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Flash Vacuum Pyrolysis of Methoxy-Substituted Lignin Model Compounds

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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. FVP of $PhCH_2CH_2OPh$ (PPE), a model of the dominant β-O-4 linkage in lignin, proceeds by C−O and C−C cleavage, in a 37:1 ratio, to produce styrene plus phenol as the dominant products and minor amounts of toluene, bibenzyl, and benzaldehyde. From the deuterium isotope effect in the FVP of $PhCD_2CH_2OPh$, it was shown that C−O cleavage occurs by homolysis and by 1,2-elimination in a ratio of 1.4:1, respectively. Methoxy substituents enhance the homolysis of the β-O-4 linkage, relative to PPE, in o-CH_3O-$C_6H_4OCH_2CH_2Ph$ (o-CH_3O-PPE) and $(o\text{-}CH_3O)_2$-$C_6H_3OCH_2CH_2Ph$ ($(o\text{-}CH_3O)_2$-PPE) by a factor of 7.4 and 21, respectively. The methoxy-substituted phenoxy radicals undergo a complex series of reactions, which are dominated by 1,5-, 1,6-, and 1,4-intramolecular hydrogen abstraction, rearrangement, and β−scission reactions. In the FVP of o-CH_3O-PPE, the dominant product, salicylaldehyde, forms from the methoxyphenoxy radical by a 1,5-hydrogen shift to form 2-hydroxyphenoxymethyl radical, 1,2-phenyl shift, and β-scission of a hydrogen atom. The 2-hydroxyphenoxymethyl radical can also cleave to form formaldehyde and phenol in which the ratio of 1,2-phenyl shift to β-scission is ca. 4:1. In the FVP of o-CH_3O-PPE and $(o\text{-}CH_3O)_2$-PPE, products (ca. 20 mol %) are also formed by C−O homolysis of the methoxy group. The resulting phenoxy radicals undergo 1,5- and 1,6-hydrogen shifts in a ratio of ca. 2:1 to the aliphatic or benzylic carbon, respectively, of the phenethyl chain. In the FVP of $(o\text{-}CH_3O)_2$-PPE, o-cresol was the dominant product. It was formed by decomposition of 2-hydroxy-3-hydroxymethylbenzaldehyde and 2-hydroxybenzyl alcohol, which are formed from a complex series of reactions from the 2,6-dimethoxyphenoxy radical. The key step in this reaction sequence was the rapid 1,5-hydrogen shift from 2-hydroxy-3-methoxybenzyloxy radical to 2-hydroxymethyl-6-methoxyphenoxy radical before β-scission of a hydrogen atom to give the substituted benzaldehyde. The 2-hydroxybenzyl alcohols rapidly decompose under the reaction conditions to o-benzoquinone methide and pick up hydrogen from the reactor walls to form o-cresol.

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 byproduct 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, despite the extensive research to expand the use of lignin, the efforts have been only moderately successful.[1a,2] This can be attributed to the structural diversity of lignin and the dependence of its chemical structure 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.[1,5−7] 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 to 650 °C) for short periods of time (typically less than 2 s).[5] At temperatures above 700 °C, fast pyrolysis maximizes gas yields (up to 80 wt %).[1,8] However, despite the extensive research into the pyrolysis of biomass and lignin, the fundamental chemical reactions that lead to the complex array of products

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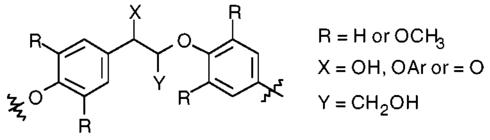
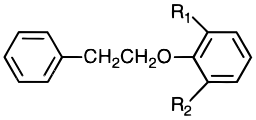
remains poorly understood, and as a result, there is little insight into how to control the product selectivity.[9] Currently, the most detailed mechanistic insights on lignin pyrolysis have been obtained from model compound studies.[9−13] However, most of these studies have been done at relatively low temperature (less than 450 °C) with long residence times (greater than 5 min) or slow heating rates. This makes it difficult to extrapolate the results to the moderate temperature, short contact-time reaction conditions 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 investigation uses flash vacuum pyrolysis to study the mechanistic pathways in the pyrolysis of lignin model compounds at 500 °C. Flash vacuum pyrolysis (FVP) or flash vacuum thermolysis has been used for decades by organic chemists for mechanistic investigations, preparative organic synthesis, and preparation of fullerene fragments[14] and highly reactive intermediates.[15] A special variation of this experiment, very-low-pressure pyrolysis (VLPP), has been 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.[16]



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 only by the number of methoxy groups on the aromatic ring.[1,17] 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 thermodynamics of the free-radical polymerization.[1] The dominant interunit linkages in lignin are 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. These structures account for approximately 48−60% and 6−8%, respectively, of the total interunit linkages in lignin,[1,17] and they are exemplified by the structure above. If this structure is stripped for all its substituents, the skeletal remnant would be phenethyl phenyl ether ($C_6H_5CH_2CH_2OC_6H_5$, PPE), the simplest model of the β-O-4 linkage, and the starting point for this mechanistic investigation.

This investigation will focus on FVP of lignin model compounds containing the β-O-4 linkage at 500 °C and the impact of methoxy substituents on the reaction pathways. The compounds that will be investigated are PPE and its methoxy derivatives, *o*-CH_3O-PPE and (*o*-$CH_3O)_2$-PPE (see below). These model compounds not only contain the dominant structural features found in lignin, but methoxyaromatics are also import structures in low-rank coal and they are a valuable commodity chemical.[18]



PPE $R_1 = R_2 = H$
o-CH_3O-PPE $R_1 = OCH_3$ $R_2 = H$
(*o*-$CH_3O)_2$-PPE $R_1 = R_2 = OCH_3$

Results and Discussion

FVP. Before the mechanistic pathways can be addressed, some of the characteristic features of FVP need be discussed that are important for the mechanistic interpretation of the data. In FVP, the pressure during the pyrolysis stays below 10^{-3} Torr (typically 2×10^{-5}−2×10^{-4} Torr). Thus, the residence time in the hot zone depends on the molecular velocity and the reactor geometry and is independent of the pressure and the rate of addition of the substrate.[15] Under these conditions, the residence time in the hot zone is estimated to be ca. 10 ms,[15a] and the steady-state concentration of substrate is 10^{-8}−10^{-9} mol L^{-1}. At these low concentrations, only fast bimolecular reactions, such as radical−radical couplings, can occur in addition to unimolecular reactions. For example, Trahanovsky et al. showed that in the FVP of di-α-ethylbenzyl oxalate at 570 °C and 0.05 mmHg, unimolecular elimination of the methyl radical from 1-phenyl-1-propyl radical was faster than bimolecular coupling to produce 3,4-diphenylhexane.[19] Stable radicals, such as benzyl and phenoxy, can couple or they can be transformed into molecular species by wall-associated hydrogen transfer reactions. These hydrogen-transfer

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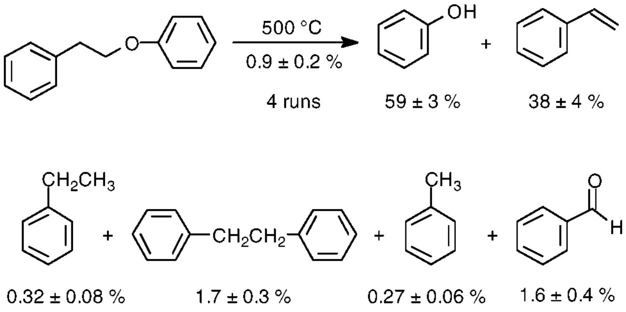
reactions have been reported in both FVP and VLPP experiments.[20,21]

At the low pressures used in these FVP experiments, heat transfer is accomplished by collision of the substrate with the quartz chips and the reactor tube walls. To compare the effect of substituents on the conversion and product distributions, the history of the pyrolysis tube must not be a variable in the experiment. In many cases, carbonaceous residues, from decomposition of reactive intermediates, are used to passivate active sites on the reactor surface (i.e., a seasoned or well-conditioned reactor). However, these residues can inhibit heat transfer from the tube walls to the substrate and decrease the conversion. Carbonaceous residues are a significant problem in industrial pyrolysis reactors because it affects the heat and mass transport properties of the system and shortens the lifetime of the heating coils.[22] These residues can be removed by heating to 600−800 °C in a mixture of steam and air. In preliminary studies on the FVP of 2-phenyl-2-hydroxyethyl phenyl ether ($PhCH(OH)CH_2$-OPh, α-HO-PPE), the conversion was found to steadily decrease from 52.3 to 28.4% over five sequential pyrolysis runs, although the product distribution did not significantly change (including the amount of dehydration product).[23] One explanation is that active sites on the quartz chips were passivated by deposition of carbonaceous deposits. Another explanation is that the carbonaceous residues reduce the heat transfer to the substrate and the rate of reaction is reduced because the effected reaction temperature is lower. To remove any carbonaceous deposits in the reactor so that all compounds were exposed to the same reactor conditions, the tube was "burned out" at 800 °C in a stream of air after every run. Surprisingly, this treatment enhanced the conversions of α-HO-PPE to ca. 90% (approximately a factor of 2 higher than the pyrolysis with new quartz chips), but the product distribution remained the same. Preliminary FVP experiments on *o*-CH_3O-PPE in a tube cleaned at 800 °C produced a significant amount (27 mol %) of rearranged starting material 2-methoxy-(6-(2-phenylethyl)phenol and 2-methoxy-4-(2-phenylethyl)phenol), and the product distribution was altered from FVP experiments run on a tube that was not burned out. A similar change in the product distribution and increase in rearranged products was observed in acid-catalyzed pyrolysis of surface-immobilized PPE and *o*-CH_3O-PPE.[12] Thus, it appeared that burning out the tube at 800 °C produced acidic sites of the quartz surface that altered the reaction pathways. (The activity of the tube could be reduced, but not eliminated, by base washing). Heterogeneous reactions at acidic sites on the quartz surface were a little bit surprising since these reactions are typically slow, since they have relatively low preexponential factors and moderate activation energies, compared to desorption, which has a very high preexponential factor and usually a lower activation energy.[16,22] Moreover, as the temperature increases, the residence time of a molecule on the surface decreases. Thus, only very fast heterogeneous reactions can occur under the FVP conditions used in these experiments. The possibility that the rearranged products arose from recombination of the initially formed radicals from C−O homolysis ($PhCH_2CH_2^\bullet$ and $^\bullet OC_6H_4OCH_3$) is unlikely since no phenoxyphenols were found. Trahanovsky found that the FVP of unsymmetrical oxalates, at 650 °C and 0.05 mmHg, led to statistical scrambling of the benzyl groups, indicating intermolecular coupling of benzyl radicals.[24] Thus, to remove the residues from the reactor without activating the quartz chips, a new cleaning procedure was developed that involved heating the tube to 600 °C for 1 h in air, after every run. With this modified procedure, replicate pyrolyses were remarkably reproducible with similar product distributions, excellent mass balances (typically >95%), and consistent conversions (±15%). Changing the injection rate by a factor of 2 (50−100 mg h^{-1}) did not change the product distribution. To check the long-term reproducibility of the pyrolysis reactor to ensure that the relative reactivity of the substituted phenethyl phenyl ethers could be compared over time, the pyrolysis of *o*-CH_3O-PPE was repeated after every three to five pyrolyses as a control sample (that was sensitive to surface acidity). Similar pyrolysis results (conversion, mass balances, and product yields) have been obtained for more than 15 runs of the control sample. Although the possibility that some fraction of the reaction is catalyzed by the reactor surface cannot be eliminated, these control experiments indicate that surface reactions are minimized.

Scheme 1



FVP of PPE. The major products from the FVP of PPE at 500 °C are shown in Scheme 1 (average mol % from four runs). As a consequence of the low conversions (0.9 ± 0.2%), the reproducibility and the mass balances (96 ± 2%) were less consistent than those found at higher conversions (see the Experimental Section). In addition to these products, a small amount (0.6 ± 0.4%) of rearranged PPE, *o*-(2-phenylethyl)phenol and *p*-(2-phenylethyl)phenol (91:9 mole ratio), was also found. At higher temperatures (550 and 600 °C), the conversion of PPE increased, but the product distribution did not change and the yield of the rearranged products was <1%.[25] As discussed above, it appears that the very small amounts

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[25] At 600 °C, the conversion of PPE was 46.8%, and the mass balance was 99.6%. The pyrolysis products included phenol (56.2 mol %), styrene (40.1 mol %), benzene (1.5 mol %), benzaldehyde (0.7 mol %), toluene (0.6 mol %), ethylbenzene (0.35 mol %), bibenzyl (0.2 mol %), and *o*-(2-phenylethyl)phenol (0.1 mol %) and *p*-(2-phenylethyl)phenol (0.1 mol %).

of rearranged products were formed from surface acidity of the quartz chips. In the pyrolysis of surface-immobilized PPE (by covalent attachment to an inert silica surface) in the presence of a small particle, dispersed acid catalyst, the product mixture was dominated by ether cleavage, aromatic alkylation reactions to form *o*-(2-phenylethyl) and *p*-(2-phenylethyl)phenol, and the absence of alkenes (polymerized).[12] In the FVP of PPE and substituted PPEs, the yield of styrene is always too low on the basis of the reaction stoichiometry, and it is proposed that some of the styrene is lost by surface mediated reactions.

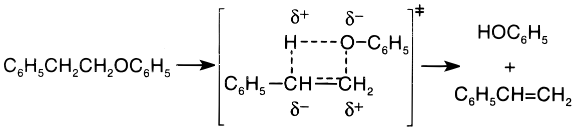
Decomposition of PPE will occur by cleavage of the weakest bond in the molecule. The $D°_{CO}$ and $D°_{CC}$ of PPE are estimated as 65 kcal mol^{-1},[11,26–28] and 72 kcal mol^{-1},[11] respectively. Homolysis of the C−O bond forms the phenoxy radical and the phenethyl radical (eq 1). The phenoxy radical will pick up a hydrogen atom from the walls of the reactor to make phenol. Unimolecular decomposition of the phenoxy radical to form the cyclopentadienyl radical and CO should not be competitive, log $k = -1.0$ s^{-1}, at 500 °C (log k (s^{-1}) = 11.4−43.9/θ where $\theta = 2.303RT$ kcal mol^{-1}).[29] The phenethyl radical could produce styrene (eq 3) or ethylene (eq 4) by β-scission of a hydrogen atom ($\Delta H°_{3,298} = 31.6$ kcal mol^{-1}) or a phenyl radical ($\Delta H°_{4,298} = 35.6$ kcal mol^{-1}), respectively.[27] The relative contribution of these pathways can be calculated from the reaction enthalpy and the intrinsic activation energy (since $\Delta H° = E_f - E_b$). The intrinsic activation energy for the addition of a hydrogen atom to an olefin is typically 1−2 kcal mol^{-1},[30] while addition of a phenyl radical to an olefin is ≥5 kcal mol^{-1}.[31] Thus, the activation energy for β-scission of a hydrogen atom, E_3, is estimated as 33 kcal mol^{-1} and for the phenyl radical E_4 is estimated as 41 kcal mol^{-1}. For an analogous elimination reaction, the Arrhenius parameters for the loss of a hydrogen atom from but-3-en-1-yl radical ($CH_2{=}CHCH_2CH_2^{\bullet}$) to form 1,3-butadiene has been estimated as log k (s^{-1}) = 13.5 − 34.8/θ.[32] The preexponential factor for the β-scission reaction can be estimated from the relationship $\ln(A_f/A_b) = \Delta S_c°/R$ and the preexponential factor of the back-reaction and the reaction entropy ($\Delta S°_{3,\ 298} = 17.4$ cal mol^{-1} K^{-1} and $\Delta S°_{4,\ 298} = 29.4$ cal mol^{-1} K^{-1}).[33,34] The preexponential factor for addition of a hydrogen atom to *cis*- and *trans*-2-butene and butadiene is $10^{11.1}$ M^{-1} s^{-1} and $10^{10.6}$ M^{-1} s^{-1}, respectively,[32,35] while the addition of the phenyl radical to ethylene has been measured as $10^{9.2}$ s^{-1}.[36] Thus, the Arrhenius parameters for β-scission of a hydrogen atom and phenyl radical from the phenethyl radical are log k_3 (s^{-1}) = 13.4−33/θ and log k_4 (s^{-1}) = 14.2−41/θ.[37] Therefore, the β-scission of a hydrogen atom (log $k_3 = 4.1$ s^{-1}) should be ca. 30 times faster than β-scission of a phenyl radical (log $k_4 = 2.6$ s^{-1}) at 500 °C. The yield of benzene from this pathway is predicted to be 0.7 mol % (taking into account the other pathways of styrene formation, see below) but benzene can also be formed from additional pathways (see below). The isolated yield of benzene, 0.48 ± 0.08 mol %, was lower than that predicted, but these small quantities are difficult to quantitate in our sample handling procedure as a consequence its volatility.

$$C_6H_5CH_2CH_2OC_6H_5 \rightarrow C_6H_5CH_2CH_2\bullet + \bullet OC_6H_5 \qquad (1)$$

$$C_6H_5CH_2CH_2OC_6H_5 \rightarrow C_6H_5CH_2\bullet + \bullet CH_2OC_6H_5 \qquad (2)$$

$$C_6H_5CH_2CH_2\bullet \rightarrow C_6H_5CH{=}CH_2 + H\bullet \qquad (3)$$

$$C_6H_5CH_2CH_2\bullet \rightarrow C_6H_5\bullet + CH_2{=}CH_2 \qquad (4)$$



(5)

In the FVP of *o*-CH_3O-PPE and (*o*-$CH_3O)_2$-PPE, the small amount of benzene (<1.5 mol %) that is formed most likely arises from the β-scission of the phenethyl radical. In the pyrolysis of an analogous alkyl phenyl ether, *n*-butyl phenyl ether, products were proposed to be formed by C−O homolysis (log k (s^{-1}) = 16.0−65.5/θ) and by 1,2-elimination (log k (s^{-1}) = 13.6−57.4/θ).[38,39] For PPE, the polar transition state for the formation of styrene will be stiffer than that for the formation of 1-butene as a consequence of the developing conjugation with the aromatic ring (eq 5). This results in an increased barrier to phenyl rotation and a decrease in entropy (ca. 2 cal mol^{-1} K^{-1}).[40] With this adjustment to the Arrhenius parameters above, the ratio of C−O homolysis to 1,2-elimination for PPE is predicted to be 3.5:1 at 500 °C. Therefore, in the pyrolysis of PPE, the major products,

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[26] Previously,[11] the heat of formation of the phenoxy radical was taken as 9.6 kcal mol^{-1} from the average value from three different studies. Using the recommended value of 87 kcal mol^{-1} for the BDE (O−H) of phenol (Wayner, D. D. M.; Lusztyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737), the $\Delta H_f°$(PhO) is calculated to be 11.9 kcal mol^{-1} from the $\Delta H_f°$(H) = 52.1 kcal mol^{-1} and $\Delta H_f°$(PhOH) = −23 kcal mol^{-1}.[27] The $\Delta H_f°$(PhO) has also been measured as 12.1 kcal mol^{-1} from the pyrolysis of anisole.[28] If these new values are averaged with those previously reported, the heat of formation of the phenoxy radical as $\Delta H_f°$(PhO), = 11.2 ± 1.5. Therefore, BDE (C−O) in PPE is increased to 64.7 kcal mol^{-1}.

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[32] Weissman, M.; Benson, S. W. *Int. J. Chem. Kinet.* **1984**, *16*, 307. The reaction entropy and enthalpy are estimated to be $\Delta S_p° = 17.5$ cal mol^{-1} K^{-1} and $\Delta H°_{298} = 32.4$ kcal mol^{-1}. For the reverse reaction, the preexponential factor is estimated as $10^{11.1}$ M^{-1} s^{-1}.[33]

[33] Thermochemical data (and estimates) for $\Delta H_f°$, $S°$, $\Delta G°$, and K are generally expressed for a standard state of 1 atm. Experimental rate constants are typically measured in concentration units (M). To calculate the preexponential factor for β-scission, the thermochemical estimates ($\Delta S_p°$) need to converted to concentration units ($\Delta S_c°$) by the relationship $\Delta S_c° = \Delta S_p° - \Delta nR \ln(R'T)$, where Δn is the change in the numbers of moles in the reaction and $R' = 0.0821$ atm K^{-1} M^{-1}.[34]

[34] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley & Sons: New York, 1976.

[35] Kerr, J. A.; Parsonage, M. J. *Evaluated Kinetic Data on Gas-Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds*; CRC: London, 1972.

[36] (a) Yu, L.; Lin, M. C. *Combust. Flame* **1995**, *100*, 169. (b) Fahr, A.; Stein, S. E. *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1988; p 1023. Rate constant for addition of phenyl radical to ethylene is log k (M^{-1} s^{-1}) = 8.86−4.5/θ and log k (M^{-1} s^{-1}) = 9.4−6.2/θ, respectively. We will use an average preexponential of $10^{9.2}$ M^{-1} s^{-1}.

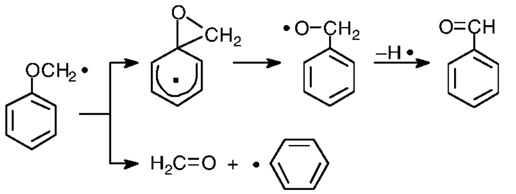
[37] For comparison, the rate constants for the β-scission of hydrogen atom and a phenyl radical from 1,2-diphenylethyl radical were estimated as log k (s^{-1}) = 13.6−41/θ and log k (s^{-1}) = 14.6−52/θ, respectively.[31]

[38] Walker, J. A.; Tsang, W. *J. Phys. Chem.* **1990**, *94*, 3324.

styrene and phenol, could be produced by two competing pathways: (a) C−O homolysis and (b) 1,2-elimination. Unfortunately, it is difficult to deconvolute these two pathways experimentally in the decomposition of PPE since both routes lead to the same products. However, if PPE is 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 a primary deuterium isotope effect in breaking the C−D bond, while the homolytic cleavage would be unaffected by the substitution. In the pyrolytic 1,2-elimination of hydrogen halide from ethyl chloride, ethyl bromide, and their deuterated analogues, the measured isotope effect (k_H/k_D) was 2.0−2.2 at 500 °C.[39] Since only a small difference in conversions is expected for PPE and PPE-d_2, the pyrolyses were run in succession (see the Experimental Section). The average conversion for three runs of PPE-d_2 was 0.55 ± 0.05%, and the average conversion of two runs of PPE was 0.71 ± 0.05%.[41] Hence, the ratio of C−O homolysis to 1,2-elimination for PPE is calculated to be 1.4:1 assuming a deuterium isotope effect (k_H/k_D) of 2.1, which is very similar to the ratio reported in the pyrolysis of *n*-butyl phenyl ether.[38] Thus, the 1,2-elimination also contributes to the decomposition of PPE at low pressures (in the absence of a chain reaction).[11]

The small amounts of toluene, bibenzyl, and benzaldehyde that were observed in the FVP of PPE can be formed from C−C homolysis (eq 2). The difference in the C−O and C−C bond strengths is estimated to be −7 kcal mol^{-1}, while the entropy difference ($\Delta\Delta S°_{298}$) is approximately zero (but depends on the method used to estimate the entropy for the phenethyl radical).[27,42] The selectivity between the pathways is predicted to be 100:1 in the absence of 1,2-eliminations. Comparing the yield of phenol from C−O homolysis (34 mol %, calculated by subtracting the contribution from 1,2-elimination) to benzaldehyde,[43] the experimental ratio C−O to C−C homolysis is 21:1. The yield of products from C−C homolysis is higher than that predicted but not outside the typical uncertainties in the thermochemical estimates of BDEs, ±2 kcal mol^{-1}, and $S°_{298}$, ±1 cal mol^{-1} K^{-1}.[34] The toluene and benzaldehyde could also form from a free radical chain reaction, but at the low pressures used in the FVP experiments, bimolecular reactions are unlikely. Moreover, from the previous studies on the pyrolysis of PPE, the product selectivity for phenol plus styrene and toluene plus benzaldehyde was 3.1 ± 0.3 at 375 °C and independent of concentration (which varied from the neat liquid (3.8 M) to the dilute gas (5×10^{-3} M)). From an estimation of the Arrhenius parameters for the hydrogen abstraction reactions, the selectivity is predicted to decrease to 2.2 at 500 °C.[11] Therefore, in these FVP experiments, the product selectivity is inconsistent with a free radical chain pathway.

In the FVP of PPE, a majority of the benzyl radicals formed from C−C homolysis will couple to form bibenzyl as a consequence of their fast termination rate constant ($10^{9.8}$ M^{-1} s^{-1}).[31] The phenoxymethyl radical ($PhOCH_2^{\bullet}$) will produce benzaldehyde ($\log k$ (s^{-1}) = $12.5 - 21/\theta$)[44] by a rate-determining 1,2-phenyl shift, to form the benzyloxy radical ($PhCH_2O^{\bullet}$), followed by loss of a hydrogen atom (eq 6). β-Scission of a hydrogen atom from $PhCH_2O^{\bullet}$ ($\log k$ (s^{-1}) = $13.9 - 17.2/\theta$) to form benzaldehyde is approximately 100−1000-times faster than forming $H_2C{=}O$ and $Ph^{\bullet}$ ($\log k$ (s^{-1}) = $14.0 - 24.5/\theta$).[45] β-Scission of $PhOCH_2^{\bullet}$ would also produce $H_2C{=}O$ and the $Ph^{\bullet}$ (eq 7). On the basis of the enthalpy of the reaction ($\Delta H°_{298}$ = 27.6 kcal mol^{-1}), the intrinsic activation energy (1 kcal mol^{-1}),[46,47] and assuming the entropy for losing $H_2C{=}O$ from $PhCH_2O^{\bullet}$ and $PhOCH_2^{\bullet}$ are similar, the β-scission (eq 7) is estimated to have Arrhenius parameters of $\log k_7$ (s^{-1}) = $14.0 - 28.6/\theta$. At 500 °C, $PhOCH_2^{\bullet}$ is predicted to form a 4:1 ratio of benzaldehyde to benzene plus formaldehyde. As previously discussed, the benzene yield was difficult to quantitate, so the ratio of this pathway for PPE cannot be determined. However, these pathways are important in the FVP of *o*-CH_3O-PPE and (*o*-CH_3O)$_2$-PPE (see below). In the FVP of *o*-CH_3O-PPE, the yield of products from rearrangement to β-scission of the substituted phenoxymethyl radical is 4.3:1, which is in good agreement with our predictions.



(6)

(7)

FVP of *o*-CH_3O-PPE. The major products from FVP of *o*-CH_3O-PPE at 500 °C are shown in Scheme 2 (average mol %). The conversion and mass balance for six FVP runs on *o*-CH_3O-PPE was 3.8 ± 0.2% and 98.2 ± 4.6%, respectively. Surprisingly, salicylaldehyde was the dominant pyrolysis product rather than guaiacol, which was predicted from the reaction pathways of PPE. At 550 and 600 °C, similar pyrolysis products were obtained, but the yield of salicylaldehyde and phenol increased at the expense of the guaiacol. Only a small amount (5 ± 2 mol %) of rearranged starting material (2-methoxy-6-(2-phenylethyl)phenol) was observed, indicating that the surface-mediated, acid-catalyzed reactions are of minor importance. However, the styrene yields were poor based on the ratio of phenolic products to styrene plus ethylbenzene (2.9:1). Independent FVP of styrene at 500 °C

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[39] The most common four-centered elimination reaction is the loss of hydrogen halide from alkyl halides to produce olefins. These reactions are characterized by highly polar cyclic transition states and preexponential factors that fall into the range of $10^{13.5\pm1.0}$ s^{-1} [40] (compared to the preexponential factors for homoloysis $10^{16\pm1}$).[34] In the pyrolysis of substituted α-phenethyl chlorides, a Hammett plot found the rates of elimination correlated with σ^+ and the slope, ρ, was −1.36 (at 335 °C) indicating that moderate carbocationic character developed on the carbon containing the leaving group in the transition state. (a) Maccoll, A. *Chem. Rev.* **1969**, *69*, 33 and references therein. (b) Maccoll, A.; Thomas, P. J. *Progress in Rection Kinetics* **1967**, *4*, 119 and references therein.

[40] O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1967**, *71*, 2903.

[41] Using the Students *t* test at the 90% confidence levels, the conversion for PPE-d_2 and PPE is 0.55 ± 0.08% and 0.71 ± 0.2%, respectively.

[42] Entropy of phenoxy radical 73.7 cal mol^{-1} K^{-1}. Colussi, A. J.; Zabel, F.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 161.

[43] This ratio can also be calculated by the yield of benzyl fragments (i.e., toluene plus 2 × bibenzyl), but toluene and *o*-cresol (0.45 ± 0.05 mol %) are also formed by C−C homolysis of *o*-(2-phenylethyl)phenol.

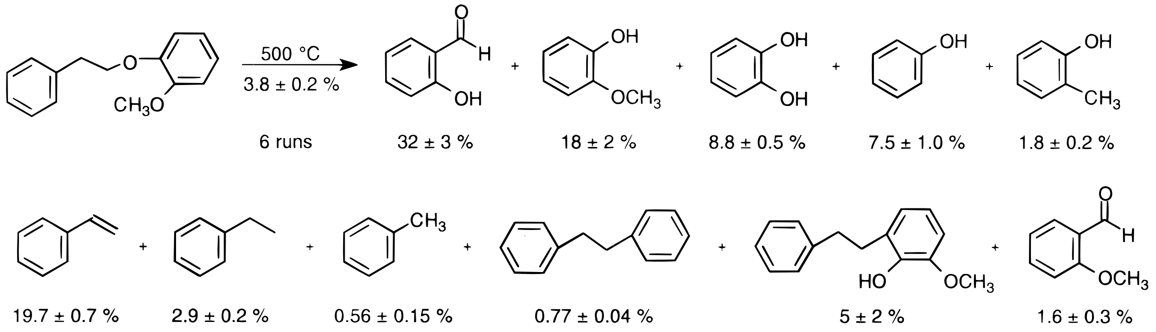
[44] Mulcahy, M. F. R.; Tucker, B. G.; Williams, D. J.; Wilmshurst, J. R. *Aust. J. Chem.* **1967**, *20*, 1155.

[45] Brezinsky, K.; Litzinger, T. A.; Glassman, I. *Int. J. Chem. Kinet.* **1984**, *16*, 1053.

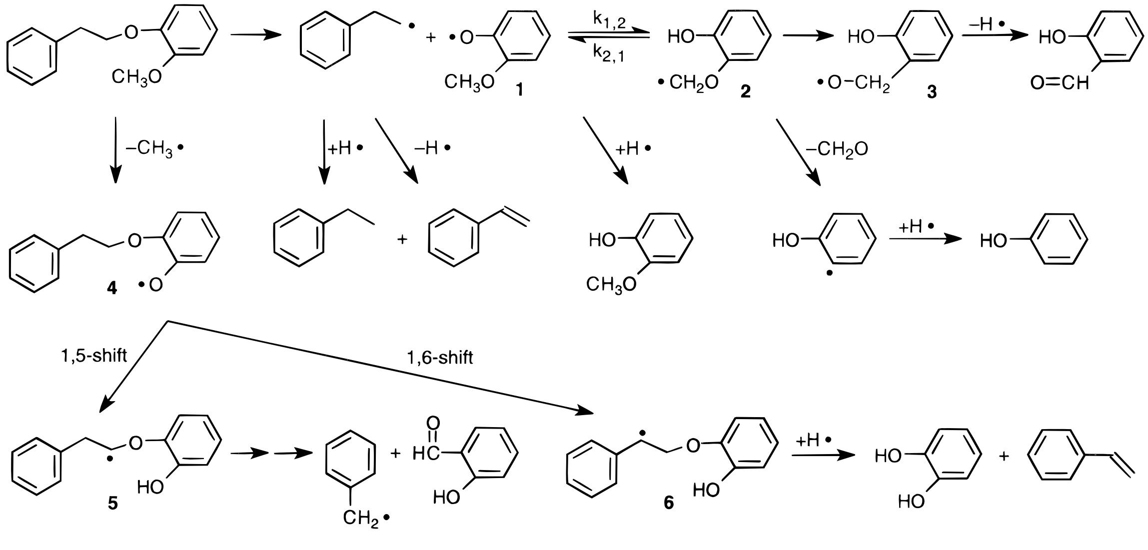
[46] Brezinsky[45] assumed that the reaction of the phenyl radical with formaldehyde had no intrinsic activation energy (i.e., $\Delta H° = E_a$), while the addition of phenyl radical to the oxygen of formaldehyde was estimated to have an intrinsic activation energy of 1 kcal mol^{-1} from Mulder's data[47] and $\Delta H°_{298}(PhOCH_2^{\bullet})$ = 25 kcal mol^{-1}.[11]

[47] Schráa, G.-J.; Arends, I. W. C. E.; Mulder, P. *J. Chem. Soc., Perkin Trans. 2* **1994**, 189.

Scheme 2



Scheme 3



provided quantitative recovery of unreacted styrene. This indicates that styrene could be reacting with the other products in the trap, with hydrogen atoms, or with acidic sites on the reactor surface. Since a carbonaceous residue was found on the reactor surface, it most likely arises from the decomposition of styrene by an unknown pathway. It is interesting to note that the ratio of styrene to ethylbenzene decreases in the FVP of PPE, *o*-CH_3O-PPE, and *o*-$(CH_3O)_2$-PPE from 119:1, to 6.8, to 3.5, respectively, while the conversion and yield of hydrogen atoms, from β-scission of reactive intermediates increase.

The decomposition of *o*-CH_3O-PPE is ca. four times faster than that for PPE. On the basis of the FVP results for PPE, the major products should arise from 1,2-elimination and C−O homolysis. The methoxy substituent is predicted to have little effect on the rate of 1,2-elimination on the basis of the similar Arrhenius parameters obtained in the 1,2-elimination of isobutylene from phenyl *tert*-butyl ether ($\log k\ (s^{-1}) = 14.3 \pm 0.2 - 50.4 \pm 0.7/\theta$) and *p*-methoxyphenyl *tert*-butyl ether ($\log k\ (s^{-1}) = 14.5 \pm 0.3 - 50.2 \pm 0.9/\theta$).[48] At 500 °C, the *p*-methoxy substituent enhanced the 1,2-elimination in phenyl *tert*-butyl ether by a factor of 1.8. The *o*-methoxy group is predicted to accelerate the homolysis of the β-O-4 linkage since *o*-and *p*-methoxy groups lower the bond dissociation energy of anisole by 4 kcal mol^{-1},[20] which corresponds to a rate enhancement of 13.5 at 500 °C. In the pyrolysis of *o*-CH_3O-PPE, the methoxy substituent enhances the C−O homolysis by a factor of 8.5 (corresponding to $\Delta\Delta H°_{298} = 3.3$ kcal mol^{-1}) based on the deuterium isotope effect in the FVP of PPE. The C−O bond of the methoxy group can also cleave, but it is expected to be approximately four times slower than that for O−CH_2CH_2Ph bond based on the average Arrhenius parameters for the homolysis of anisole ($PhOCH_3$) and phenetole ($PhOCH_2CH_3$).[49,50] Thus, C−O homolyses of the β-O-4 linkage and the methoxy group are predicted to be the dominant pathways for the decomposition of *o*-CH_3O-PPE.

The free-radical reaction pathways for the formation of the major products from the FVP of *o*-CH_3O-PPE are shown in Scheme 3. Homolysis of the C−O bond produces the phenethyl and *o*-methoxyphenoxy radical. The phenethyl radical forms styrene and benzene (0.31 ± 0.08 mol %) in a 64:1 ratio, which is in good agreement with the 30:1 ratio estimated above. The *o*-methoxyphenoxy radical (**1**) can pick up hydrogen from the reactor walls to form guaiacol or abstract hydrogen internally from the methoxy substituent through a six-centered transition state to form the *o*-hydroxyphenoxymethyl radical (**2**). To determine if the 1,5-hydrogen shift reaction is competitive

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(48) (a) Martin, G.; Martinez, H.; Ascanio, J. *Int. J. Chem. Kinet.* **1989**, *21*, 193. (b) Martin, G.; Martinez, H.; Ascanio, J. *Int. J. Chem. Kinet.* **1990**, *22*, 1136.

(49) Mirokhin, Y.; Mallard, G.; Westly, F.; Herron, J.; Frizzell, D.; Hampson, R. *NIST Chemical Kinetics Database*; National Institute of Standards and Technology, Gaithersburg, MD, 1998.

(50) Data from the NIST chemical kinetic database for the pyrolysis for anisole (five different studies) was plotted on the same graph and fit to a common Arrhenius equation, $\log k\ (s^{-1}) = 15.8 - 65/\theta$. The same procedure was used for two studies on the pyrolysis of phenetole, $\log k\ (s^{-1}) = 15.7_5 - 62.7/\theta$. At 500 °C, the ratio of the rate constants is 3.98:1.

with other reactions, estimates of the Arrhenius parameters are needed. Unfortunately, there are very few reports of Arrhenius parameters for the hydrogen abstraction of phenoxy radicals with hydrocarbons.[11,51−53] Previously, the rate constants for hydrogen abstraction by phenoxy radicals were assumed to be similar to those for benzyl radicals.[11,53] Thus, for hydrogen-transfer reactions where one center is aliphatic and one center is benzylic, the rate constant is anchored to the average value for the reaction between ethyl radical and toluene $\log k$ (per hydrogen, $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) $= 7.5 \pm 0.2 - 9.6 \pm 0.6/\theta$.[54] If this base reaction is normalized to the hypothetical thermoneutral reaction,[55] we obtain $\log k$ (per hydrogen, $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) $= 8.05 - 15.7/\theta$. We estimate the 1,5-hydrogen shift of **1** to **2** to have $\Delta H^\circ_{298} = 8.9$ kcal mol^{-1} and $\Delta S^\circ_{298} = 2.6$ cal mol^{-1} K^{-1}.[56,57] The preexponential factor for the 1,5-hydrogen shift is expected to be similar to that for other reactions involving 6-centered transition states, such as the ene or Cope reaction, which typically have preexponential factors in the range of $10^{11.5\pm1.5}$ s^{-1}.[40] Some of the earlier experimental investigations into 1,5-hydrogen shifts of alkyl radicals measured Arrhenius parameters with preexponential factors of $10^{9.5}$ s^{-1} ($\Delta S^\ddagger = -17.5$ cal mol^{-1} K^{-1}), which is lower than expected.[58] The loss of entropy in the transition state for the 1,5-hydrogen shift of **1** is predicted to be smaller ($\Delta S^\ddagger = -7$ to -12 cal mol^{-1} K^{-1}, corresponding to a $\log A = 11-12$ s^{-1}) than that for the alkyl radical since the aromatic ring holds the reactive functional groups in close proximity. Intramolecular hydrogen bonding is well documentated in salicylaldehyde and guaiacol.[59] Theoretical calculations (MP-SAC2/6-311G**) on the 1,5-isomerization of 2-methyl-1-hexyl radical found $\Delta S^\ddagger = -7.5$ cal mol^{-1} K^{-1},[60] which agreed well with the $\Delta S^\ddagger = -8.4$ cal mol^{-1} K^{-1} measured for the 1,5-isomerization of 3-methyl-2-hexyl radical.[61] The preexponential factor for the intramolecular hydrogen abstraction by 2-methylbenzoyloxy radical ($\mathrm{CH_3C_6H_4CO_2^\bullet}$) to form 2-carboxybenzyl radical ($\mathrm{^\bullet CH_2C_6H_4CO_2H}$) has been measured as $10^{10.5}$ s^{-1} ($T_\mathrm{m} = 256$ K, $\Delta S^\ddagger = -12.2$ cal mol^{-1} K^{-1}).[62] Although there is a significant variation between the experimental and theoretical[63] preexponential factors for the 1,5-hydrogen shift, we will use an average preexponential factor of $10^{11\pm1}$ s^{-1} ($\Delta S^\ddagger = -10$ cal mol^{-1} K^{-1}). If ΔH°_{298} and ΔS°_{298} are split equally between forward and reverse reaction, and the preexponential factor of the base reaction is increased to reflect intramolecular nature of the 1,5-hydrogen shift (10^{11} s^{-1}), the rate constant estimated for **1** going to **2** is $\log k_{1,2}$ (s^{-1}) $= 11.3 - 20.2/\theta$ and the reverse reaction would have $\log k_{2,1}$ (s^{-1}) $= 10.7 - 11.3/\theta$. At 500 °C, $\log k_{1,2} = 5.6$ s^{-1} and $\log k_{2,1} = 7.5$ s^{-1}. Thus, the 1,5-hydrogen shift is fast, and at higher concentrations, it might even compete with bimolecular reactions (see below).

From the discussion of the reaction pathways of $\mathrm{PhOCH_2^\bullet}$, it is predicted that **2** will also undergo a 1,2-phenyl shift to form the *o*-hydroxybenzyloxy radical (**3**), which can lose a hydrogen atom via β-scission to form salicylaldehyde ($\log k$ (s^{-1}) $= 12.5 - 21/\theta$), which is the major pyrolysis product.[44] The rate constant for **1** picking up hydrogen from the reactor walls cannot be determined, so it is unclear what fraction of **1** forms guaiacol since it can also be formed by the 1,2-elimination. The loss of formaldehyde via β-scission of **2** will be competitive with rearrangement to form **3**. Mulder has estimated the rate constant for β-scission of **2** to be $\log k$ (s^{-1}) $= 14 - 28.4/\theta$ from the ratio of salicylaldehyde to phenol (3.9:1 at $T_\mathrm{m} = 500$ °C) produced in the pyrolysis of dimethoxybenzene.[47] In the FVP of *o*-CH$_3$O-PPE, the ratio of salicylaldehyde to phenol is 4.3:1, which is in good agreement with Mulder's data. The possibility that phenol arises from the pyrolysis of salicylaldehyde was ruled out since independent pyrolysis determined that it was stable under the FVP conditions. On the basis of the rate constant for the β-scission of $\mathrm{PhCH_2O^\bullet}$ reported above, **3** is not expected to contribute to the formation of phenol. Hence, formation of the major product, salicylaldehyde, and phenol is consistent with the formation of the key radical intermediate, **2**, from **1**.

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(51) The rate constant estimates for the reaction of phenoxy radical with anisole has been reported as $\log k$ ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) $= 8.62 - 16.06/\theta$,[28] but it was assumed that the alkyl radical would be conjugated through the oxygen to the aromatic ring (i.e., a resonance-stabilized center). Thus, the rate constant is that reported for the hydrogen abstraction by the benzyl radical from bibenzyl.[31] In the hydrogen abstraction reaction between *tert*-butoxy radicals and substituted toluenes and anisoles, the Hammett plots correlated with σ^+ and σ, respectively, indicating that in the anisoles, direct conjugation with the aromatic ring is not important. (a) Sakurai, H.; Hosomi, A. *J. Am. Chem. Soc.* **1967**, *89*, 458. (b) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Org. Chem.* **1970**, *35*, 993.

(52) Denisov, E. *Handbook of Antioxidants*; CRC Press: New York, 1995.

(53) Phenoxy radicals abstract hydrogen atoms slightly faster (1−6-fold at 375 °C) than benzyl radicals. (a) Stein, S. E. In *Chemistry of Coal Conversion*; Schlosberg, R., Ed.; Plenum: New York, 1985; p 13. (b) Franz, J. A.; Alnajjar, M. S.; Barrows, R. D.; Kaisaki, D. L.; Camaioni, D. M.; Suleman, N. K. *J. Org. Chem.* **1986**, *51*, 1446. (c) Bockrath, B.; Bittner, E.; McGrew, J. *J. Am. Chem. Soc.* **1984**, *106*, 135.

(54) (a) Paputa, M. C.; Price, S. J. W. *Can. J. Chem.* **1979**, *57*, 3178. (b) Daly, M.; Price, S. J. W. *Can. J. Chem.* **1976**, *54*, 1814. (c) LaLonde, A. C.; Price, S. J. W. *Can. J. Chem.* **1971**, *49*, 3367. (d) Koski, A. A.; Price, S. J. W.; Trudell, B. C. *Can. J. Chem.* **1976**, *54*, 482. (e) Zhang, H.-X.; Ahonkhai, S. I.; Back, M. H. *Can. J. Chem.* **1989**, *67*, 1541.

(55) By thermochemical balance ($\Delta H^\circ_{298} = -12.2$ kcal mol^{-1} and $\Delta S^\circ_{298} = 5.2$ cal mol^{-1} K^{-1}) the reverse reaction ($\mathrm{PhCH_2^\bullet + CH_3CH_3}$) has $\log k$ (per hydrogen, $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) $= 8.6 - 21.8/\theta$. Assuming no polar effects in the hydrogen transfer reaction, the Evans−Polanyi correlation ($E = \alpha(\Delta H^\circ_\mathrm{rxn}) + C$) can be used with $\alpha = 0.5$, i.e., a symmetrical transition state, and C is determined from the base reaction. To construct the hypothetical thermoneutral reaction for reaction between aliphatic and benzylic centers, $C = E_\mathrm{base} - 0.5(\Delta H^\circ_\mathrm{base})$.

(56) The ΔH°_{298} of o-$\mathrm{CH_3OC_6H_4O^\bullet}$ is estimated as -24.7 kcal mol^{-1} from the ΔH°_{298} of phenoxy radical (11.2 kcal mol^{-1})[26] and group additivity, $-\mathrm{C_B{-}H} + \mathrm{C_B{-}O} + \mathrm{O{-}C_BC} + \mathrm{C{-}H_3C}$.[34,57] Another method to estimate this number uses the O−H BDE of guaiacol, (ΔBDE 3.9 kcal mol^{-1}, relative to phenol in solution)[64] estimated as 83.1 kcal mol^{-1} in the gas phase,[26] and the $\Delta H^\circ_\mathrm{f}$ (guaiacol) $= -58$ kcal mol^{-1}.[27] The ΔH°_{298} of o-$\mathrm{CH_3OC_6H_4O^\bullet}$ is estimated as -27.0 kcal mol^{-1}. The ΔH°_{298} of o-$\mathrm{^\bullet CH_2OC_6H_4OH}$ is estimated as -17.1 kcal mol^{-1} from ΔH°_{298} of $\mathrm{C_6H_5OCH_2^\bullet}$ (25 kcal mol^{-1})[11] and group additivity ($-\mathrm{C_B{-}H} + \mathrm{C_B{-}O} + \mathrm{O{-}C_BH}$). Another method to estimate this number uses the BDE of the $\mathrm{OCH_2{-}H}$ bond as 93.3 kcal mol^{-1}, which is assumed to be similar to that of dimethyl ether.[11] The H°_{298} of o-$\mathrm{^\bullet CH_2OC_6H_4OH}$ is estimated as -16.8 kcal mol^{-1} by this procedure. An average value for the 1,5-hydogen shift (8.9 kcal mol^{-1}) will be used.

(57) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

(58) Dóbé, S.; Bérces, T.; Réti, F.; Márta, F. *Int. J. Chem. Kinet.* **1987**, *19*, 895 and references therein. The rate constant for the 1,5-hydrogen shift from 1-hexyl to 2-hexyl radical has been measured as $\log k$ (s^{-1}) $= 9.5 - 11.6/\theta$.

(59) For recent examples, see: (a) Chung, G.; Kwon, O.; Kwon, T. *J. Phys. Chem. A* **1998**, *102*, 2381. (b) Fujimaki, E.; Fujii, A.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **1999**, *110*, 4238.

(60) Viskolcz, B.; Lendvay, G.; Seres, L. *J. Phys. Chem. A* **1997**, *101*, 7119.

(61) Larson, C. W.; Chua, P. T.; Rabinovitch, B. S. *J. Phys. Chem.* **1972**, *76*, 2507.

(62) Wang, J.; Tsuchiya, M.; Sakuragi, H.; Tateno, T. *Chem. Lett.* **1992**, 563.

(63) Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508. Theoretical calculations (UMP2/6-31G*) on a series of 1,5-hydrogen atom transfer reactions to oxygen from the Barton reaction, Norrish Type II reaction, alcohol radical cation rearrangement, and retro-ene reaction have also found lower $\Delta S^\ddagger$ (-3.6, -4.8, -7.1, and -4.9 cal mol^{-1} K^{-1}, respectively) than that found experimentally.

Catechol can arise from the pyrolysis of guaiacol since the *o*-hydroxy substituent lowers the bond dissociation energy of anisole by 7 kcal mol^{-1}.[20] The FVP of guaiacol was investigated at 500 °C, the average conversion from two runs was 4.5 ± 0.8%, and the mass balance was 98.2 ± 0.5%. The major products were catechol (66 ± 3%) and salicyladehyde (21 ± 2%). The conversion of guaiacol is in good agreement with that estimated from the reported rate constants (6.7%).[20] In the FVP of *o*-CH_3O-PPE, the ratio of guaiacol to catechol is 2:1. Therefore, pyrolysis of guaiacol is only a minor pathway for the formation of catechol. Catechol could also be formed by β-scission of a methyl group from the **1** to form *o*-benzoquinone, which could pick up hydrogen from the reactor walls to form catechol. However, Mulder did not observe catechol or *o*-benzoquinone in the pyrolysis of 1,2-dimethoxybenzene or 2,3-dihydro-1,4-benzodioxin.[47] The cleavage of the methyl group from **1** is estimated to have an activation energy of 41.5 kcal mol^{-1} based on the $\Delta H°_{298} = 34.5$ kcal mol^{-1}, and the intrinsic activation energy for the addition of a methyl radical to a olefin $E_a = 7$ kcal mol^{-1}.[27,30] The preexponential factor for β-scission should be similar to that for loss of a methyl radical from 1-phenyl-1-propyl radical, $10^{14.8}$ s^{-1}.[27] Thus, the rate constant for β-scission of a methyl radical from **1** to form *o*-benzoquinone is estimated as $\log k$ (s^{-1}) = 14.8−41.5/θ. At 500 °C, β-scission ($\log k = 3.1$ s^{-1}) is not competitive with intramolecular hydrogen abstraction and loss of formaldehyde.

Another possible pathway for the formation of catechol is by C−O homolysis of the methoxy group to produce a methyl radical and $PhCH_2CH_2OC_6H_4O^\bullet$ (**4**). Cleavage of the $O-CH_3$ bond is estimated to be ca. four times slower than cleavage of the phenethyl group.[50] Cleavage of **4** to form the phenethyl radical and *o*-benzoquinone is predicted to be slow ($\log k = 3.7$ s^{-1}) from the estimates above. Thus, intramolecular hydrogen abstraction can occur at the β- or α-carbons, i.e., a 1,5- or 1,6-hydrogen shift, to form **5** and **6**, respectively. Theoretical calculations at the MP-SAC2/6-311G** level on the isomerization of the 2-methyl-1-hexyl radical predict that the 1,5-hydrogen shift will be responsible for over 70% of the isomerization, but 1,6-hydrogen shifts could contribute as much as 11−26% depending on the pressure and temperature (800−1500 K).[60] The ring strain for both 1,5- and 1,6-hydrogen shifts of the alkyl radicals were estimated to be less than 2 kcal mol^{-1}. The calculated activation energy for the 1,5-hydrogen shift for the 2-methyl-1-hexyl radical was 13 kcal mol^{-1} and agreed reasonably well with the experimental activation energies of 11.6 and 11.2 kcal mol^{-1} for the 1-hexyl and 3-octyl radicals, respectively.[58] The calculated activation energy for the 1,6-hydrogen-transfer reaction was 15.1 kcal mol^{-1}, which agrees with the activation energy suggested by Larson et al. of 16 kcal mol^{-1}.[61] In PPE, bimolecular hydrogen abstraction by the phenoxy radical is favored at the benzylic site (α-carbon) over the β-carbon by a 3:1 ratio at 375 °C.[11] Taking into account the ring strain, entropy effects ($10^{0.33}$),[60] and activation energy for hydrogen abstraction,[11] the ratio of 1,5- to 1,6-hydrogen shift is estimated as 2.5:1, indicating that the 1,6-hydrogen transfer should be competitive. 1,6-Hydrogen shift forms **6**, which can cleave to produce styrene and *o*-hydroxyphenoxy radical, which can pick up hydrogen to form catechol. Intramolecular 1,5-hydrogen abstraction from the β-carbon produces **5**. In the liquid-phase pyrolysis of PPE, $C_6H_5CH_2CH(^\bullet)OC_6H_5$ undergoes a 1,2-phenyl shift to form $C_6H_5CH_2CH(O^\bullet)C_6H_5$ ($\log k$ (s^{-1}) > 11.5 − 18/θ) and cleaves to produce benzaldehyde and the benzyl radical.[11] In an analogous fashion, **5** can undergo a rearrangement and β-scission to form salicyladehyde and the benzyl radical. Since salicyladehyde is also formed from rearrangement of **1** and toluene is formed from C−C homolysis, the contribution of the 1,5-hydrogen shift cannot be determined from the product yields. However, the yield of catechol is ca. 1.8 times larger than that estimated (taking into account the small amount formed by pyrolysis of guaiacol), indicating that C−O homolysis of the methoxy group is faster than predicted or the ratio of 1,5- to 1,6-hydrogen shifts is <2.5. (A ratio of 1.75 is measure in the FVP of (*o*-CH_3O)$_2$-PPE; see below.)

The small amounts of toluene, bibenzyl, and *o*-methoxybenzaldehyde are formed from C−C homolysis to produce the benzyl radical and the *o*-methoxyphenoxymethyl radical. The benzyl radicals can pick up hydrogen to form toluene or couple to form bibenzyl. The *o*-methoxyphenoxymethyl radical can undergo 1,2-phenyl shift and loss of a hydrogen atom to form *o*-methoxybenzaldehyde. The ratio of cleavage of the β-O-4 linkage to C−C homolysis was determined to be 50:1 from the ratio of salicyladehyde, guaiacol, plus phenol to *o*-methoxybenzaldehyde, since toluene is also formed from the cleavage of the methoxy group. This ratio is ca. 2.5 times larger than that found for PPE, but the amount of products from C−C homolysis is still larger than expected from the thermochemical estimates. However, the *o*-methoxy group can also enhance C−C homolysis by providing a small amount of additional stabilization to the phenoxymethyl radical. In the abstraction of methyl hydrogens from substituted anisoles by *tert*-butoxy radical, the *p*-methoxy substituent enhanced the relative rate of hydrogen abstraction (per hydrogen) by a factor of 1.3, indicating the methoxy substituent must either destabilize the ground state or stablize the radical center.[51b]

FVP of (*o*-CH_3O)$_2$-PPE. The major products (mol %) from the FVP of (*o*-CH_3O)$_2$-PPE are shown in Scheme 4. The average conversion and mass balance for six runs was 11 ± 1% and 99 ± 2%, respectively. The reaction mixtures were surprisingly complex, and the major product was *o*-cresol (24 mol %) and not 2-hydroxy-3-methoxybenzaldehyde (8.8 mol %), which would be predicted from the reaction pathways of *o*-CH_3O-PPE. Three unidentified products were also formed with molecular weights of 196 (2.8 ± 0.8%) and 210 (2.3 ± 0.4%) and 210 (2.2 ± 0.6%) that did not contain phenolic groups (i.e., did not silylate with BSTFA, see the Experimental Section).

The decomposition of (*o*-CH_3O)$_2$-PPE is only 2.8 times faster than *o*-CH_3O-PPE, indicating the second methoxy group does not enhance the homolysis of the β-O-4 linkage as much as the first. This was also found in the solution-phase bond dissociation energies (BDEs, relative to phenol) of *o*-methoxyphenol (ΔBDE (O−H) = 3.9 kcal mol^{-1})[64] and 2,6-dimethoxyphenol (ΔBDE (O−H) = 5.1 kcal mol^{-1}).[65,66] The methoxy substituents are not predicted to substantially enhance the 1,2-elimination, as

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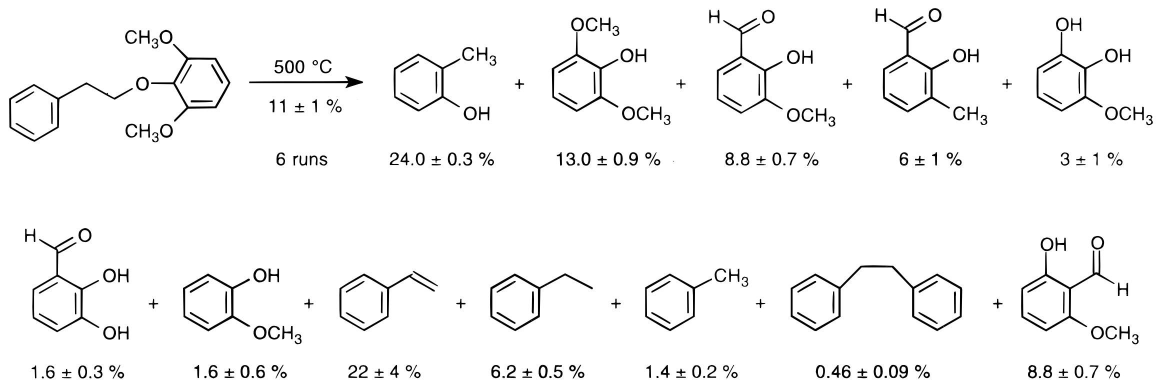
[64] Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736.

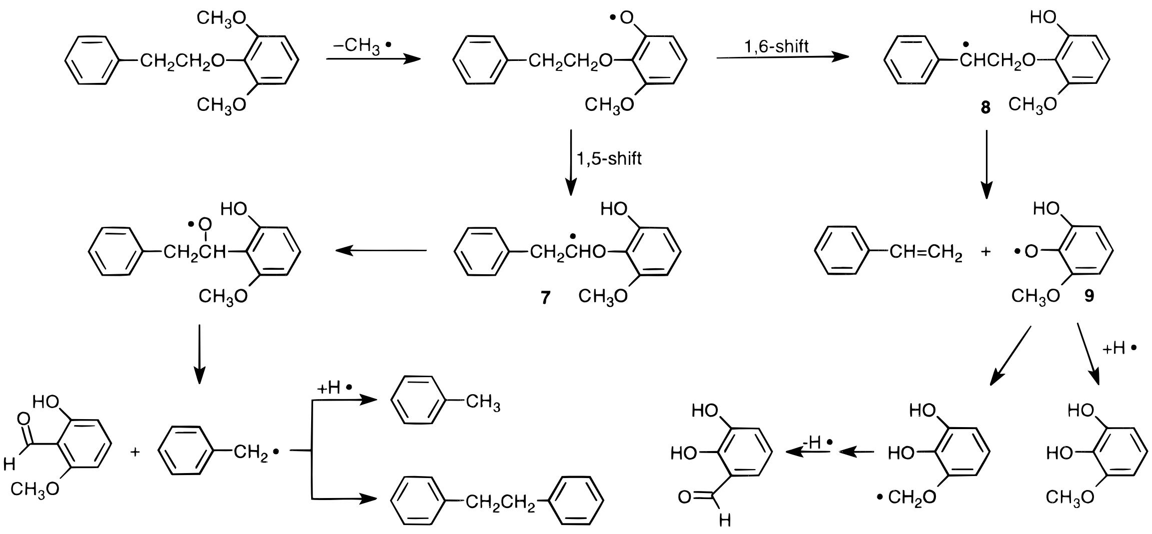
[65] Lucarini, M.; Pedrielli, P.; Pedulli, G. F. *J. Org. Chem.* **1996**, *61*, 9259.

[66] BDE for substituted phenols have also been calculated with density functional theory (B3LYP). Wright, J. S.; Carpenter, D. J.; McKay, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1997**, *119*, 4245.

Scheme 4



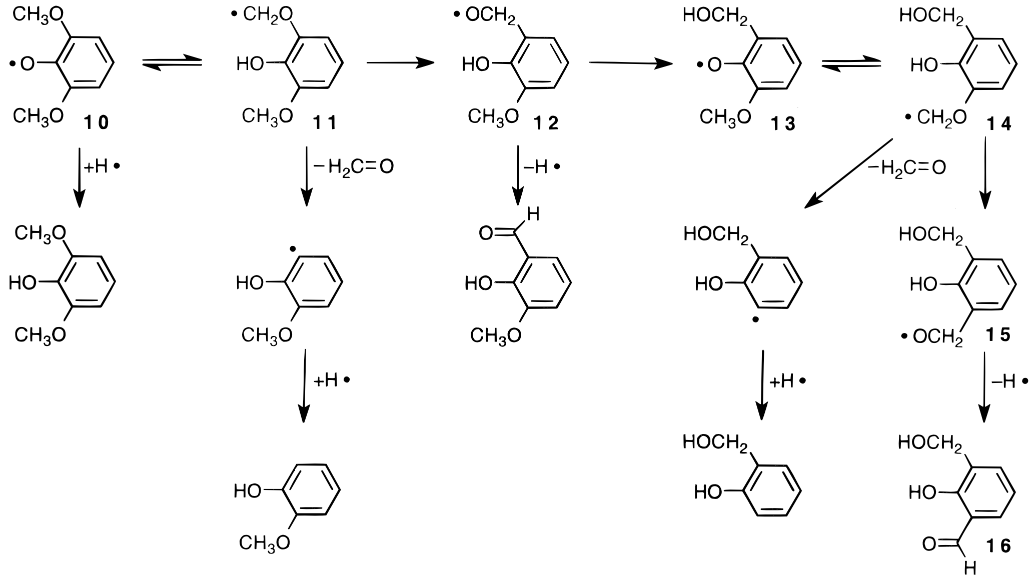
Scheme 5



discussed above, but the contribution of the 1,2-elimination to this reaction cannot be determined since C−O homolysis produces the same products. As for *o*-CH_3O-PPE, the major decomposition pathway for (*o*-$CH_3O)_2$-PPE should be by C−O homolysis of the β-O-4 linkage and the methoxy groups. As previously discussed, the methoxy group should cleave ca. four times slower than the β-O-4 linkage. Homolysis of the methoxy group forms a methyl radical and a phenoxy radical that can intramolecularly abstract hydrogen from the α- or β-carbons (Scheme 5). β-Scission of the aryloxy radical, to form 3-methoxy-1,2-benzoquinone and the phenethyl radical, is predicted to be slower than intramolecular hydrogen abstraction, as previously discussed. As opposed to *o*-CH_3O-PPE, 1,5- and 1,6-hydrogen shifts give unique products that allow the contribution of these pathways to be determined from the product yields. The 1,5-hydrogen shift forms **7**, which can undergo a 1,2-phenyl shift, as observed in the liquid-phase pyrolysis of PPE, and β-scission to give 2-hydroxy-6-methoxybenzaldehyde (8.8 mol %) and the benzyl radical, which will dimerize or pick up hydrogen from the walls of the reactor.[11] 1,6-Hydrogen shift forms **8**, which can undergo β-scission to form styrene and the 2-hydroxy-6-methoxyphenoxy radical (**9**). The reaction pathways for **9** should be similar to that for **1**. Thus, **9** can pick up hydrogen from the reactor walls to form 3-methoxycatechol (3 mol %). Phenoxy radical **9** can also intramolecularly abstract hydrogen from the methoxy substitutent (1,5-hydrogen shift), rearrange by a 1,2-phenyl shift, and lose a hydrogen atom to give 2,3-dihydroxybenzaldehyde (1.6 mol %). The 2,3-hydroxyphenoxymethyl radical can undergo β-scission to give formaldehyde and 2,3-dihydroxyphenyl radical, which will pick up hydrogen to form catechol (0.8 ± 0.2 mol %). 3-Methoxycatechol could also be formed from decomposition of 2,6-dimethoxyphenol. FVP of 2,6-dimethoxyphenol was investigated at 500 °C, and the average conversion and mass balances for two runs were 5.1 ± 0.3% and 99 ± 6%, respectively. The major products were 3-methoxycatechol (56 mol %), 2,3-dihydroxybenzaldehyde (21 mol %), *o*-cresol (10.9 mol %), and 2-hydroxy-3-methoxybenzaldehyde (9.5 mol %). Therefore, ca. 10% of the 3-methoxycatechol arises from decomposition of 2,6-dimethoxyphenol. From the yield of 2-hydroxy-6-methoxybenzaldehyde relative to 3-methoxycatechol (minus the contribution from decomposition of 2,6-dimethoxyphenol), catechol, plus 2,3-dihydroxybenzaldehyde, the ratio of 1,5- to 1,6-hydrogen shift is 1.75:1.

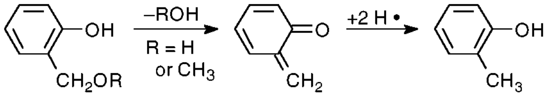
Pyrolysis of (*o*-$CH_3O)_2$-PPE by homolysis of the β-O-4 linkage gives the 2,6-dimethoxyphenoxy radical (**10**) and the phenethyl radical. The 2,6-dimethoxyphenoxy radical is predicted to undergo a series of reactions similar to that outlined for radicals **1** and **9**, but these pathways should also lead to the formation of the major product, *o*-cresol (see Scheme 6). Thus, **10** can pick up hydrogen to form 2,6-dimethoxyphenol (13 mol %) or can intramolecularly abstract hydrogen from the methoxy substituents to form **11**. This radical can rearrange by a 1,2-phenyl shift (major pathway) to form 2-hydroxy-3-methoxybenzyloxy radical (**12**), or **11** can lose formalde-

Scheme 6



hyde to give 2-hydroxy-3-methoxyphenyl radical, which will pick up a hydrogen to form guaiacol (1.6 mol %). The benzyloxy radical **12** can form 2-hydroxy-3-methoxybenzaldehyde (6 mol %) by β-scission of a hydrogen atom or undergo intramolecular hydrogen abstraction from the phenol to produce the 2-hydroxymethyl-6-methoxyphenoxy radical (**13**). This hydrogen transfer reaction is estimated to be highly exothermic ($\Delta H°_{298} = -16.6$ kcal mol^{-1}, and $\Delta S°_{298} = 1.5$ cal mol^{-1} K^{-1}) and, thus, very rapid.[34,57] A rate constant for this 1,5-hydrogen shift can be estimated by anchoring it to the hydrogen abstraction reaction between hydroxyl radical and phenol.[67] Previously, the preexponential factor for 1,5-hydrogen shift was estimated to be 10^{11} s^{-1}. Thus, the rate constant for the intramolecular hydrogen abstraction between the benzyloxy radical and phenol is predicted to be (log k (s^{-1}) = 11.3−6.8/θ) with a rate constant of log $k = 9.4$ s^{-1} at 500 °C, which is competitive with the rate constant for β−scission of a hydrogen atom from **12** to form 2-hydroxy-3-methoxybenzaldehyde, (assumed to be the same as for the phenoxymethyl radical, log $k = 9.0$ s^{-1}).[45] In the FVP of *o*-CH_3O−PPE, this reaction pathway could also occur for **3** to form the 2-hydroxymethylphenoxy radical which could pick up hydrogen to form 2-hydroxybenzyl alcohol. As discussed below, FVP of 2-hydroxybenzyl alcohol can produce *o*-cresol which was found in the FVP of *o*-CH_3O−PPE in 1.8 ± 0.2 mol % yield. The phenoxy radical **13** can undergo a 1,5-hydrogen shift to form 2-hydroxy-3-hydroxymethylphenoxymethyl radical (**14**). β-Scission of a hydroxy radical from **13** to form the 6-methoxy-*o*-benzoquinone methide is unlikely as a consequence of the large reaction enthalpy ($\Delta H°_{298} = 52.3$ kcal mol^{-1}).[68] The phenoxymethyl radical **14** can rearrange to form **15** and lose a hydrogen atom to form 2-hydroxy-3-hydroxymethylbenzaldehyde (**16**) or lose formaldehyde and pick up a hydrogen from the reactor walls to form 2-hydroxybenzyl alcohol. The benzyloxy radical **15** can also undergo a 1,5-hydrogen shift to form the 2,6-di(hydroxymethyl)phenoxy radical, which could pick up hydrogen to form 2,6-di(hydroxymethyl)phenol. However, this product would not be stable to the reaction conditions and would undergo additional reaction (see below).

It is predicted that **16** and 2-hydroxybenzyl alcohol would form *o*-cresol by degrading to *o*-quinone methides, which are known to form *o*-cresol under these reaction conditions. For example, the pyrolyses of 2-hydroxybenzyl alcohol[69] and 2-methoxymethylphenol[70] have been previously studied and were shown to produce *o*-benzoquinone methide (6-methylene-2,4-cyclohexadien-1-one) by elimination of water or methanol, respectively (eq 8). The elimination reaction occurs at 190 °C in solution,[71] and the *o*-benzoquinone methide can be trapped by electron-rich dienophiles, such as styrene, to give chroman derivatives.[72] In the gas phase at 500−650 °C, the elimination is quantitative. Although the origin of the *o*-cresol as the dominant product in the gas-phase pyrolysis of chroman was not completely evident, it was suggested that hydrogen atoms initiated the reaction.[73] Mulder has suggested that *o*-benzoquinone methide reacts with hydrogen atoms[69,74] ($k_{add} = 10^{9-10}$ M^{-1} s^{-1})[49] or hydrogen donors



(8)

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(67) The rate constant for the reaction of hydroxy radical with phenol is $k = 2.62 \times 10^8$ (T/298)^2 M^{-1} s^{-1} exp (+1.31 kcal mol^{-1}/RT),[49] and the reaction enthalpy is $\Delta H°_{298} = -32.9$ kcal mol^{-1}.[27] Splitting $\Delta H°$ equally between the forward and reverse reaction, the activation energy for the hypothetical thermoneutral reaction is 15.1 kcal mol^{-1}.

(68) Reaction enthalpy estimated for β-scission of hydroxy radical from 2-hydroxymethylphenoxy radical to form *o*-benzoquinone. The $\Delta H°_{298}$ (2-hydroxymethylphenoxy radical) = −32.5 kcal mol^{-1} was calculated from the $\Delta H°_{298}$ (PhO) and group additivity. $\Delta H°_{298}$ *o*-benzoquinone methide) = 10.5 kcal mol^{-1} was calculated from the $\Delta H°_{298}$ (*o*-benzoquinone) = −25 kcal mol^{-1},[27] and group additivity (−COC_BCO (−24.3 kcal mol^{-1}) was calculated from $\Delta H°_{298}$ (*o*-benzoquinone) and other known group contributions.[57]

(69) Dorrestijn, E.; Epema, O. J.; van Scheppingen, W. B.; Mulder, P. *J. Chem. Soc., Perkins Trans. 2* **1998**, 1173.

(70) (a) Gardner, P. D.; Sarrafizadeh, R. H.; Brandon, R. L. *J. Am. Chem. Soc.* **1959**, *81*, 5515. (b) Cavitt, S. B.; Sarrafizadeh, R. H.; Gardner, P. D. *J. Org. Chem.* **1962**, *27*, 1211.

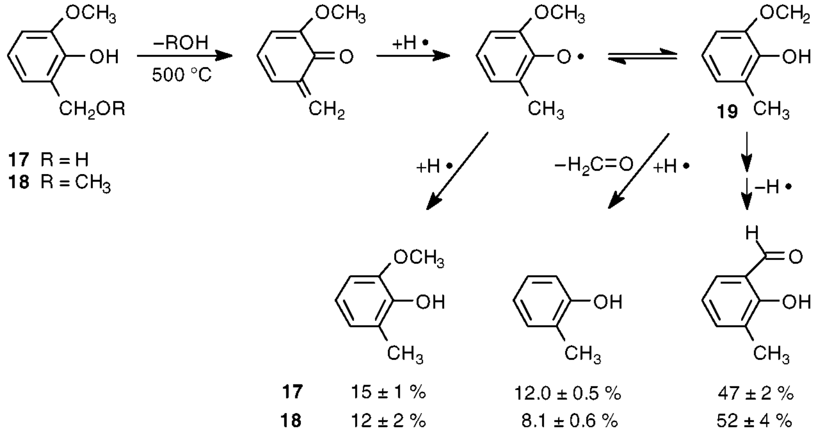
(71) Dorrestijn, E.; Kranenburg, M.; Ciriano, M. V. Mulder, P. *J. Org. Chem.* **1999**, *64*, 3012.

(72) Yato, M.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1990**, *112*, 5341.

(73) Paul, G. C.; Gajewski, J. J. *J. Org. Chem.* **1993**, *58*, 5060.

(74) Dorrestijn, E.; Pugin, R.; Nogales, M. V. C.; Mulder, P. *J. Org. Chem.* **1997**, *62*, 4804.

Scheme 7



(such as toluene) by reverse radical disproportionation[74] to form *o*-cresol. Even in VLPP of 2-hydroxybenzyl alcohol, *o*-benzoquinone methide produced *o*-cresol.[69] In this case, *o*-cresol was proposed to arise from wall-mediated hydrogen-transfer reactions to form the *o*-methylphenoxy radical and then *o*-cresol. Addition of a hydrogen atom to the methylene carbon is estimated to be ca. 3.6 kcal mol^{-1} more favorable than addition to the carbonyl oxygen.[74] To determine the reaction pathways of the *o*-benzoquinone methide under our reaction conditions, the FVP of 2-hydroxy-3-methoxybenzyl alcohol (**17**) and 2-methoxy-6-methoxymethylphenol (**18**) was investigated (since we were unable to synthesize the reaction intermediate **16**).

The FVP of **17** was investigated at 500 °C (Scheme 7). The compound proved to be very reactive, and it decomposed in the sublimation chamber (T < 343 K). The reaction mixtures were analyzed as the trimethylsilyl ethers since the underivatized starting material decomposed in the GC. Small amounts of starting material (15 ± 5%) were recovered in the pyrolysis, but the mass balances were very poor (21.6 ± 0.7%), and significant amounts of char were formed at the entrance and exit of the furnace (ca. 50% of the starting mass). The major low molecular weight products from three FVP runs of **17** were 2-hydroxy-3-methylbenzaldehyde (47 ± 2 mol %), 2-methoxy-6-methylphenol (15 ± 1 mol %), and *o*-cresol (12.0 ± 0.5 mol %) in addition to a series of unresolvable products at long GC retention time (i.e., high molecular weight). In an attempt to minimize the decomposition of the starting material in the sublimation chamber and improve mass balances, we attempted the FVP of the methyl ether of hydroxybenzyl alcohol, i.e., **18**. The conversion from three FVP runs was quantitative and the mass balance improved to 29 ± 2% but significant amounts of char were still produced (47 ± 15%). The same products were formed as in the pyrolysis of **17**, 2-hydroxy-3-methylbenzaldehyde (52 ± 4 mol %), 2-methoxy-6-methylphenol (12 ± 2 mol %), *o*-cresol (8.1 ± 0.6 mol %), and an unknown product with *m*/*e* 150. In the absence of a trapping agent, it has been reported that *o*-benzoquinone methide undergoes self-condensation, via Diels−Alder reaction, to form the dimer at −100 °C,[75] and upon warming to room temperature a trimer (dominant)[70] and tetramer are formed. In the FVP of **18**, no oligomeric products from the self-condensation of *o*-benzoquinone methide could be identified by GC−MS when the reaction products were dissolved in acetone. But when the reaction products were dissolved in toluene, new peaks were found that had molecular weights corresponding to dimer (272), trimer (408), and tetramer (544). *o*-Benzoquinone methide also under goes reactions with nucleophiles such as acetic acid and methanol.[76] Additional peaks were found on the GC−MS that contained the molecular weights and appropriate fragmentation patterns for the adducts of the phenolic products and 3,5-dimethylphenol (standard used for GC quantitation) with *o*-benzoquinone methide. Therefore, it appears that *o*-benzoquinone methide is formed in the FVP of **17** and **18**.

o-Benzoquinone methide has also been shown to undergo Diels−Alder reactions with electron-rich olefins, such as phenyl vinyl ether, ethyl vinyl ether, styrene, or isoprene.[72,76] To determine if the unknown products in the FVP of (o-CH$_3$O)$_2$-PPE with *m*/*e* of 210 were adducts of *o*-benzoquinone methide with styrene (a reaction product), the FVP of **18** was run with a large excess of stryene in the trap. Small amounts of 2-phenylchroman (*m*/*e* 210) were produced, but this product had a different retention time than that of the unknown products form the pyrolysis of (o-CH$_3$O)$_2$-PPE.

The major products in the pyrolysis **17** and **18** can be rationalized by loss of water or methanol to form the *o*-benzoquinone methide, which can pick up hydrogen from the reactor walls to make 2-methyl-6-methoxyphenoxy radical (see Scheme 7). This radical can pick up hydrogen to form 2-methoxy-6-methylphenol or intramolecularly abstract hydrogen to form the phenoxymethyl radical (**19**). This radical intermediate can form *o*-cresol by loss of formaldehyde and picking up a hydrogen atom, or 2-hydroxy-3-methylbenzaldehyde by 1,2-phenyl shift followed by β-scission of a hydrogen atom. The 2-hydroxy-3-methylbenzyloxy radical can undergo intramolecular hydrogen abstraction from the phenol to form the 2-hydroxymethyl-6-methylphenoxy radical, which can pick up a hydrogen to give 2-hydroxymethyl-6-methylphenol. This product would not be stable and undergo additional decomposition to 2,6-dimethylphenol. A carefully examination of the GC and GC-MS traces found that a small amount of 2,6-dimethylphenol was formed.

In the FVP of (o-CH$_3$O)$_2$-PPE, **16** is predicted to quickly undergo elimination of water to form the substituted

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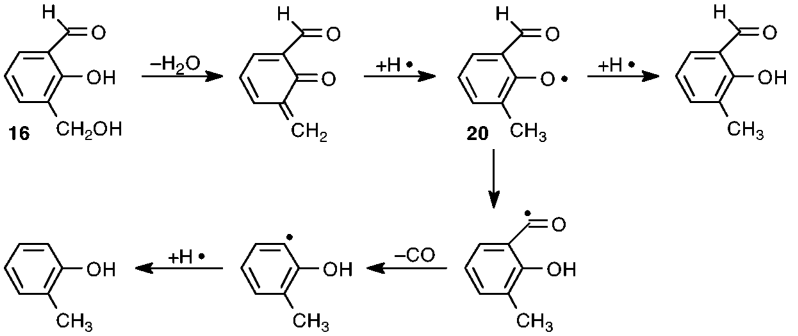
[75] Letulle, M.; Guenot, P.; Ripoll, J.-L. *Tetrahedron Lett.* **1991**, *32*, 2013.

[76] Bolon, D. *J. Org. Chem.* **1970**, *35*, 3666.

Scheme 8



o-benzoquinone methide (see Scheme 8). Examination of the silylated reaction mixture by GC−MS found a small amount of **16**. As observed in other studies, the *o*-benzoquinone methide will pick up hydrogen atoms from the wall of the reactor to form the 2-formyl-6-methylphenoxy radical (**20**) and 2-hydroxy-3-methylbenzaldehyde (6 mol %). The phenoxy radical **20** could abstract hydrogen from the aldehyde and decarbonylate to form the 2-hydroxy-3-methylphenyl radical, which will pick up hydrogen to form *o*-cresol. The activation barrier for 1,4-hydrogen-transfer reactions is typically 20 kcal mol^{-1}.[60] The hydrogen-abstraction reaction is thermoneutral since the C−H BDE of benzaldehyde (86.9 kcal mol^{-1})[77] is similar to the O−H BDE of phenol (87 kcal mol^{-1})[26] and the reaction entropy is $\Delta S°_{298} = 5.3$ cal mol^{-1} K^{-1}. The preexponential factor of 1,4-hydrogen transfer reactions has been estimated as 10^{11} s^{-1} [61] and theoretically calculated as $10^{11.8}$ s^{-1} for the 2-methyl-1-hexyl radical.[60] Intramolecular 1,4-hydrogen shifts have also been measured in solution for substituted 2-hydroxyphenols by kinetic EPR. The average preexponential factor was $10^{11.6\pm0.4}$ s^{-1} (at ca. 298 K).[78] Therefore, an average preexponential factor of $10^{11.5}$ s^{-1} will be used. Thus, a rough estimate of the rate constant for 1,4-hydrogen transfer (splitting $\Delta S°_{298}$ equally between the forward and the reverse reaction) is $\log k$ (s^{-1}) $= 11.5-20/\theta$ (at 500 °C, $\log k = 10^{5.8}$ s^{-1}). After hydrogen abstraction, decarbonylation will be very fast ($\log k = 6.3$ s^{-1}),[79] and the aryl radical will pick up hydrogen to give cresol. A similar 1,4-hydrogen abstraction reaction has been reported in the FVP of *N*-(2-allyloxybenzylidene)aniline at 650 °C.[80] The major product, 2-cyanophenol, was rationalized by 1,4-hydrogen abstraction by the phenoxy radical from the imine carbon atom, followed by β-scission to give 2-cyanophenol and the phenyl radical. Thus, the rapid 1,4-hydrogen shift seems reasonable.

Comparison of FVP Results with Other Pyrolysis Conditions. The product distribution from the pyrolysis of PPE,[11] *o*-CH_3O-PPE, and (*o*-CH_3O)$_2$-PPE in the liquid phase and the gas phase (3×10^{-2} M) at 375 °C[81] are quite different from that obtained from the FVP at higher temperatures. At lower temperatures and high concentrations, pyrolysis occurs instead by a free-radical chain pathway to form styrene plus the substituted phenol as the major products and toluene plus the substituted benzaldehyde as minor products. These two sets of products are formed in a ratio of 3:1 for PPE and 5:1 for *o*-CH_3O-PPE and (*o*-CH_3O)$_2$-PPE. The products are formed by hydrogen abstraction by the chain carrying phenoxy and benzyl radicals at the α- and β-carbons to form $PhCH(^\bullet)CH_2OAr$ and $PhCH_2CH(^\bullet)OAr$ followed by β-scission of the former and 1,2-phenyl shift and β-scission of the latter. This free-radical chain reaction was also found to occur under condition of restricted diffusion, which could be imposed by the macromolecule structure of lignin.[12] At the lower temperatures (375 °C) and low conversions (<10%), the methoxy groups do not cleave to any significant extent and dihydroxybenzenes are not observed. At high concentrations, the chain-carrying methoxyphenoxy radicals undergo bimolecular hydrogen abstraction reactions rather than intramolecular hydrogen abstraction. However, a small amount of salicyladehyde (<0.5 mol %) was formed in the liquid-phase pyrolysis of *o*-CH_3O-PPE at 375 °C. In the gas phase (3×10^{-2} M) at 375 °C, the yield of salicyladehyde increased, but it was still a minor product (<2 mol %). However, this was predicted on the basis of the rate constant estimates for the reaction pathways for the methoxyphenoxy radical discussed above. Steady-state analysis of the reaction pathways for **1**, described in Scheme 3, with the addition of a bimolecular hydrogen abstraction step (k_H) predicts that $d[\mathbf{1}]/dt \approx k_H[\mathbf{1}][o\text{-}CH_3O\text{-PPE}]$ since $k_{2,1} + k_{\mathbf{2}\rightarrow\mathbf{3}} + k_{\mathbf{2}\rightarrow\text{phenol}} \approx k_{2,1}$ at 375 °C. Assuming the rate constant for hydrogen abstraction by **1** is similar to that for the phenoxy radical ($\log k_H$ (M^{-1} s^{-1}) $= 8.3-14.4/\theta$),[11] the ratio of bimolecular to unimolecular reactions from **1** is predicted to be ca. 1:13 at 3×10^{-2} M. The experimental ratio of ca. 15:1 indicates that either the estimated equilibrium between **2** and **1** (250 at 375 °C) must be too small or the unimolecular reactions of **2** to **3** and phenol are slower than estimated (or both). This example highlights the current difficulties in predicting product yields from thermochemical kinetic estimates of oxygen-containing substrates in which many of the parameters are not well defined. Moreover, thermochemical estimates do not take into account any polar effects, from the electrophilic phenoxy radicals, which can alter the product distribution in these reactions.[82] Therefore, additional flash pyrolysis experiments will be run at higher substrate concentrations to determine the competition between the unimolecular and bimolecular reaction pathways.

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Summary

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 reaction pathways were significantly more complex than initially expected and were dominated by free-radical reactions, molecular rearrangements, and concerted eliminations. As opposed to liquid-phase studies where the presence of methoxy substituents serve only to accelerate the rate of decomposition, under FVP conditions, the methoxy-substituted phenoxy radicals undergo a complex series of reactions, which are dominated by 1,5-, 1,6-, and 1,4-intramolecular hydrogen abstraction, rearrangement, and β-scission reactions. The product distributions were generally consistent with the thermochemical kinetic analysis of the reaction pathways except that the ratio of C−O to C−C homolysis was too low. However, more thermochemical kinetic data is needed for the prediction and modeling of reaction pathways in oxygen containing substrates. The thermochemical estimates[34,57] do not take into account polar[82] or hydrogen bonding effects[23] in reactions of polar radicals, such as the electrophilic phenoxy radical, and in many cases, the group additivity parameters are not known for radical sites adjacent to heteroatoms. Moreover, our energy resource of the future, which include low-rank coal and biomass, contain higher concentrations of oxygen-containing species. To maximize the efficient utilization these energy resources, fundamental thermochemical kinetic data is needed on hydrogen abstraction, rearrangements, and elimination reactions of oxygen-, nitrogen-, and sulfur-containing substrates. In support of this effort, we will continue our investigations into reaction pathways of the key structural found in lignin and low-rank coal[83] to gain fundamental insight into the reaction pathways of oxygen-containing substrates.

Experimental Section

The synthesis of PPE and PPE-d_2 ($PhCD_2CH_2OPh$) has been previously described.[11] These compounds were purified by vacuum fractional distillation: PPE, 99.9% purity by GC: bp 123−124 °C (1.5 mmHg); and PPE-d_2, 99.4% purity by GC (H/(H + D) = 0.035 for the benzylic site): bp 118−119 °C (0.4 mmHg). 2-Hydroxy-3-methoxybenzyl alcohol was purchased from Aldrich and used as received (purity 98.7% by GC). Attempts to purify the alcohol by recrystallization were unsuccessful. 2-Methoxy-6-methoxymethylphenol (96.1% purity by GC) was prepared from 2-hydroxy-3-methoxybenzyl alcohol by heating in methanol at 150 °C in a sealed tube as previously described.[84] ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, using TMS and an internal standard in $CDCl_3$. Elemental analysis was performed by Galbraith Laboratories, Inc.

Phenethyl *o*-Methoxyphenyl Ether (*o*-CH_3O-PPE). 2-Phenylethyl tosylate[85] was stirred with guaiacol (2.2 equiv) in DMF with K_2CO_3 (6.6 equiv) at room temperature for 62 h under argon. The reaction mixture was poured into water and extracted with benzene (3 × 150 mL). The combined organic layers were washed with 0.5 M NaOH (3 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. Vacuum fractional distillation (2×) afforded *o*-CH_3O-PPE in 99.8% purity by GC (30% yield): bp 109−110 °C (0.05 mmHg); ^{1}H NMR δ 7.31−7.16 (m, 5H), 6.91−6.85 (m, 4H), 4.14 (t, 2H, $J = 7.7$ Hz), 3.80 (s, 3H), 3.13 (t, 2H, $J = 7.5$ Hz); ^{13}C NMR δ 149.2, 148.0, 137.7, 128.8, 128.2, 126.2, 120.9, 120.6, 113.0, 111.7, 69.4, 55.6, 35.5; MS *m*/*z* (relative internsity) 228 (32), 124 (16), 109 (11), 105 (100), 103 (12), 91 (9), 79 (18), 77, (32), 52 (10), 51 (13). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06; O, 14.02. Found: C, 79.43; H, 7.14; O, 13.42.

Phenethyl 2,6-Dimethoxyphenyl Ether (*o*-CH_3O)$_2$-PPE. The sodium salt of 2,6-dimethoxyphenol was prepared by the slow addition of a solution of 2,6-dimethoxyphenol (35.39 g, 0.23 mol) in DMF (150 mL) to a suspension of sodium hydride (5.22 g, 0.22 mol) in DMF (50 mL) at room temperature. After the addition, the mixture was heated to 55 °C for 1 h and then cooled to room temperature. A solution of 2-phenylethyl tosylate[85] (31.28 g, 0.11 mol) in DMF (200 mL) was added. The reaction mixture was stirred for 39 h at room temperature and then heated to 50 °C for 5 h. The reaction mixture was poured into water and extracted with benzene (3 × 150 mL). The combined organic layers were washed with 0.5 M NaOH (3 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The crude reaction mixture was passed through a silica gel column (8 in. × 1 in.) eluting with hexanes/toluene (10:1) to remove the dark color. The solvent was removed under reduced pressure, and the residue was fractionally distilled under vacuum to afford (*o*-CH_3O)$_2$-PPE in 99.5% purity by GC (yield: 11.9 g, 0.046 mol, 42%): bp 138−139 °C (0.025 mmHg); ^{1}H NMR δ 7.27−7.17 (m, 5H), 6.92 (br t, 1H, $J = 8.5$ Hz), 6.51 (br d, 2H, $J = 8.5$ Hz), 4.19 (t, 2H, $J = 7.7$ Hz), 3.73 (s, 6H), 3.09 (t, 2H, $J = 7.7$ Hz) ^{13}C NMR δ 153.2, 138.0, 136.6, 128.5, 127.8, 125.7, 123.2, 104.8, 73.3, 55.4, 36.1; MS *m*/*z* (relative internsity) 258 (36), 154 (45), 139 (10), 110 (6), 106 (9), 105 (100), 103 (10), 95 (11), 93 (5), 79 (15), 77 (18), 65 (6), 51 (7). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02; O, 18.58. Found: C, 74.44; H, 7.17; O, 18.39.

FVP. The FVP apparatus was based on the design reported by Trahanovsky.[19,24] The pyrolysis tube consisted of a quartz tube (62.5 cm × 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 in. × 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 in the hot zone. The quartz tube was heated with a Carbolite three zone furnace (45 × 3.8 cm i.d.), 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 that was 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 $<10^{-4}$ mmHg (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}. After the reaction, the trap was opened, and the products were washed out with a high-purity acetone containing internal standards (cumene, dimethylphenol, and diphenyl ether). Analytical GC analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 7673 autosampler and a J & W Scientific 30 m × 0.25 mm DB-1 methylsilicone capillary column (0.25 μm film thickness). The samples were analyzed by GC−MS at 70 eV with a Hewlett-Packard 5972A/5890 Series II GC−MS system equipped with a capillary column identical to that used for GC analysis. Reaction mixtures were

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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. Reaction mixtures were also converted into their trimethylsilyl ethers with *N*,*O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) in pyridine and analyzed by GC and GC−MS. Product yields were calculated from the average of three to six injections with a typically standard deviation of <2%. 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 (o-CH_3O)$_2$-PPE).

In the FVP of PPE, four pyrolyses were run, and the product yields were reasonably consistent. However, the conversion varied slightly between two sets of runs made ca. 1 month apart with conversions of 1.14 and 0.95% for the first set and 0.67 and 0.74% for the second. Just before the first set of PPE runs were made, the control sample was found to have a higher conversion, 4.8%, than normal, 3.8 ± 0.2%, which brings these values into question. The latter runs of PPE were made at the same time as the runs of the deuterated PPE.

In the FVP of (o-CH_3O)$_2$-PPE, three unidentified products were formed with *m*/*e* 196, 210, and 210. The products did not silylate with BSTFA in pyridine, indicating that they contain no hydroxyl groups. By comparing the MS fragmentation pattern and GC retention times of authentic samples, the unknown products were not $PhCOCH_2Ph$ (196), $PhCH_2CH_2Ph$ (196), stilbene oxide (196), PhCOCOPh (210), or $PhCH_2CH_2CH_2CH_2Ph$ (210). The mass spectra of the three products are listed below: (a) *m*/*e* (relative intensity) 196 (4), 106 (9), 105 (100), 104 (18), 103 (6), 91 (10), 79 (7), 78 (2), 77 (9); (b) *m*/*e* (relative intensity) 210 (2), 106 (9), 105 (100); 104 (27), 103 (7), 91 (3), 79 (8), 78 (3), 77 (11); (c) *m*/e (relative intensity) 210 (2), 106 (9), 105 (100), 104 (26), 103 (7), 91 (4), 79 (9), 78 (3), 77 (11).

In the FVP of 2-methoxy-6-methoxymethylphenol, experiments were conducted to trap the *o*-benzoquinone methide intermediate. A standard FVP run was made and a yellow pyrolysate was found in the trap. At 77 K, the trap was opened, and styrene (26-fold excess) was washed down the walls of the trap followed by toluene. The trap was allowed to warm to −70 °C in a dry ice/2-propanol bath and was held at − 70 °C for 1 h. The trap was then warmed to room temperature over 30 min. The reaction mixture was analyzed by the standard method. The GC chromatograms contained a large hump at 25−30 min (300 °C) that contained the molecular weights for the dimer (272), trimer (408), and tetramer (544). Unique mass spectra for each of the oligomers could not be resolved, but all had the characteristic loss of 137, the 2-hydroxy-3-methoxybenzyl fragment. A dominant peak with *m*/*e* 274 was also observed with fragmentation pattern *m*/*e* (relative intensity) 275 (16), 274 (89), 138 (28), 137 (100), 122 (17), 77 (18). In the presence of styrene, a new peak appeared with *m*/e of 240, which is consistent with the Diels−Alder product between 6-methoxy-*o*-benzoquinone methide and styrene: *m*/*e* (relative intensity) 241 (17), 240 (100), 225 (5, $M^+ - CH_3$), 209 (12, $M^+ - OCH_3$), 208 (11), 207 (10), 149 (24, $M^+ - PhCH_2$), 136 (39, $M^+ - PhCH{=}CH_2$), 135 (28), 115 (11), 107 (19), 106 (12), 91 (24), 78 (15), 77 (14), 65 (24). Only one isomer was found, which is consistent with the trapping of *o*-benzoquinone methide and styrene, which exclusively formed 2-phenylchroman.[72] Products were also found by GC−MS that were consistent with trapping of the 6-methoxy-*o*-benzoquinone methide with the phenolic products: (a) adduct with 2-methoxy-6-methylphenol *m*/*e* (relative intensity) 275 (15), 274 (82), 138 (26), 137 (100), 122 (15), 94 (15), 77 (16), (b) adduct with 3,5-dimethylphenol (standard use in the GC quantitation) 258 (M^+,44), 138 (13), 137 (100), 122 (10), 121(58), 91 (10), 77 (14); and (c) adduct with *o*-cresol 245 (17), 244 (100), 229 (58) 211 (16), 201 (14), 169 (10), 137 (22), 77 (11).

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