Table II. <sup>13</sup>C NMR Spectral Data of 24

			ALC: 1 12 12 12 12 12 12 12 12 12 12 12 12 1
 mult (carbon no.)	ZZ (major)	ZE + EZ	EE (minor)
 $\begin{array}{c} \text{CH} (4, 10) \\ \text{CH}_2 (2, 12) \\ \text{CH} (1, 13) \\ \text{CH} (5, 9) \\ \text{CH} (14, 15) \\ \text{CH}_2 (16) \\ \text{CH}_2 (6, 8) \\ \text{CH} (7) \end{array}$	59.5 49.8 43.0 40.7 38.8 35.8 27.2 21.7	$\begin{array}{c} 60.2,54.5\\ 50.2,54.5\\ 42.4,43.2\\ 41.5,40.5\\ 38.7,37.7\\ 33.1\\ 26.8,26.6\\ 20.2 \end{array}$	54.4 55.2 43.3 41.2 38.4 31.1 (est) 26.5 19.9 (est)
			=:(-=-)

 $C_hH$ ), 43.3, 43.0, 39.5 (3 × CH), 30.7 ( $C_fH_2$ ), 28.6 ( $C_aH_2$ ), 26.7 ( $C_rH_2$ ); UV (EtOH)  $\lambda_{max}$  275 ( $\epsilon$  290), and end absorption; IR (KBr disc) 3350 cm<sup>-1</sup> (br).

3,11-Bis(dimethylamino)-3,11-diazahexacyclo-[11.2.1.0<sup>2,12</sup>.0<sup>4,15</sup>.0<sup>5,9</sup>.0<sup>10,14</sup>]hexadecane (27). A mixture of 0.88 g (3.57 mmol) of 25, 30 mL of acetonitrile, 5.0 mL (61.6 mmol CH<sub>2</sub>O) of 35% formalin, and 1.80 g (28.6 mmol) of NaBH<sub>3</sub>CN was stirred at room temperature while 30 drops of acetic acid was added over 2 h. After the mixture was stirred for 3 h more, 10 mL of concentrated hydrochloric acid was added, and the solvent was removed. The residue was dissolved in 15% sodium hydroxide and extracted five times with 25-mL portions of ether. Drying with sodium sulfate and concentration gave 1.4 g (130%) of crude 27, which was recrystallized from hexane and sublimed: mp 98-103 °C; empirical formula,<sup>10</sup> C<sub>18</sub>H<sub>30</sub>N<sub>4</sub> (m/e 302, 6.7% of base peak at 43); <sup>1</sup>H NMR  $\delta$  3.21 (br s, 2 H), 3.13 (br s, 2 H), 2.35-2.20 (m, 2 H), 2.30 (s, 12 H), 2.06 (m, 2 H), 2.0-1.8 (m, 4 H), 1.8-1.7 (m, 2 H), 1.53 (d, J = 11 Hz, 1 H), 1.41 (d, J = 11 Hz, 1 H), 1.4-1.2 (m, 2 H); <sup>13</sup>C NMR  $\delta$  63.8, 57.2 (C<sub>d</sub>H and C<sub>h</sub>H), 45.8, 42.7, 40.6 (3 × CH), 41.4 (CH<sub>3</sub>), 31.0 (C<sub>r</sub>H<sub>2</sub>), 29.2 (C<sub>a</sub>H<sub>2</sub>), 27.0 (C<sub>c</sub>H<sub>2</sub>).

(3 × CH), 41.4 (CH<sub>3</sub>), 31.0 (C<sub>1</sub>H<sub>2</sub>), 29.2 (C<sub>a</sub>H<sub>2</sub>), 27.0 (C<sub>a</sub>H<sub>2</sub>). 3,11-Dinitroso-3,11-diazapentacyclo[11.2.1.0<sup>4,15</sup>.0<sup>5,5</sup>.0<sup>10,14</sup>]hexadecane (24). Treatment of 3.87 g (17.7 mmol) of diamine 13 with sodium nitrite under the same conditions as in the preparation of 23 gave 3.5 g of crude product, which was recrystallized from ethyl acetate to give 24 as brownish crystals, mp 126–126.5 °C. The mass spectrum showed no parent ion, but the 246 peak (p – 30) peak matched for C<sub>14</sub>H<sub>20</sub>N<sub>3</sub>O,<sup>10</sup> as expected if one nitroso group had been lost. <sup>1</sup>H NMR, exceedingly complex; <sup>13</sup>C NMR is shown in Table II, with assignments to conformations.

**3,11-Diamino-3,11-diazapentacyclo**[11.2.1.0<sup>4,15</sup>.0<sup>5,9</sup>.0<sup>10,14</sup>]**hexadecane** (26). Reduction of 3.78 g of nitroso compound 24 with 3.0 g of lithium aluminum hydride under the same conditions and workup as for 25 gave 3.0 g of an oil, which gave 2.53 g of a light yellow oil upon Kugelrohr distillation: empirical formula,<sup>10</sup> C<sub>14</sub>H<sub>24</sub>N<sub>4</sub>; <sup>1</sup>H NMR  $\delta$  3.06 (d, J = 9 Hz, 2 H), 3.05 (br s, 4 H), 2.7–2.6 (m, 2 H), 2.5–2.3 (m, 2 H), 2.20 (dd, J = 9.0, 6.1 Hz, 2 H), 2.2–2.0 (m, 2 H), 2.0–1.75 (m, 6 H), 1.66–1.50 (m, 2 H), 1.48 (dt, J = 12.5, 10.3 Hz, 2 H); <sup>13</sup>C NMR  $\delta$  68.7 (C<sub>d</sub>H), 65.7 (C<sub>h</sub>H<sub>2</sub>), 44.8, 42.2, 39.5 (3 × CH), 39.0 (C<sub>a</sub>H<sub>2</sub>), 27.7 (C<sub>f</sub>H<sub>2</sub>), 22.4 (C<sub>g</sub>H<sub>2</sub>).

3,11-Bis (dimethylamino)-3,11-diazapentacyclo-[11.2.1.0<sup>4,15</sup>.0<sup>5,9</sup>.0<sup>10,14</sup>]hexadecane (29) was made by reductive methylation of 26, using the same conditions as in the preparation of 27, in 87% crude yield. Sublimation and recrystallization from hexane gave 27: empirical formula,<sup>10</sup> C<sub>18</sub>H<sub>32</sub>N<sub>4</sub> (m/e 304, 1.2% of base peak at 260); mp 96-101 °C; <sup>1</sup>H NMR  $\delta$  2.93 (br t, 2 H), 2.66 (d, J = 7.7 Hz, 2 H), 2.5-2.4 (m, 2 H), 2.37-2.30 (m, 2 H), 2.30 (s, 12 H), 2.2-2.0 (m, 2 H), 2.0-1.9 (m, 2 H), 1.85-1.65 (m, 5 H), 1.55-1.35 (m, 3 H); <sup>13</sup>C NMR  $\delta$  57.6 (C<sub>d</sub>H), 43.7 (C<sub>h</sub>H<sub>2</sub>), 43.2, 42.6, 40.5 (3 × CH), 39.0 (CH<sub>3</sub>), 38.0 (C<sub>a</sub>H<sub>2</sub>), 28.0 (C<sub>t</sub>H<sub>2</sub>), 22.7 (C<sub>c</sub>H<sub>2</sub>).

( $C_gH_2$ ). **3**, 11 - **B** is (diethylamino) - 3, 11 - diazahexacyclo-[11.2.1.0<sup>2,12</sup>.0<sup>4,15</sup>.0<sup>5,9</sup>.0<sup>10,14</sup>]hexadecane (28) was prepared by reductive ethylation of 25 with acetaldehyde, using the same method as for the methyl derivative 27, giving a crude yield of 100%. Purer 20 was obtained by Kugelrohr distllation, as an oil; empirical formula, <sup>10</sup>  $C_{22}H_{38}N_4$  (present at m/e 358, 25.3% of base peak at 286); <sup>1</sup>H NMR  $\delta$  3.25–3.14 (m, 4 H); ethyl group ABX<sub>3</sub> pattern,  $\delta_A$  2.50,  $\delta_B$  2.78,  $\delta_X$  1.03,  $J_{AB}$  = 12.5 Hz,  $J_{AX}$  = 6.9 Hz,  $J_{BX}$  = 7.2; 2.34 (br s, 2 H), 2.25–2.0 (m, 4 H), 1.97–1.87 (br m, 2 H), 1.86–1.75 (m, 2 H), 1.7–1.58 (br m, 2 H), 1.50 (dt, J = 10.5, 1.6 Hz, 1 H), 1.35 (dt, J = 10.5, 1.6 Hz, 1 H); <sup>13</sup>C NMR  $\delta$  63.9, 61.3 ( $C_d$ H and  $C_h$ H), 46.0, 43.0, 40.8 (3 × CH), 44.7 (CH<sub>2</sub>CH<sub>3</sub>), 30.1 ( $C_f$ H<sub>2</sub>), 29.3 ( $C_a$ H<sub>2</sub>), 26.7 ( $C_g$ H<sub>2</sub>), 13.5 (CH<sub>2</sub>CH<sub>3</sub>).

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**Registry No.** 5, 14882-64-5; 7, 63904-59-6; 8, 63904-60-9; 9, 87858-39-7; 10, 87783-20-8; 11, 87783-21-9; 12, 87783-22-0; 13, 87783-23-1; 14, 87783-24-2; 15, 87858-40-0; 15 didehydro, 87858-41-1; 16, 63904-58-5; 17, 87783-25-3; 18, 87783-26-4; 19, 87801-37-4; 20, 87783-28-6; 21, 87783-29-7; 22, 87783-30-0; 23, 87783-31-1; 24, 87783-32-2; 25, 87783-33-3; 26, 87783-34-4; 27, 87783-35-5; 28, 87783-36-6; 29, 87783-37-7; 2,5-dimethoxy-2,5-dihydrofuran, 332-77-4; cyclopentadiene, 542-92-7.

# Coal Liquefaction Model Studies: Radical-Initiated and Phenol-Inhibited Decomposition of 1,3-Diphenylpropane, Dibenzyl Ether, and Phenethyl Phenyl Ether

Kevin E. Gilbert

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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The thermal decompositions of 1,3-diphenylpropane (1), dibenzyl ether (2), and phenethyl phenyl ether (3) have been studied in the temperature range of 138-250 °C in the presence of various free-radical initiators. Thermodynamic calculations of the conversion of 1 to toluene and styrene indicate the reaction is unfavorable below 300 °C, and 1 was found to be unreactive with di-tert-butyl peroxide (TPO) at 138 °C, di-tert-butyl diazene (TBD) at 200 °C, and 1,1,2,2-tetraphenylethane (TPE) at 250 °C. Reactions of 2 to toluene and benzaldehyde and of 3 to phenol and styrene were calculated to be energetically favorable at these temperatures. 2 reacted in the presence of TPO, TBD, and TPE to give toluene, benzaldehyde, and 1,2-diphenylethane in a free-radical chain process. 3 reacted in the presence of TBD and TPE to give phenol and styrene but did not react with TPO. Reaction of 2 can be inhibited with 2,6-di-tert-butyl-4-methylphenol. With TPO as the initiator the reaction was -0.61 order in phenol, while with TBD as the initiator the reaction was -1.1 order in phenol. The change in reaction order is due to changes in the rates of the various hydrogen-tranfer reactions. The hindered phenol did not inhibit reaction processes are discussed.

The thermal decompositions of 1,3-diphenylpropane (1), dibenzyl ether (2) and phenethyl phenyl ether (3) as neat

liquids or as solutions in hydrogen-donating solvents have been found to proceed by free-radical chain reactions in

	· · · · · · · · · · · · · · · · · · ·	- · · · · · · · · · · · · · · · · · · ·	$\Delta G$ , kcal/mol			
reaction	$\Delta H$	$\Delta S$	100 °C	200 °C	300 °C	400 °C
$1 \longrightarrow PhCH_3 + Ph \checkmark$	17.66	32.5	5.5	2.3	-0.96	-4.2
$2 \longrightarrow \mathbf{PhCH}_{3} + \mathbf{PhCHO}$	1.23	53.0	-18	-24	-29	-34
$3 \longrightarrow PhOH + Ph$	10.30	33.9	-2.3	-5.7	-9.1	-12.5

Scheme I

Ph 
$$X$$
 Ph  $\rightarrow$  Ph  $X$  + Ph  $Y$  H  
1, X = Y = CH<sub>2</sub>  
2, X = O; Y = CH  
3, X = CH<sub>2</sub>; Y = O

the temperature range of 310-390 °C.<sup>1</sup> The evidence, in the form of products (Scheme I), reaction orders, rates, activation parameters, and initiation by benzyl phenyl ether, was consistent with this interpretation; however, inhibition of these radical chain reactions has not been demonstrated. Inhibition of radical chain processes in the temperature range of 300-400 °C is not well understood, and it is not known if standard chain inhibitors such as hindered phenols will function as inhibitors in this temperature range.<sup>2</sup> Herein we report on the effect of hindered phenols on the thermal decomposition of 1-3 in the temperature range of 140-350 °C, on methods for initiating the chain decomposition of 1-3 in this temperature range. and on the kinetic and thermodynamic barriers to the radical reactions of 1-3.

Inhibition of radical chain autoxidations and polymerizations have been studied in the temperature range of 0-130 °C.<sup>2</sup> Hindered phenols such as 2,6-di-tert-butyl-4methylphenol function as inhibitors in these reactions by reacting with either the initiator radical or the chaincarrying radical to give phenoxy radicals which are inactive or less reactive in chain-transfer reactions and terminate to give stable products. The effect of temperature on phenolic inhibitors is not well documented, and the upper temperature limit on the use of phenolic inhibitors is unclear. Also the ability of phenols to scavenge carbon radicals is open to question. The rate constant for hydrogen abstraction from phenol by alkoxy radicals is approximately 10<sup>6</sup> times faster than the corresponding rate for polystyryl radicals.<sup>3</sup> Ivanov et al. have found that hindered phenols do not react with methyl radical at 78 °C in the absence of oxygen.<sup>4</sup> As reported here, a large number of phenols have no effect on the decomposition of 1 at 350 °C while Stock has found that phenols catalyze the decomposition of 2 at these temperatures.<sup>5</sup> This lack of an inhibitory effect may be due to the instability of the termination products derived from phenoxy radicals or an increased reactivity of phenoxy radicals in hydrogen abstraction reactions at higher temperatures. Therefore, the effect of hindered phenols on the decomposition of 1-3 has been studied over a wide range of temperatures to determine if phenols could inhibit these radical chain reactions and if so over what range of conditions. These studies were also undertaken because coals are known to contain significant amounts of phenols, and the effect of these phenols



on liquefaction is of interest.

## **Results and Discussion**

The self-initiated thermal decomposition of 1 was unaffected by any of a large number of compounds in the liquid phase at 350 °C (Chart I). The products formed and the reaction rates were identical with those obtained in the absence of these compounds. Stock has found that hindered phenols have no effect on the decomposition of 1 at 400 °C, while they catalyze the decomposition of 2 to give benzaldehyde and toluene.<sup>5</sup> A radical chain mechanism for the catalyzed decomposition has not yet been demonstrated. Since no effects with hindered phenols were observed at elevated tempertures, a study of the effects of hindered phenols on the decomposition of 1-3 at lower temperatures was undertaken.

Prior to a study of the effects of phenols on 1-3 the thermodynamics of the reactions of 1-3 to give the products derived from radical chain reactions needed to be determined and methods for initiating the radical chain reactions developed. The thermodynamics of the overall conversion of 1 to toluene and styrene, 2 to toluene and benzaldehyde, and 3 to phenol and styrene have been examined by using the thermochemical kinetics methods of Benson.<sup>6</sup> The reaction free energies have been calculated over the temperature range of interest and are given in Table I. These calculations suggest that reaction of 1 will be unfavorable at temperature below 300 °C, as might be expected since the entropic contribution from generating two molecules is not sufficient to overcome the enthalpic difference between a C-C single bond and a C-C double bond. Replacement of a  $CH_2$  group by an oxygen and the resultant formation of an aldehyde greatly changes the thermodynamics, with the decomposition of 2 being favored at all temperatures of interest. This reflects the much greater bond strength of the carbonyl group relative to the C–O single bond. The oxygen atom in 3 has a much less profound effect than the oxygen atom in 2, reflecting

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<sup>(6)</sup> Benson, S. M. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976.

Table II. Reaction of 1-3 with Various Initiators

		reaction <sup>a</sup>			
initiator	temp, °C	1	2	3	
AIBN	80	NR	NR	NR	
TPO	138	NR	+	NR	
TBD	180-200	NR	+	+	
(Ph) <sub>2</sub> CHCH(Ph) <sub>2</sub>	250	NR	+	+	
	350	+	+	+	

 $^{a}$  NR = no reaction, and a plus indicates reaction.

Table III

substrate	concn, M	initiator	concn, M	$\log R_{i}$	temp, °C
DBE (2)	2.2	AIBN	0.51		
. ,	1.77	TPO	1.12	-4.19	138
	2.0	TBD	0.51	-4.19	180
	2.0	TPE	0.16	-4.56	250
	2.9	BPE	0.09	-3.24	350
PPE (3)	1.77	TPO	1.12		
. ,	2.0	TBD	0.51	-5.08	200
	2.52	TPE	0.15	-4.52	265
	2 93	BPE	013	-3.90	350

the fact that no carbonyl is formed from 3. However, the decomposition of 3 is favored over the temperature range of interest.

The thermal decompositions of 1-3 have been studied in the presence of several free-radical initiators [AIBN/80 °C, di-tert-butyl peroxide (TPO)/138 °C, di-tert-butyldiazene (TBD)/180-200 °C, and 1,1,2,2-tetraphenylethane/250 °C], and the results are summarized in Table II. In all cases where reaction occurred the products were those expected from the radical chain reaction. 1,3-Diphenylpropane (1) does not react with any of the freeradical initiators below 300 °C; in all cases no loss of 1 was observed, and no toluene, styrene, or 1,3,4,6-tetraphenylhexane was found. 2 reacts with all initiators except AIBN,<sup>7</sup> while 3 does not react at temperatures below 180 °C and reacts only slowly at that temperature. The difference in reactivity between 1, 2, and 3 indicates that the lack of reactivity of 1 is not an experimental artifact but is due to thermodynamic or kinetic factors. The radical chain decomposition of 1 is begun by hydrogen abstraction from 1 by an initiator radical, in this case *tert*-butoxy radical, which is known to react rapidly with similar hydrocarbons.<sup>8</sup> The activation energy for  $\beta$  scission has been estimated as 28 kcal/mol,<sup>9</sup> and the rate constant for  $\beta$ scission varies from 1 to 1000 s<sup>-1</sup> over the 140-250 °C temperature range of these experiments. Thus a kinetic barrier to reaction appears unlikely, and a thermodynamic barrier to reaction is proposed to account for the results. As will be discussed in more detail below, both 2 and 3 react by radical chain reactions in the presence of lowtemperature initiators, with the rate-controlling reaction being hydrogen transfer between 2 and 3 and the chaincarrying radical.

**Reaction of Dibenzyl Ether with Di**-tert-butyl **Peroxide.** Dibenzyl ether (2) reacts with di-tert-butyl peroxide (TPO) at 138 °C to give toluene, benzaldehyde, and 1,2-diphenylethane (4) in a 1.1:2:0.65 ratio. The reaction is 0.68 order in 2 over the concentration range of 1.1-3.1 M and 0.62 order in TPO over the concentration

Table IV. Reaction of 2 with 110 and 12.	Table IV.	Reaction	of 2	with	TPO	and	TBD
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[DBE], M	[I], M	[ArOH], M	log R <sub>i</sub>	rxn order
3.07 2.38 1.77 1.46 1.15 1.77	1.12 1.55 1.12 0.61	TPO	-4.07 -4.15 -4.19 -4.29 -4.37 -4.11 -4.19 -4.36	0.68 0.62
1.77 2.38 1.77 1.15	1.12 1.12	0.87 0.58 0.37 0.29 0.14 0.29	-4.85 -4.68 -4.52 -4.49 -4.36 -4.41 -4.49 -4.62	-0.61 0.67
3.1 2.0 1.3 2.0 2.0	0.51 0.82 0.51 0.36 0.51	TBD 1.15 0.89 0.57 0.29	$\begin{array}{r} -3.97 \\ -4.19 \\ -4.32 \\ -3.95 \\ -4.19 \\ -4.27 \\ -4.82 \\ -4.69 \\ -4.47 \\ -4.16 \end{array}$	0.93 0.5 -1.10

<sup>a</sup> TPO. <sup>b</sup> TPD.

range of 0.61-1.55 M (Tables III and IV). The chain length, given by the ratio of benzaldehyde to 4, is three. A mechanism consistent with these results is given in Scheme II. Reaction is initiated by thermal cleavage of

## Scheme II

$$I-I \xrightarrow{k_{i}} 2I^{*}$$

$$I^{*} + DBE \xrightarrow{k_{H}} I-H + DBE^{*}$$

$$DBE^{*} \xrightarrow{k_{B}} Ph-CH_{2}^{*} + Ph-CHO$$

$$PH-CH_{2}^{*} + DBE \xrightarrow{k_{H}} Ph-CH_{3} + DBE^{*}$$

$$2Ph-CH_{2}^{*} \xrightarrow{k_{T}} PhCH_{2}CH_{2}Ph$$

$$\frac{-\partial[DBE]}{\partial t} = ek_{i}[I] + \left(\frac{ek_{i}[I]}{k_{t}}\right)^{1/2} k_{H}[DBE]$$

TPO to give two *tert*-butoxy radicals which may abstract hydrogen from 2 or self-react to give molecular products which do not start a chain process.<sup>10</sup> The dibenzyl ether radical rapidly undergoes  $\beta$  scission to give benzaldehyde and benzyl radical.<sup>11</sup> Benzyl radical may abstract hydrogen from more 2 or may recombine to give 4. Given the amount of toluene and 4 formed, termination and hydrogen transfer from 2 to benzyl radical are of similar magnitude. Analysis of this reaction scheme using the steady-state approximation gives a two-term expression for the loss of 2. At higher temperatures where the chains are very long, the first term in the rate expression can be ignored. However, in this case the chain lengths are short, and both terms contribute. By use of literature values for

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<sup>(9)</sup> Poutsma, M. L.; Dyer, C. W. J. Org. Chem. 1982, 47, 4903.

<sup>(10)</sup> Bell, E. R.; Rust, F. F.; Vaughan, W. E. J. Am. Chem. Soc. 1950, 72, 337.

<sup>(11)</sup> Livingston, R.; Zeldes, H. Fuel 1982, 61, 1254.

the rate of initiation  $(\log k_i = 15.6 - 37.4/\theta T)^{12}$  and termination  $(\log k_T = 9.5)^{13}$  and on the assumption that the efficiency of initiation is 0.3,<sup>14</sup> the reaction rate can be calculated as a function of the concentration of 2 and TPO with good agreement with the experimentally determined values. This reaction scheme accounts for the reaction order in 2 and TPO and the formation of 4 and benzaldehyde. The ratio of toluene to 4 makes it clear that hydrogen transfer is slow at these temperatures and is rate controlling in the radical chain process.

Addition of 2,6-di-*tert*-butyl-4-methylphenol to the reaction mixture of 2 and TPO decreases the rate of loss of 2 and surpresses the formation of 4, while still giving toluene benzaldehye as products. The reaction is 0.67 order in 2 and -0.53 order in phenol over the concentration range of 0.1-0.9 M. A mechanism consistent with this data is given in Scheme III. This is a general reaction, scheme

#### Scheme III

$$I-I \xrightarrow{k_i} 2I^*$$
 (1)

$$I^* + DBE \xrightarrow{\kappa_2} I - H + DBE^*$$
 (2)

$$I* ArOH \longrightarrow I-H + ArO*$$
(3)

$$DBE* \longrightarrow Ph-CH_2* + Ph-CHO$$
 (4)

$$Ph-CH_2^* + DBE \xrightarrow{\sim} Ph-CH_3 + DBE^*$$
 (5)

$$Ph-CH_2^* + ArOH \xrightarrow{\sim} Ph-CH_3 + ArO^*$$
(6)

$$ArO* + DBE \xrightarrow{\kappa_7} ArOH + DBE*$$
(7)

$$2ArO* \longrightarrow$$
 products (8)

$$\frac{-\partial [\text{DBE}]}{\partial_t} = \frac{R_i k_2 [\text{DBE}]}{k_2 [\text{DBE}] + k_3 [\text{ArOH}]} + \frac{k_5 [\text{DBE}]}{k_6 [\text{ArOH}]} \left[ \frac{R_i k_2 [\text{DBE}]}{k_2 [\text{DBE}] + k_3 [\text{ArOH}]} \right]$$
(9)

and at these temperatures several of the reactions do not contribute. Thus the very short chain lengths obtained in the absence of phenol suggests that  $k_5$  will be small relative to  $k_6$  while the greater stability of phenoxy radicals relative to benzyl radicals suggests that the  $k_7$  will also be very small.<sup>15</sup> Under these experimental conditions all of the reaction can be accounted for by using only the first term of the rate expression. From autoxidation studies it is known that  $k_3 > k_2^{16}$  while [2] > [ArOH]; thus the terms in the denominator are of similar magnitude. Numerical analysis with estimates for  $k_2$ ,  $k_3$ , and the efficiency of initiation yields a calculated reaction order in 2 of 0.7 and in phenol of -0.55 (Table V). In these experiments the phenol is an efficient inhibitor and functions by effectively competing for the initiator radicals and by scavenging any benzyl radicals formed, thus preventing chain propagation.

**Reaction of 2 with Di-***tert*-**butyldiazene.** DBE (2) reacts with di-*tert*-butyldiazene (TBD) at 180 °C to 200 °C to give toluene, benzaldehyde, and 4 in approximately a 6:8:1 ratio. The reaction is first order in 2 and 0.5 order

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in TBD. The chain length is eight at 180 °C (Tables III and IV). A mechanism similar to that given in Scheme II is consistent with the data. This appears to be a simple chain reaction with the chain length increasing with increasing temperature.

Addition of 2,6-di-*tert*-butyl-4-methylphenol to the reaction mixture of 2 and TBD gives results similar to those obtained with TPO. Toluene and benzaldehyde are still the major products, the formation of 4 is surpressed, and the reaction rate is decreased. However, the reaction is first order in 2 and inverse first order in phenol. Scheme III can be used to analyze these results. Since the chain length has increased,  $k_5$  has become more important. At 180 °C benzyl radical abstraction from 2 is competitive with hydrogen transfer from phenol and with termination. Reaction 7 in Scheme III is probably not important since inhibition still occurs. The rate of loss of 2 can now be expressed with a two-term rate equation (eq 10). The one

$$\frac{-\partial [\text{DBE}]}{\partial t} = \frac{R_{i}k_{2}[\text{DBE}]}{k_{2}[\text{DBE}] + k_{3}[\text{ArOH}]} \left[1 + \frac{k_{5}[\text{DBE}]}{k_{6}[\text{ArOH}]}\right]$$
(10)

term expression used in the TPO case is not applicable as it would predict a -0.5 order in phenol and not the -1.10order observed. Addition of the second term combined with estimates for  $k_5$  and  $k_6$  leads to the calculated reaction order of -1.0 in phenol (Table V). In these experiments phenol competes for the initiator radicals as well as the chain-carrying radicals and continues to function as an inhibitor. As the temperature increases from 140 to 180 °C, the competition for benzyl radical between 2 and phenol becomes more equal, but the phenol continues to function as an inhibitor because reaction 7 is not yet important.

**Reaction of DBE with 1,1,2,2-Tetraphenylethane.** DBE (2) reacts with 1,1,2,2-tetraphenylethane at 250 °C to give toluene and benzaldhyde. The reaction appears to be a simple chain process following the mechanism given in Scheme II.

Addition of 2,6-*tert*-butyl-4-methylphenol to the reaction of 2 and TPE has no effect on the rate or the products formed. Apparently reaction 7 has become significant as the temperature has increased from 180 to 250 °C. Further studies on this point are continuing with a search for an initiator that functions between 200 and 250 °C.

**Reaction of Phenethyl Phenyl Ether (3) with Various Initiators.** PPE (3) does not react with TPO at 138 °C and is recovered unchanged. It reacts only slowly with TBD at 180 °C to give phenol and styrene with the initial rates and concentrations as given in Table III. 2,6-Di-*tert*-butyl-4-methylphenol does inhibit the reaction of **3** with TBD at 180 °C; however, a complete study of the inhibited reaction was not undertaken because the uninhibited reaction was so slow.

PPE reacts with TPE at 250 °C to give phenol and styrene; hindered phenols have no effect on the reaction.

#### Conclusions

In summary it should be noted that DBE is an excellent model compound. It decomposes over a wide temperature range with no thermodynamic barrier to reaction, reacts with a wide variety of initiators to give stable products, and allows study of the kinetic barriers to reaction in these radical chain reactions. Finally the wide temperature range for decomposition permits investigation of the temperature dependence of inhibition by hindered phenols.

Conversely, the all-carbon system 1,3-diphenylpropane demonstrates a thermodynamic barrier to reaction with

<sup>(16)</sup> Howard, J. A.; Ingold, K. U. Can. J. Chem. 1964, 42, 2324.

			$ek:[1]^{-1/2}$	log	R <sub>i</sub>
[DBE], M	[I], M	10 <sup>5</sup> ek <sub>i</sub> [I]	$10^{\circ} \frac{10^{\circ}}{k_{\rm T}} k_{\rm H}[\rm DBE]$	calcd	obsd
3.07	1.12	2.21	6.30	-4.07	-4.07
1.77		2.21	3.63	-4.23	-4.19
1.15		2.21	2.36	-4.34	-4.37
1.77	1.55	3.06	4.27	-4.18	-4.11
	1.12	2.21	3.63	-4.23	-4.19
	0.61	1.20	2.68	-4.41	-4.36
$= 0.3, \log k_{\rm i} = -4.18,$	$\log k_{\rm T} = 9.0, \log$	$k_{\rm H} = 2.14$			
		TP	O Inhibited		
				lo	g R <sub>i</sub>
[DBE], M	[ArOH], M	$R_{i}k_{2}[DBE]$	$k_2$ [DBE] + $k_3$ [ArOH]	calcd	obsd
1.77	0.87	0.2114	14078	-4.82	-4.85
	0.37	0,2114	7637	-4.55	-4.52
	0.14	0.2114	4674	-4.34	-4.36
2.38	0.29	0.2843	7596	-4.43	-4.41
1.77		0.2114	6607	-4.49	-4.49
1.15		0.1374	5601	-4.61	-4.62
= 1, $\log k_i = -4.18$ , lo	$\log k_2 = 3.20, \log k_2$	$e_3 = 4.11$			
		TB	D Inhibited		
				log	R <sub>i</sub>
[DBE], M	[ArOH], M	1st term $ imes$ 10 <sup>5</sup>	2nd term $ imes$ 10 <sup>5</sup>	caled	obsd
2.0	1.15	1.541	0.174	-4.74	-4.82
	0.89	1.900	0.225	-4.63	-4.69
	0.57	2.665	0.351	-4.44	-4.47
	0.29	4.114	0.690	-4.16	-4.16
$k_{\rm T} = -4.03, \log k_{\rm T} = 9.$	5, $\log k_2 = 3.61$ , l	$\log k_3 = 4.55, \log k_3$	$k_5 = 2.60, \log k_6 = 3.60$		

Table V. Calculated Rates of Reaction of 2 and TPO and TBD **TPO** Uninhibited

Table VI. Physical Properties

property	TPO	TBD	TPE
$T_{\rm c}, ^{\circ}{\rm C}$ $P_{\rm c}, {\rm atm}$	231 22.5	231 22.5	
$P_t$ , atm density, <sup>a</sup> g/mL	3.24 (140) 0.91	13.8 (200) 0.87	$\begin{array}{c} 0 \\ 0.82 \end{array}$

<sup>a</sup> At temperature of initiator use.

no reaction observed below 300 °C. This suggests that all-carbon systems will not cleave to stryene and toluene by any process below 300 °C and that attempts to develop coal liquefaction processes based on lower temperature thermal chemistry will not be successful. This also suggests that free-radical initiators will have no effect on coal liquefaction.

Phenols can inhibit carbon-centered free-radical chain processes up to approximately 200 °C. This result should be compared to previous autoxidation studies where temperature limits of 135 °C were found, presumably due to the extremely rapid nature of autoxidations at higher temperatures. These results suggest that phenoxy radicals are unable to abstact benzylic hydrogens at temperatures below 200 °C, thus accounting for effectiveness of inhibition.

### **Experimental Section**

Compounds 1-3 were prepared as previously.<sup>1</sup> Di-tert-butyl peroxide was obtained commercially and was distilled prior to use. Di-tert-butyldiazene was prepared by the procedure of Stowell.<sup>17</sup> 1,1,2,2-Tetraphenylethane was prepared by the reaction of diphenylbromomethane with magnesium.<sup>18</sup> All of the phenols were obtained commercially and were used as received.

The vapor pressures of TPO and TBD were estimated from plots of log (vapor pressure) vs. 1/T (K). The critical tempertures and pressures were calculated by standard methods,<sup>19</sup> and Raoult's law was assumed. The volume expansion was also calculated by standard methods.<sup>19</sup> Table VI gives the calculated values used in this work.

Pyrolyses were carried out in thick-walled Pyrex ampules that were degassed and sealed under high vacuum. Temperatures of 138 °C were obtained with a boiling xylene bath while temperatures of 180 °C and higher were obtained with a eutectic salt bath or a fluidized sand bath. Analyses were by gas chromatography using either a fused silica capillary column with DB-5 as the stationary phase or an 8 ft  $\times 1/4$  in. Dexsil packed column. An FID detector and an electronic integrator were used throughout and molar calibration factors were obtained for all compounds.

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Registry No. 1, 1081-75-0; 2, 103-50-4; 3, 40515-89-7; TPO, 110-05-4; TBD, 927-83-3; TPE, 632-50-8; 2,6-di-tert-butyl-4methylphenol, 128-37-0.

<sup>(17)</sup> Stowell, J. C. J. Org. Chem. 1967, 32, 2360.

<sup>(18)</sup> Turk, A.; Chanan, H. "Organic Syntheses, Wiley: New York, 1955; Collect. Vol. 3, p 121.
(19) Chilton, C. H.; Perry, R., Eds. "Chemical Engineers Handbook",

<sup>5</sup>th ed. McGraw-Hill: New York, 1973; pp 3-226-3-250.