

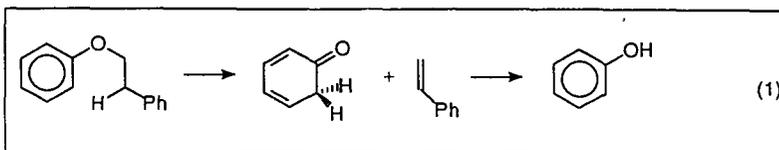
**THERMOLYSIS OF PHENETHYL PHENYL ETHER.
A MODEL OF ETHER LINKAGES IN LOW RANK COAL.**

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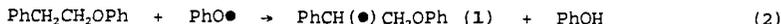
INTRODUCTION

Currently, an area of interest and frustration for coal chemists has been the direct liquefaction of low rank coal. Although low rank coals are more reactive than bituminous coals, they are more difficult to liquefy and offer lower liquefaction yields under conditions optimized for bituminous coals.¹ Solomon, Serio, and co-workers have shown that in the pyrolysis and liquefaction of low rank coals, a low temperature cross-linking reaction associated with oxygen functional groups occurs before tar evolution.^{2,3} A variety of pretreatments (deminerzalization, alkylation, and ion-exchange) have been shown to reduce these retrogressive reactions and increase tar yields,^{2,3} but the actual chemical reactions responsible for these processes have not been defined. In order to gain insight into the thermochemical reactions leading to cross-linking in low rank coal, we have undertaken a study of the pyrolysis of oxygen containing coal model compounds.⁴ Solid state NMR studies suggest that the alkyl aryl ether linkage may be present in modest amounts in low rank coal.⁵ Therefore, in this paper, we will investigate the thermolysis of phenethyl phenyl ether (PPE) as a model of β -aryl ether linkages found in low rank coal, lignites, and lignin, an evolutionary precursor of coal. Our results have uncovered a new reaction channel that can account for 25% of the products formed. The impact of reaction conditions, including restricted mass transport, on this new reaction pathway and the role of oxygen functional groups in cross-linking reactions will be investigated.

Background The thermolysis of PPE has been previously studied under a variety of conditions. Liquid-phase studies by Klein⁹ and Gilbert¹⁰ found phenol and styrene as the primary decomposition products, but different mechanisms were proposed to rationalize the data. Klein proposed a concerted retro-ene reaction based on the first-order reaction kinetics (1.16 ± 0.12 in PPE) which was



unaffected by tetralin, and the Arrhenius parameters, $\log A = 11.1 \pm 0.9 \text{ s}^{-1}$ and $E_a = 45 \pm 2.7 \text{ kcal mol}^{-1}$. It was proposed that secondary decomposition of styrene produced the minor amounts of toluene and ethylbenzene that were detected. Gilbert proposed a free radical chain mechanism for the decomposition of PPE based on the fractional reaction order (1.21 in PPE), the rate acceleration by added free radical initiator, and the Arrhenius parameters, $\log A = 12.3 \text{ s}^{-1}$ and $E_a = 50.3 \text{ kcal mol}^{-1}$. The chain propagation steps are shown below. PPE has also been studied under coal liquefaction



conditions, i.e. in tetralin under high pressure of hydrogen,¹¹ and under catalytic hydrolysis conditions, with iron and zinc metal.¹² In both these studies, the dominant products were phenol and ethylbenzene, since under these reaction conditions, styrene would be hydrogenated to ethylbenzene.

EXPERIMENTAL

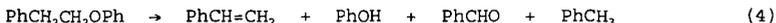
Phenethyl phenyl ether was synthesized by alkylation of phenol with phenethyl tosylate with K_2CO_3 in dimethylformamide. Vacuum fractional distillation afforded PPE in $> 99.9\%$ purity by GC. Biphenyl was purified by successive recrystallization from ethanol and benzene/hexanes while *p*-phenylphenol, 2-naphthol, and *p*-benzylphenol were recrystallized from benzene/hexanes until

purity was > 99.9% by GC. Tetralin was purified by washing with conc H₂SO₄ until the layers were no longer colored, 10% Na₂CO₃, water, dried over Na₂SO₄, filtered, and fractionally distilled under vacuum from sodium two times taking the center cut. Purity was 99.4 % by GC. The synthesis of the surface-attached phenethyl phenyl ethers, ~PhCH₂CH₂OPh (~PPE-3) and ~PhOCH₂CH₂Ph (~PPE-1) has been previously reported.⁶ Two-component surfaces were prepared by co-attachment of the phenols in a single step,⁷ and had final purities of >99.7% (by GC). Surface coverages are listed in Table 2.

Thermolyses of PPE in the fluid and gas phase were performed in a fluidized sand bath (±1 °C) in Pyrex tubes, degassed by six freeze-pump-thaw cycles, and sealed under vacuum (ca. 10⁻⁵ Torr). Tubes were rinsed with acetone (high purity) containing standards, analyzed by GC and GC/MS, and quantitated by the use of internal standards with measured GC detector response factors. Thermolyses of surface-immobilized PPE were performed at 375 ± 1 °C in T-shaped tubes sealed under high vacuum (ca. 10⁻⁶ Torr). The volatile products were collected as they formed in a cold trap (77 K), analyzed by GC and GC/MS, as above. The surface-attached products were removed from the silica surface as the corresponding phenols by a base hydrolysis procedure,⁸ silylated to the trimethylsilyl ethers, and analyzed as above. All products were identified by their mass spectra and whenever possible, by comparison to an authentic sample.

RESULTS AND DISCUSSION

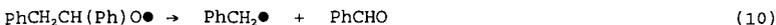
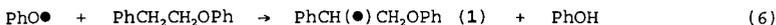
Phenethyl Phenyl Ether Thermolysis of PPE in the liquid phase at 345 °C (1.2% conversion) produced styrene (36 mol%) and phenol (38 mol%), as the major products, and toluene (11 mol%) and benzaldehyde (12 mol%) as the minor products (eq 4). Small amounts



of Ph(CH₂)₂Ph (0.7 mol%), Ph(CH₂)₃Ph (0.7 mol%), PhH (0.6 mol%) and PhCH₂CH₃ (0.3 mol%) were also formed. As the conversion increased, several secondary products, Ph(CH₂)₃Ph, PhCH₂CH₃, 1,3,5-triphenylpentane, and 1-phenoxy-2,4-diphenylbutane, grew in at the expense of the styrene. The material recovery decreased steadily with increasing conversion (based on recovered products), from 99.9% at 1.2% conversion, to 85% recovery at 17.9% conversion. The addition of 0.82 mol% and 7.0 mol%, 2,3-dimethyl-2,3-diphenylbutane, as a free radical initiator, increased the rate of reaction by 25% and 200%, respectively, while not altering the product distribution.

Thermolysis of PPE was also investigated at 375 °C with biphenyl (BP), as an inert diluent, (see Table 1) and in the gas phase from 28 - 260 kPa. Although the rate of decomposition is slower than in the liquid, the product composition is much simpler with PhCH=CH₂, PhOH, PhCHO, and PhCH₃ as the dominant products (>95%). The product selectivity, i.e. (PhCH=CH₂ + PhOH) / (PhCHO + PhCH₃), is independent of PPE concentration and conversion, if secondary products are taken into account. This indicates PhCHO and PhCH₃ are formed by a primary reaction pathway competitive with PhCH=CH₂ and PhOH. Additionally, a kinetic order of 1.30 ± 0.03 was determined from the slope of a log-log plot of initial rates vs. concentration.

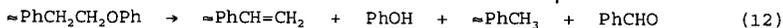
A free radical chain pathway can be written for the thermal decomposition of PPE which can rationalize the primary and secondary products, acceleration by a free radical initiator, and the fractional kinetic order. Secondary products arise from the



reaction of $\text{PhCH}_2\bullet$, 1, and 2 with $\text{PhCH}=\text{CH}_2$. Steps 8-11 have been added to the mechanism proposed by Gilbert¹⁰ to explain the formation of PhCHO and PhCH_3 as primary products of a competitive reaction path. Although 1 is estimated to be ca. 7 kcal mol⁻¹ more stable than 2,¹³ the unexpected competition between eq 8 with eq 6 can be rationalized by polar effects in the hydrogen transfer reaction between the electrophilic phenoxy radical and PPE (eq 8). Polar effects have been reported in the hydrogen abstraction reaction between the *t*-butoxy radical and substituted anisoles. A Hammett plot shows a good σ_p correlation with $\rho = -0.4$ indicating the development of cationic character in the transition state which can be stabilized by the adjacent oxygen.¹⁴ Additionally, there is precedence for the competitive formation of products from the thermodynamically less stable radical of tetralin (2-tetralyl radical)¹⁵ and 1,4-diphenylbutane (1,4-diphenyl-2-butyl radical)⁸ at these temperatures. Since radical 2 does not have a facile β -scission route, it undergoes a 1,2-phenyl shift from oxygen to carbon (eq 9). β -Scission of the rearranged radical affords benzaldehyde and the chain carrying benzyl radical (eq 10). The chain length of the reaction, i.e. the number of chain turnovers per number of free radical formed, is ca. 10. Analogous intramolecular 1,2-phenyl shifts have been reported in the thermal decomposition of phenetole ($\text{PhOCH}_2\text{CH}_3$)¹⁶ and anisole at 400 °C.¹⁷ Also, spectroscopic and kinetic data have been obtained for the rearrangement of 1,1-diphenylethoxy radical ($\text{Ph}_2\text{C}(\text{CH}_3)\text{O}\bullet$) to 1-phenyl-1-phenoxyethyl radical ($\text{PhC}(\text{CH}_3)(\bullet)\text{OPh}$).¹⁸

The thermolysis of PPE was also studied in tetralin, a model liquefaction solvent, at various concentrations (Table 1). Dilution of PPE with tetralin or BP decreased the rate of decomposition in a similar fashion but the product selectivity increased from 3 to 9 as the tetralin concentration increased. This is a consequence of changing the chain carrying radical from phenoxy to the tetralyl radical. Hydrogen abstraction at the carbon adjacent to the oxygen to form 2 is enhanced for the electrophilic phenoxy radical as a consequence of favorable polar contributions. However, this polar effect is not present for hydrocarbon radicals such as tetralyl, and hydrogen abstraction to form 2 is less favorable resulting in an increase in product selectivity. Similar changes in the selectivity were obtained when diphenylmethane, PhCH_2Ph , was used as the hydrogen donating solvent.

Surface-Immobilized Phenethyl Phenyl Ether Thermolysis of surface-immobilized PPE, $\sim\text{PhCH}_2\text{CH}_2\text{OPh}$ ($\sim\text{PPE-3}$), at 375 °C at low conversions produces the products shown in eq 12. The selectivity

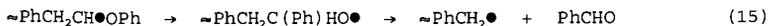
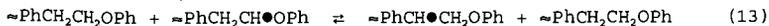


of the reaction ($\sim\text{PhCH}=\text{CH}_2 + \sim\text{PhCH}_2\text{CH}_3 + \text{PhOH}$) / ($\sim\text{PhCH}_3 + \text{PhCHO}$) is slightly larger than that found for PPE as a consequence of the para-silyloxy substituent on the aromatic ring. This substituent enhances the hydrogen abstraction at the benzylic carbon and favors the production of $\sim\text{PhCH}=\text{CH}_2$ and PhOH. A similar increase in selectivity is observed for the thermolysis of *p*-(CH_3)₂SiOPhCH₂CH₂OPh, as a model of surface attached PPE, where in the gas phase at 375 °C, the selectivity is 4.4 ± 0.5. As for PPE, a free radical chain mechanism can be written for the decomposition of surface-immobilized PPE. Restricted mass transport does not affect the new reaction pathway, i.e. hydrogen abstraction at the β -carbon, rearrangement, and β -scission, to form $\sim\text{PhCH}_3$ and PhCHO.

The influence of co-attached aromatics on the rate and selectivity of the thermolysis of $\sim\text{PPE-3}$ are shown in Table 2. No new products were detected for the two component surfaces. Dilution of $\sim\text{PPE-3}$ with biphenyl ($\sim\text{BP}$) or naphthalene ($\sim\text{Naph}$) results in a decrease in the rate of decomposition compared to the high coverage $\sim\text{PPE-3}$. However, in the presence of $\sim\text{DPM}$, a rate acceleration was observed compared to $\sim\text{PPE-3}$ diluted with $\sim\text{BP}$ or $\sim\text{Naph}$, which is in contrast to that observed in the fluid phase (Table 1). These results suggest that rapid hydrogen transfer reactions involving DPM are occurring on the surface that allows radical centers to migrate to the reactive substrate, i.e. $\sim\text{PPE}$. Evidently, the orientation of the molecules on the surface enhances the rate of hydrogen transfer, through the A-factor, relative to hydrogen transfer reactions in a nonconstrained environment, i.e. the fluid phase. A similar rate acceleration via radical relay processes has been

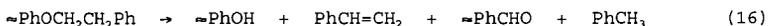
reported in the thermolysis of surface-immobilized diphenylpropane and diphenylbutane in the presence of hydrogen donors.^{7,8}

Interpretation of the selectivity data is more complicated. Surprisingly, the inert spacers increase the selectivity (Table 2). Since these spacers should not effect the thermodynamics of hydrogen abstraction, the packing of the molecules on the surface must be hindering the 1,2-phenyl shift such that a bimolecular hydrogen transfer reaction and β -scission (eq 13 and 14) can compete with rearrangement (eq 15).⁹ This hypothesis is currently



being investigated with the thermolysis of $\sim\text{PPE-3}$ and surface-attached benzene ($\sim\text{PhH}$), which should not hinder the rearrangement but still dilute the molecules on the surface. Therefore, the change in the selectivity for $\sim\text{DPM}/\sim\text{PPE-3}$ is likely a consequence of two factors. First, the methylene linkage in DPM allows the phenyl ring to rotate away from the adjacent $\sim\text{PPE}$ such that the 1,2-phenyl shift should not be hindered, thus decreasing the selectivity (theoretically back to that observed for high coverage $\sim\text{PPE-3}$). Second, since $\sim\text{DPM}$ can participate in a radical relay process, an increase in selectivity would be expected for this nonpolar radical, $\sim\text{PhCHO}\bullet$, compared to the electrophilic phenoxy radical. It is interesting to note that in the fluid phase, dilution of PPE with an 8-fold excess of DPM increases the selectivity by a factor of 2.6, which is similar to the factor of 2.4 found for the surface-immobilized substrates.

The thermolysis of $\sim\text{PhOCH}_2\text{CH}_2\text{Ph}$, $\sim\text{PPE-1}$, at 375 °C produces the products shown in eq 16. The rate of decomposition is enhanced



relative to $\sim\text{PPE-3}$ as a consequence of the para-silyloxy substituent. As for PPE and $\sim\text{PPE-3}$, a free radical chain mechanism can account for the products. Based on the selectivity, surface-immobilization does not appear to hinder the 1,2-phenyl shift to form $\sim\text{PhCHO}$ and PhCH_3 . However, $\sim\text{PhCHO}$ undergoes free radical decomposition to form a surface-attached phenyl radical as shown in eq 17. The bond dissociation energy of benzaldehyde (87 kcal mol⁻¹) is similar to that of toluene ($\text{PhCH}_2\text{-H}$, 88 kcal mol⁻¹).¹⁹



At 13% conversion, over 41% of the $\sim\text{PhCHO}$ has decomposed by decarbonylation to produce $\sim\text{PhH}$ (73%) by hydrogen abstraction, $\sim\text{PhPh}$ (14%) by aromatic substitution, and $\sim\text{PhCH}_2\text{Ph}$ (13%) by coupling with a gas phase benzyl radical. Stein has shown that the selectivity for hydrogen abstraction vs. arylation of toluene by the phenyl radical is 5.2 ± 0.5 at 400 °C in the gas phase.²⁰ Therefore, even in the presence of hydrogen donors, the phenyl radical could lead to arylation, which would form a more refractory linkage, i.e. a cross-link. These results show how decomposition of ether linkages may lead to cross-linking in low rank coal. Additionally, aromatic methoxy groups (ArOCH_3), which are present in high concentrations in low rank coals, could rearrange to aromatic aldehydes ($\text{ArOCH}_2\bullet \rightarrow \text{ArCH}_2\text{O}\bullet \rightarrow \text{ArCHO}$), under free radical reaction conditions. Subsequent decarbonylation could again lead to cross-linking.

SUMMARY

Investigations into the pyrolysis mechanisms of model β -aryl ether linkages have provided fundamental insights into the role of oxygen functional groups in retrogressive reactions. A previously undetected reaction pathway has been found for the free radical decomposition of PPE in the fluid phase and under conditions of restricted diffusion. Under conditions of restricted mass transport, the rates and product selectivities can be altered by the physical and chemical structure of the neighboring molecules. In the presence of a hydrogen donor, radical migration can occur on the surface to transport radical sites to reactive molecules. Pyrolysis of the β -aryl ether linkage can lead to cross-linking reactions by the free radical decomposition of benzaldehyde to the

highly reactive phenyl radical, which can undergo aromatic substitution reactions competitively with hydrogen abstraction.

ACKNOWLEDGEMENTS

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Table 1. Effect of Diluents on the Thermolysis of PPE at 375 °C

Diluent	Diluent ^a /PPE	Rate *10 ⁵ Ms ⁻¹	Selectivity ^b
None	--	32.8	2.8
BP	1.03	25.7	2.7
Tetralin	0.96	14	6.0
BP	4.54	5.1	2.9
Tetralin	3.87	6.5	9.3
BP	8.42	2.1	3.1
Tetralin	8.05	2.4	9.5
DPM	8.76	2.6	8.1
BP	19.1	0.67	3.7

^aBP = biphenyl; DPM = diphenylmethane

^bPhCH=CH₂+PhOH/PhCH₃+PhCHO

Table 2. Product Selectivity in the Thermolysis of Surface Attached PPE at 375 °C

Surface Comp.	Coverage (mmol g ⁻¹)	Rate (% h ⁻¹)	Selectivity ^a
≈PPE-3	0.54	8.3	5±1
≈PPE-3/≈BP	0.050/0.536	3.6	21±2
≈PPE-3/≈Naph	0.072/0.45	3.4	20±5
≈PPE-3/≈DPM	0.059/0.48	8.5	12±2
≈PPE-1	0.50	81	3.1±0.3 ^b

^a(≈PhCH=CH₂ + ≈PhCH₂CH₃+PhOH) / (≈PhCH₃+PhCHO)

^bPhCH=CH₂/PhCH₃