

## Thermolysis of Phenethyl Phenyl Ether: A Model for Ether Linkages in Lignin and Low Rank Coal

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The thermolysis of phenethyl phenyl ether (PPE) was studied at 330–425 °C to resolve the discrepancies in the reported mechanisms of this important model of the  $\beta$ -ether linkage found in lignin and low rank coal. Cracking of PPE proceeded by two competitive pathways that produced styrene plus phenol and two previously undetected products, benzaldehyde plus toluene. The ratio of these pathways, defined as the  $\alpha/\beta$  selectivity, was  $3.1 \pm 0.3$  at 375 °C and independent of the PPE concentration. The kinetic order over ca.  $10^3$  variation in the initial concentration from the neat liquid, in solutions with biphenyl, and in the gas phase was  $1.29 \pm 0.02$ . The rate expression for the decomposition in the liquid phase was  $\log(k/M^{-0.29} \text{ s}^{-1}) = (11.4 \pm 0.1) - (46.4 \pm 1.0)/2.303RT$ . The reaction could be accelerated by the addition of a free-radical initiator or a hydrogen bonding solvent, such as *p*-phenylphenol, but the product composition was altered with the latter. Thermolysis of PPE in tetralin, a model hydrogen donor solvent, increased the  $\alpha/\beta$  selectivity to 7 and accelerated the formation of secondary products. All the data was consistent with a free-radical chain mechanism for the decomposition of PPE. Styrene and phenol are produced by hydrogen abstraction at the  $\alpha$ -carbon,  $\beta$ -scission to form styrene and the phenoxy radical, followed by hydrogen abstraction. Benzaldehyde and toluene are formed by hydrogen abstraction at the  $\beta$ -carbon, 1,2-phenyl migration from oxygen to carbon,  $\beta$ -scission to form benzaldehyde, and the benzyl radical, followed by hydrogen abstraction. Thermochemical kinetic estimates indicate that product formation is controlled by the relative rate of hydrogen abstraction at the  $\alpha$ - and  $\beta$ -carbons by the phenoxy radical (dominant) and benzyl radical (minor) since  $\beta$ -scission and 1,2-phenyl migration are fast relative to hydrogen abstraction. The electrophilic phenoxy radical has an inherently lower  $\alpha/\beta$  selectivity than the nonpolar benzyl radical because it benefits from the polar effects of the  $\alpha$ -oxygen at the  $\beta$ -carbon. The rate of the 1,2-phenyl migration was much faster than interconversion of 1-phenoxy-2-phenyl-1-ethyl radical and 1-phenoxy-2-phenyl-2-ethyl radical, and an activation barrier of  $<18 \text{ kcal mol}^{-1}$  was estimated for the 1,2-phenyl migration. Thermolysis of  $\text{PhCD}_2\text{CH}_2\text{OPh}$  and  $\text{PhCH}_2\text{CD}_2\text{OPh}$  was consistent with the previous results, indicating that there was no significant contribution of a concerted retro-ene pathway to the thermolysis of PPE.

### Introduction

Lignin represents a potentially enormous, but underutilized, renewable resource of aromatic chemicals and liquid fuels.<sup>1–3</sup> It is the second most abundant, naturally occurring biopolymer, found in the cell walls of all vascular plants, and millions of tons of technical lignin are produced annually as a byproduct of commercial pulping processes. There have been numerous studies on the pyrolysis of separated lignins and lignin model compounds.<sup>3–13</sup> However, as a consequence of the

difficulty in isolating lignin without significantly altering its structure, the pyrolysis behavior of lignins isolated by different methods, such as ball milling or solvent extraction, can vary dramatically.<sup>7,8</sup> Consequently, the study of simple model compounds has the potential to be extremely valuable in providing detailed kinetic and mechanistic insights into the degradation of the basic building blocks of lignin.<sup>7,10–13</sup> In the low temperature ( $<600 \text{ °C}$ ) pyrolysis of lignin, one unresolved mechanistic question is the relative importance of the concerted retro-ene, free radical, and ionic reaction pathways.<sup>4a,7</sup> A more detailed understanding of the molecular processes and kinetics involved in the pyrolysis of lignin could enhance lignin utilization and provide insight into the design of a commercial pyrolysis process based on an understanding of the underlying chemistry. This paper, describing the thermolysis of phenethyl phenyl ether (PPE), is the first in a series of papers investigating the thermal decomposition of compounds that model structural features found in lignin and low rank coal. Mechanistic insights gained from this study would be valuable to the

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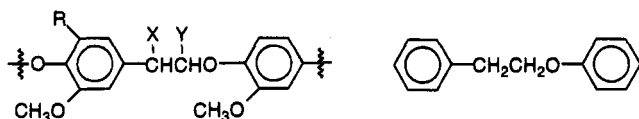
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thermal processing of biomass and low rank coals, which have an established evolutionary link to lignin, the coalification of lignocellulosic materials,<sup>14</sup> and the structural analysis of lignin.<sup>15</sup>

Lignin is a complex, heterogeneous, three-dimensional polymer formed from the enzyme-initiated, dehydrogenative, free-radical copolymerization of *trans-p*-coumaryl alcohol, *trans*-coniferyl alcohol, and *trans*-sinapyl alcohol with the proportions of these monomers differing between hardwoods, softwoods, and grasses. The dominant interunit linkage, which can account for up to half the total number of linkages, is the arylglycerol- $\beta$ -aryl ether linkage, referred to as the  $\beta$ -O-4 linkage, exemplified by the structure below.<sup>15,16</sup> If this structure is stripped of

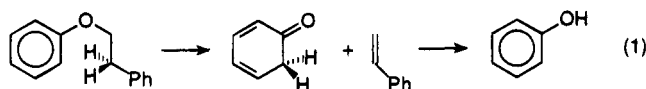


R = H, OCH<sub>3</sub>  
X = H, OH, OAr  
Y = CH<sub>3</sub>, CH<sub>2</sub>OH

Phenethyl phenyl ether

all its substituents, the skeletal remnant would be phenethyl phenyl ether (PPE), the simplest model of the  $\beta$ -ether linkage. Therefore, the thermal decomposition of PPE was studied as the prototypical model of the  $\beta$ -ether linkage in lignin.<sup>17</sup>

The thermolysis of PPE has been previously studied under a variety of conditions. Liquid-phase studies by Klein and Virk<sup>10</sup> and Gilbert and Gajewski<sup>11</sup> found phenol and styrene as the primary decomposition products, but different mechanisms were proposed to explain the data. Klein and Virk investigated the thermolysis of PPE in the liquid phase and in tetralin, a hydrogen donor solvent, from 300–550 °C in a stainless steel reactor and proposed a concerted retro-ene mechanism based on first-order reaction kinetics ( $1.16 \pm 0.12$  in PPE) which were unaffected by tetralin, and the Arrhenius parameters,  $\log A = 11.1 \pm 0.9 \text{ s}^{-1}$  and  $E_a = 45 \pm 2.7 \text{ kcal mol}^{-1}$ . Minor



amounts of toluene and ethylbenzene were proposed to arise from the secondary decomposition of styrene. Gilbert and Gajewski<sup>11</sup> studied the thermolysis of PPE in the liquid and gas phase from 350–390 °C in glass ampules and proposed a free-radical chain mechanism based on the fractional reaction order (1.21 in PPE), acceleration by a free radical initiator (benzyl phenyl ether), and the Arrhenius parameters,  $\log A = 12.3 \text{ s}^{-1}$ <sup>18</sup>

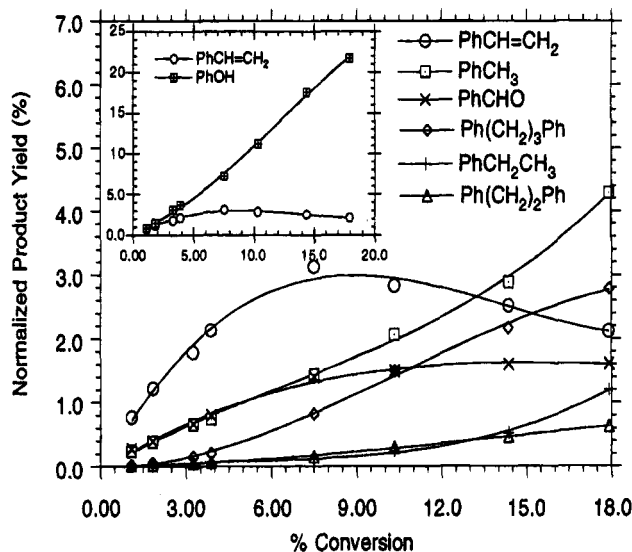
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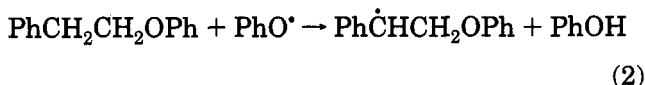
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(18) Units in ref 11 do not conform to the magnitude of the reaction order.



**Figure 1.** Normalized yields of products from the thermolysis of phenethyl phenyl ether in the liquid phase at 345 °C. Inset graph has an expanded y-axis.

and  $E_a = 50.3 \text{ kcal mol}^{-1}$ . The chain propagation steps are shown in eqs 2 and 3.



PPE has also been studied under coal liquefaction conditions, i.e., in tetralin under high pressure of hydrogen,<sup>19</sup> and under catalytic hydrolysis conditions, with iron or zinc metal.<sup>20</sup> In both these studies, the dominant products were phenol and ethylbenzene, since styrene is hydrogenated to ethylbenzene under these reaction conditions. Klein has also studied the hydrous pyrolysis of PPE in supercritical water and determined that the primary products were phenol, styrene, and phenethyl alcohol.<sup>21</sup>

In this paper, the thermolysis of PPE is investigated in the neat liquid, in solution with a nonreactive or with a hydrogen donor solvent, and in the gas phase from 330 to 425 °C in order to resolve the discrepancies in the reported reaction mechanisms. Data are limited to low conversion so primary reactions and initial kinetic behavior can be studied to delineate the thermal decomposition of this prototypical model of the  $\beta$ -ether linkage found in lignin and low rank coal.

## Results

**Liquid Phase.** The thermolysis of purified PPE was studied at 345 °C in degassed sealed Pyrex tubes in which ca. 98% of the material was present in the liquid phase. The normalized yields of the major products are plotted as a function of conversion in Figure 1. At the lowest conversion level studied (ca. 1%), the dominant products

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Table 1. Thermolysis of Liquid Phase and Gas Phase PPE at Various Temperatures

temp (°C)	liquid phase <sup>a</sup>				gas phase (139 ± 5 kPa) <sup>a</sup>			
	time (min)	% convn <sup>b</sup>	rate <sup>c</sup> (M s <sup>-1</sup> )	$\alpha/\beta^d$	time (min)	% convn <sup>b</sup>	rate <sup>c</sup> (M s <sup>-1</sup> )	$\alpha/\beta^d$
425	5	23.3	$3.6 \times 10^{-3}$	2.3	5	8.1	$8.6 \times 10^{-6}$	3.0
400	5	8.6	$1.4 \times 10^{-3}$	2.5	10	3.2	$1.5 \times 10^{-6}$	3.1
390	5	5.2	$8.5 \times 10^{-4}$	2.7	20	5.4	$1.2 \times 10^{-6}$	3.0
375	10	4.6	$3.3 \times 10^{-4}$	2.8	120	11.7	$4.3 \times 10^{-7}$	3.2
360	10	1.6	$1.2 \times 10^{-4}$	2.6	90	3.1	$1.6 \times 10^{-7}$	3.2
345	20	1.9	$6.7 \times 10^{-5}$	2.9	180	2.9	$6.5 \times 10^{-8}$	3.7
330	40	1.4	$2.5 \times 10^{-5}$	3.0	480	2.1	$1.8 \times 10^{-8}$	4.5

<sup>a</sup> Based on the average of two runs. <sup>b</sup> Based on recovered products. <sup>c</sup> See Experimental Section. <sup>d</sup>  $\alpha/\beta$  selectivity, see text for definition.

were PhCH=CH<sub>2</sub> (36 mol %), PhOH (38 mol %), PhCH<sub>3</sub> (11 mol %), and PhCHO (12 mol %). Formation of significant quantities of benzaldehyde and toluene was surprising since, in previous studies<sup>10,11</sup> benzaldehyde was not observed and toluene formation was attributed to the secondary decomposition of styrene.<sup>10</sup> The formation of this additional set of products was studied under a variety of reaction conditions and will be discussed below. Minor amounts of Ph(CH<sub>2</sub>)<sub>2</sub>Ph (0.7 mol %), Ph(CH<sub>2</sub>)<sub>3</sub>Ph (0.7 mol %), PhH (0.6 mol %), and PhCH<sub>2</sub>CH<sub>3</sub> (0.3 mol %) were also detected. The mass balance at this conversion was excellent with recovered PPE and products accounting for 99.9% of the starting charge. As the conversion increased, the ratios of PhOH/PhCH=CH<sub>2</sub> and PhCH<sub>3</sub>/PhCHO increased rapidly above unity, presumably because of secondary reactions of PhCH=CH<sub>2</sub> and PhCHO. Simultaneously, several secondary products, Ph(CH<sub>2</sub>)<sub>3</sub>Ph, PhCH<sub>2</sub>CH<sub>3</sub>, PhH, 1,3,5-triphenylpentane, and 1-phenoxy-2,4-diphenylbutane, grew in. However, these products accounted for only a part of the deficiency in PhCH=CH<sub>2</sub> and PhCHO, and the mass balance steadily decreased with increasing conversion. At the highest conversion level studied (17.9% conversion based on recovered products), the mass balance was only 85%. Since the product yields were conversion dependent, the remaining experiments were run to low conversions, whenever possible, to ensure the observation of primary products and to obtain a good mass balance.

A series of runs were made at 330–425 °C in the liquid phase, and the data are listed in Table 1. All runs were made in duplicate, and there was excellent agreement in rates ( $\pm 10\%$ ) and product distributions between the runs. Reaction times were adjusted to maintain a relatively low conversion in order to emphasize the primary thermolysis products. Initial liquid phase rates, expressed in concentration units (M s<sup>-1</sup>), are based on accumulated products and the estimated liquid density at the various temperatures used in this study (see Experimental Section). Since >94% of the material is in the liquid phase and conversion in the gas phase is much slower, the reaction was approximated as occurring only in the liquid phase, and the rates (M s<sup>-1</sup>) were adjusted for the percentage of PPE in the liquid phase as a function of temperature. By the reaction stoichiometry, the ratio of the number of moles of PhOH (C<sub>6</sub> fragment) to PhCH=CH<sub>2</sub> (C<sub>8</sub> fragment) and PhCH<sub>3</sub> (C<sub>7Tot</sub>) to PhCHO (C<sub>7Alid</sub>) should be unity if all the primary and secondary products are taken into account (see below). The C<sub>6</sub>/C<sub>8</sub> and the C<sub>7Tot</sub>/C<sub>7Alid</sub> balances for the liquid phase runs were  $1.25 \pm 0.25$  and  $1.23 \pm 0.17$ , respectively, and the mass balance for recovered starting materials and products was  $98 \pm 6\%$ , indicating that all the major products had been accounted for. The selectivity for the formation of PhOH and PhCH=CH<sub>2</sub> relative to the two new products, PhCH<sub>3</sub> and PhCHO, was calculated from

Table 2. Thermolysis of PPE in the Gas Phase at 375 °C

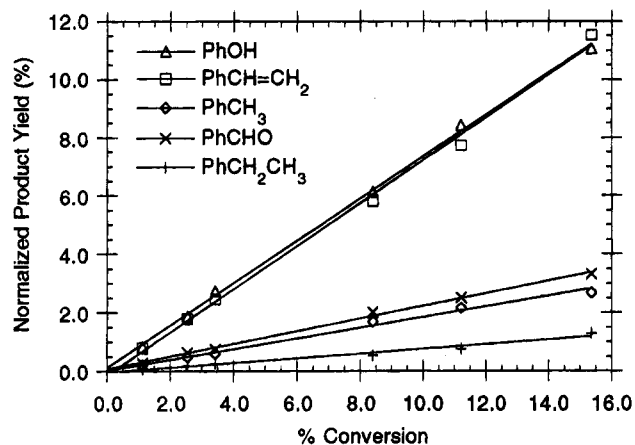
PPE <sup>a</sup> (M × 10 <sup>2</sup> )	P <sup>b</sup> (kPa)	time (min)	% convn	rate <sup>c</sup> (M s <sup>-1</sup> )	$\alpha/\beta^d$
4.07	219	15	1.6	$7.9 \times 10^{-7}$	3.1
2.84	153	10	1.1	$5.9 \times 10^{-7}$	3.2
2.79 <sup>e</sup>	150	20	2.4	$5.7 \times 10^{-7}$	3.0
2.64	142	30	3.4	$5.2 \times 10^{-7}$	3.2
2.88	155	60	8.4	$6.8 \times 10^{-7}$	2.9
2.75	148	90	11.2	$5.7 \times 10^{-7}$	3.1
2.59	139	120	15.4	$5.6 \times 10^{-7}$	3.9
1.28 <sup>e</sup>	68	60	6.6	$2.3 \times 10^{-7}$	3.4 <sup>f</sup>
0.52	28	121	10.7	$7.8 \times 10^{-8}$	4.5 <sup>f</sup>
0.47	25	121	12.2	$8.0 \times 10^{-8}$	4.6 <sup>f</sup>

<sup>a</sup> Moles of PPE/Pyrex tube volume. <sup>b</sup> Estimated from the ideal gas law. <sup>c</sup> See Experimental Section. <sup>d</sup>  $\alpha/\beta$  selectivity; see text for definition. <sup>e</sup> Average of two runs. <sup>f</sup> Run performed in large reaction tubes (33 mL).

the fragment balances of (C<sub>6</sub> + C<sub>8</sub> fragments)/C<sub>7</sub> fragments =  $\alpha/\beta$  selectivity = (PhOH + PhCH=CH<sub>2</sub> + PhCH<sub>2</sub>CH<sub>3</sub> + Ph(CH<sub>2</sub>)<sub>3</sub>Ph + 1,3,5-triphenylpentane + 1-phenoxy-2,4-diphenylbutane)/(PhCHO + PhH + PhCH<sub>3</sub> + 2 PhCH<sub>2</sub>CH<sub>2</sub>Ph + Ph(CH<sub>2</sub>)<sub>3</sub>Ph) which accounts for the primary and secondary products. As shown in Table 1, the  $\alpha/\beta$  selectivity increased slightly as the reaction temperature decreased.

**Gas Phase.** Thermolysis of PPE was also studied in the gas phase (139 ± 5 kPa) at 330–425 °C (see Table 1). The product composition was similar to that found in the liquid phase except there were smaller quantities of secondary products. The mass balances ( $99 \pm 4\%$ ) and C<sub>6</sub>/C<sub>8</sub> ( $1.03 \pm 0.07$ ) and C<sub>7Tot</sub>/C<sub>7Alid</sub> ( $0.93 \pm 0.1$ ) fragment balances were improved and closer to their ideal values. The  $\alpha/\beta$  selectivity was slightly larger in the gas phase than in the liquid phase. Thermolysis of PPE was also performed in the gas phase from 25 to 219 kPa at 375 °C, and the results are contained in Table 2. Attempts to decrease the concentration further were not successful as a consequence of sample handling losses. A slight increase in the  $\alpha/\beta$  selectivity was observed for the thermolyses performed at lowest pressures in the large (33 mL) reaction tubes indicating that the glass reaction vessel may alter the selectivity (see below). A series of runs were performed at  $148 \pm 6$  kPa at 375 °C, and the product distribution as a function of conversion is shown in Figure 2. The gas phase thermolysis does not have the complication of significant amounts of secondary reactions which were observed in the liquid phase (Figure 1). It is clearly seen in Figure 2 that PhCH<sub>3</sub> and PhCHO are formed in a one-to-one ratio as well as PhOH and PhCH=CH<sub>2</sub>, and these four materials are the primary reaction products.

**Diluents.** Thermolysis of PPE was studied at 375 °C in biphenyl as an inert solvent, and the data are compiled in Table 3. The amounts of PPE and biphenyl were chosen to keep the total volume constant, and the



**Figure 2.** Normalized yields of products for the thermolysis of phenethyl phenyl ether in the gas phase ( $148 \pm 6$  kPa) at  $375$  °C.

**Table 3.** Thermolysis of Liquid Phase PPE in Diluents at  $375$  °C

diluents <sup>a</sup>	diluent/ PPE	PPE <sup>b</sup> (M)	time <sup>c</sup> (min)	% convn	rate <sup>a</sup> (M s <sup>-1</sup> ) <sup>a</sup>	$\alpha/\beta^d$
none		3.82	10	4.5	$3.3 \times 10^{-4}$	2.8
BP	0.95	2.15	10	4.4	$1.8 \times 10^{-4}$	2.7
tetralin	0.96	2.14	10	3.5	$1.4 \times 10^{-4}$	6.0
HOBP	1.00	2.23	10	9.6	$4.0 \times 10^{-4}$	4.4
BP	1.99	1.45	10	3.3	$8.8 \times 10^{-5}$	2.7
BP	4.00	0.893	10	2.8	$4.5 \times 10^{-5}$	2.6
tetralin	3.87	0.913	10	3.9	$6.5 \times 10^{-5}$	8.9
BP	7.93	0.508	20	5.2	$2.3 \times 10^{-5}$	3.1
tetralin	7.98	0.505	20	5.8	$2.5 \times 10^{-5}$	7.2
DPM	8.76	0.426	10	3.3	$2.6 \times 10^{-5}$	8.1
BP	8.42	0.483	20	4.9	$2.1 \times 10^{-5}$	3.1
HOBP	8.27	0.552	20	13.6	$6.6 \times 10^{-5}$	10.0

<sup>a</sup> BP = biphenyl, HOBP = *p*-phenylphenol, DPM = diphenylmethane. <sup>b</sup> See Experimental Section for estimates of densities. <sup>c</sup> Heating time is 1 min. <sup>d</sup>  $\alpha/\beta$  selectivity; see text for definition.

reaction time was varied to maintain a low conversion. No additional products were detected when biphenyl was added. The  $\alpha/\beta$  selectivity increased slightly from the neat liquid to 0.48 M PPE in biphenyl. At 0.23 M PPE (diluted 18.9-fold with biphenyl), the average  $\alpha/\beta$  selectivity from two runs was significantly higher ( $3.8 \pm 0.1$ ) than in runs at lower dilution. The origin and the significance of this anomalous selectivity is unknown at this time. Dilution of PPE with *p*-phenylphenol (HOBP) increased the rate of decomposition and altered the product distribution compared to dilution with biphenyl. In these runs, the yields of ethylbenzene increased, while the yields of PhCH=CH<sub>2</sub>, PhCH<sub>3</sub>, and PhCHO decreased. Although the secondary products of these reactions were not investigated in detail, the dominant new product had *m/z* of 274 and a fragmentation pattern consistent with a product from acid-catalyzed addition of *p*-phenylphenol to styrene (i.e., 2-(1-phenylethyl)-4-phenylphenol). Hung and Stock have reported that phenols and carboxylic acids enhanced the rate of decomposition of benzyl phenyl ether and dibenzyl ether by hydrogen bonding to the ether oxygen and enhancing the rate of initiation.<sup>22</sup> At this time, it is difficult to determine whether hydrogen bonding is similarly altering the free-radical reactions for PPE or whether the phenol is acting as an acid catalyst and producing carbenium ion intermediates, since both pathways can produce the observed results.

The thermolysis of PPE was also studied in the presence of tetralin, a hydrogen donor solvent typically used to model the recycle solvent in coal liquefaction. A comparison of thermal decomposition of PPE in tetralin and biphenyl at  $375$  °C is shown in Table 3. At similar concentrations, the rate of decomposition is approximately the same ( $\pm 30\%$ ) for the two diluents, but the  $\alpha/\beta$  selectivity increased from ca. 3 in biphenyl to ca. 7 in tetralin. A similar 2.3-fold increase in the  $\alpha/\beta$  selectivity was observed in comparisons made at  $345$  °C and  $400$  °C. A series of runs were made at  $375$  °C at an 8:1 dilution of tetralin to PPE and conversions ranging from 2–12%. The major products were phenol, styrene, toluene, and benzaldehyde, but the fragment balances were poor even at low conversion and diverge from unity as the conversion increased. For example, at 2.3% conversion ( $375$  °C, 5 min), the  $C_6/C_8$  and  $C_{7Tol}/C_{7Ald}$  fragment balances were 1.4 and 2.5, respectively. This was a consequence of the reduction of styrene by tetralin to form toluene, ethylbenzene, 1,3-diphenylpropane, and methylnaphthalenes.<sup>22</sup> Additional products from reaction of the tetralin were also found, such as naphthalene, 2,3-dihydromethylindene, methylindene, and tetralin dimers. As a consequence of the poor fragment balances, the  $\alpha/\beta$  selectivity of 7 is probably a lower limit. A comparison was also made with diphenylmethane (DPM) as a hydrogen donor, see Table 3, which should not be involved in as much secondary chemistry. The rate of decomposition and the fragment balances were similar to that reported in biphenyl, but the  $\alpha/\beta$  selectivity was enhanced by a factor of 2.6 to 8.1. These studies indicate that the chemical structure and concentration of the solvent can alter the  $\alpha/\beta$  selectivity in the thermolysis of PPE.

**Additives.** The sensitivity of the decomposition of PPE to extraneous variables was also investigated. In order to make rate comparisons, a Pyrex tube containing PPE (as a control sample) was placed beside the reaction tube containing PPE with the additives, and the thermolyses were run for the same reaction time. Thermolysis of two different batches of PPE prepared by the same procedure produced similar selectivities and rates ( $\pm 25\%$ ). Decomposition of PPE was investigated under reaction conditions similar to that used by Klein, i.e., stainless steel tubing bomb,<sup>10</sup> to determine if the reaction conditions could suppress the formation of benzaldehyde and toluene. Thermolysis of PPE at  $400$  °C in a stainless steel tube gave a product distribution,  $\alpha/\beta$  selectivity, and rate similar to PPE in a Pyrex tube. Addition of a free-radical initiator, 2,3-dimethyl-2,3-diphenylbutane, in 0.82 mol % and 7.0 mol %, increased the rate of reaction in the liquid phase at  $345$  °C by 25% and 200%, respectively, while not changing the product distribution. Increasing the surface/volume ratio, via the addition of Pyrex chips or a fumed silica (Cab-O-Sil M-5,  $200$  m<sup>2</sup> g<sup>-1</sup>), did not have a significant perturbation on the rate of decomposition or the product distribution in the liquid phase at  $375$  °C. However, in a series of thermolyses in the gas phase ( $132$ – $155$  kPa) at  $375$  °C with the reaction tube 1/3 full of glass chips, the  $\alpha/\beta$  selectivity increased from  $3.3 \pm 0.4$  to  $6.3 \pm 0.4$ , and the mol % of ethylbenzene increased from  $4.0 \pm 0.3$  to  $5.5 \pm 0.7$ . Another instance of glass-catalyzed decomposition has been reported by Gilbert and Gajewski in the thermolysis of dibenzyl ether, in which the reaction rate and kinetic order were sensitive to the glass ampules.<sup>11</sup> In the acid-catalyzed cracking of a surface-immobilized phenethyl phenyl ether ( $=SiOC_6H_4-$

CH<sub>2</sub>CH<sub>2</sub>OPh) dispersed with a small particle silica-alumina catalyst, the reaction was characterized by products from ether cleavage, aromatic alkylation, and dealkylation, and most notably the near absence of alkenes, which were consistent with carbenium ion intermediates.<sup>23</sup> At this point, it is unclear whether the glass surface produces true ionic intermediates or whether hydrogen bonding alters the free-radical reactions and enhances the rate of initiation,<sup>22</sup> thus increasing the yields of ethylbenzene (see Discussion), since both pathways can lead to the observed results. A plot (not shown) of the relative yield of ethylbenzene at low conversion against the log [PPE] (13 points) provided a linear correlation ( $R = 0.974$ ) with the yields of ethylbenzene increasing (ca. a factor of 7.7) with decreasing concentration of PPE. The  $\alpha/\beta$  selectivity was also observed to increase slightly (ca. 40%) as the concentration of PPE decreased from 3.8 M to  $4.7 \times 10^{-3}$  M. These results indicate that the decomposition of PPE is weakly catalyzed by the Pyrex tubes used in this investigation. However, this has a minor impact on the rates and product selectivities in the liquid phase and should not interfere with the mechanistic interpretation of the data.

**Deuterated PPE.** Two isotopically labeled derivatives of PPE, PhCD<sub>2</sub>CH<sub>2</sub>OPh and PhCH<sub>2</sub>CD<sub>2</sub>OPh, were prepared by the coupling of the corresponding deuterated 2-phenylethyl tosylates<sup>24</sup> with phenol. The fraction of residual protium ( $H/(H + D)$ ) could be determined both by mass spectrometry, since there is no  $(M - 1)^+$  peak for PPE, and by <sup>1</sup>H NMR, and the measured values were in good agreement: PhCD<sub>2</sub>CH<sub>2</sub>OPh, 0.031 and 0.039, respectively, and PhCH<sub>2</sub>CD<sub>2</sub>OPh, <0.002 and 0.004, respectively.

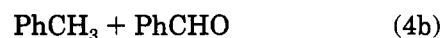
The thermolysis of PhCD<sub>2</sub>CH<sub>2</sub>OPh was carried out in the liquid and gas phase (114 kPa) at 375 °C under the same reaction conditions as used for unlabeled PPE. The rate of decomposition in the liquid phase (3.7% conversion, 20 min, 11.6% h<sup>-1</sup>) decreased by a factor of 2.6 compared to PPE (30% h<sup>-1</sup>), and the  $\alpha/\beta$  selectivity decreased from 2.8 to  $1.6 \pm 0.3$ . GC-MS analysis of the trimethylsilylated reaction mixture, in order to remove any contribution from OD, showed that the silylated phenol contained  $16 \pm 2\%$  deuterium in the aromatic ring based on the intensities of the 168, 167, and 166 masses, compared to the mass spectrum of an undeuterated trimethylsilylated phenol. GC-MS analysis also showed that the benzaldehyde contained no deuterium, indicating that the deuterium label did not scramble to any significant extent between the  $\alpha$ - and  $\beta$ -positions during the reaction. Analysis of the reaction mixture by <sup>2</sup>H NMR showed the phenol was only deuterated in the ortho position. In the gas phase, a run for 60 min at 375 °C produced 4.4% conversion and an  $\alpha/\beta$  selectivity of  $2.0 \pm 0.1$ . The deuterium content of the phenol, analyzed as the trimethylsilyl ether, was  $20 \pm 0.5\%$ , and the isotopic distribution of the remaining products were similar to that found in the liquid phase. The similarity in the results obtained from these liquid and gas phase experiments indicate that the glass reaction tube is *not* catalyzing isotopic exchange in the gas phase.

The thermolysis of PhCH<sub>2</sub>CD<sub>2</sub>OPh was studied in the gas phase (113 kPa) in order to limit the formation of

secondary products and to obtain good mass and fragment balances. The rate of decomposition at 375 °C was similar ( $\pm 20\%$ ) to that of the undeuterated PPE, but the  $\alpha/\beta$  selectivity increased from 3.2 to  $9.4 \pm 1.4$ . Analysis of the reaction mixture by GC-MS showed the toluene contained ca. 10% PhCH<sub>2</sub>D and the benzaldehyde was 100% PhCDO. GC-MS analysis of the trimethylsilylated reaction mixture indicated the phenol contained a small, but reproducible, excess of deuterium  $3.4 \pm 1.3\%$ . The results on the thermolysis of both isotopically labeled substrates shows a significant deuterium isotope effect on product selectivities. As a bench mark, a maximum primary deuterium isotope effect of 2.4 is calculated at 375 °C based on the ground state zero point energies for C-H and C-D stretching vibrations, in the absence of tunneling.

## Discussion

The cracking of PPE proceeds by two competitive pathways, defined as the  $\alpha/\beta$  selectivity, that produce PhOH plus PhCH=CH<sub>2</sub> and two previously undetected products,<sup>10,11</sup> PhCHO plus PhCH<sub>3</sub>. For the neat liquid,



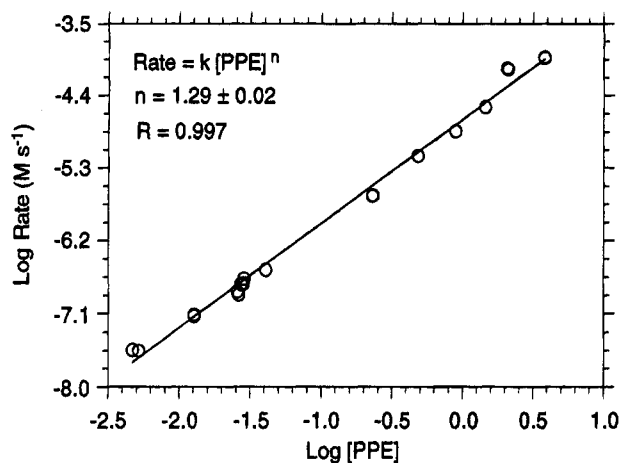
in solutions with biphenyl, and in the gas phase, the average  $\alpha/\beta$  selectivity is  $3.1 \pm 0.3$  at 375 °C. A mild concentration dependence is observed in the gas phase. The selectivity can also be altered by the presence of hydrogen bonding or hydrogen donor solvents. The isomeric dibenzyl ether (PhCH<sub>2</sub>OCH<sub>2</sub>Ph, DBE)<sup>25</sup> and the all-carbon analogue, 1,3-diphenylpropane (PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph, DPP),<sup>26</sup> thermally decompose by a free-radical chain pathway. The involvement of a retro-ene mechanism was eliminated for DBE<sup>11,25</sup> and DPP<sup>26</sup> based on the fractional kinetic order, 1.43 and 1.59, respectively, and the deuterium distribution in the products obtained from the thermolysis of DBE with tetralin-*d*<sub>10</sub><sup>25</sup> and DPP-1,1,3,3-*d*<sub>4</sub>.<sup>26</sup> In order to distinguish between a retro-ene pathway, which must have first-order kinetics, and a free-radical pathway, the kinetic order for thermolysis of PPE was determined by a log-log plot of the initial rate of product formation at low conversion as a function of initial concentration. As shown in Figure 3, a plot of the rate of phenol formation in the liquid phase, diluted with biphenyl, and in the gas phase at 375 °C provides a kinetic order  $n = 1.29 \pm 0.02$  ( $R = 0.996$ ). If the data are separated into two sets, the liquid phase set has  $n = 1.47 \pm 0.08$  ( $R = 0.990$ ) and the gas phase set has  $n = 1.06 \pm 0.04$  ( $R = 0.997$ ). The difference in the kinetic orders between the liquid and gas phase is *not* an indication of a change in the reaction mechanism to a concerted retro-ene pathway, based on the similar deuterium content of the phenol recovered in the thermolysis of PhCD<sub>2</sub>CH<sub>2</sub>OPh in the liquid phase (3.8 M) and in the gas phase (114 kPa,  $2.1 \times 10^{-2}$  M) at 375 °C and the *concentration independent*  $\alpha/\beta$  selectivity, but probably represents a change in the dominant chain termination reaction (see below).<sup>11</sup> A fractional kinetic order,  $n = 1.22$  ( $R = 0.995$ ), was also obtained for the thermolysis of PPE

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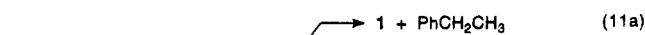
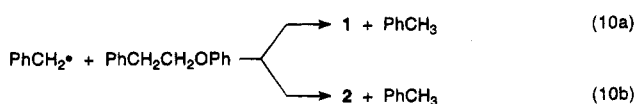
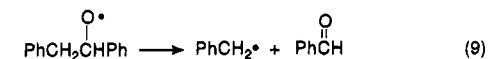
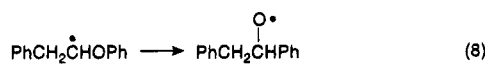
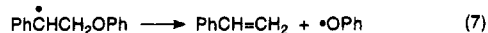
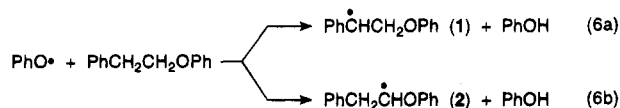
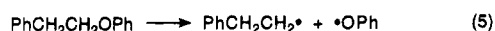
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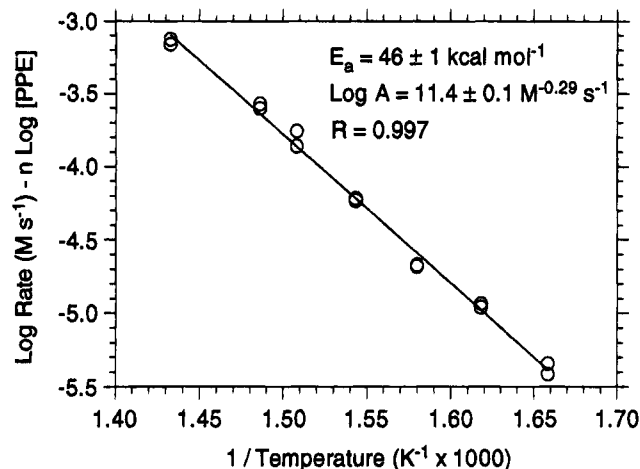
**Figure 3.** Differential kinetic order plot for the initial rate of phenol formation in the liquid phase, neat and diluted with biphenyl, and in the gas phase at 375 °C.

in tetralin, in contrast to the first-order kinetics reported by Klein and Virk.<sup>10</sup> The fractional kinetic order provides strong evidence that PPE does not decompose by a retro-ene pathway in the gas or liquid phase. An Arrhenius plot (Figure 4) of the data in Table 1 for the thermolysis of PPE in the liquid phase provides  $E_a = 46.4 \pm 1.0$  kcal mol<sup>-1</sup> and a log A of  $11.4 \pm 0.1$  M<sup>-0.29</sup> s<sup>-1</sup>. These values are very similar to those reported by Klein,  $E_a = 45.0 \pm 2.7$  kcal mol<sup>-1</sup> and log A =  $11.1 \pm 0.9$  s<sup>-1</sup>,<sup>10</sup> and a little lower than those reported by Gilbert,  $E_a = 50$  kcal mol<sup>-1</sup> and log A =  $12.3$  s<sup>-1</sup>.<sup>11,18</sup>

On the basis of the primary and secondary products, the fractional kinetic order, the rate acceleration by the addition of a free-radical initiator, the concentration independent  $\alpha/\beta$  selectivity, and the thermolysis of PPE-*d*<sub>2</sub>, a free-radical chain mechanism is proposed for the thermal decomposition of PPE, as shown in eqs 5–11.



In the remaining discussion, each mechanistic step will be discussed sequentially with literature and thermochemical analysis as supporting information. The origin



**Figure 4.** Arrhenius plot for the thermolysis of phenethyl phenyl ether in the liquid phase.

of the secondary products, the possibility of a retro-ene reaction, and the relevance of this work to the pyrolysis of macromolecules will also be discussed.

**Initiation Reaction.** The reaction is most probably initiated by homolytic cleavage of the weakest bond in the molecule. The  $D^\circ_{\text{CO}}$  is estimated at 63 kcal mol<sup>-1</sup> using group additivity<sup>27</sup> and assuming that  $D^\circ(\text{PhCH}_2\text{-CH}_2\text{H})$  is equal to that of ethane<sup>28</sup> and  $\Delta H_f(\text{PhO}) = 9.6$  kcal mol<sup>-1</sup>.<sup>29,30</sup> For experimental calibration, the extrapolated high pressure rate constant for the homolysis of the C–O bond in phenetole ( $\text{PhOCH}_2\text{CH}_3$ ) has been measured by two different groups by the very low pressure pyrolysis technique to be  $\log k/s^{-1} = 15.3 - 60.4/\theta$ ,<sup>31</sup> where  $\theta = 2.303RT$  in kcal mol<sup>-1</sup> and  $\log k/s^{-1} = 15.5 - 61.9/\theta$ .<sup>32</sup> The  $D^\circ_{\text{CC}}$  is estimated as 72 kcal mol<sup>-1</sup> based on the  $\Delta H_f(\text{PhCH}_2)$  of 48.5 kcal mol<sup>-1</sup>.<sup>26,30</sup> and the assumption that  $D^\circ_{\text{CH}}$  in anisole is similar to that in dimethyl ether<sup>27b</sup> and  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{H}$ .<sup>33</sup> With a 9 kcal mol<sup>-1</sup> difference in the C–O and C–C bond strengths of PPE, a rate difference of  $>10^3$  would be predicted at 375 °C for the homolytic cleavage.

**Hydrogen Abstraction by the Phenoxy Radical To Produce 1.** The phenoxy radical can abstract hydrogen at the benzylic position of PPE to form phenol and 1, with an estimated reaction enthalpy of  $-0.1$  kcal

(27) (a) Benson, S. W. *Thermochemical Kinetics*; Wiley-Interscience: New York, 1976. (b) NIST Structures and Properties Database and Estimation Program Version 1.1. Stein, S. E.; Rukkers, J. M.; Brown, R. L. NIST Reference Database 25, 1991.

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(29) The heat of formation of the phenoxy radical,  $\Delta H_f(\text{PhO})$ , has been determined as 9.6 kcal mol<sup>-1</sup> based on two different studies on the thermal decomposition of anisole. (Back, M. H. *J. Phys. Chem.* **1989**, *93*, 6881 and references therein.) Colussi et al.<sup>31</sup> obtained a value of 11.4 kcal mol<sup>-1</sup> from the homolytic cleavage of phenetole, but when this value is corrected for the revised heat of formation of the ethyl radical,<sup>28</sup>  $\Delta H_f(\text{PhO}) = 9.7$  kcal mol<sup>-1</sup>. Even though these studies were performed by different techniques, they are in good agreement and an average value of 9.6 kcal mol<sup>-1</sup> will be used. A recent measurement of the homolysis of phenetole in a single-pulse shock tube,  $\log k/s^{-1} = 15.7 - 64.2/\theta$  provided a significantly larger calculated heat of formation of the phenoxy radical, 13.2 kcal mol<sup>-1</sup>, which is in disagreement with four other measurements by three different groups.<sup>30</sup>

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mol<sup>-1</sup> and entropy of 0.2 cal mol<sup>-1</sup> K<sup>-1</sup>.<sup>34</sup> If  $k_7/k_{6a}$  [PPE]  $\gg 1$ , the rate of product formation will be controlled by the hydrogen abstraction reaction. Therefore, in order to calibrate the relative rates of hydrogen abstraction (eq 6a) to  $\beta$ -scission (eq 7), estimates of the Arrhenius parameters for these reactions are needed. Although there are numerous examples of hydrogen abstraction reactions of phenoxy radicals with substituted phenols and hydroperoxides, there are very few reports of Arrhenius parameters for the hydrogen abstraction of phenoxy radicals with hydrocarbons.<sup>35</sup> This is a consequence of the experimental difficulties associated with the relatively slow hydrogen abstraction and the very rapid recombination rates of the phenoxy radical. On the basis of the relative rates of hydrogen abstraction of benzyl<sup>36</sup> and 2-allylbenzyl radicals<sup>37</sup> with OH of substituted phenols and the benzylic CH of aromatic hydrocarbons, and the principle of microscopic reversibility, it is predicted that the phenoxy radical abstracts hydrogen from the benzylic position of aromatic hydrocarbons slightly faster (ca. 1–6-fold at 375 °C) than the benzyl radical.<sup>38,39</sup> For experimental calibration, the ratio of the solution phase rate constants for hydrogen abstraction by the phenoxy/benzyl radicals from tetralin at 60 °C is estimated to be  $1.6 \text{ M}^{-1} \text{ s}^{-1}/1.3 \text{ M}^{-1} \text{ s}^{-1} = 1.2$ . This was calculated from the absolute rate constant for hydrogen transfer to the phenoxy radical from 9,10-dihydroanthracene (DHA),  $110 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>40</sup> and  $k_{\text{DHA}}/k_{\text{tetralin}}$  of 70 at 60 °C in chlorobenzene.<sup>41</sup> For the reaction of benzyl radical with tetralin,<sup>42</sup> the estimated Arrhenius parameters were adjusted for Franz's<sup>37</sup> and Bockrath's<sup>36</sup> relative rates ( $\log k/\text{M}^{-1} \text{ s}^{-1} = 8.6 - 12.9/\theta$ ). Thus, it is estimated that  $k_{6a} \geq k_{10a}$  (the rate constant for hydrogen abstraction by the benzyl radical at the  $\alpha$ -carbon of PPE to produce 1). To evaluate  $k_{10a}$ , we anchor our estimate to an average value for the hydrogen transfer between benzyl radical and deuterium-labeled toluene<sup>26,42</sup> and 2-allylbenzyl radical with *m*-xylene<sup>37</sup> ( $\log k$  (per hydrogen)/M<sup>-1</sup> s<sup>-1</sup> =  $8.0 - 16.2/\theta$ ). We estimate reaction 10a to have

$\Delta H^\circ_{298} = -3.5 \text{ kcal mol}^{-1}$  and  $\Delta S^\circ_{298} = -0.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Since the hydrogen transfer is a relatively symmetrical process, we will assume an Evans–Polanyi  $\alpha = 0.5$  and split  $\Delta H^\circ$  and  $\Delta S^\circ$  equally between the forward and reverse reaction, since  $\Delta H^\circ = E_f - E_r$  and  $\Delta S^\circ = R \ln (A_f/A_r)$ .<sup>42</sup> Thus, we estimate  $\log k_{6a} \geq \log k_{10a}/\text{M}^{-1} \text{ s}^{-1} = 8.3 - 14.4/\theta$ .

**$\beta$ -Scission of 1.**  $\beta$ -Scission of 1 to form styrene and the chain-carrying phenoxy radical is predicted to be very rapid based on the rate constant for the  $\beta$ -scission of 1-phenyl-2-phenoxypropyl radical (PhCH(•)CH(CH<sub>3</sub>)OPh):  $\log k_{\text{trans}}/\text{s}^{-1} = 13.4 - 16.9/\theta$  ( $\Delta H^\circ_{298}$  (trans) =  $11.7 \text{ kcal mol}^{-1}$ ,  $\Delta S^\circ_{298} = 36.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ ) and  $\log k_{\text{cis}}/\text{s}^{-1} = 13.4 - 19.3/\theta$ .<sup>43</sup> Since the reaction enthalpy and entropy for the  $\beta$ -scission of 1,  $10.6 \text{ kcal mol}^{-1}$  and  $34.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ , respectively, are similar to 1-phenyl-2-phenoxypropyl radical, and the intrinsic activation barrier for the reverse reaction for should be slightly smaller for styrene than for  $\beta$ -methylstyrene since substituents at the carbon atom of the alkene which is attacked exert steric effects on the rate of addition,<sup>44</sup> the rate of  $\beta$ -scission of 1 should be of similar magnitude to 1-phenyl-2-phenoxypropyl radical. The activation energy for the  $\beta$ -scission of the 1-phenyl-2-phenoxypropyl radical is ca.  $11 \text{ kcal mol}^{-1}$  lower than the calculated barrier for 1,3-diphenyl-1-propyl radical.<sup>26</sup> This is a consequence of the weaker C–O bond and is not attributed to a polar transition state in the cleavage.<sup>44</sup> On the basis of these thermochemical estimates,  $\beta$ -scission, eq 7, will be at least  $10^3$  times faster than hydrogen abstraction, i.e.,  $k_7/k_{6a}$  [PPE]  $> 10^3$ , at 375 °C over the concentration range [PPE] =  $3.8 - 0.005 \text{ M}$ .

**Hydrogen Abstraction by the Phenoxy Radical To Form 2.** The formation of PhCH<sub>3</sub> and PhCHO can be explained by a competitive free-radical pathway in which hydrogen abstraction at the  $\beta$ -carbon forms 2, 1,2-phenyl migration, and  $\beta$ -scission produces PhCHO and the chain carrying benzyl radical, eqs 6b and 8–10b. Although radical 2 is estimated to be ca.  $7.4 \text{ kcal mol}^{-1}$  less stable than 1,<sup>27</sup> there is precedence for the competitive formation of products from the analogous thermodynamically less stable radical of tetralin (2-tetralyl radical)<sup>42,45</sup> and 1,4-diphenylbutane (1,4-diphenyl-2-butyl radical)<sup>26,46</sup> at similar temperatures. Additionally, selectivities in hydrogen transfer reactions have long been rationalized by enthalpy changes, steric requirements, and polar effects in the transition state.<sup>47</sup> Radical centers on atoms more electronegative than carbon are considered electrophilic, and phenoxy and *tert*-butoxy radicals, for example, seek out sites of higher electron density.<sup>48</sup> In the hydrogen abstraction reaction by the *tert*-butoxy radical with substituted toluenes<sup>49</sup> and anisoles<sup>50</sup> in 1,1,2-trichlorotrifluoroethane at 45 °C, the Hammett plots show good correlations with  $\rho$  values of  $-0.35$  and  $-0.41$ , respectively, indicating the development of cationic character in the transition state. For the substituted tolu-

(34) Estimated  $\Delta H^\circ_{298}$  and  $\Delta S^\circ_{298}$  were not corrected to the reaction temperature (typically 648 K) since the  $\Delta C_p$  corrections are small and within the accuracy of the estimation procedures.

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enes, a  $\sigma^+$  correlation was observed, while for the substituted anisoles, a correlation with  $\sigma$  provided a better fit to the data indicating that direct conjugation with the aromatic ring was not important in the latter. Therefore, on the basis of polar effects, the rate of hydrogen abstraction by the electrophilic phenoxy radical at the  $\beta$ -carbon would be enhanced compared to abstraction by a nonpolar radical, such as the benzyl radical, as a consequence of the adjacent oxygen which can stabilize the developing cationic character of the transition state.

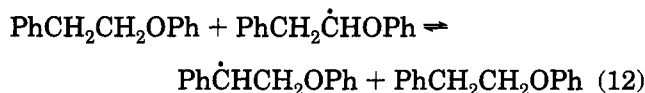
One disadvantage of using polar effects to rationalize the product selectivity is that there are no defined limits on the magnitude of this effect. To obtain a more quantitative description of relative rates of hydrogen transfer at the  $\alpha$ - and  $\beta$ -carbons, we will assume that the Evans–Polanyi relationship, which has been used to correlate the rates of hydrogen transfer between carbon centered radicals with changes in the C–H bond energies in the absence of steric effects,<sup>47</sup> can be applied to hydrogen abstraction by the phenoxy radical. If we arbitrarily assume an Evans–Polanyi  $\alpha = 0.5$ , typical for nonpolar hydrocarbon radicals,<sup>47</sup> and similar pre-exponential factors for hydrogen abstraction at the  $\alpha$ - and  $\beta$ -carbons, an  $\alpha/\beta$  selectivity of 18 is calculated at 375 °C, since hydrogen abstraction is slow compared to  $\beta$ -scission and the rearrangement (see below). The ratio of the pre-exponential factors for the hydrogen transfer from an aliphatic/benzylic site in 1,3-diphenylpropane to the benzyl radical has been estimated as ca.  $10^{0.5}$  ( $\Delta\Delta S^\circ_{298} = 3.1 \text{ cal mol}^{-1} \text{ K}^{-1}$ ).<sup>26,42</sup> If we assume that this difference holds for the hydrogen abstraction at the  $\alpha$ - and  $\beta$ -carbons in PPE ( $\Delta\Delta S^\circ_{298} = 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ ), the  $\alpha/\beta$  selectivity will decrease to ca. 5.6 which is close to the measured value of 3.0. If an Evans–Polanyi  $\alpha = 0.63$  is used, which has been suggested for the electrophilic peroxy radical ( $\text{ROO}^\bullet$ ),<sup>47</sup> an  $\alpha/\beta$  selectivity of 2.6 is calculated at 375 °C assuming the differences in the pre-exponential factors discussed above. Hence, it may not be necessary to invoke polar effects to rationalize the product selectivity. However, until the Arrhenius parameters for hydrogen abstraction by phenolic radicals with aromatic hydrocarbons are accurately measured, the contribution of polar effects to the hydrogen abstraction reaction remain a viable rationalization.

### 1,2-Phenyl Migration from Oxygen to Carbon.

The next step in the mechanism for the formation of benzaldehyde is the rearrangement of 1-phenoxy-2-phenyl-1-ethyl radical to 1,2-diphenylethoxy radical (eq 8). Although 1,2-migration of an aryl group from carbon to a carbon-centered radical has been extensively investigated following the discovery of the rearrangement of the 2-methyl-2-phenylpropyl (“neophyl”) radical,<sup>51</sup> there are few detailed investigations of neophyl-like rearrangements from carbon to a heteroatom. This is ironic since the first example of a free-radical rearrangement in solution was the isomerization of triphenylmethoxy radical to diphenylphenoxyethyl radical (*O*-neophyl rearrangement).<sup>52</sup> However, 1,2-phenyl migration from oxygen to carbon has been reported in the thermolysis of

alkyl aryl ethers, such as anisole, phenetole, and isopropyl phenyl ether, based on the observed products.<sup>51,53–55</sup>

In the thermolysis of PPE, the distribution of products will represent the relative rates of the hydrogen abstraction reactions at the  $\alpha$ - and  $\beta$ -carbons (eqs 6a and 10a vs 6b and 10b) if the 1,2-phenyl migration is faster than the exothermic hydrogen transfer reaction shown in eq 12



which will interconvert **2** and **1** ( $\beta$ -scission of **2** is predicted to be very slow, since the reaction enthalpy is ca.  $14 \text{ kcal mol}^{-1}$  larger than that for  $\beta$ -scission of **1**).<sup>42</sup> Steady-state treatment of the chain steps 6–10 and 12 leads to an expression 13 for the dependence of  $\text{PhOH}/\text{PhCH}_3$

$$\frac{\text{PhOH}}{\text{PhCH}_3} = \frac{k_{10a}/k_{10} + k_{12}[\text{PPE}]/k_8}{1 - (k_{6a}/k_6) + k_{-12}[\text{PPE}]/k_7} \quad (13)$$

$\text{PhCH}_3$  (i.e., the  $\alpha/\beta$  selectivity in the absence of secondary reactions) on [PPE] where  $k_6 = k_{6a} + k_{6b}$  and  $k_{10} = k_{10a} + k_{10b}$ . On the basis of the concentration independent  $\alpha/\beta$  selectivity (see Tables 2 and 3), reaction 12 must not be competitive with 1,2-phenyl migration, i.e.,  $k_{12}[\text{PPE}]/k_8 < 0.1$  and  $k_{-12}[\text{PPE}]/k_7 < 0.1$ . To get a lower limit on  $k_8$ ,  $k_{12}$  needs to be estimated. For the hydrogen transfer reaction where one center is aliphatic and the other is benzylic, the rate constant is anchored to the average reported value for the reaction between ethyl radical and toluene  $\log k$  (per H)/ $\text{M}^{-1} \text{ s}^{-1} = 7.5 \pm 0.2 - 9.6 \pm 0.6/\theta$ .<sup>56</sup> By thermochemical balance ( $\Delta H^\circ_{298} = -12.2 \text{ kcal mol}^{-1}$  and  $\Delta S^\circ_{298} = 5.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ ), the reverse reaction,  $\text{PhCH}_2^\bullet + \text{CH}_3\text{CH}_3$ , has  $\log k$  (per H)/ $\text{M}^{-1} \text{ s}^{-1} = 8.6 - 21.8/\theta$ .<sup>56</sup> If this base reaction is normalized to the hypothetical thermoneutral reaction, we obtain  $\log k$  (per H)/ $\text{M}^{-1} \text{ s}^{-1} = 8.05 - 15.7/\theta$  for the reaction between an aliphatic–benzylic center. We estimate reaction 12 to have  $\Delta H^\circ_{298} = -7.4 \text{ kcal mol}^{-1}$  and  $\Delta S^\circ_{298} = -2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ . If  $\Delta H^\circ$  and  $\Delta S^\circ$  are split equally between the forward and reverse reaction ( $\alpha = 0.5$ ), then we estimate  $\log k_{12}/\text{M}^{-1} \text{ s}^{-1} = 8.1 - 12.0/\theta$ .<sup>56</sup> Thus, a lower limit for reaction 8 is predicted to be  $\log k_8/\text{s}^{-1} \geq 5.6$  at 375 °C for the neat liquid (3.8 M). Assuming a typical *A* factor for the 1,2-phenyl migration,  $10^{11.5} \text{ s}^{-1}$  (see below), we estimate  $E_8 < 18 \text{ kcal mol}^{-1}$ . Unfortunately, there are no detailed mechanistic studies on the rate of the *O*-neophyl rearrangement to base an estimate of the barrier for the rearrangement of **2** to 1,2-diphenylethoxy radical. For the all-carbon case, the neophyl rearrangement occurs rapidly for 2-methyl-2-phenylpropyl radical with  $\log k/\text{s}^{-1} = 11.55 - 11.82/\theta$ .<sup>51c</sup> The spiro[2.5]octadienyl radical has been detected by optical spectroscopy (opening to the 2-phenylethyl radical with  $\log k/\text{s}^{-1} = 9.2 - 2.8/\theta$ )<sup>57</sup> and is generally accepted as a shallow minimum on the

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reaction coordinate.<sup>51</sup> In the *O*-neophyl rearrangement of 1,1-diphenylethoxy radical, a similar intermediate, displaying an absorption spectrum similar to the cyclohexadienyl radical, was formed within a 17 ps laser pulse and decayed with a lifetime of 312 ns at room temperature to 1-phenyl-1-phenoxyethyl radical.<sup>58</sup> Since hydrogen abstraction by the alkoxy radical was detected, cyclization to form the spiro intermediate must be reversible with rate-determining ring opening. For a 1,2-phenyl migration from sulfur to carbon, Alnajjar and Franz have measured the Arrhenius parameters for the thermoneutral rearrangement of  $\alpha$ -(phenylthio)benzyl radical to diphenylmethylthio radical at 160–215 °C:  $\log k/s^{-1} = 10.6 - 21.4/\theta$ .<sup>60</sup> This activation energy is higher<sup>51c</sup> and the *A* factor is a little lower (typically  $10^{11.5-11.8}$ ) than that found in the all-carbon analogues.<sup>51,61a</sup> The estimated enthalpy for the formation of the thiaspiro[2.5]octadienyl intermediate (although semiempirical calculations predict a transitional structure) from the  $\alpha$ -(phenylthio)benzyl radical was 19.4 kcal mol<sup>-1</sup> which is consistent with a small barrier for ring opening.<sup>60</sup>

As opposed to the neophyl rearrangement, the enthalpy for the rearrangement of **2** to 1,2-diphenylethoxy radical is endothermic by 5.4 kcal mol<sup>-1</sup>. The enthalpy for the conversion of **2** ( $\Delta H^\circ_{f,298} = 41.6$  kcal mol<sup>-1</sup>) to the oxaspiro[2.5]octadienyl radical intermediate ( $\Delta H^\circ_{f,298} = 66.3$  kcal mol<sup>-1</sup>)<sup>62,63</sup> is estimated to be 24.7 kcal mol<sup>-1</sup>. Assuming a small barrier for C–O bond cleavage (2 kcal mol<sup>-1</sup>),<sup>57,60</sup> the activation energy for the rearrangement is estimated to be 26.7 kcal mol<sup>-1</sup>. This estimated activation energy is ca. 9 kcal mol<sup>-1</sup> larger than that calculated from the experimentally determined ratio of PhOH/PhCH<sub>3</sub> and an estimate of  $k_{12}$ . For the all-carbon case, group additivity estimates of the enthalpy for conversion of the radical to the bridged intermediate also tend to exceed the measured activation energy for the reaction.<sup>61,64</sup> For example, estimates of the enthalpy of

forming the bridged intermediate of 2-methyl-2-phenylpropyl radical ranges between 10.9 and 16.9 kcal mol<sup>-1</sup> while the measured activation energy is 11.8 kcal mol<sup>-1</sup>. This discrepancy has been attributed to failure of group additivity to reflect the steric compression associated with the formation of *gem*-dialkyl-substituted three-membered rings (Thorpe–Ingold effect).<sup>61</sup> However, in the absence of *gem*-dialkyl substituents, as in the rearrangement of the 2-phenylethyl radical, group additivity still overestimates the reaction enthalpy.<sup>64,65</sup> This highlights the need for thermochemical data on spiro[2.*n*]octadiene systems, since group additivity appears to fail even in the absence of the Thorpe–Ingold effect.<sup>61,64,65</sup>

**$\beta$ -Scission of 1,2-Diphenylethoxy Radical.** The rate constant for  $\beta$ -scission of the 1,2-diphenylethoxy radical is very rapid, and the hydrogen abstraction to form 1,2-diphenylethanol does not effectively compete. There have been many studies on the rate constant ratio of  $k_\beta/k_a$ , where  $k_\beta$  is the rate constant for  $\beta$ -scission and  $k_a$  is the rate constant for hydrogen abstraction from a hydrogen donor, in which  $k_\beta$  was found to increase with increasing stabilization of the expelled radical.<sup>66</sup> For the cumyloxy radical in CCl<sub>4</sub> containing toluene, the relative activation energies [ $E_\beta - E_a$ ] = 4.9 kcal mol<sup>-1</sup> and preexponential factors  $\log(A_\beta/A_a) = 4$  M and the rate constant for  $\beta$ -scission, to form acetophenone and a methyl radical ( $\log k_\beta/s^{-1} = 12.4 - 8.6/\theta$ ), have been determined.<sup>67</sup> The Arrhenius parameters for the  $\beta$ -scission of the 2-phenylethoxy radical to form formaldehyde and a benzyl radical have also been measured with  $\log k_\beta/s^{-1} = 10.89 - 4.8/\theta$  (the low *A* value was attributed to a substantial degree of solvent organization and freezing out a rotation about the benzyl carbon atom in the transition state).<sup>67,68</sup> The  $\beta$ -scission of the 1,2-diphenylethoxy radical ( $\Delta H^\circ_{298} = -8$  kcal mol<sup>-1</sup>) is anticipated to be even more rapid than the 2-phenylethoxy radical ( $\Delta H^\circ_{298} = -1.2$  kcal mol<sup>-1</sup>)<sup>27</sup> as a consequence of the more favorable reaction enthalpy.

#### Hydrogen Abstraction by the Benzyl Radical.

The benzyl radical can abstract hydrogen at the  $\alpha$ - and  $\beta$ -carbons to produce **1** and **2** and toluene. Previously, we estimated  $\log k_{6a} \geq \log k_{10a}/M^{-1} s^{-1} = 8.3 - 14.4/\theta$ . On the basis of the rate constant for hydrogen abstraction between PhCH<sub>2</sub>• and ethane (discussed above), we estimate  $\log k_{10b}/M^{-1} s^{-1} = 8.5 - 17.6/\theta$  by equally splitting ( $\alpha = 0.5$ )  $\Delta H^\circ_{298} = 3.9$  kcal mol<sup>-1</sup> and  $\Delta S^\circ_{298} = 1.8$  cal

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(63) The  $D^{\circ}(c-C_6H_5H, 1,3\text{-cyclohexadiene}) = 76$  kcal mol<sup>-1</sup> (Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152). A stabilization energy of 1 kcal mol<sup>-1</sup> is given for the cyclopropyl substituent. The experimentally determined heat of formation of the cyclopropylcarbinyl radical provided a bond dissociation energy of methylcyclopropane as  $97.4 \pm 1.6$  kcal mol<sup>-1</sup> for a stabilization energy of 3.2 kcal mol<sup>-1</sup> for the cyclopropyl substituent (McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3*(4), 359) which is approximately 30% of the resonance stabilization energy found in the allyl radical (11.5 kcal mol<sup>-1</sup>; Herdon, W. C. *J. Org. Chem.* **1981**, *46*, 2119). Since the resonance stabilization energies of the pentadienyl and heptatrienyl radicals are 17.8 and 21.0 kcal mol<sup>-1</sup>, respectively, the additional pseudoallylic stabilization provided by the cyclopropane ring of the pentadienyl radical is estimated to be 1 kcal mol<sup>-1</sup>, approximately 30% of the difference in the resonance energy (i.e., 3.2 kcal mol<sup>-1</sup>).

(64) The estimated activation energy for the rearrangement of the 2-phenylethyl radical is 20.7 kcal mol<sup>-1</sup>, obtained from a combination of the estimated enthalpy of reaction, 17.9 kcal mol<sup>-1</sup>,<sup>65</sup> and the reported activation barrier for cleavage of the spiro[2.5]octadienyl radical, 2.8 kcal mol<sup>-1</sup>.<sup>57</sup> The estimated activation energy is larger than the reported upper limit for the rearrangement  $\log k/s^{-1} < 11.55 - 18.5/\theta$ .<sup>57</sup> The reported value of  $\log k/s^{-1} < 10.75 - 16.9/\theta$  was adjusted for comparison with the rearrangement of the 2-methyl-2-phenylpropyl radical at constant *A*.

(65) We obtain  $\Delta H^\circ_f(\text{PhCH}_2\text{CH}_2) = 55.2$  kcal mol<sup>-1</sup> from  $\Delta H^\circ_f(\text{PhCH}_2\text{CH}_3) = 7$  kcal mol<sup>-1</sup>,<sup>27b</sup>  $D(\text{PhCH}_2\text{CH}_2\text{H})$  equal to  $D(\text{CH}_3\text{CH}_2\text{H}) = 100.3$  kcal mol<sup>-1</sup>,<sup>28</sup> and heat of formation of H• (52.1 kcal mol<sup>-1</sup>).<sup>27</sup> The enthalpy for formation of spiro[2.5]octa-4,6-diene is calculated to be 50.2 kcal mol<sup>-1</sup> using group additivities with a cyclopropyl ring strain of 27.6 kcal mol<sup>-1</sup> and 1,3-cyclohexadiene ring strain of 4.8 kcal mol<sup>-1</sup>.<sup>27a</sup> The enthalpy for the formation of the spiro[2.5]octadienyl radical is then calculated to be 73.1 kcal mol<sup>-1</sup>, and the enthalpy for the formation of the spiro intermediate from the 2-phenylethyl radical is  $73.1 - 55.2 = 17.9$  kcal mol<sup>-1</sup>.

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$\text{mol}^{-1} \text{K}^{-1}$  between the forward and reverse reaction. In the thermolysis of PPE in tetralin and diphenylmethane, the  $\alpha/\beta$  selectivity increases by a factor of ca. 2.5, compared to PPE diluted with biphenyl (see Table 3). The hydrogen donor solvent can quench the chain carrying benzyl and phenoxy radicals, but the solvent radicals do not have an irreversible decay route at these elevated temperatures and continue the chain by hydrogen abstraction with PPE.<sup>11b,42</sup> Thus, for neat PPE, the  $\alpha/\beta$  selectivity is a composite of selectivity for abstraction by phenoxy radical (dominant) and benzyl radical (minor) at the  $\alpha$ - and  $\beta$ -carbons. The  $\text{PhO}^\bullet$  radical has an inherently lower  $\alpha/\beta$  selectivity than  $\text{PhCH}_2^\bullet$  because it benefits from the polar effects of the  $\alpha$ -oxygen at the  $\beta$ -carbon. Thus, in a donor solvent,  $\text{PhO}^\bullet$  is largely replaced by the donor solvent radicals and the  $\alpha/\beta$  selectivity increases. Since the  $\Delta\Delta H^\circ_{298}$  for hydrogen abstraction by  $\text{PhO}^\bullet$  and  $\text{PhCH}_2^\bullet$  at the  $\alpha$ - and  $\beta$ -carbons is identical, but the observed  $\alpha/\beta$  selectivity for  $\text{PhCH}_2^\bullet$  (and tetralyl and diphenylmethyl radicals) is different from that for  $\text{PhO}^\bullet$ , this is clear evidence that polar effects must be responsible for the enhanced selectivity in hydrogen abstraction at the  $\beta$ -carbons by the electrophilic phenoxy radical. Interestingly, the predicted  $\alpha/\beta$  selectivity for the benzyl radical based on thermochemical kinetic estimates presented above,  $k_{10a}/k_{10b} = 7.6$  at 375 °C, is of similar magnitude to that experimentally observed for PPE in DPM and tetralin, 8.1 and 7, respectively.

**Secondary Products and Chain Length.** The secondary products,  $\text{Ph}(\text{CH}_2)_3\text{Ph}$ , 1,3,5-triphenylpentane, 1-phenoxy-2,4-diphenylbutane,  $\text{PhH}$ , and  $\text{PhCH}_2\text{CH}_2\text{Ph}$ , can be readily explained by free-radical reactions of the primary products. 1,3-Diphenylpropane, 1,3,5-triphenylpentane, and 1-phenoxy-2,4-diphenylbutane can be formed from the addition of  $\text{PhCH}_2^\bullet$ , 1,3-diphenyl-1-propyl radical, and 1, respectively, to styrene,<sup>66,69</sup> followed by hydrogen abstraction. The rate constant for the addition of benzyl radical to styrene has been estimated as  $\log k_{\text{Add}}/\text{M}^{-1} \text{s}^{-1} = 7.5 - 7.6/\theta$  on the basis of values for the polymerization of styrene<sup>26</sup> adjusted for difference between addition of a secondary and a primary radical to an olefin.<sup>70</sup> The  $\beta$ -scission of the 1,3-diphenyl-1-propyl radical is estimated as  $\log k_{\beta}/\text{s}^{-1} = 14.8 - 28.3/\theta$ .<sup>26</sup> Thus, at 375 °C, addition competes with dissociation,  $k_{\text{Add}}/k_{\beta} = 0.54 \text{ M}^{-1}$ . Since the activation energy for  $\beta$ -scission is typically greater than that for hydrogen abstraction,<sup>42</sup>  $\beta$ -scission is favored at high temperatures while hydrogen abstraction is favored by high concentration of hydrogen donor. Hence, these secondary products are much more prominent in the condensed phase than the gas phase (see Figures 1 and 2). Benzene arises from hydrogen abstraction from benzaldehyde ( $D^\circ(\text{Ph}(\text{C}=\text{O})\text{H}) = 87 \text{ kcal mol}^{-1}$ )<sup>71</sup> to give the benzoyl radical, followed by rapid decarbonylation<sup>42a,72</sup> to the phenyl radical and hydrogen abstraction. Although aromatic substitution by the phenyl radical is facile, albeit reversible, at these tem-

peratures,<sup>70,73</sup> no aryl-substituted products were identified, although addition of phenyl radicals to styrene is most likely a minor pathway for the formation of bibenzyl.<sup>74</sup> The major route for bibenzyl formation is probably coupling of the benzyl radicals. Surprisingly, no significantly quantities of products were detected for the termination of the phenoxy radical. In aqueous solution, phenoxy radicals decompose by second-order kinetics<sup>75,76</sup> to afford 2,2', 2,4', and 4,4'-dihydroxybiphenyls as the predominant products (ca. 80%) in a ratio of 0.73:1.73:1.00<sup>76a</sup> and 2- and 4-phenoxyphenols as minor products (ca. 10%).<sup>76</sup> For coupling of phenoxy radicals in nonpolar solvents, the formation of the initial keto dimer is reversible and the rate-controlling step is enolization, which can be enhanced with an acid catalyst.<sup>75a</sup> In the gas phase at 665 °C, thermolysis of phenol produced dibenzofuran which most likely arises from condensation of 2,2'-dihydroxybiphenyl, in addition to water, solid residue, CO, H<sub>2</sub>, benzene, indene, and higher aromatics.<sup>77</sup> Similarly, thermolysis of 1- and 2-naphthol in the liquid phase at 400 °C afforded binaphthalenediols as the initial products which rapidly cyclized to the dinaphthofurans.<sup>78</sup> In an effort to detect the termination products from the phenoxy radicals, the reaction mixtures from the thermolysis of PPE in the liquid phase were analyzed after trimethylsilylation, and after base extraction, acidification, and trimethylsilylation (since 2,2'-dihydroxybiphenyl coelutes with PPE on the GC). Only very small amounts of 2,2'-dihydroxybiphenyl were detected with poor reproducibility, and no dibenzofuran or phenoxyphenol isomers were detected. Gilbert and Gajewski suggested that termination could also occur by disproportionation between the phenoxy radical and 1, but no significant quantities of  $\beta$ -phenoxystyrene were detected.<sup>11a</sup> Moreover, on the basis of the disproportion-recombination ratios of hydrocarbon radicals, which typically are 0.01–0.3,<sup>79</sup> recombination is predicted to be the dominant reaction for the hydrocarbon radicals. Therefore, the phenoxy radical must not form significant quantities of termination products or else these termination products are difficult to detect by GC analysis, i.e., high molecular weight.

The kinetic chain length (rate of chain propagation relative to the rate of chain termination, which is assumed equal to the rate of initiation at steady state) for the decomposition of PPE can be estimated as  $(\text{PhOH} + \text{PhCH}_3)/2\text{PhCH}_2\text{CH}_3$  at low conversion where secondary reactions to form ethylbenzene are small, since termination products for the phenoxy radical are not defined. In the liquid phase, the chain length decreases from  $89 \pm 3$  at 330 °C to  $25 \pm 2$  at 400 °C. If it is assumed that no chain termination occurs through the

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phenoxy radical, then the chain length can also be estimated as  $(\text{PhCH}_3 + \text{PhOH})/2\text{PhCH}_2\text{CH}_2\text{Ph}$ . At 375 °C, the chain length calculated from the initiation reaction  $(\text{PhCH}_2\text{CH}_3)$  is  $34 \pm 2$ , while that calculated from the chain termination reaction  $(\text{PhCH}_2\text{CH}_2\text{Ph})$  is  $33 \pm 4$ . The excellent agreement between these numbers indicates that at high temperatures, phenoxy radicals predominantly undergo reactions that produce other radical intermediates and chain termination reactions are very inefficient. These chain lengths are also smaller than those reported for DBE, ca. 140 at 458 °C,<sup>42a</sup> and DPP, >100 at 365 °C,<sup>26</sup> and although the factors affecting the chain length are complex, one obvious difference between PPE, DBE, and DPP is the the weaker C–O bond for PPE which leads to an enhanced initiation rate. In the gas phase (148 ± 6 kPa) at 375 °C, the chain length calculated from termination (of the benzyl radical) is  $37 \pm 6$ , which is similar to that found in the liquid phase. However, the experimentally measured kinetic order is observed to change from  $1.47 \pm 0.08$  in the liquid phase to  $1.06 \pm 0.04$  in the gas phase. This likely indicates a change in the dominant chain termination reaction in the gas phase. Since enolization of the keto dimer is the rate-limiting step in termination of the phenoxy radical,<sup>75</sup> the glass walls of the reaction vessel could assist in this enolization step and enhance the efficiency of phenoxy radical termination. The kinetic treatment for a wall-catalyzed termination reaction is similar to that found for the second-order coupling of radicals that require the participation of a third body. In these cases, the net effect is to reduce the reaction order by one-half.<sup>75b,c</sup> However, a similar reaction order could arise from coupling of the phenoxy or benzyl radical with 1 or 2.<sup>11</sup> Therefore, until the termination products from the phenoxy radical are identified, the explanation for the change in the reaction order is tentative.

**Exploration of the Retro-Ene Reaction and the Thermolysis of PPE-*d*<sub>2</sub>.** The conversion of PPE to phenol and styrene by a retro-ene pathway was investigated in more detail by the thermolysis of deuterated PPE, since rough estimates of the activation energy for reaction 1 indicate that it might be competitive with the free-radical chain reaction. The rate constants for the retro-ene reaction have been measured in the gas phase for alkyl vinyl ethers and alkyl allyl ethers,  $\log k/s^{-1} = 11.8 \pm 0.5 - 43 \pm 2/\theta$ <sup>80</sup> and  $\log k/s^{-1} = 11.6 \pm 0.4 - 42 \pm 1.3/\theta$ ,<sup>81</sup> respectively, and are relatively insensitive to substitution unless they impose steric interference.<sup>82,83</sup> The activation energy for the retro-ene reaction for PPE can be calculated by two different methods. In the first method, it is recognized that  $E_1$  is made up of three additive terms: (1)  $\Delta H^\circ$  for the conversion of PPE to styrene and phenol, 10.6 kcal mol<sup>-1</sup>,<sup>27</sup> (2)  $\Delta H^\circ_{\text{isom}}$ , the difference in enthalpy between phenol and 2,4-cyclohexa-

dien-1-one ( $\Delta H^\circ_{f,298} = -17 \pm 3$  kcal mol<sup>-1</sup>),<sup>84</sup> 6.0 kcal mol<sup>-1</sup>; and (3) the intrinsic activation energy for the reverse reaction of 2,4-cyclohexadien-1-one with styrene, which had not been measured. A crude estimate of the last reaction can be made by using the  $E_a$  for a simple ene reaction and assuming that substituents will have little impact on the aromatic transition state. Thus, for the reaction of butene and acetaldehyde, the intrinsic activation barrier is calculated to be 36.9 kcal mol<sup>-1</sup>, from the reaction enthalpy,  $-4.1$  kcal mol<sup>-1</sup>,<sup>27b</sup> and the reported activation barrier for the retro-ene reaction, ca. 41 kcal mol<sup>-1</sup>.<sup>80d,81a</sup> Therefore, an upper limit for the activation barrier for the retro-ene reaction of PPE is calculated to be 53.5 kcal mol<sup>-1</sup> (based on the three additive terms,  $E_1 = 10.6 + 6.0 + 36.9$  kcal mol<sup>-1</sup>). In the second method,  $E_1$  is calculated by anchoring the estimate to the measured average activation energy for the decomposition of alkyl vinyl ethers (43 kcal mol<sup>-1</sup>)<sup>80</sup> and adding the energy requirement for the loss of aromaticity in the transition state to form the cyclohexadienone intermediate. The latter value is estimated from the difference in the activation barriers for the Claisen rearrangement of allyl vinyl ether to 4-pentenal, and allyl phenyl ether to *o*-allylphenol, which produces 6-allyl-2,4-cyclohexadien-1-one as an intermediate. This difference should reflect the additional energy required in the transition state to form the cyclohexadienone intermediate. The rate constant for the rearrangement of allyl vinyl ether has been measured in the gas phase,  $\log k/s^{-1} = 11.7 - 30.6/\theta$ , and in di-*n*-butyl ether,  $\log k/s^{-1} = 9.9 - 26.3/\theta$  (calculated at 180 °C from  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ).<sup>85</sup> Although part of the discrepancy in activation energies can be attributed to reaction media, the preexponential factor for the latter appears low, and an average activation energy of ca. 28 kcal mol<sup>-1</sup> will be used. For the rearrangement of allyl tolyl ether, the rate constant has been measured in diphenyl ether as  $\log k/s^{-1} = 11.2 - 33.1/\theta$ .<sup>86</sup> Thus, the difference in the activation energies for the Claisen rearrangement of allyl vinyl ether and allyl phenyl ether is 5 kcal mol<sup>-1</sup>. Therefore, the estimated activation energy for the retro-ene reaction of PPE is estimated to be 48 kcal mol<sup>-1</sup>.<sup>87,88</sup> (43 kcal mol<sup>-1</sup> for the rearrangement of alkyl vinyl ether plus 5 kcal mol<sup>-1</sup> for the loss of aromaticity in the transition state) by the second method. The rate constant for the retro-ene reaction for PPE is estimated as  $\log k/s^{-1} = 11.7 - 50/\theta$ , based on the average activation energy calculated by the two different methods<sup>87</sup> above and assigning a typical preexponential factor of 11.7 for the retro-ene reaction.<sup>51</sup> In the liquid phase at 375 °C, the ratio of the experimentally measured rate constants for the free-radical reaction ( $\log k/M^{-2.9} s^{-1} = 11.4 - 46/\theta$ ) to the estimated retro-ene reaction (above) is 11:1, indicating that a small amount of the PhOH and PhCH=CH<sub>2</sub> could be produced by a concerted pathway. Therefore, the thermolysis of

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(87) Poutsma has estimated an activation barrier for the retro-ene reaction for DPP as 59 kcal mol<sup>-1</sup>.<sup>26</sup> Since the retro-ene reaction on terminal alkenes typically have activation energies ca. 11 kcal mol<sup>-1</sup> larger than the alkyl vinyl ethers, an activation barrier of 48 kcal mol<sup>-1</sup> is predicted for PPE. (a) Blades, A. T.; Sandhu, H. S. *Int. J. Chem. Kinet.* **1971**, *3*, 187. (b) Tsang, W. *Int. J. Chem. Kinet.* **1973**, *5*, 929.

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PPE-*d*<sub>2</sub> was studied to probe for a small contribution of the retro-ene reaction to the decomposition of PPE.

For PhCD<sub>2</sub>CH<sub>2</sub>OPh, the retro-ene reaction would incorporate deuterium into the ortho position of phenol, while for PhCH<sub>2</sub>CD<sub>2</sub>OPh, no aromatic deuterium should be found in the phenol product. Thermolysis of PhCH<sub>2</sub>CD<sub>2</sub>OPh at 375 °C in the gas phase (113 kPa), where secondary reactions are minimized, produced phenol which contained 3.4 ± 1.3% aromatic deuterium, by GC-MS analysis of the trimethylated phenol, indicating that deuterium can exchange into the aromatic ring of phenol under the reaction conditions. King and Stock<sup>88</sup> have studied the exchange reaction of phenol with tetralin-*d*<sub>12</sub> and naphthalene-*d*<sub>8</sub> at 427 °C and concluded that phenol-*d* forms by a free-radical process and not by an electrophilic substitution reaction<sup>89a</sup> or reaction with the glass reaction tube.<sup>89b</sup> Thermolysis of an equal molar mixture of phenol and tetralin-*d*<sub>12</sub> at 400 °C for 600 min produced 66% D in the recovered phenol (39% ortho and 27% para) while thermolysis with 11 mol % benzyl phenyl sulfide, a free-radical initiator, at 400 °C for 10 min produced 59% D in the recovered phenol (49% ortho and 10% para).<sup>88</sup> Thermolysis of PhCD<sub>2</sub>CH<sub>2</sub>OPh in the liquid and gas phase (114 kPa) produced 16% and 20% aromatic D in the ortho position of the phenol by GC-MS and <sup>2</sup>H NMR analysis. The similarity in these results indicates that the glass reaction tube is *not* catalyzing isotopic exchange in the gas phase.<sup>89b</sup> In order to estimate the amount of aromatic D in the phenol from the free-radical exchange reaction in PhCD<sub>2</sub>CH<sub>2</sub>OPh based on the thermolysis of PhCH<sub>2</sub>CD<sub>2</sub>OPh, the selectivity and deuterium isotope effect for the hydrogen abstraction at the α- and β-carbons must be taken into account. On the basis of the α/β-selectivity in the thermolysis of PhCH<sub>2</sub>CD<sub>2</sub>OPh (9.4 ± 1.4) and PhCD<sub>2</sub>CH<sub>2</sub>OPh (2.0 ± 0.1) in the gas phase at 375 °C, deuterium abstraction will be favored in the α-position of PhCD<sub>2</sub>CH<sub>2</sub>OPh by a factor of 4.7 (i.e., 9.4/2.0) over the β-position of PhCH<sub>2</sub>CD<sub>2</sub>OPh. Therefore, it is predicted that the free-radical exchange reaction will produce 16 ± 8% aromatic D in the recovered phenol from the thermolysis of PhCD<sub>2</sub>CH<sub>2</sub>OPh. Therefore, the deuterium labeling experiments confirm that there is no significant contribution of a retro-ene reaction to the decomposition of PPE, but these experiments cannot be used to probe for a small fraction (<10%) of a concerted pathway in the presence of the free-radical reaction, as a consequence of the exchange reaction.

Additional evidence against the participation of a retro-ene reaction in the thermolysis of PPE is provided by the absence of this pathway in the pyrolysis of other alkyl phenyl ethers. In the very low pressure pyrolysis of ethyl phenyl ether, only homolytic cleavage of the C-O bond was observed (see above for Arrhenius parameters).<sup>31,32</sup> In the shock tube studies on *n*-butyl phenyl ether, rearrangement to 1-butene and phenol, log *k*/s<sup>-1</sup> = 13.6 - 57.4/θ, was competitive with C-O homolysis, log *k*/s<sup>-1</sup> = 16 - 65.6/θ.<sup>30</sup> However, the Arrhenius parameters for the rearrangement were consistent with a 1,2-elimination involving a four-center transition state, which typically

has log *A* = 13.6 s<sup>-1</sup><sup>30,90</sup> instead of log *A* = 11.7 s<sup>-1</sup> typically found in the retro-ene reaction.<sup>80</sup> A 1,2-elimination was also proposed in the gas phase pyrolysis of *tert*-butyl phenyl ether to form phenol and 2-methylpropene, log *k*/s<sup>-1</sup> = 14.1 - 50.3/θ.<sup>91</sup> On the basis of these rate expressions, the rate of the 1,2-elimination is estimated to be competitive with the retro-ene reaction in the pyrolysis of alkyl aryl ethers. Therefore, great care needs to be taken to deconvolute these two potential parallel reaction pathways for the decomposition of alkyl phenyl ethers. Nevertheless, in the absence of experimental evidence to support the retro-ene reaction, the activation barrier for conversion to the cyclohexadienone intermediate must be significantly larger than the estimate value (>5 kcal mol<sup>-1</sup>). Additional insight into the transition state of the retro-ene reaction is currently under investigation by theoretical calculations.

#### Relevance to the Thermolysis of Macromolecules.

In the cross-linked macromolecular structure of lignin and biomass, thermally generated reactive intermediates may experience restricted diffusional constraints. In order to model the impact of restricted mass transport in free-radical reactions, the thermolysis of model compounds covalently anchored to an inert silica surface via a *p*-silyloxy linkage, ≡SiOC<sub>6</sub>H<sub>4</sub>R, have been studied.<sup>92</sup> Preliminary results from the thermolysis of surface-immobilized phenethyl phenyl ether at 375 °C indicate that restricted mass transport does not hinder the free-radical chain reaction or the product selectivity.<sup>17,23</sup> Therefore, the results gained from these simple model studies are relevant to processes that can occur in constrained environments, such as macromolecules. Preliminary data on the thermolysis of 1-phenyl-2-phenoxypropane at 375 °C in the gas phase (231 kPa), where secondary reactions of the alkenes are minimized, afforded phenol plus *cis*- and *trans*-β-methylstyrene and toluene plus acetophenone in a 16:1 ratio, indicating that the free-radical chain reaction described for PPE (eqs 5-11) also applies to substituted phenethyl phenyl ethers.<sup>17a</sup> The impact of substitution on the rate and selectivity of the decomposition reaction will be the subject of future investigations.

#### Conclusion

The thermolysis of phenethyl phenyl ether was investigated to resolve the discrepancies in the reported mechanisms<sup>10,11</sup> for this important model of the β-ether linkage found in lignin and low rank coal.<sup>7-9,43</sup> The cracking of PPE proceeds by two competitive pathways, defined by the α/β selectivity, that produce PhOH plus PhCH=CH<sub>2</sub> and two previously undetected products,<sup>10,11</sup> PhCHO plus PhCH<sub>3</sub>. The α/β selectivity is 3.1 ± 0.3 and is independent of concentration. From studies in the neat liquid, in solution with donor and nondonor solvents, and in the gas phase at 330-425 °C, the data is consistent with a free-radical chain mechanism for the decomposition of PPE. However, the reaction can be altered by

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hydrogen-bonding solvents. The product selectivity is determined by the relative rates of hydrogen abstraction at the  $\alpha$ - and  $\beta$ -carbons since  $\beta$ -scission and 1,2-phenyl migration from oxygen to carbon are rapid relative to hydrogen abstraction. This selectivity, and thus the product distribution, can be altered by a hydrogen donor solvent, which might be found in the liquefaction of coal or biomass,<sup>1-3</sup> by changing the dominant chain carrying radical from the phenoxy radical to the hydrocarbon solvent radical. This study also highlights the need for thermochemical data for the reactions of molecules containing heteroatoms. Specifically, more data are needed on hydrogen abstraction of aryloxy radicals with hydrocarbons, 1,2-phenyl migrations involving heteroatoms and their spirocyclic intermediates, and concerted reactions of ethers and alcohols in order to meet the current challenges for the efficient utilization of highly oxygenated macromolecules such as biomass, lignin, and low rank coal which contain up to 45, 31, and 20 wt % oxygen, respectively.<sup>15,93</sup>

### Experimental Section

**General.** Analytical analyses were performed on a gas chromatograph equipped with an autosampler and a 30 m  $\times$  0.25 mm DB-1 methylsilicone capillary column (0.25  $\mu$ m film thickness).<sup>46</sup> Detector response factors were determined relative to cumene, 2,5-dimethylphenol, and 1,4-diphenylbutane as internal standards or were estimated based on carbon number. Mass spectra were obtained at 70 eV on a GC-MS equipped with a capillary column identical to that used for GC analysis. Product identification was made by comparison of GC retention times and MS fragmentation patterns with authentic samples or based on the mass spectral fragmentation pattern and comparison with the NIST spectral library. <sup>1</sup>H, <sup>13</sup>C, and <sup>2</sup>H NMR spectra were obtained at nominally 400, 100, and 60 MHz, respectively, in CDCl<sub>3</sub> or CHCl<sub>3</sub>. Chemical shifts are reported in ppm relative to TMS.

Biphenyl was purified by successive recrystallizations from ethanol and benzene/hexanes, and *p*-phenylphenol was recrystallized from benzene/hexanes until purities were >99.9% by GC. Tetralin was washed with concd H<sub>2</sub>SO<sub>4</sub> until the layers were no longer colored, 10% Na<sub>2</sub>CO<sub>3</sub>, and water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and fractionally distilled under vacuum from sodium two times, taking the center cut. Purity was 99.4% by GC with naphthalene as the dominant impurity. 2,3-Dimethyl-2,3-diphenylbutane was recrystallized from ethanol and dried under vacuum over P<sub>2</sub>O<sub>5</sub> before use. The preparation of 1,3,5-triphenylpentane has been previously reported.<sup>26</sup>

Vapor pressures for PPE at various temperatures were estimated by the method of Lee and Kesler.<sup>94</sup> Critical parameters were estimated using Joback's group contribution method.<sup>94</sup> Liquid densities of PPE were estimated by the modified Rackett technique with the density at the boiling point estimated by the Tyn-Calus method.<sup>94</sup> The calculated densities of PPE at 425, 400, 390, 375, 360, 345, and 330 °C are 0.696, 0.728, 0.740, 0.757, 0.774, 0.790, and 0.806 g mL<sup>-1</sup>, respectively. Since the conversion in the gas phase was much lower than in the liquid, the reaction was approximated as occurring only in the liquid phase, and the rates were adjusted to account for the decreased PPE in the liquid phase. Estimates of the percent of material in the liquid phase were made on the basis of vapor pressure, ideal gas law, and the volume of the head space. The percentages varied from 98.5% at 330 °C to 94.2% at 425 °C. The densities of biphenyl, diphenylmethane, and tetralin at elevated temperatures were estimated from reported critical parameters.<sup>94</sup> The concentrations

of PPE in biphenyl or tetralin were based on the assumption of ideal mixing. Concentrations in the gas phase were calculated from the ideal gas law and measured tube volumes.

**Phenethyl Phenyl Ether.** 2-Phenylethyl tosylate<sup>25</sup> was stirred with phenol (1.2 equiv) in DMF with K<sub>2</sub>CO<sub>3</sub> (5 equiv) at room temperature for 24 h under argon. The reaction mixture was poured into H<sub>2</sub>O and extracted with toluene (2  $\times$  150 mL). The combined organic layers were washed with 0.5 M NaOH (3  $\times$  50 mL), H<sub>2</sub>O (1  $\times$  100 mL), and brine (1  $\times$  50 mL), dried over MgSO<sub>4</sub>, and filtered, and the solvent was removed under reduced pressure. Vacuum fractional distillation afforded PPE in >99.9% purity by GC (41% yield): bp 123–124 °C (1.5 mm) [lit.<sup>11</sup> 125–126 °C (1 mm)]; MS *m/z* (relative intensity) 198 (24), 105 (100), 104 (13), 103 (12), 94 (5), 91 (10), 79 (17), 77 (34).

**Deuterated 2-Phenethyl Phenyl Ethers.** 2-Phenylethyl-1,1-*d*<sub>2</sub> tosylate and 2-phenylethyl-2,2-*d*<sub>2</sub> tosylate were prepared by the method of Ettinger et al.<sup>25</sup> 2-Phenylethanol-1,1-*d*<sub>2</sub> was prepared by the reduction of methyl phenylacetate with LiAlD<sub>4</sub> (Aldrich, 98 atom % D). 2-Phenylethanol-2,2-*d*<sub>2</sub> was prepared from phenyl acetic acid by multiple isotopic exchanges with CH<sub>3</sub>CH<sub>2</sub>OD/CH<sub>3</sub>CH<sub>2</sub>ONa followed by reduction with LiAlH<sub>4</sub>. The deuterium content of the 2-phenylethanol, determined by mass spectrometry since the alcohol has no (M - 1)<sup>+</sup> peak, were >99% for PhCH<sub>2</sub>CD<sub>2</sub>OH (M<sup>+</sup>, 124) and 92% for PhCD<sub>2</sub>CH<sub>2</sub>OH (M<sup>+</sup>, 124) with 8% PhCHDCH<sub>2</sub>OH (M<sup>+</sup>, 123). The tosylates were coupled with phenol as described above and purified by vacuum fractional distillation. **2-Phenylethyl-2,2-*d*<sub>2</sub> phenyl ether** (42% yield, purity 99.4% by GC): bp 118–119 °C (0.4 mm); <sup>1</sup>H NMR  $\delta$  7.31–7.22 (m, 7H), 6.93–6.87 (m, 3H), 4.12 (s, 2H), 3.05 (t, see below). The NMR integration of the residual protium compared to oxymethylene gave H/(H + D) = 0.039; <sup>13</sup>C NMR  $\delta$  158.7, 138.1, 129.3, 128.9, 128.3, 126.3, 120.6, 114.5, 68.3, 35.4, 35.2, 35.0, 34.8, 34.6; MS *m/z* (relative intensity) 200 (25), 199 (1), 107 (100), 106 (16), 105 (12), 93 (15), 79 (13), 78 (15), 77 (31). Isotopic abundance can be determined from the M<sup>+</sup> peak since there is no (M - 1)<sup>+</sup> peak (see MS of PPE above). The residual protium in the sample is H/(H + D) = 0.031, which is in good agreement with the NMR result. **2-Phenylethyl-1,1-*d*<sub>2</sub> phenyl ether** (53% yield, purity 99.9% by GC): bp 89–90 °C (0.05 mm); <sup>1</sup>H NMR  $\delta$  7.31–7.21 (m, 7H), 6.93–6.87 (m, 3H), 3.06 (s, 2H). The NMR integration of residual protium in the oxymethylene compared to the benzylic methylene gave H/(H + D) = 0.004; <sup>13</sup>C NMR  $\delta$  158.7, 138.1, 129.3, 128.8, 128.3, 126.3, 120.6, 114.5, 68.1, 67.9, 67.6, 67.4, 67.2, 35.4; MS *m/z* (relative intensity) 200 (26), 199 (0), 107 (100), 106 (11), 105 (11), 91 (12), 79 (10), 78 (15), 77 (27). The residual protium of the sample determined by GC-MS is <0.002. See the supplementary material for copies of the <sup>1</sup>H and <sup>13</sup>C NMR spectra.

**Thermolysis Procedure.** Pyrex tubes with internal volumes of ca. 0.6, 3.7, or 33 mL were washed with detergent, rinsed extensively with distilled water, acetone, CH<sub>2</sub>Cl<sub>2</sub>, and ethanol, dried at 140 °C, and cooled under argon. The appropriate amount of material was weighed into the tubes, connected to a high vacuum line via Swagelok fittings and Teflon ferrules, degassed by a minimum of three freeze-pump-thaw cycles, and sealed at <2  $\times$  10<sup>-3</sup> Pa. The tubes were fastened to a metal holder in the horizontal position and heated to 120 °C for 5 min in a drying oven. This preheating step helped to minimize the temperature fluctuations during the first few minutes of reaction. Samples analyzed after the preheating step confirmed that no detectable decomposition had occurred. The warm samples were placed into a fluidized sand bath controlled by a proportioning controller with a K-type thermocouple. The temperature drift was monitored by a RTD placed beside the sample with the output sent to a strip chart recorder. The temperature stability during a run was  $\pm$ 1 °C with a heating time of ca. 1 min. Tubes were cooled with flowing air, removed from the sample holder, and frozen in liquid nitrogen. The tubes were opened, the samples dissolved in high purity acetone (GC/GC-MS grade solvent), and the standards added in acetone. No attempts were made to analyze the gases. The yields of products were the average of three to six injections with typical standard deviations of

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(94) Reid, R. C.; Prausnitz, J. N.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987; Chapters 2, 3, and 7.



<1% for the autosampler and <3% for manual injection. Conversion was calculated based on the recovered products and the charge of PPE.

In several thermolyses, the reaction tubes were filled one-third full of Pyrex chips, from crushed reaction tubes, in order to increase the surface/volume ratio. In liquid phase runs, the chips were thoroughly washed with acetone to remove products. In the gas phase runs, a small plug of clean glass wool was inserted ca. one-third the distance from the top of the tube in order to retain the Pyrex chips. After the reaction, the top of the warm tube above the glass wool plug was placed in liquid nitrogen, and the products were condensed away from the glass chips, allowing good recovery of products and unreacted PPE. In runs with fumed silica (Cab-O-Sil grade M5, 200 m<sup>2</sup> g<sup>-1</sup>, Cabot Corp.), standards were added in acetone, and the mixture was filtered through a 0.45 μm HPLC syringe filter eluting with acetone and analyzed by GC. For reactions in the stainless tubing bomb, a reactor was fashioned out of Swagelok fittings and stainless steel tubing with an internal volume of 0.6 mL. The tube was purged with argon before sealing.

Thermolysis of PPE diluted with *p*-phenylphenol produced a major, new secondary product. GC-MS analysis found a *m/z* (relative intensity) 274 (100) and 259 (95) indicating loss of CH<sub>3</sub> similar to that found for 1,1-diphenylethane. This fragmentation pattern is similar to that found for 2-(1-phenylethyl)phenol formed from the acid-catalyzed reaction of styrene and phenol.<sup>95</sup> GC-MS analysis of the silylated reaction mixture (BSTFA/pyridine) found an increase in the molecular weight of the product, *m/z* (relative intensity) 346 (100) and 331 (88). On the basis of the molecular weight and the mass spectral fragmentation patterns, this product was tentatively assigned as an adduct of styrene and *p*-phenylphenol, i.e., 2-(1-phenylethyl)-4-phenylphenol.

In the thermolysis of PhCD<sub>2</sub>CH<sub>2</sub>OPh at 375 °C in the liquid phase (20 min, 3.7% conversion), GC-MS analysis of the reaction mixture provided information on the deuterium distribution in the products by comparison of the mass spectral fragmentation patterns and normalized ion intensities with those of the undeuterated samples. The mass spectra of selected products are as follows: *m/z* (relative intensity) deuterated toluene 95 (48), 94 (100), 93 (95), 92 (32); benzal-

dehyde 107 (8), 106 (100), 105 (92), 77 (96); deuterated phenol 95 (25), 94(100); trimethylsilylated deuterated phenol 168 (2), 167 (15), 166 (46), 153 (10), 152 (43), 151 (100). For comparison, an undeuterated trimethylsilylated phenol was run for comparison of the intensity of the isotope peaks (<sup>13</sup>C, <sup>29</sup>Si, and <sup>30</sup>Si): *m/z* 168 (2), 167 (9), 166 (59). All deuterated and undeuterated samples were run three times and the results averaged. Similar isotopic distributions were observed in the GC-MS analysis of the gas phase thermolysis of PhCD<sub>2</sub>CH<sub>2</sub>OPh. The trimethylsilylated phenol had *m/z* 168 (3), 167 (16), 166 (46). For <sup>2</sup>H NMR analysis, the thermolysis mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and extracted with 1 M NaOH (2 × 10 mL), the combined basic layers were acidified to pH < 5 with HCl and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 7 mL), the combined organic layers were washed with brine (1 × 7 mL), dried over MgSO<sub>4</sub>, and filtered, and the solvent was removed under reduced pressure. Analysis of the sample dissolved in CHCl<sub>3</sub> (with a trace of acetone-*d*<sub>6</sub>) by <sup>2</sup>H NMR indicated only ortho-deuterated phenol. A similar extraction procedure performed on phenol-*d*<sub>6</sub> showed no exchange of the aromatic deuteriums by GC-MS analysis.<sup>89c</sup>

Thermolysis of gas phase (113 kPa) PhCH<sub>2</sub>CD<sub>2</sub>OPh at 375 °C provided 7.0% conversion in 60 min. The mass spectra of selected products are as follows: *m/z* (relative intensity) deuterated toluene 93 (11), 92 (78), 91 (100); deuterated ethyl benzene 109 (7), 108 (49), 93 (100), 91 (91); deuterated benzaldehyde 108 (6), 107 (100), 105 (91), 77 (95); deuterated phenol 95 (11), 94 (100); trimethylsilylated phenol 167 (9), 166 (51).

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**Supporting Information Available:** Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of PhCD<sub>2</sub>CH<sub>2</sub>OPh and PhCH<sub>2</sub>CD<sub>2</sub>OPh (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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