arise from the decomposition of benzaldehyde (confirmed by independent pyrolysis) and is observed as a mass spectral fragmentation product. The m/z at 105 is from fragmentation of the PPE, which decreases in intensity as the molecular ion (m/z 198) decreases. Thus, the pyrolysis MBMS experiment gives primarily unimolecular products and little bimolecular reactions. However, small quantities of additional products are formed with m/z 154, 168, and 180 that appear to be coupling products from the radicals formed in the reaction (phenoxy, benzyl, and phenyl, from decomposition of benzaldehyde to form biphenyl, dibenzofuran, and stilbene), but they also could arise from surface catalyzed reactions. Attempts to increase the yield of these products by addition of a free radical

initiator, such as benzyl phenyl ether, were unsuccessful. Thus, the origin of these products is still under investigation.

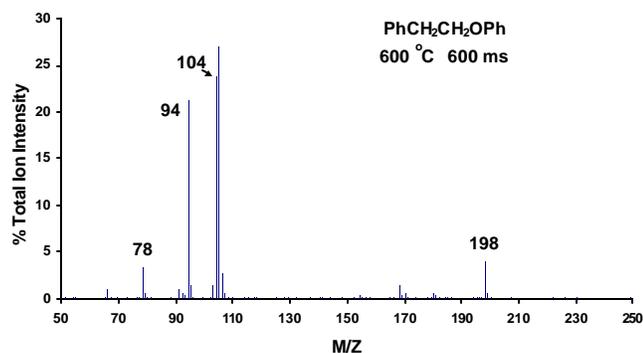
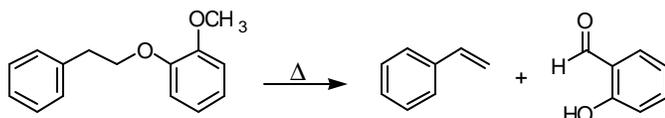


Figure 2. Average spectra of products detected by MBMS from the pyrolysis of PPE at 600 °C and a residence time of 0.6 s.

The pyrolysis MBMS of *o*-CH₃O-PPE was run at 500, 550 and 600 °C at residence times of 0.3 and 0.6 s. The mass spectrum from a run at 500 °C and a residence time of 0.3 s is shown in the Figure 3. The mass at *m/z* 228, 124, and 105 are from mass spectrometer fragmentation of the starting material (see Figure 3), and there is little thermal decomposition of the material. At 600 °C with a residence time of 0.6 s, all the starting material is consumed (see Figure 4) indicating that the *o*-methoxy derivative is more reactive than PPE. The dominant products arise from C-O homolysis and form styrene and hydroxybenzaldehyde (*m/z* 122). Guaiacol (*m/z* 124) was a minor product in the reaction. Independent pyrolysis of guaiacol at 600 °C indicated that it was not stable under these reaction conditions but formed catechol (*m/z* 110) as the major product and small amounts of hydroxybenzaldehyde and phenol. Independent pyrolysis of hydroxybenzaldehyde at 600 °C produced small amounts of phenol (*m/z* 94). Small amounts of toluene and *o*-methoxybenzaldehyde (*m/z* 138) were also found which arise from C-C homolysis.



The major products are very similar to those formed in the FVP of *o*-CH₃O-PPE at 500 °C indicating that unimolecular reactions are dominant. *o*-Hydroxybenzaldehyde is formed by C-O homolysis to give the *o*-methoxyphenoxy radical, intramolecular hydrogen abstraction to form *o*-hydroxyphenoxy radical, 1,2-phenyl shift to form *o*-hydroxybenzyloxy radical followed by β-scission of hydrogen. In solution phase at lower temperatures, bimolecular hydrogen abstraction is the dominant reaction and two sets of products are formed: guaiacol plus styrene, and toluene plus *o*-methoxybenzaldehyde, in a 3:1 ratio (at 375 °C).

The FVP of (*o*-CH₃O)₂-PPE produced a complex set of products.⁵ Surprisingly, the dominant product was *o*-cresol (24 mol%), 2,6-dimethoxyphenol (13 mol%), and styrene (22 mol%). These products were formed by C-O homolysis followed by hydrogen abstraction, rearrangement, and β-scission reactions. The mass spectra of the products detected by MBMS from the pyrolysis of (*o*-CH₃O)₂-PPE at 600 °C and a residence time of 0.6 s is shown in Figure 5. The spectrum is surprisingly simple (compared to the FVP results). The dominant products appear to be styrene (*m/z* 104), cresol (*m/z* 108), *o*-hydroxybenzaldehyde (*m/z* 122), and benzene (*m/z* 78). Independent pyrolysis of 2,6-dimethoxyphenol at 600 °C produced a complex set of products with *m/z* 138, 126, 124, 110, 108. This indicates that 2,6-dimethoxyphenol is not a major primary product since its major decomposition products are not observed to a significant extent. More studies are needed to determine the origin of

these products. As a consequence of the decomposition and mass spectral fragmentation of the products, it is difficult to determine the primary and secondary products. Thus, the data will be analyzed by multivariate factor analysis to determine which masses (i.e., products) are correlated.⁸ Results from this data analysis will be presented and the mechanisms of the decomposition of these lignin model compounds will be discussed.

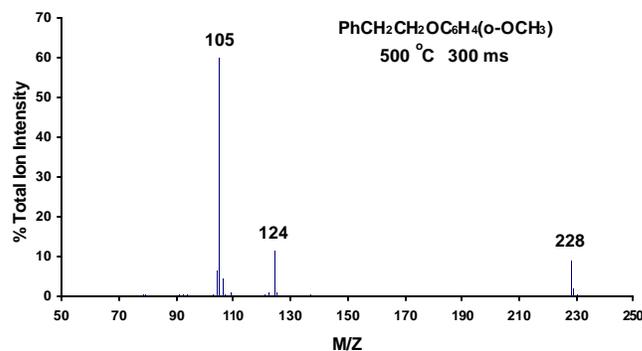


Figure 3. Average spectra of products detected by MBMS from the pyrolysis MBMS of (*o*-CH₃O)-PPE at 500 °C.

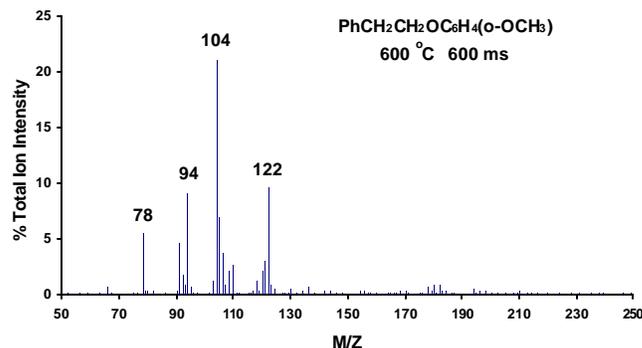


Figure 4. Average spectra of products detected by MBMS from the pyrolysis *o*-CH₃O-PPE at 600 °C and 0.6 s residence time.

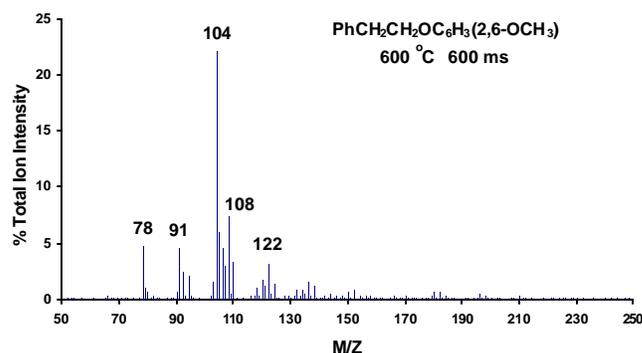


Figure 5. Average spectra of products detected by MBMS from the pyrolysis *o*-CH₃O-PPE at 600 °C and 0.6 s residence time.

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