Pyrolysis Mechanisms of Lignin Model Compounds
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ABSTRACT

The flash vacuum pyrolysis of lignin model compounds was studied under conditions optimized for the production of liquid products to provide mechanistic insight into the reaction pathways that lead to product formation. The major reaction products can be explained by cleavage of the C–O ether linkage by a free radical or concerted 1,2-elimination.

Keywords: pyrolysis, lignin, depolymerization

1. INTRODUCTION

The thermochemical conversion of lignin, the second-most abundant naturally occurring biopolymer and a by-product of the pulping process, has received an enormous amount of attention as a consequence of its availability and its potential to produce higher value products [1]. However, these efforts to expand the use of lignin have been only moderately successful [2]. To enhance the economic production of higher value products from lignin, it will be necessary to understand those factors that maximize product yields and promote product selectivity. Currently, the most promising method to maximize the yields of liquid products from biomass (up to 60 wt% moisture-free organic liquids on a dry feed basis) is by fast or flash pyrolysis in which the sample is rapidly heating to moderate temperatures (typically 500 °C) for short periods of time (typically less than 2 s). To provide mechanistic insight into the reaction pathways that lead to product formation under conditions optimized for the production of liquid products, we have initiated a systematic study of the pyrolysis mechanisms of lignin model compounds at high temperatures (500 °C) and short contact times by flash vacuum pyrolysis (FVP). In this investigation, we will focus on the thermal
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degradation of the β-O-4 linkage, the dominant interunit linkage in lignin, by studying the FVP of phenethyl phenyl ether (PPE) and phenethyl o-methoxyphenyl ether (o-CH₃O-PPE).

![Chemical structures](Image)

2. EXPERIMENTAL

The synthesis of phenethyl phenyl ether, phenethyl-1,1-d₂ phenyl ether, and phenethyl o-methoxyphenyl ether has been previously described [3]. The flash vacuum pyrolysis apparatus was based on the design reported by Trahanovsky [4] and has been previously reported [5]. All experiments were run at 500 °C and pressures <10⁻³ Torr. Products were analyzed by GC and GC-MS and identified by comparison of GC retention times and mass spectral fragmentation patterns with authentic samples.

3. RESULTS AND DISCUSSION

The products from the FVP of PPE at 500 °C are shown below (average mol % from three runs). The major products, styrene and phenol, can be produced by two competing pathways: a) homolytic cleavage of the weakest bond in the molecule (D°C-O estimated as 63 kcal mol⁻¹) to give PhO• and PhCH₂CH₂• which can form phenol and styrene by addition and β-scission of a hydrogen atom, respectively, or b) 1,2-elimination to produce the phenol and styrene directly [3]. Unfortunately, it is very difficult to deconvolute these two pathways in the decomposition of PPE since both routes lead to the same products. However, the rate of 1,2-elimination should be slower for PhCD₂CH₂OPh than for PPE as a consequence of
primary deuterium isotope effect in breaking the C–D bond, while the homolytic cleavage of the C–O bond should not be influenced by the substitution of deuterium for hydrogen. The % conversion for the FVP of PhCD₂CH₂OPh was approximately 20 % slower than that for PPE under identical reaction conditions indicating that 1,2-elimination contributes to the decomposition of the β-O-4 ether linkage, although a quantitative contribution can not be obtained. The small amounts of toluene, bibenzyl, and benzaldehyde that are observed in the FVP of PPE can be formed from the homolysis of the C-C bond (Δ₀°C-C estimated as 72 kcal mol⁻¹) [3]. Under the low pressure reaction conditions, a majority of the benzyl radicals couple to form bibenzyl. The phenoxymethyl radical (PhOCH₂•) produces benzaldehyde by a 1,2-phenyl shift, to form the benzyloxy radical (PhCH₂O•), followed by loss of a hydrogen atom.

The major products from the FVP of o-CH₃O-PPE at 500 °C are show below. The six FVP runs were obtained over a twelve week period and there was no significant trends in conversions or product yields as a function of time indicating that the pyrolysis conditions were reproducible over this long period of time. The average conversion and mass balance from the six FVP runs was 3.8 ± 0.2 and 98.2 ± 4.6 %, respectively. The conversion is a factor of ca. four larger for o-CH₃O-PPE than for PPE. This is expected based on substituent effects since the o- and p-methoxy substituent have been shown to weaken the O–CH₃ bond in anisole by 4 kcal mol⁻¹ [6].
On the basis of the results from the FVP of PPE, the major products from the FVP of \( o\text{-CH}_3\text{O-PPE} \) should arise from C–O homolysis and 1,2-elimination followed by degradation of the primary labile products. 1,2-Elimination of \( o\text{-CH}_3\text{O-PPE} \) produces styrene and guaiacol which can undergo further degradation to catechol [6]. Homolysis of the \( \beta \)-ether linkage forms the phenethyl radical and \( o\text{-methoxyphenoxy} \) radical (\( o\text{-CH}_3\text{OC}_6\text{H}_4\text{O}^* \)). The phenethyl radical can undergo facile \( \beta \)-scission to form styrene and a hydrogen atom. The \( o\text{-methoxyphenoxy} \) radical can abstract hydrogen to form guaiacol, but a more favorable pathway, as a consequence of a lower reaction entropy, is internal hydrogen abstraction through a six-centered transition state to form the \( o\text{-hydroxyphenoxy} \) radical (\( o\text{-HOC}_6\text{H}_4\text{O}^* \)). This radical can undergo a 1,2-phenyl migration from oxygen to carbon to form the \( o\text{-hydroxybenzyloxy} \) radical (\( o\text{-HOCC}_6\text{H}_4\text{O}^* \)) followed by \( \beta \)-scission of a hydrogen atom to form \( o\text{-hydroxybenzaldehyde} \). The \( o\text{-hydroxyphenoxy} \) radical can also undergo \( \beta \)-scission to form formaldehyde and the phenoxy radical, which can pick up a hydrogen atom to form phenol. The small quantities of toluene, bibenzyl, and \( o\text{-methoxybenzaldehyde} \) arise for the cleavage of the C–C bond, as observed for PPE.

ACKNOWLEDGEMENTS

Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. M. J. Cooney was supported by an appointment to ORNL Postdoctoral Research Associate program administered jointly by Oak Ridge Institute for Science and Education and ORNL.

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