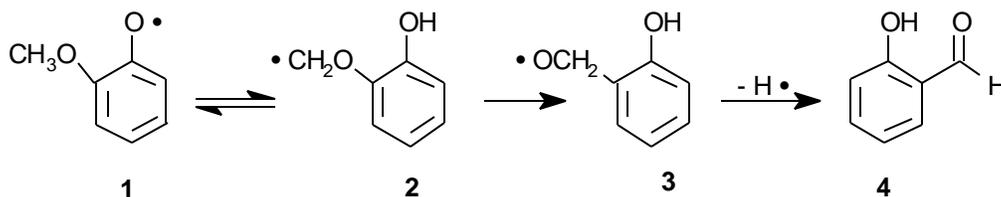


Pyrolysis Mechanisms of Lignin Model Compounds: Flash Vacuum Pyrolysis of Methoxy-Substituted Aromatics

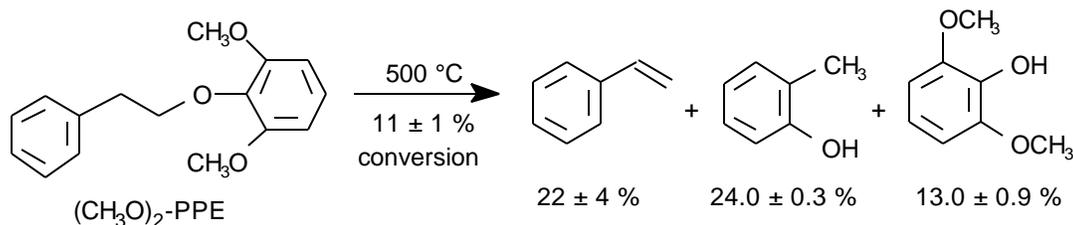
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The thermochemical conversion of lignin into higher value products is of great interest. To enhance the economic production of liquid products from lignin, it is necessary to understand those factors that maximize product yields and promote product selectivity. However, the fundamental chemical reactions that lead to the complex array of products remains poorly understood, and there is little insight into how to control product selectivity. Therefore, we are investigating the pyrolysis of compounds which model key structural features found in lignin under a variety of pyrolysis conditions to gain mechanistic insight into the reaction pathways and products.

The flash vacuum pyrolysis (FVP) of methoxy-substituted β -O-4 lignin model compounds has been studied at 500 °C to provide mechanistic insight into the primary reaction pathways that occur under conditions of fast pyrolysis. The methoxy-substituents enhance the homolysis of the β -O-4 linkage in *o*-CH₃O-C₆H₄OCH₂CH₂Ph (*o*-CH₃O-PPE) and (*o*-CH₃O)₂-C₆H₃OCH₂CH₂Ph ((*o*-CH₃O)₂-PPE) relative to PhOCH₂CH₂Ph (PPE) by a factor of 9 and 24, respectively. The methoxy-substituted phenoxy radicals undergo a complex series of reactions, which are dominated by 1,5- and 1,6-intramolecular hydrogen abstraction, rearrangement, and β -scission reactions. For example, in the FVP of *o*-CH₃O-PPE, the dominant product, salicylaldehyde (**4**), forms from **1** by a 1,5-hydrogen shift, followed by a 1,2-phenyl shift, and β -scission of a hydrogen atom. Radical **2** can also cleave to form formaldehyde and phenol.



In the FVP of (*o*-CH₃O)₂-PPE, *o*-cresol was unexpectedly found as the dominant product. The mechanistic origin of this product and the complex reaction pathways of this methoxy substituted lignin model compound will be discussed in the presentation.



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