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**Keywords:** pyrolysis mechansisms, lignin pyrolysis, model compounds

## ABSTRACT

Despite the extensive research into the pyrolysis of lignin, the underlying chemical reactions that lead to product formation are poorly understood. Detailed mechanistic studies on the pyrolysis of biomass and lignin under conditions relevant to current process conditions could provide insight into utilizing this renewable resource for the production of chemicals and fuel. Currently, flash or fast pyrolysis is the most promising process to maximize the yields of liquid products (up to 80 wt %) from biomass by rapidly heating the substrate to moderate temperatures, typically 500 °C, for short residence times, typically less than two seconds. To provide mechanistic insight into the primary reaction pathways under process relevant conditions, we are investigating the flash vacuum pyrolysis (FVP) of lignin model compounds that contain a $\beta$-ether linkage and $\alpha$- or $\gamma$-alcohol, which are key structural elements in lignin. The dominant products from the FVP of $PhCH_2CH_2OPh$ (PPE), $PhC(OH)HCH_2OPh$, and $PhCH_2CH(CH_2OH)OPh$ at 500 °C can be attributed to homolysis of the weakest bond in the molecule (C-O bond) or 1,2-elimination. Surprisingly, the hydroxy-substituent dramatically increases the decomposition of PPE. It is proposed that internal hydrogen bonding is accelerating the reaction.

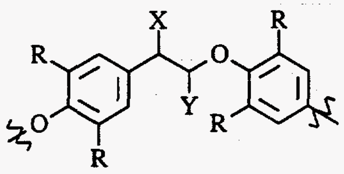
## INTRODUCTION

Over the past two decades, a good deal of attention has focused on the thermochemical conversion of renewable resources into higher value products [1]. 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. However, in spite of the extensive research to expand the use of lignin, the efforts have been only moderately successful [2]. This can be attributed to the structural diversity of lignin and the dependence of the chemical structure of lignin on the method of isolation [3]. To enhance the economic production of higher value products from lignin, it is necessary to understand those factors that maximize product yields and promote product selectivity. Over the past two decades, significant advances have been made in maximizing the yields of solid (charcoal) [4], liquid and gaseous products from biomass by pyrolysis [1,5,6]. While slow pyrolysis at low temperatures and long residence times produces charcoal, fast or flash pyrolysis produces high yields of liquid products (up to 60 wt% moisture-free organic liquids on a dry feed) by rapidly heating biomass to moderate temperatures (typically 500 °C, but ranging from 400-650 °C) for short periods of time (typically less than 2 s). At temperatures above 700 °C, fast pyrolysis maximizes gas yields (up to 80 wt%). However, despite the extensive research into the pyrolysis of biomass and lignin, the fundamental chemical reactions that lead to the complex array of products remains poorly understood, and as a result, there is little insight into how to control the product selectivity [7]. Currently, the most detailed mechanistic insights on lignin pyrolysis have been obtained from model compound studies [7,8]. However, most of these studies have been done at relatively low temperature (less than 450 °C) with long residence times (greater than 5 min) or slow heating rates. This makes it difficult to extrapolate these results to the moderate temperature, short contact-time reaction condition found in fast pyrolysis. Therefore, additional model compound studies are needed under conditions relevant to current process conditions (i.e., fast pyrolysis) to provide insight into controlling the reaction chemistry and product distribution to enhance the utilization of lignin.

There are many methods to rapidly heat compounds to high temperature, each with their own set of advantages and disadvantages. This paper investigates the flash vacuum pyrolysis of lignin model compounds at 500 °C. Flash vacuum pyrolysis (FVP) or flash vacuum thermolysis (FVT) has been used for decades by organic chemists for the preparation of highly reactive intermediates, for mechanistic investigations, and for preparative organic synthesis [9]. There are many different designs of flash vacuum pyrolysis apparatus operating at pressures from 1 atmosphere to $<10^{-4}$ mm Hg depending on the specific application and method of detection of the products [9]. However, all flash pyrolysis experiments are characterized by short contact times (sample typically remains in the hot zone for 0.001 - 1 s), low steady-state concentrations of the reactants and products in the hot zone, and rapid quenching of the products to low temperatures, typically 77 K. This method has been used to study thermally labile intermediates by a variety of spectroscopic methods (for example, NMR, UV-Vis, FTIR, Raman, and photoelectron spectroscopy). A special variation of this experiment, very low-pressure pyrolysis (VLPP), was developed to directly measure the reactive intermediates (i.e., free-radicals) from unimolecular reactions and very fast bimolecular reactions (i.e., $10^{11}$ L $mol^{-1}s^{-1} \geq k \geq 10^{6}$ L $mol^{-1}s^{-1}$) by mass spectrometry [10].

Flash vacuum pyrolysis seems ideally suited for the mechanistic investigation of the pyrolysis of lignin model compounds under conditions relevant to large scale fast pyrolysis reactors. Initial experiments can be run at low pressure ($<10^{-3}$ mm Hg) to characterize the primary reaction pathways and reactive intermediates that occur at moderate temperatures (500 °C) with a minimum of interference from bimolecular reactions. Next, the pyrolysis can be investigated at higher pressures (0.1 mm Hg to 1 atmosphere) under a flow of inert gas ($N_2$) to determine the more complex secondary reactions. A focus of this project is to characterize and quantitate the products, and to determine the origin and efficiency of their production. With the reaction pathways defined for the production of the products, we can focus on changing the experimental conditions to promote product selectivity.

Lignin is a complex, heterogeneous, three-dimensional polymer formed from the enzyme-initiated, dehydrogenative, free-radical polymerization of three *p*-hydroxycinnamyl alcohol precursors that differ by the number of methoxy groups on the aromatic ring [1a,11]. Softwood lignin is formed from *trans*-coniferyl alcohol (4-hydroxy-3-methoxycinnamyl alcohol), hardwood lignin is formed from coniferyl and *trans*-sinapyl alcohol (4-hydroxy-3,5-dimethoxycinnamyl alcohol), and grass lignin is formed from coniferyl, sinapyl and *trans-p*-courmaryl alcohol (4-hydroxycinnamyl alcohol). As opposed to other biopolymers such as cellulose, lignin has many different types of linkages between monomer units. This arises from the distribution of the π-electron density throughout the phenylpropene monomer unit and the thermodynamic principles governing radical addition reactions [1a]. The dominant interunit linkage in lignin is the arylglycerol-β-aryl ether linkage, commonly referred to as the β-O-4 linkage, and the arylglycerol-α-aryl ether linkage, referred to as the α-O-4 linkage, which accounts for approximately 48-60 % and 6-8 %, respectively, of the total interunit linkages [1a,11], exemplified by the structure below. If this structure is stripped for all its substituents, the skeletal remnant would be phenethyl phenyl ether, the simplest model of the β-O-4 linkage, and the starting point for this mechanistic investigation.

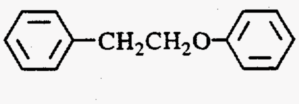


R = H or $OCH_3$

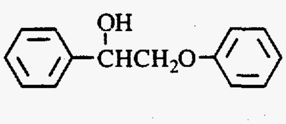
X = OH, OAr or =O

Y = $CH_2OH$ or $CH_2OR$

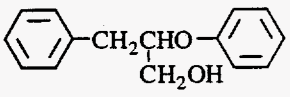
In this paper, the flash vacuum pyrolysis of lignin model compounds will be studied to determine the primary reaction that occurs at 500 °C and low pressures ($<10^{-3}$ Torr) and the impact of substituents on the reaction pathways. As a consequence of the complexity of the pyrolysis reactions and the thermal sensitivity of the products, a graded approach is used to solve this problem in which simple model compounds are thoroughly studied to provide a solid foundation to assist in the interpretation of more complex model compounds and lignin. This investigation will focus on FVP of the β-O-4 linkage, and the impact of hydroxy functional groups on the reaction pathways. To our knowledge, this is the first investigation of the reaction pathways of the γ-alcohol (i.e. β–$CH_2OH$-PPE).



PPE



α–HO-PPE



β–$CH_2OH$–PPE

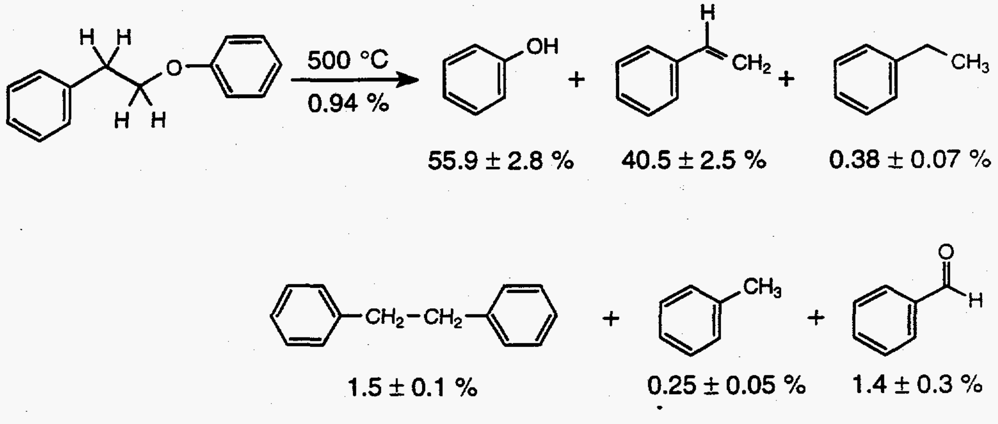
## EXPERIMENTAL

The synthesis of PPE and $PhCD_2CH_2OPh$ has been previously described [12]. The preparation of α–HO-PPE was accomplished by alkylation of α–bromoacetophenone with phenol ($K_2CO_3$ in DMF), reduction with lithium aluminum hydride, and recrystallization with hexanes/toluene. The preparation of β-$CH_2OH$-PPE was accomplished by alkylation of the enolate of ethyl phenoxyacetate (by the reaction of lithium hexamethyldisilazide with ethyl phenoxyacetate in THF at -78 °C) with benzyl bromide, reduction with lithium aluminum hydride, and purification by reverse phase flash chromatography. All compounds were >99.5 % pure by GC analysis.

The FVP apparatus was based on the design reported by Trahanovsky [13, 14] and available from Kontes. The pyrolysis tube consisted of a quartz tube (62.5 cm x 2.5 cm) with a 34/45 male joint on one end and a 90° bend with a size 40 o-ring joint on the other end. The tube was packed with short pieces (1/4" x 6 mm OD) of quartz tubing to a length of ca. 40 cm and held in place by a small plug of quartz wool. The quartz chips prevent streaming of the substrate and increase residence time in the hot zone. The quartz tube was heated with a Carbolite three zone furnace (45 x 3.8 cm (ID)) and the temperature was maintained within ± 1 °C of the setpoint (500 °C) over a length of 30 cm (out of total heated zone of 40 cm). The sample (typically 100-200 mg) was weighed into a sublimation tube made from a 34/45 female joint and connected to the horizontal quartz pyrolysis tube. The pyrolysis tube was connected by a size 40 o-ring joint to a trap which is cooled with liquid nitrogen. To prevent products from condensing in the tube before the cold trap, the pyrolysis tube was warmed with a heating tape at the exit of the furnace. At the start of a pyrolysis experiment, the system was pumped down to $<10^{-4}$ mm Hg (measured after the cold trap), the furnace was equilibrated at 500 °C, and the sublimation chamber was enclosed in an aluminum cylinder wrapped with a heating tape. The temperature of the sublimation tube (monitored by a thermocouple in the aluminum cylinder) was increased to provide a throughput of 50 - 100 mg $h^{-1}$. Under these conditions, the residence time (i.e., contact time) is estimated to be ca. 10 ms and the steady state concentration of materials in the hot zone is $10^{-8}$-$10^{-9}$ mol $L^{-1}$ such that only fast bimolecular reactions can occur in the hot zone, such as radical-radical couplings [9]. After the reaction, the trap was opened, products were washed out with a high purity acetone containing internal standards (cumene, dimethylphenol, and diphenyl ether), and the samples are analyzed by GC-MS at 70 eV and quantitated by GC with measured response factors. Products were identified by comparison of GC retention time and mass spectral fragmentation patterns with authentic samples or based on MS fragmentation patterns and comparison with the NIST spectral library. After each run, the tube was "burned out", by blowing air through the tube at 600 °C for 1 h, to remove any carbonaceous deposits (which were visible in the pyrolysis of phenethyl 2,6-dimethoxyphenyl ether). Duplicate pyrolyses were remarkably reproducible with similar mol % of products, mass balances (typically >95 %), and conversions (± 15%). Changing the injection rate by a factor of two (50 to 100 mg $h^{-1}$) did not change the product distributions. To check the long term reproducibility of the pyrolysis runs to ensure that the relative reactivity of the substituted phenethyl phenyl ethers could be compared over time, the pyrolysis of phenethyl *o*-methoxyphenyl ether was run after every 3-5 pyrolyses and compared to previous pyrolyses. Currently, similar pyrolysis results (% conversion, mass balances, and product yields) have been obtained over the span of a six week period (over 30 pyrolyses).

## RESULTS AND DISCUSSION

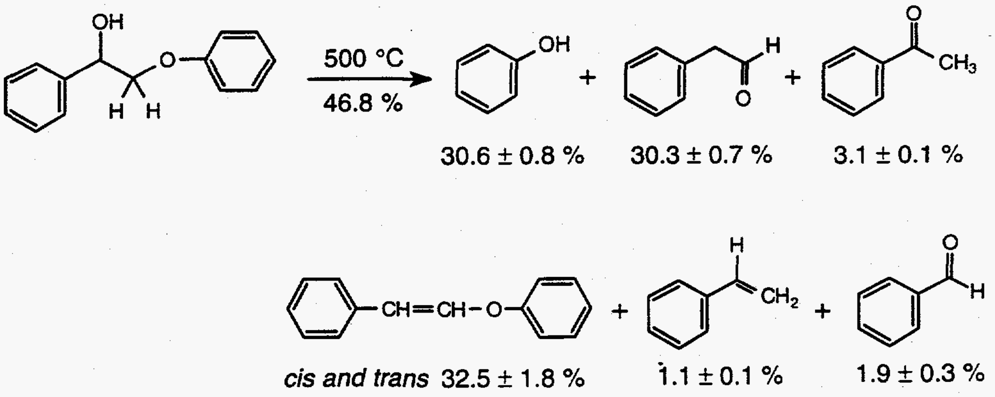
**FVP of PPE.** The major products from the FVP of PPE at 500 °C are shown below (average mol % from three runs). As a consequence of the low % conversions (0.94 ± 0.16 %), the



reproducibility and the mass balances were not as good as that found at higher conversions. In addition to the products shown below, a small amount (typically, ≤1 % of the starting material) of rearranged PPE, *o*-(2-phenylethyl)phenol and *p*-(2-phenylethyl)phenol, was also found. At higher temperatures (550 and 600 °C), the conversion of PPE increased to form the products shown above, but the yield of the rearranged products did not increase (ca. 1 % of the starting material). Recombination of the phenoxy and phenethyl radicals (see below) to form the rearranged products seems unlikely on the basis that no cross-coupling products, phenoxyphenol or 1,4-diphenylbutane, were observed. Trahanovsky has shown that FVP (650 °C and 0.05 mm Hg) of an unsymmetrical oxalate, benzyl *p*-chlorobenzyl oxalate, lead to statistical scrambling of the benzyl group indicating intermolecular coupling of benzyl radicals [14]. Therefore, the rearranged products were attributed to a small amount of acid catalysis from the quartz chips. In the decomposition of an analogous alkyl phenyl ether, *n*-butyl phenyl ether, it was proposed that products were formed by C-O homolysis (log k ($s^{-1}$) = 16.0 - 65.5 / 2.303 RT (kcal $mol^{-1}$)) and by 1,2-elimination (log k ($s^{-1}$) = 13.6 - 57.4 / 2.303 RT (kcal $mol^{-1}$)) [15]. At 500 °C, the ratio of homolysis to 1,2-elimination is 1.3. Therefore, in the pyrolysis of PPE, the major products, styrene and phenol, could 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 $PhCH_2CH_2$• which can gain and lose a hydrogen atom, respectively, or b) 1,2-elimination to produce the phenol and styrene products directly. Unfortunately, it is very difficult to deconvolute these two pathways in the decomposition of PPE since both routes lead to the same products. However, if PPE were substituted with deuterium in the benzylic position ($PhCD_2CH_2OPh$, PPE-$d_2$), the rate of 1,2-elimination would be slower, as a consequence of the deuterium isotope effect in breaking the C-D bond, while the homolytic cleavage should not be influenced by the substitution (since β-scission of $PhCD_2CH_2$• is fast compared to C-O homolysis). At 500 °C, a maximum rate difference (in the absence of tunneling) of $k_H/k_D = 2.1$ is predicted. In the pyrolytic 1,2-elimination of hydrogen halide from ethyl chloride, ethyl bromide, and their deuterated analogues, the measured isotope effect was ($k_H/k_D$) 2.0 - 2.2 at 500 °C [16]. Comparison of the % conversion from three FVP runs of PPE-$d_2$ and PPE under similar conditions found that the deuterated PPE reacted approximately 20 % slower than PPE indicating that the 1,2-elimination contributes to the decomposition of PPE at low pressures. At higher pressures, radicals produced from C-O homolysis can start a chain reaction and the contribution of 1,2-elimination will most likely be small.

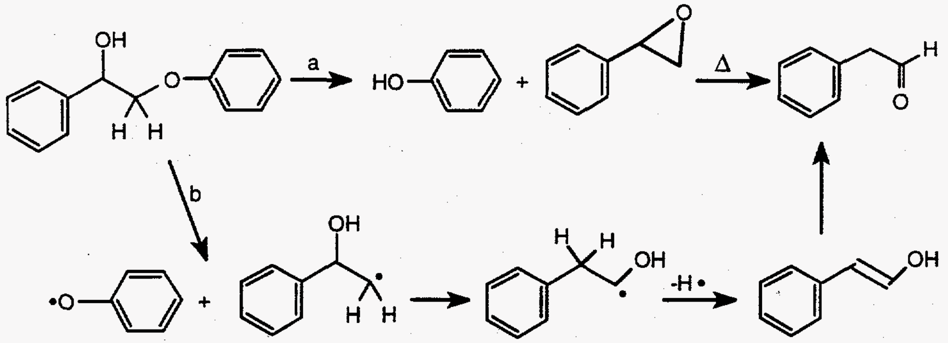
The small amounts of toluene, bibenzyl, and benzaldehyde that are observed can be formed from the homolysis of the C-C bond ($D°_{C-C}$ estimated as 72 kcal $mol^{-1}$). Under the low pressure reaction conditions, a majority of the benzyl radicals couple to form bibenzyl. The phenoxymethyl radical ($PhOCH_2$•) produces benzaldehyde by a 1,2-phenyl shift, to form the benzyloxy radical ($PhCH_2O$•), followed by loss of a hydrogen atom. In support of this mechanism, the benzaldehyde formed in the FVP of PPE-$d_2$ contained no deuterium.

**FVP of α-HO-PPE.** The major products from the FVP of α-HO-PPE at 500 °C are shown below (average mol % from three runs). The reproducibility and mass balances (98.5 ± 1.5 %) of these runs are excellent. Surprisingly, the α-hydroxy group dramatically accelerates the rate of decomposition (46.8 ± 0.4 % conversion, 23.4 ± 0.9 % without dehydration) of PPE. The major reaction is the 1,2-elimination of the α-hydroxy group to form the more refractory vinyl ether. The most studied 1,2-eliminations involve loss of hydrogen halide from alkyl halides to form alkenes, although loss of water, alcohol, ammonia, and hydrogen sulfide from alcohols, ethers, amines, and mercaptans have also been reported [15-17]. The transition state is proposed to be highly polar and electron donating species at the α-carbon dramatically accelerate the reaction while electron donating substituents at the β–carbon have only a small effect [17]. Since the aromatic ring is typically substituted with a *p*-hydroxy or *p*-alkoxy group in lignin, it is predicted that 1,2-elimination will be an dominant reaction pathway in lignin pyrolysis. It would be

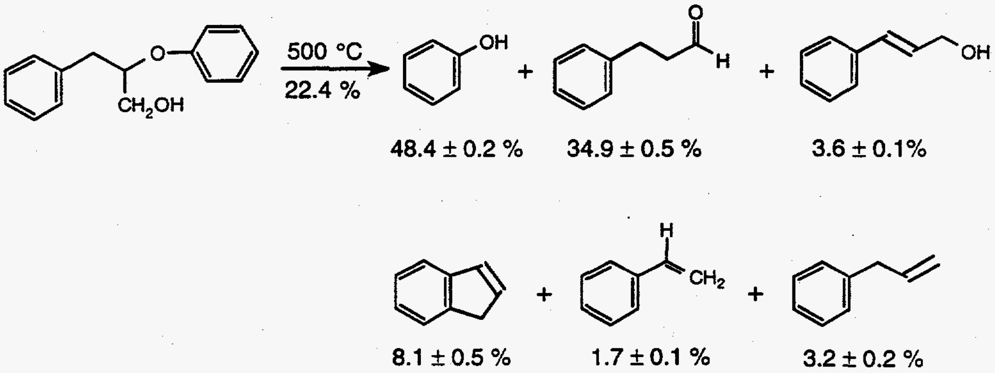


beneficial to find reaction conditions to minimize the dehydration reaction since it produces a more refractory product with the ejection of hydrogen (as water) from a carbon rich material.

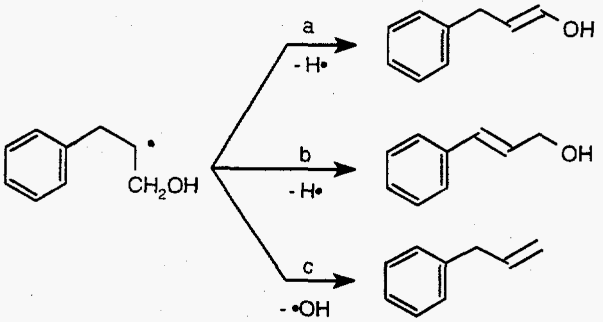
On the basis of the FVP results of PPE, we would predict that the dominant products from the FVP of α-HO-PPE would be phenol and acetophenone ($PhCOCH_3$) by the C-O homolysis or 1,2-elimination pathway. Surprisingly, acetophenone is a minor product indicating that 1,2-elimination is not a significant pathway in the decomposition of α-HO-PPE. The formation of phenol and phenylacetaldehyde could arise from two different pathways as shown below: a) intramolecular attack of the hydroxyl group on the β–carbon to eliminate phenol and styrene oxide which can undergo additional decomposition by pyrolysis; or b) homolysis of C-O bond, 1,2-phenyl shift, followed by loss of a hydrogen atom and tautomerization. Alkaline cleavage of lignin model compounds at low temperatures (220-300 °C) was shown to proceed through an epoxide intermediate by an internal displacement reaction [18]. Pyrolysis of substituted styrene oxides have been shown to produce alkyl benzyl ketones (or aldehydes). For example, pyrolysis of 3,4-dimethoxyphenyloxirane at 500 °C produces 3,4-dimethoxyphenylacetaldehyde as the major product [19]. To determine the contribution between these two possible pathways, we are currently synthesizing α-hydroxy-α-deuterophenethyl phenyl ether ($PhC(OH)DCH_2OPh$). Pathway (a) will provide phenylacetaldehyde labeled with deuterium in the benzylic position ($PhCHDCHO$) while pathway (b) will produce phenylacetaldehyde labeled in the aldehydic position ($PhCH_2CDO$). The contribution from the two pathways will be deduced from the mass spectrum fragmentation pattern of the phenylacetaldehyde produced in the FVP of $PhC(OH)DCH_2OPh$.



**FVP of β–$CH_2OH$-PPE.** The major products from the FVP of β-$HOCH_2$-PPE at 500 °C are shown below (average mol % from three runs). The reproducibility of the % conversion (22.4 ± 0.7 %) and mass balances (100.4 ± 0.4 %) of these runs are excellent. As observed for α-HO-PPE, the rate is dramatically accelerated by the addition of the hydroxy group to the β-ether linkage. As predicted from the documented substituent effects on 1,2-elimination reactions, dehydration of the primary alcohol is a minor pathway for β-$HOCH_2$-PPE, since there are no electron donating substituents to stabilize the polar transition state as found in α-HO-PPE [17]. The dominant pyrolysis products can be rationalized by C-O homolysis, followed by β-scission of a hydrogen or a hydroxyl radical (see below). Thermochemical estimates predict that pathway (a) should be favored over (b) and (c) by 5-6 kcal $mol^{-1}$ [20] and $PhCH_2CH_2CHO$ is found to be the dominant product. However, it is impossible to rule out a contribution of a 1,2-elimination in the formations of $PhCH_2CH_2CHO$ and $PhCH=CHCH_2OH$. The origin of the indene is unclear,



but it has been shown that $PhCH{=}CHCH_2\bullet$ can cyclize to indene [21]. However, under the low pressure conditions, hydrogen abstraction from $PhCH_2CH{=}CH_2$ is unlikely and thermochemical



estimates indicate that the homolysis of the C-O bond in $PhCH{=}CHCH_2OH$ would be slow at 500 °C [20]. Nevertheless, the indene most likely arises from decomposition of $PhCH{=}CHCH_2OH$.

**Impact of the hydroxy group on the decomposition of the β-ether linkage.** One surprising outcome of this investigation was the dramatic increase in the decomposition of PPE by the addition of a hydroxy-substituent. The average % conversion without dehydration for the FVP of PPE, α-HO-PPE, and β-$HOCH_2$-PPE at 500 °C was 0.96 %, 23.4 %, and 22.4 %. Thermochemical estimates, assuming C-O homolysis is the rate determining step, predict a β-hydroxy substituent might enhance the decomposition by a factor of 1-4 [22]. However, we observe rate enhancements greater than a factor of 20. One possible explanation for the similar rate enhancement for an α- and γ-hydroxy group is that internal hydrogen bonding is accelerating the C-O homolysis. Suryan, Kafafi, and Stein have measured the C-O bond dissociation energy of a series of substituted anisoles and found that the bond weakening caused by the *o*-hydroxy group was 4.7 kcal $mol^{-1}$ greater than that for the *p*-hydroxy group [23]. This additional stabilization was attributed to internal hydrogen bonding and not a destabilizing interaction in the guaiacol molecule. In α-HO-PPE and β-$HOCH_2$-PPE, molecular mechanics calculations indicate that the hydroxy group can interact with the ether oxygen without a significant energy penalty. The 20 fold rate enhancement in the decomposition of hydroxy-substituted PPE's at 500 °C corresponds to a difference of ca. 4.5 kcal $mol^{-1}$ in C-O bond strengths (assuming all products arise from C-O homolysis). Additionally, King and Stock have reported that hydrogen bonding by phenols or benzoic acid enhance the rate of decomposition of benzyl phenyl ether and dibenzyl ether [24]. However, it is still remarkable for weak hydrogen bonding interactions to have such a dramatic influence on the reaction chemistry at high temperatures. Therefore, to further investigate the potential role of hydrogen bonding in the decomposition of hydroxy-substituted PPE's, the methyl ether of α-HO-PPE and β-$HOCH_2$-PPE will be synthesized and subjected to FVP. This will remove the hydrogen bonding interactions and the conversions should be more similar to that found for PPE if hydrogen bonding is important.

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