

# Model Compound Studies of the $\beta$ -O-4 Linkage in Lignin: Absolute Rate Expressions for $\beta$ -Scission of Phenoxyl Radical from 1-Phenyl-2-phenoxyethanol-1-yl Radical

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Arrhenius rate expressions were determined for  $\beta$ -scission of phenoxyl radical from 1-phenyl-2phenoxyethanol-1-yl, PhC•(OH)CH<sub>2</sub>OPh (V). Ketyl radical V was competitively trapped by thiophenol to yield PhCH(OH)CH<sub>2</sub>OPh in competition with  $\beta$ -scission to yield phenoxyl radical and acetophenone. A basis rate expression for hydrogen atom abstraction by *sec*-phenethyl alcohol, PhC•(OH)-CH<sub>3</sub>, from thiophenol,  $\log(k_{abs}/M^{-1} s^{-1}) = (8.88 \pm 0.24) - (6.07 \pm 0.34)/\theta$ ,  $\theta = 2.303RT$ , was determined by competing hydrogen atom abstraction with radical self-termination. Self-termination rates for PhC•(OH)CH<sub>3</sub> were calculated using the Smoluchowski equation employing experimental diffusion coefficients of the parent alcohol, PhCH(OH)CH<sub>3</sub>, as a model for the radical. The hydrogen abstraction basis reaction was employed to determine the activation barrier for the  $\beta$ -scission of phenoxyl from 1-phenyl-2-phenoxyethanol-1-yl (V):  $\log(k_{\beta}/s^{-1}) = (12.85 \pm 0.22) - (15.06 \pm 0.38)/\theta$ ,  $k_{\beta}(298 \text{ K})$  ca. (64.0 s<sup>-1</sup> in benzene), and  $\log(k_{\beta}/s^{-1}) = (12.50 \pm 0.18) - (14.46 \pm 0.30)/\theta$ ,  $k_{\beta}(298 \text{ K}) =$ 78.7 s<sup>-1</sup> in benzene containing 0.8 M 2-propanol. B3LYP/cc-PVTZ electronic structure calculations predict that intramolecular hydrogen bonding between the  $\alpha$ -OH and the –OPh leaving group of ketyl radical (V) stabilizes both ground- and transition-state structures. The computed activation barrier, 14.9 kcal/mol, is in good agreement with the experimental activation barrier.

## Introduction

Lignin is one of the most abundant naturally occurring biopolymers. The development of detailed knowledge of the chemistry of lignin is a desirable undertaking since large volumes of lignin produced as waste in the pulp and paper industry provide a potentially important raw material base for value-added aromatic compounds. The structure of lignin is a complicated network of aromatic ethers connected by several types of linkages in which arylglycerol  $\beta$ -aryl ether or  $\beta$ -O-4 linkages predominate,<sup>1</sup> Scheme 1. A fundamental understanding of the decomposition pathways of lignin model compounds is important in quantifying the thermal reaction pathways of lignin-like structures under hydropyrolysis conditions,<sup>2</sup> understanding the fate of lignin in the geosphere, and understanding the practical consequences of lignin reactivity, such as mechanisms of paper yellowing.<sup>3</sup>

The radiative degradation of lignin is considered to be responsible for photoyellowing of paper made from me-

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#### **SCHEME 1**



chanical pulps due to the formation of light-absorbing chromophores formed by the reactions of oxidatively produced phenoxyl radicals. A variety of pathways leading to the formation of "yellowing precursors", substituted phenoxyl radicals, have been proposed.<sup>4–10</sup> An important

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# SCHEME 2



variable for prediction of the course of lignin thermal or photooxidative dissolution is the lifetime of the ketyl radical II. In an early study, a lignin model ketyl radical PhCH<sup>•</sup>(OH)CH<sub>2</sub>OPh was examined by laser flash photolysis techniques.<sup>11</sup> The authors reported that the ketyl radical undergoes rapid fragmentation with a lifetime  $(\tau)$ of about 0.5  $\mu$ s at ambient temperature to yield phenoxyl radical. This was a surprising result in view of the activation barrier for scission of a related lignin model radical, PhCH·CH(CH<sub>3</sub>)OPh,  $E_a = 16$  kcal/mol<sup>12</sup> and  $\tau >$ 1 s. In a recent study,<sup>4</sup> the rapid fragmentation rate reported in the transient absorption experiment was questioned. A rough estimate of the expected barrier based on thermochemical kinetic estimates was published<sup>13</sup> for a calculated lifetime on the order of seconds at 298 K, but no actual kinetic measurements were carried out. If the lifetime of the ketyl radical is seconds, instead of microseconds, then alternate pathways (e.g., radical-radical disproportionation reactions) to yield an aryl ketone (III) become available to compete with  $\beta$ -scission.<sup>14</sup> Formation of phenoxyl radicals could then occur by direct photolysis of, e.g., III. The relative importance of the thermal (Scheme 2, path A) versus photochemical scission (path B) pathways leading to phenoxyl radical intermediates generated from  $\beta$ -guiacoxybenzyl alcohols depends on the lifetime of the ketyl radical in the lignin matrix. If the lifetime of the phenoxyl radical precursor is short as suggested by transient absorption experiments, then  $\beta$ -scission of ketyl radicals will lead directly to phenoxyl radicals. The phenoxyl radicals undergo reactions yielding quinones and related structures possessing light-absorbing chromophores. An

unambiguous measurement of the rate constants for  $\beta$ -scission would allow the importance of the various proposed pathways to be assessed, as well as providing an important rate-describing step in the hydropyrolysis of lignin.

Thus, we undertook a kinetic study of the scission of the 1-phenyl-2-phenoxyethanol-1-yl radical (V). The Arrhenius parameters for  $\beta$ -scission were determined in an analogous manner to our previous quantitative study of the  $\beta$ -scission of the phenoxyl radical from 1-phenyl-2phenoxypropyl radical (VI).<sup>12</sup> In the present study, we also apply ab initio electronic structure calculations to investigate the  $\beta$ -scission energetics as well as the role of intramolecular hydrogen bonding, depicted below, in controlling the rate of scission through stabilization of ground and/or transition states.



#### **Results and Discussion**

The approach used in this work is analogous to previous kinetic studies.<sup>12</sup> The lifetime of the 1-phenyl-2-phenoxyethanol-1-yl radical (V) was expected to be sufficiently long to be trapped by a suitable hydrogen atom donor, allowing relative rates to be obtained from product studies.  $\beta$ -Scission yields the enol of acetophenone, which rearranges to the observed product, acetophenone, and phenoxyl radical, observed as phenol, eq 1. The competing abstraction pathway forms 1-phenyl-2-phenoxyethanol, eq 2. Under the conditions of short extent of conversion of hydrogen donor, the relation  $k_{\beta}$  (s<sup>-1</sup>) ~ [DH]  $k_{abs}$  (M<sup>-1</sup> s<sup>-1</sup>) holds, and the relative rate of  $\beta$ -scission to hydrogen abstraction can be

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<sup>(14)</sup> Reaction of the ketyl with oxygen by disporoportionation or radical hydrogen transfer to another carbonyl compound.

determined from the ratio of acetophenone to 1-phenyl-2-phenoxyethanol, eq 3. Applying independently determined values of  $k_{abs}$  to the relative rates,  $k_{\beta}/k_{abs}$ , yields values of  $k_{\beta}$ . The Arrhenius parameters describing the  $\beta$ -scission of phenoxyl radical from the  $\beta$ -O-4 linkage of the 1-phenyl-2-phenoxyethanol-1-yl radical (V) were thus obtained.

PhC<sup>•</sup>(OH)CH<sub>2</sub>OPh 
$$\xrightarrow{k_{\beta}}$$
  
PhC(OH)=CH<sub>2</sub> + PhO<sup>•</sup>(+DonorH →) HOPh (1)

PhC<sup>•</sup>(OH)CH<sub>2</sub>OPh + DonorH  $\xrightarrow{k_{abs}}$ PhCH(OH)CH<sub>2</sub>OPh (2)

$$k_{\beta}/k_{abs}[DH] = [PhC(OH)=CH_2]/$$
  
[PhCH(OH)CH<sub>2</sub>OPh] (3)

**Determination of Rate Constants for Abstraction** of Hydrogen from Thiophenol by 1-Phenylethanol-1-yl Radical. A convenient means of determining the basis reaction rate, eq 2 above, would have been to compete the self-termination of the abstracting radical, PhC<sup>•</sup>C(OH)CH<sub>2</sub>OPh, to form dimers, with the abstraction process. However, self-termination of the ketyl radical was found to proceed essentially exclusively by disproportionation, with no more than a few percent of dimers formed. It thus was impractical to compete self-termination with abstraction. The radical PhC•(OH)CH<sub>3</sub>, which undergoes nearly exclusive dimerization, was thus employed, with the necessary assumption that the abstraction rate is identical to the ketyl radical V. The rate constants of abstraction of hydrogen atom from thiophenol by a number of radicals have been reported.<sup>15–17</sup> These rate expressions for the transfer of hydrogen from thiophenol serve as important rate standards for the competitive measurements of intramolecular radical reactions. No rate expressions for the reaction of thiophenol with ketyl radicals have been reported. We measured an absolute rate expression for hydrogen abstraction using the competition between the abstraction of hydrogen by 1-phenylethanol-1-yl radical (substituted for V) with the self-termination of 1-phenylethanol-1-yl radical to yield the corresponding termination products, pinacol coupling products *meso-* and  $d_1/[PhCH(OH)CH_3]_2$  by combination and sec-phenethyl alcohol and acetophenone by disproportionation. Acetophenone was used as the photoprecursor to generate 1-phenylethanol-1-yl radical since it is photoreduced by aliphatic alcohols with quantum yields of 0.5-0.7 yielding acetophenone pinacols.<sup>18-20</sup> The reaction suite involved in the photoreduction of

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acetophenone through a ketyl radical intermediate is outlined in eqs 4-10.

$$PhCOCH_{3} + h\nu \rightarrow [PhCOCH_{3}]^{*1} \rightarrow [PhCOCH_{3}]^{*3} \quad (4)$$

 $PhC^{\bullet}(OH)CH_3 + PhSH \rightarrow PhCH(OH)CH_3 + PhS^{\bullet}$  (8)

 $2PhC^{\bullet}(OH)CH_3 \rightarrow meso- + d, l-[PhCH(OH)CH_3]_2$  (9)

 $2PhC^{\bullet}(OH)CH_3 \rightarrow PhCH(OH)CH_3 + PhCOCH_3$  (10)

Upon irradiation, the low-lying triplet state of acetophenone, [PhCOCH<sub>3</sub>]\*<sup>3</sup>, abstracts hydrogen from 2-propanol to form two hemipinacol radicals, eq 5. Equations 6 and 7 depict the reduction of ground-state acetophenone by transfer of a hydrogen atom from ketyl radicals. By increasing the acceptor ketone concentration, the rate of the transfer reaction (eq 6) can be adjusted to be faster than coupling of ketyl radicals (eqs 9 and 10).<sup>21</sup> The absence of any cross-coupling or self-combination products of 2-propanol-1-yl radicals indicates that acetophenone ketyl radical (PhC•(OH)CH<sub>3</sub>) is the only radical in appreciable concentration in solution. In the presence of thiophenol, the acetophenone ketyl radical abstracts hydrogen, eq 8, to form the corresponding alcohol with a rate constant,  $k_{\rm abs}$ , in competition with radical termination,  $k_{\rm t}$  (eqs 9 and 10), by combination and disproportionation to form the dimer, 2,3-diphenyl-2,3-butanediol, sec-phenethyl alcohol, and acetophenone. The thiophenoxyl radical, PhS<sup>•</sup>, undergoes cross- and symmetric termination (not shown), with no consequence on the measured product ratios at short reaction times. (Acetophenone ketyl radical can both be oxidized by thiyl radicals to form acetophenone and reduced by mercaptans to form sec-phenethyl alcohol.<sup>22</sup> However, this side reaction does not complicate the kinetic analysis to determine the competitive rate constant,  $k_{\rm abs}/k_{\rm t}$ , although it does significantly lower the mercaptan concentrations that can be employed in kinetic experiments.) The disproportionation of acetophenone ketyl radicals to yield acetophenone and the corresponding alcohol, eq 10, does not appear to be significant; only some 2% dispro-

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portionation relative to coupling has been observed.<sup>19a,23</sup> The combination-to-disproportionation ratio,  $k_{dis'}k_{com}$ , for 1-phenylethanol-1-yl radical was determined by measuring the dimer and *sec*-phenethyl alcohol concentrations of the reaction mixtures from irradiation of the radical precursor in the absence of thiophenol as a function of temperature. The *sec*-phenethyl alcohol formed by the disproportionation pathway ranged from 3% to 5% of the dimer, 2,3-diphenyl-2,3-butanediol (30–110 °C), and the average value of  $k_{dis'}k_{com}$  (0.04) was used to correct the *sec*-phenethyl alcohol concentration for disproportionation.

At short reaction times (1-5 s), i.e., less than 1% consumption of acetophenone and less than 10% consumption of thiophenol, the rate of formation of the *sec*-phenethyl alcohol and the rate of formation of the dimer in steady-state concentrations of ketyl radical are given by eqs 11 and 12. The product alcohol produced by reaction of the ketyl radical with the donor [PhCH(OH)-CH<sub>3</sub>]<sub>tr</sub> and [PhCH(OH)CH<sub>3</sub>]<sub>dis</sub> terms in eq 11 and 12 refers to the *sec*-phenethyl alcohol (PhCH(OH)CH<sub>3</sub>) formed by the hydrogen transfer reaction (eq 5) and that formed by disproportionation of ketyl radicals (eq 10).

 $d[PhCH(OH)CH_3]_{tr}/dt = k_{abs}[PhSH]_{av}[PhC^{\bullet}(OH)CH_3] (11)$  $d([dimer] + [PhCH(OH)CH_3]_{dis})/dt = k_t[PhC^{\bullet}(OH)CH_3]^2 (12)$ 

Under steady-state conditions, dividing the integral of eq 11 by the square root of the integral of eq 12 yields eq 13, which relates the rate constant of abstraction,  $k_{abs}$ , with the termination rate constant,  $k_{\rm t}$ , the photolysis time,  $\Delta t$ , thiophenol, dimer, and *sec*-phenethyl alcohol concentrations. The concentrations of reactants and products were corrected for density changes of benzene at the reaction temperatures.<sup>24</sup> The concentrations of PhCH(OH)CH<sub>3</sub>, eq 14, and the dimer, 2,3-diphenyl-2,3butanediol, eq 15, were measured in the acetophenone solutions of 0.8 M 2-propanol in benzene in the presence of thiophenol (0.002-0.008 M) upon irradiation under steady-state conditions. The Arrhenius expression, log- $(k_{\rm abs}/(k_{\rm t})^{1/2} = (2.99 \pm 0.24) - (4.49 \pm 0.34)/\theta$ , was determined from the data obtained at the temperature range 25-100 °C.

$$k_{abs} = (k_t)^{1/2} [PhCH(OH)CH_3]_{corr} / [PhSH]_{av} [dimer]_{corr}^{1/2} (\Delta t)^{1/2}$$
(13)

$$[PhCH(OH)CH_3]_{corr} = [PhCH(OH)CH_3] - k_{dis}/k_{com}[dimer] (14)$$

$$[dimer]_{corr} = [dimer] + [dimer]k_{dis}/k_{com}$$
 (15)

Equations 13–15, where dimer = *meso-* and *d*,*l*-2,3-diphenylbutane-2,3-diol, allow for the determination of

 $k_{\rm abs}$  if the self-termination rate constants are available for the temperature range. The self-termination rate constants for small, carbon-centered radicals can be accurately calculated by using the Smoluchowski equation, eq 16. The diffusion coefficient,  $D_{AB}$ , can either be calculated by an empirical approach such as the Spernol-Wirtz (SW) treatment or measured experimentally.<sup>25,26</sup> Other terms include Avogadro's number, *N*, the fraction of cage encounter radical pairs that undergo reaction,  $\sigma$ , taken to be equal to the statistical population of singlet radical pairs, 1/4, and the collision diameter of the diffusing species,  $\rho$ . Estimation of the latter value is probably the greatest source of error in the Smoluchowski equation, perhaps 15% for small radicals in nonassociating media. A detailed description of the use of diffusion coefficients in the calculation of self-termination rate constants is given in the Supporting Information (Table 1S). The diffusion coefficients were measured in benzene and a benzene solution containing 0.8 M 2-propanol by Taylor's dispersion method using sec-phenethyl alcohol as a model for the corresponding ketyl radical.<sup>27</sup>

$$2k_{\rm t} = (8\pi/1000)\sigma\rho D_{\rm AB}N \tag{16}$$

There are negligibly small differences between the termination rate constants for Ph(C<sup>•</sup>)(OH)CH<sub>3</sub> in benzene, calculated by the SW treatment (using diffusion coefficients for the parent alcohol (PhCH(OH)CH<sub>3</sub>) estimated from solvent viscosities), and those calculated using experimentally measured diffusion coefficients (exp) in benzene:  $\log(2k_t/M^{-1} s^{-1})_{sw} = 11.92 - 2.93/\theta$ ; log- $(2k_t/M^{-1} s^{-1})_{exp} = 11.64 \pm 0.16 - 2.76 \pm 0.23/\theta^{.28}$  On the other hand, in a mixed solvent system (e.g., 0.8 M 2-propanol in benzene), the SW approach is expected to fail due to solvent-solvent and solvent-solute association;<sup>29</sup> thus, diffusion coefficients of sec-phenethyl alcohol in this mixed solvent were experimentally measured by Taylor's dispersion method and used in the Smoluchowski equation to obtain self-termination rate constants. The Arrhenius expression for self-termination,  $\log(2k_t/M^{-1} s^{-1}) = 12.08 \pm 0.14 - 3.16 \pm 0.18/\theta$ , was employed to determine the abstraction rate constant,  $k_{abs}$ , eq 13, in the mixed solvent. The Arrhenius expression determined for termination permits us to calculate an Arrhenius expression for  $k_{abs}$  from the temperature dependent relative rate data. The activation parameters, in the mixed solvent system (0.8 M 2-propanol in benzene),  $\log(k_{abs}/M^{-1} s^{-1}) = (8.88 \pm 0.24) - (6.07 \pm 0.34)/\theta$ ,  $\theta = 2.303 RT$  kcal/mol, and the rate constant at 298 K,  $2.7~\times~10^4~M^{-1}~s^{-1}\!,$  are compared with those obtained for  $\alpha$ -(phenylthio)benzyl and other carbon-centered radicals,<sup>15–17</sup> Table 1.

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<sup>(28)</sup> Figure 1S (Supporting Information) shows the variation of selftermination rate constants for 1-phenylethanol-1-yl radical calculated using *sec*-phenethyl alcohol as a radical model with temperature.

<sup>(29)</sup> SW only corrects for differences between solute and solvent size. No electrostatic interactions are accounted for by this empirical recipe.

 TABLE 1. Arrhenius Parameters for the Abstraction of Hydrogen by 1-Phenylethanol-1-yl, Alkyl, and Benzylic

 Radicals from Thiophenol<sup>a</sup>

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	radical	$\log(A/M^{-1} s^{-1})$	$E_{\rm a}$ (kcal/mol)	$k_{\rm abs}$ (25 °C) (×10 <sup>4</sup> M <sup>-1</sup> s <sup>-1</sup> )	solvent
PhCH'SPh $8.60 \pm 0.04$ $6.64 \pm 0.07$ $0.58$ nonane <sup>e</sup>	PhC•(OH)CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> • CH <sub>3</sub> CH•CH <sub>3</sub> (CH3)3C• PhCH <sub>2</sub> •	$\begin{array}{c} 8.88 \pm 0.22 \\ 9.41 \pm 0.13 \\ 9.26 \pm 0.19 \\ 9.26 \pm 0.26 \\ 8.27 \pm 0.14 \end{array}$	$\begin{array}{c} 6.07 \pm 0.34 \\ 1.74 \pm 0.21 \\ 1.70 \pm 0.21 \\ 1.50 \pm 0.20 \\ 3.79 \pm 0.24 \end{array}$	2.68 13 600 10 500 14 700 31.3	0.8 M 2-propanol in benzene <sup>b</sup> nonane <sup>c</sup> nonane <sup>c</sup> nonane <sup>c</sup> hexane <sup>d</sup>
	PhCH <sup>•</sup> SPh	$8.60\pm0.04$	$6.64\pm0.07$	0.58	nonane <sup>e</sup>

<sup>a</sup> Errors are in 2*a*. <sup>b</sup> This study. <sup>c</sup> Reference 13. <sup>d</sup> Reference 14. <sup>e</sup> Reference 15.

TABLE 2. Product Distributions from the Photolysis of 1,2-Diphenyl-2-hydroxy-3-phenoxypropanone in Benzene at 100.0  $^\circ C$ 

time (s)	me s) PhCOH PhOH		$\begin{array}{c} PhCOCH_{3} \\ products \\ (mol \times 10^{4})^{a} \end{array}$	$\begin{array}{c} (PhCO)_2\\ products\\ (mol \times 10^4)^a \end{array}$	PhCOR <sup>1</sup>	R <sup>2</sup> OH		
10	1.0	2.6	2.4	0.44	2.01	0.06		
20	1.8	8.6	9.1	2.6	8.5	0.09		
30	4.9	13	17	2.9	11	tr.		
<sup>a</sup> P	<sup><i>a</i></sup> PhCOR <sup>1</sup> = PhCOCH <sub>2</sub> OPh; $R^{2}OH = PhCH(OH)CH_{2}OPh$ .							



**FIGURE 1.** The variation of the product ratio [PhCH(OH)-CH<sub>2</sub>OPh]/[PhCOCH<sub>3</sub>] with the concentration of thiophenol at ( $\bigcirc$  71.3 °C, ( $\triangle$ ) 91.2 °C, ( $\bullet$ ) 101.0 °C, ( $\bullet$ ) 118.7 °C, and ( $\square$ ) 142.3 °C in the photolysis of 1,2-diphenyl-2-hydroxy-3-phenoxypropanone (ROH = PhCH(OH)CH<sub>2</sub>OPh).

β-Scission of Phenoxyl Radical from 1-Phenyl-2-Phenoxyethanol-1-yl Radical. 1,2-Diphenyl-2-hydroxy-3-phenoxypropanone, eq 17, was used as the photoprecursor for the ketyl radical in benzene and in benzene containing 0.8 M 2-propanol (e.g., eq 17). Benzaldehyde, phenol, acetophenone, 2-phenoxyacetophenone, 1,2-diphenylethane-1,2-dione, and 1-phenyl-2-phenoxyethanol are formed as major products from the photolysis of 1,2diphenyl-2-hydroxy-3-phenoxypropanone, Table 2.

Figure 1 shows a linear increase in the ratio of reduced hydrocarbon (1-phenyl-2-phenoxyethanol) relative to scission products (phenol and acetophenone) with increasing thiophenol concentraton. While radical-radical termination dimers are observed (e.g., PhCOCOPh), no dimeric products derived from the parent radical V, are observed. The formation of 2-phenoxyacetophenone can be attributed to the cage disproportionation of parent radical V with a variety of partners, including benzoyl radical, eq 19, and/or oxygen-assisted disproportionation of the ketyl radical, eq 20, rather than to a self-termination reaction of this radical since only trace amounts of the alcohol, 1-phenyl-2-phenoxyethanol, are formed in the absence of thiophenol.

The possibility of the formation of acetophenone and phenol by the subsequent photolysis of the primary product 2-phenoxyacetophenone was addressed with control experiments. The concentration of 2-phenoxyacetophenone in kinetic experiments was less than  $5\times10^{-4}$  M at the typical reaction time of 5 s. Consideration of its relative absorptivity in the presence of the substrate at  $10^{-2}$  M concentrations suggests a negligible percentage of this ketone will have been photolyzed.

Examples of this category of ketone typically exhibit very low quantum yields, about 0.004, in benzene.<sup>30</sup> When 0.004 M solutions of 2-phenoxyacetophenone in benzene, were irradiated in degassed Pyrex tubes for 10-30 s, no reaction was detected, i.e., no acetophenone or phenol is observed. Equations 17-22 describe the formation and reaction of 1-phenyl-2-phenoxyethanol-1-yl radical upon photolysis of 1,2-diphenyl-2-hydroxy-3-phenoxypropanone. The reaction of O<sub>2</sub>, eq 20, is included for completeness, although the experiments were carried out in rigorously degassed media.

PhCOC(OH)PhCH<sub>2</sub>OPh  $\xrightarrow{h\nu}$ 

[PhCOC(OH)PhCH<sub>2</sub>OPh]\* (17)

 $[PhCOC(OH)PhCH_2OPh]^* \rightarrow$ 

 $PhCO' + PhC'(OH)CH_2OPh$  (18)

PhCO<sup>•</sup> + PhC<sup>•</sup>(OH)CH<sub>2</sub>OPh →

 $PhCOH + PhCOCH_2OPh$  (19)

PhC<sup>•</sup>(OH)CH<sub>2</sub>OPh +  $O_2$  →

 $PhCOCH_2OPh + HO_2^{\bullet}$  (20)

PhC<sup>•</sup>(OH)CH<sub>2</sub>OPh + PhSH →

 $PhCH(OH)CH_2OPh + PhS^{\bullet}$  (21)

 $PhC^{\bullet}(OH)CH_2OPh \rightarrow$ 

 $PhO^{\bullet} + Ph(OH) = CH_2 (\rightarrow PhCOCH_3)$  (22)

In the presence of thiophenol, abstraction of hydrogen atom ( $k_{abs}$ ), eq 21, competes with  $\beta$ -scission of the phenoxyl radicals, eq 22. The relative rate of abstraction to  $\beta$ -scission is calculated using eq 23 by plotting the product ratio [PhCH(OH)CH<sub>2</sub>OPh]/[PhCOCH<sub>3</sub>] against thiophenol concentration, Figure 1. The consumption of thiophenol in most cases is less than 2% and less than 10% when low thiophenol concentrations are used.

 $k_{\rm abs}/k_{\beta} = [PhCH(OH)CH_2OPh]/[PHCOCH_3][PhSH]$ (23)

<sup>(30) (</sup>a) Scaiano, J. C.; Netto-Ferreira, J. C. *J. Photochem.* **1986**, *32*, 253. (b) Netto-Fereira, J. C.; Avellar, I. G. J.; Scaiano, J. C. *J. Org. Chem.* **1990**, *55*, 89.



**FIGURE 2.** Arrhenius data for the scission of radical V in benzene (diamonds) and in benzene/0.8 M methanol (squares). A basis rate expression to convert relative expressions ( $k_{\beta}/k_{abs}$ ) to scission rate constants ( $k_{\beta}$ ) was measured for the radical Ph<sup>•</sup>(OH)CH<sub>3</sub> in 0.8 M 2-propanol in benzene and applied to both solvents in the above plot. The agreement of the two rate expressions reflects a parallel solvent effect for  $k_{abs}$  and  $k_{\beta}$ .



**FIGURE 3.** BLYP/cc-PVTZ geometries and energies of the non-hydrogen-bonded ground state (nHBGS), H-bonded GS (HBGS), non-H-bonded transition state (nHBTS), and the hydrogen bonded TS (HBTS). Hydrogen bonding stabilizes the TS 3.1 kcal/mol and the GS by 1.6 kcal/mol. The zpe and thermally (enthalpy) corrected activation enthalpy for  $\beta$ -scission of the H-bonded complex is 14.9 kcal/mol.

The relative rate constants,  $k_{abs}/k_{\beta}$ , were measured in benzene and in a benzene solution containing 0.8 M 2-propanol at 70–150 °C since the basis rates,  $k_{abs}$ , were measured in the mixed solvent system. The Arrhenius expression for the relative rate constants are  $(\log(k_{abs}/k_{\beta}) = (8.99 \pm 0.39)/\theta - (3.97 \pm 0.22)$  in benzene and  $(\log(k_{abs}/k_{\beta}) = (8.39 \pm 0.30)/\theta - (3.62 \pm 0.18)$  in 0.8 M 2-propanol. It is interesting to note that the relative rate of abstraction to scission is essentially identical in both solvents. This observation appears to indicate either the absence of a solvent effect on either  $\beta$ -scission or hydrogen abstraction due to hydrogen bonding interactions of the ketyl radical with the solvent or a parallel solvent effect on abstraction and scission. The relative rate constants were converted to the absolute rate constants of  $\beta$ -scission of PhC\*(OH)CH<sub>2</sub>OPh (V) using Arrhenius

**TABLE 3.** Arrhenius Parameters for  $\beta$ -Scission Reactions of Lignin Models<sup>*a*</sup>

radical	$\log(A/M^{-1} s^{-1})$	$E_{\rm a}$ (kcal/mol)	(25 °C) (s <sup>-1</sup> )
PhC•(OH)CH2OPhb	$12.85\pm0.22$	$15.06\pm0.38$	64.0
PhC <sup>•</sup> (OH)CH <sub>2</sub> OPh <sup>c</sup>	$12.50\pm0.18$	$14.46\pm0.30$	78.7
PhC•(OH)CH <sub>2</sub> OPh <sup>d</sup>			>106
PhCH•CHCH <sub>3</sub> OPh <sup>e</sup>	$13.45\pm0.26$	$16.94\pm0.52$	10.7
PhCH•CHCH <sub>3</sub> OPh <sup>f</sup>	$13.41\pm0.30$	$19.30\pm0.75$	0.18
PhCH•CH <sub>2</sub> CH <sub>2</sub> Ph <sup>g</sup>	14.8	28.3	$10^{-6}$

<sup>*a*</sup> Errors are in 2*σ* in the relative rate data.  $k_{\beta} = k_{abs}/k_{rel}$ . <sup>*b*</sup> In benzene,  $(\log(k_{abs}/k_{\beta}) = (8.99 \pm 0.39)/\theta - (3.97 \pm 0.22)$ . <sup>*c*</sup> In 0.8 M 2-propanol solution in benzene,  $(\log(k_{abs}/k_{\beta}) = (8.39 \pm 0.30)/\theta - (3.62 \pm 0.18)$ . <sup>*d*</sup> Reference 11. <sup>*e*</sup> Trans-*β*-scission, ref 12. <sup>*f*</sup> Cis-*β*-scission, ref 12. <sup>*g*</sup> Poutsma, M. L.; Dyer, C. W. *J. Org. Chem.* **1982**, *47*, 4903.

parameters for hydrogen abstraction determined for  $PhC^{\bullet}(OH)CH_3$  in 0.8 M 2-propanol in benzene.

Figure 3 displays results for the solvent mixture, 0.8 M 2-propanol in benzene (squares) and Arrhenius plots for scission,  $k_{\beta}$ . The linear least-squares regression line provides the activation parameters for the  $\beta$ -scission pathway of this lignin model ketyl radical:  $\log(k_{\beta}/s^{-1}) = (12.85 \pm 0.22) - (15.06 \pm 0.38)/\theta$  in benzene and  $\log(k_{\beta}/s^{-1}) = (12.50 \pm 0.18) - (14.46 \pm 0.30)/\theta$  in 0.8 M 2-propanol. A comparison of the rate expressions for  $\beta$ -scission with other lignin model radicals is shown in Table 3.

A decrease of ca. 2-2.5 kcal/mol in the activation barrier is observed compared to 1-phenyl-2-phenoxypropyl radical.<sup>12</sup> The rate constants at 25 °C, 64.0 s<sup>-1</sup> (benzene) and 78.7  $s^{-1}$  (2-propanol/benzene), suggest that the transient species observed by Scaiano should be attributed to some other prompt photoprocess, perhaps involving the ketone PhCOCH<sub>2</sub>OPh.<sup>11</sup> Although the rates of scission of V appear similar in benzene and 0.8 M 2-propanol in benzene, in fact, there is an unknown magnitude of error introduced by using the ketyl radical Ph<sup>•</sup>(OH)CH<sub>3</sub> to determine the basis rate for the rearrangement, since it cannot undergo intramolecular hydrogen bonding. The abstraction basis rate expression  $(k_{abs}/M^{-1} s^{-1})$  used to convert relative expressions  $(k_{\beta}/k_{abs})$ to scission rate constants  $(k_{\beta})$  was measured for the radical Ph•(OH)CH3 in 0.8 M 2-propanol in benzene and applied to both solvents. The agreement of the two rate expressions is due to either the lack of a significant solvent effect or a parallel solvent effect for  $k_{abs}$  and  $k_{\beta}$ . Resolution of this question must await development of an improved abstraction basis rate expression.

**Electronic Structure Calculations.** The potential surface of the scission of PhC<sup>•</sup>(OH)CH<sub>2</sub>OPh was examined at the B3LYP/6-31G(d) and B3LYP/cc-PVTZ levels of theory<sup>31</sup> to examine the role of intramolecular hydrogen bonding (HB) in the activated complex leading to scission of the phenoxyl radical, Table 4. Initial calculations were carried out at the B3LYP/6-31G(d) level of theory. The more extended cc-PVTZ basis set was found to give a small (~1 kcal/mol) improvement in relative energies and was deemed adequate for obtaining relative energetics at saddle points within 1-2 kcal/mol. Geometries were optimized as ground state (GS) or transition state (TS) as confirmed by vibrational calculations that revealed zero or one negative eigenvalue, respectively. A comparison of the geometries and energies of the hydrogen

Molecule	E (B3LYP/6-	E (B3LYP/cc-	zpe, hartree/	Thermal Corr. to
	31G(d)	PVTZ)	particle	Enthalpy, 298K
	hartree/particle	hartree/particle	(B3LYP/6-31G(d))	(B3LYP/6-31G(d)
				hartree/particle
H H O-H Hydrogen-bonded GS	-691.71235	-691.96554	0.234857	0.249425
H H H H Non-H-bonded GS	-691.70774	-691.963054	0.234856	0.249424
H H O H O Hydrogen-bonded TS	-691.68241	-691.93738	0.232797	0.245012
H H H O	-691.6749811	-691.932726	0.231483	0.245372
$\begin{array}{c} & & \\$	-691.71006	-691.96601	0.232154	0.247690

 
 TABLE 4.
 DFT Calculations of Hydrogen-Bonded and Non-Hydrogen-Bonded Ketyl Radicals<sup>a</sup>

 $^a$  Geometries were optimized at the B3LYP/6-31G(d) and B3LYP/ cc-PVTZ levels of theory.

bonding ground state (HBGS) and non-hydrogen-bonding ground state (nHBGS) and the hydrogen bonding transition state (nHBTS) and non-hydrogen-bonding transition state (nHBTS) are shown in Figure 2. Note that the non-hydrogen-bonded isomer is a true conformational isomer, as opposed to a geometry-constrained optimization. The most notable feature revealed by the calculations is the distortion of the transition state from the normal periplanar departure geometry of the phenoxyl radical from the forming olefin. A dihedral angle ( $\angle 1-2-9-10$ ) of 50.2° results from intramolecular hydrogen bonding between H-17 and O-10, whereas for the non-hydrogen-bonded transition structure, the dihedral is 83.7°.

At the B3LYP/cc-PVTZ level of theory, intramolecular hydrogen bonding stabilizes the transition state by ca. 3.1 kcal/mol. The ground state is stabilized to a slightly less extent, 1.6 kcal/mol. The slightly greater stabilization of the TS may be due to an increase in the polarization of the C–O bond during scission, thus favoring hydrogen bonding to a greater extent. The activation barrier for  $\beta$ -scission of the ketyl radical is 14.9 kcal/mol, in excellent agreement with experiment. The entropy loss on freezing the OH rotation in the hydrogen-bonded GS and TS is the primary difference that would be expected to affect the Arrhenius A factor in the gas-phase reaction, although it is uncertain how this would be modified in a hydroxylic solvent. The theoretical results point to a compensating stabilization of both the TS and GS by intramolecular hydrogen bonding.

<sup>(31)</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

From this work, it is clear that the scission of the ketyl radical V occurs by a conventional pathway, exhibiting a lifetime of about 0.1 s at 25 °C. Unconventional pathways, for example, the deprotonation of V, would result in the formation of a radical anion with a microsecond lifetime for C-O scission.<sup>32</sup> The present results rule out a radical anion decomposition mechanism. In a diffusionally restricted lignin matrix, even the modest scission rates found in this work would result in facile phenoxyl radical scission, such that phenolic radicals will provide an efficient yellowing process for paper. Factors such as pH and solvent properties would enhance such processes.<sup>33</sup> While substituent effects on the phenyl ring  $\alpha$  to the radical center do not significantly effect the rate of scission of phenoxyl radical from the corresponding benzyl radical,<sup>34</sup> more complex lignin models, e.g., with a methyl ether function  $\alpha$ -substituted to the radical center instead of hydroxy, or a hydroxymethyl substituent at the 2-position, may further enhance the  $\beta$ -scission pathway. Further work to examine more complex model structures of lignin is in progress.

## **Summary**

We have developed a new basis rate reaction, hydrogen atom abstraction by an aryl ketyl radical from thiophenol, andArrhenius expressions for the  $\beta$ -scission of phenoxyl radical from lignin radical model compound 1-phenyl-2-phenoxyethanol-1-yl. The observed scission rates are consistent with a conventional scission pathway. Electronic structure calculations show that intramolecular hydrogen-bond formation stabilizes both transition and ground states. The combined experimental and computational results suggest that intramolecular hydrogen bonding results in slightly greater stabilization of the TS for scission, resulting in a slight net decrease in the  $\beta$ -scission barrier for the lignin model radical.

## **Experimental Section**

**Materials.** Benzene (99.9%), 2-bromoacetophenone (98%), phenol (99+%), dimethyl sulfate (99+%), 2-phenyl-1,3-dithiane (97%), tetrahydrofuran (99.9%), styrene (99+%), *N*-methybis-trifluoroacetamide (98%, derivatization grade), bis(trimethyl-silyl)trifluoroacetamide (99+%), tetradecane (99+%), dodecane (99+%), *sec*-phenethyl alcohol (98%), 2-propanol (99.5+%), thiophenol (99+%), and butyllithium (2.5 M in hexane) were purchased from Aldrich. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Styrene and thiophenol were distilled at reduced pressure before use. 2,3-Diphenyl-2,3-butanediol was purchased from Fluka and used as received. Acetophenone (Eastman Organic Chemicals) and benzene were recrystallized at low temperature before use.

**Product Identification.** All products were identified by the comparison of their GC and GC/MS spectra with authentic samples. Gas chromatography was carried out using a HP-5 (cross linked 5% PHME siloxane) capillary GC column (15m  $\times$  0.25 mm i.d.). 1-Phenyl-2-phenoxyethanol and *sec*-phenethyl alcohol were identified and quantified by GC after converting

(33) Preliminary experiments performed on the photolysis of 2phenoxyacetophenone in ethanol showed 3-6 times increase in acetophenone formation when 0.015 M sodium hydroxide is added to the ethanolic solution. The importance of ketyl anion type intermediates on fragmentation also should be addressed. them to the trifluoroacetate and trimethylsilyl derivatives, respectively.

**2-Phenoxyacetophenone** was synthesized from 2-bromoacetophenone and phenol in the presence of potassium carbonate according to the literature procedure<sup>2</sup> in 84% yield: mp 71–72 °C (lit.<sup>25</sup> mp 71–72 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  5.26 (s, 2H), 6.90–7.01 (m, 3H), 7.25–7.31 (m, 2H), 7.47–7.51 (m, 2H), 7.58–7.61 (m, 1H), 7.98–8.01 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ 71.0, 115.1, 121.9, 128.4, 129.1, 129.8, 134.1, 158.3, 192.5; FTIR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3062, 1703, 1598, 1499, 1450, 1217, 1090 cm<sup>-1</sup>; GC– MS *mlz* 212, 105, 77.

**1-Phenyl-2-phenoxyethanol.** A solution of 2-phenoxyacetophenone (5 mmol) in methanol (50 mL) was treated with small portions of sodium borohydride (2.5 mmol) and stirred for 1 h. Saturated ammonium chloride solution (100 mL) followed by methylene chloride (200 mL) was added to the reaction mixture. The organic layer was separated, washed with water (2 × 100 mL), dried, concentrated, and recrystallized from 95% ethanol: mp 60.5–61.5 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 2.82 (s, 1H), 3.96–4.12 (m, 2H), 5.09–5.12 (d, 1H, *J* = 8.7 Hz), 6.80–7.00 (m, 3H), 7.10–7.47 (m, 7H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ 72.8, 73.5, 114.9, 121.6, 126.5, 128.4, 128.8, 129.8, 139.9, 159.4; FTIR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  3577, 2922, 2873, 1598, 1492, 1231, 1041 cm<sup>-1</sup>; GC–MS *m*/*z* 214, 108, 107, 94, 79, 77; HRMS calcd for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> 214.09938, found 214.09949.

**1,2-Diphenyl-2-hydroxy-3-phenoxypropanone** was prepared using procedures similar to those reported in the literature.<sup>35</sup> Butyllithium in hexanes (1.6 M, 6 mL) was added dropwise under nitrogen to a solution of 1-phenyl-2,6-dithiane (7.5 mmol) at -78 °C in dry tetrahydrofuran (25 mL) freshly distilled from sodium benzophenone ketyl. The solution was stirred for 2.5 h at -50 to -70 °C, and a solution of 2-phenoxyacetophenone (7.5 mmol) in tetrahydrofuran (20 mL) was added. Water (150 mL) was added and extracted to methylene chloride (3 × 100 mL) after keeping the reaction mixture in a freezer for 24–30 h under argon. The methylene chloride extract (2 × 100 mL), dried over anhyd magnesium sulfate, and concentrated to obtain the crude dithiane product (1.7 g).

A solution of the dithiane product (0.77 g) in acetonitrile (3 mL) was added quickly to a well-stirred suspension of Nchlorosuccinimide (1.02 g) and silver nitrate (1.46 g) in 80% acetonitrile 20% water (25 mL). The reaction mixture was treated with aqueous solutions of saturated sodium sulfite, sodium carbonate, and sodium chloride (1 mL each) after stirring for 5-10 min at 55 °C. A mixture of pentane and dichloromethane (1:1; 20 mL) was added to the reaction mixture and filtered through a pad of a filter aid, Celite. The organic phase of the filtrate was dried over anhyd magnesium sulfate. The crude product (0.5 g) was recrystallized three times from 95% ethanol: mp 120–121 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 4.10 (d, 1H, J = 10.5 Hz),  $\hat{4}.30$  (s, 1H), 4.95 (d, 1H, J = 10.5Hz), 6.85–8.05 (m, 15H);  $^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  75.42, 82.53, 115.1, 121.7, 125.3, 127.1, 128.1, 128.3, 128.6, 128.9, 132.8, 135.0, 138.4, 158.3, 199.4; FTIR (CH<sub>2</sub>Cl<sub>2</sub>) v 3556, 3063, 1675, 1597, 1499, 1450, 1238 cm<sup>-1</sup>; GC-MS *m*/*z* 213, 195, 120, 119, 105, 91, 77.

Kinetic Experiments. Relative Rate Constants of β-Scission to Abstraction of Hydrogen from Thiophenol by 1-Phenyl-2-phenoxyethanol-1-yl Radical. A series of solutions of 1,2-diphenyl-2-hydroxy-3-phenoxypropone (0.016– 0.02 M) and thiophenol (0.008–0.2 M) were prepared in benzene or in 0.8 M 2-propanol solution in benzene in the presence of an internal standard (tetradecane or diphenyl ether; 0.003–0.007 M). Thiophenol was freshly distilled before use. Aliquots of these solutions (50–100 µL) were added to argon-purged Pyrex tubes, degassed by three freeze–thaw cycles, and sealed. These solutions were photolyzed using a

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<sup>(34)</sup> Suleman, N. K.; Nelson, D. A. J. Org. Chem. 1989, 54, 503.

<sup>(35) (</sup>a) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231. (b) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1971**, *36*, 3553.

1000 W xenon lamp for 3-10 s at 70-150 °C in a constanttemperature bath, resulting in 0.5-10% reaction of thiophenol. A derivatization agent, N-methylbistrifluoroacetamide (10-15  $\mu$ L), was added to the contents of the reaction mixture to convert 1-phenyl-2-phenoxyethanol to its trfluoroacetate derivative and analyzed by GC after keeping the contents of the derivatized reaction mixture for 5-10 h at room temperature. Degassed and sealed, but unphotolyzed, samples were analyzed in a same manner as control reactions. The relative rate constant,  $k_{abs}/k_{\beta}$ , at each temperature was determined by using the rate equation, eq 18 (Figure 3). The thiophenol concentrations were corrected for the density variations of benzene with the temperature<sup>24</sup> and the GC area ratios of acetophenone and 1-phenyl-2-phenoxyethanol were converted-to-concentration ratios by using their molar response factors with respect to a common standard.

**Photolysis of 2-Phenoxyacetophenone.** One hundred microliter samples of 2-phenoxyacetophenone solutions in benzene (0.004 M) in the presence of an internal GC standard (tetradecane; 0.004 M) were degassed by three freeze–thaw cycles and sealed in Pyrex tubes. The sealed tubes were irradiated for 10-30 s at 100.0 °C using a 1000 W xenon lamp. The contents of the sealed tubes were analyzed by gas chromatography.

Abstraction of Hydrogen from Thiophenol by 1-Phen**yl-1-hydroxyethyl Radical.** A solution (100 µL) of acetophenone (0.05 M), thiophenol (0.0015-0.008 M), and 2-propanol (0.8 M) in benzene was added to argon-purged Pyrex tubes and degassed by three freeze-thaw cycles. The sealed tubes were irradiated with a 1000 W xenon lamp for 1-30 s at 25-102 °C. The reaction mixtures were analyzed by GC after derivatization with bis(trimethylsilyl)trifluoroacetamide to convert sec-phenethyl alcohol to its trimethylsillyl derivative. The concentrations of thiophenol, sec-phenethyl alcohol, and 1,2-diphenyl-1,2-dihydroxybutane were measured and corrected for reaction temperature. The consumption of thiophenol was less than 15% in all of the reactions. The abstraction rate constant,  $k_{abs}$ , was calculated according to the eq 10. The concentration of sec-phenethyl alcohol was corrected for disproportionation of 1-phenyl-1-hydroxyethyl radical using an estimated value of 0.04 for  $k_{dis}/k_{com}$  for the temperature range.

The termination rate constant,  $2k_t$ , for the 1-phenyl-1hydroxyethyl radical was calculated by measuring the diffusion coefficients of *sec*-phenethyl alcohol (radical model) in 0.8 M 2-propanol solution in benzene using the Smoluchowski equation.

**Diffusion Coefficients.** The diffusion coefficients of *sec*phenethyl alcohol in 0.8 M 2-propanol solution in benzene were measured at 20–70 °C by Taylor's<sup>23,24</sup> dispersion method using a stainless steel coil (length-22.8 m; internal diameter 0.0508  $\pm$  0.025 cm; coil diameter 21 cm) held at constant temperature in a Neslab RTE-211 temperature bath. A detailed description of the apparatus was described elsewhere.<sup>12</sup> The helium purged solvent was pumped through the coil at a flow rate of 0.2–0.3 mL/min using Waters associate HPLC pump with Waters 410 differential refractometer or Waters 2410 refractive index detector. The variance ( $\sigma^2$ ) of *sec*-phenethyl alcohol peak was determined by the least-squares analysis of a Gaussian curve of the refractive index data. The experimental diffusion coefficient, *D*, is related to the internal radius of the coiled tube *r*, the retention time *t*, and the variance  $\sigma^2$ , eq 24.

$$D = r^2 t/24\sigma^2 \tag{24}$$

**Combination to Disproportionation Ratio of 1-Phenylethanol-1-yl Radical.** Solutions of acetophenone (0.10 M) and 2-propanol (0.8 M) in benzene (50 mL) were degassed and sealed in Pyrex tubes. These solutions were photolyzed using a 1000 W xenon lamp at 30-110 °C for 10-60 s. The reaction mixtures were analyzed by gas chromatography. *sec*-Phenethyl alcohol was converted to its trimethylsilyl derivative before analysis. The combination to disproportionation rate constant,  $k_{\rm com}/k_{\rm dis}$ , was calculated from the rqatio of products [dimer]/ [PhCH(OH)CH<sub>3</sub>].

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**Supporting Information Available:** Supporting data for diffusion coefficients of *sec*-phenethyl alcohol and self-termination rate constants of 1-phenylethanol-1-yl radical. Data for estimation of rate constants for the abstraction of hydrogen by 1-phenylethanol-1-yl radical from thiophenol in 0.8 M 2-propanol solution in benzene. Supporting data for the relative rate constants for abstraction of hydrogen from thiophenol to  $\beta$ -scission for 1-phenyl-2-phenoxyethanol-1-yl. Plots of Arrhenius plots for self-diffusion and relative rate data. This material is available free of charge via the Internet at http://pubs.acs.org.

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