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supporting electrolyte and reactant at the same concentration as the test solution. During all measurements the temperature was kept constant within ±0.1 °C. Cyclic voltammetric experiments were performed with an oscillopolarograph (Amel 448) using the same cell as for the measurements at low polarization rates. Coulometric determinations and macroscale electrolysis at controlled potentials were carried out with a potentiostat (Amel 552) coupled with an integrator (Amel 721) and a recorder (Amel 867). In a typical run, 50–70 mg of reactant was dissolved in 20–30 mL of MeCN–0.1 M Et_4NClO_4. The solution was then electrolyzed at an appropriate potential (0.65–0.85 V), using a platinum-gauze cylinder (1.5-cm diameter) as a working electrode, with a Ag|0.1 M $AgClO_4$–MeCN as reference and a platinum spiral as a counterelectrode separated from the test solution by a fine-porosity fritted glass disks. The solution was magnetically stirred and covered with a continuous argon flow. After the current had fallen to its background value, the solution was evaporated under vacuum and the residue was taken up with benzene (10 mL). The insoluble supporting electrolyte was filtered off, and the filtrate was chromatographed. Only from indole **4**, electrolyzed in aqueous acetonitrile, was the 3-hydroxyindolenine **5c** isolated (10% yield).

Registry No. 1a, 948-65-2; **1b**, 3558-24-5; **2a**, 76794-16-6; **2b**, 82665-92-7; **3a**, 53904-10-2; **3b**, 58863-88-0; **3c**, 82665-93-8; **3d**, 82665-94-9; **4**, 10257-92-8; **5a**, 65837-35-6; **5b**, 78024-78-9; **5c**, 1213-48-5; **5d**, 82665-95-0; **10**, 74441-25-1; **11a**, 1922-77-6; **11b**, 82665-96-1; **11c**, 82665-97-2; 1-chlorobenzotriazole, 21050-95-3; 1-chloroisatin, 2959-03-7.

Coal Liquefaction Model Studies: Free Radical Chain Decomposition of Diphenylpropane, Dibenzyl Ether, and Phenyl Ether via β-Scission Reactions

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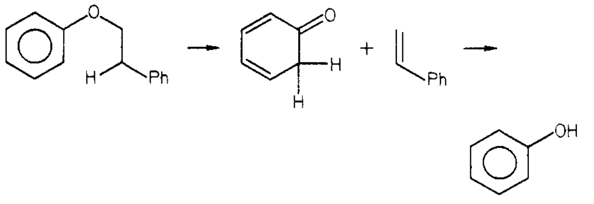
The thermal decompositions of 1,3-diphenylpropane (**1**), dibenzyl ether (**2**), and phenethyl phenyl ether (**3**) have been found to proceed by free radical chain processes. **1** gave toluene and styrene with a reaction order of 1.55, E_A = 51.4 kcal/mol, and log A = 12.5. The reaction could be initiated by benzyl phenyl ether but not by 1,2-diphenylethane. **2** gave toluene and benzaldehyde with a reaction order of 1.43, E_A = 48 kcal/mol, and log A = 12.6. The reaction could be initiated with benzyl phenyl ether. **3** gave phenol and styrene with a reaction order of 1.21, E_A = 50.3 kcal/mol, and log A = 12.3. The reaction could be initiated by benzyl phenyl ether. All of the data are consistent with free radical chain processes with the reaction order determined by the termination reaction. No evidence for concerted reactions has been found.

The thermal conversion of coal into a liquid material has been postulated to involve the formation of free radicals by the homolysis of covalent bonds in short, linear linkages which join the polycyclic clusters of coal into a polymeric network.[1] Prior studies have shown that one-atom links are stable unless substituents on the aromatic rings allow isomerization to more reactive, nonaromatic species.[2,3] Two-atom links are cleaved in a simple bond homolysis which, in most liquefaction studies, is followed by hydrogen abstraction from a hydrogen-donating solvent.[4] Three-atom links have received relatively less attention although the potential chemistry is more complex as simple homolysis reactions, radical chain processes, and concerted unimolecular reactions are all possible. Herein we report the thermal decomposition of 1,3-diphenylpropane (**1**), dibenzyl ether (**2**), and phenethyl phenyl ether (**3**), which serve as models for the thermal chemistry of three-atom linkages in coal and all of which react by free radical chain processes.

Diphenylpropane (**1**) has been reported to give equal amounts of styrene and toluene in a reaction that is 1.6 order in **1**.[5] A free radical chain process has been proposed to explain these observations. This reaction has been reinvestigated here along with studies of initiation by free radical initiators which provide further support for the free radical chain mechanism hypothesis.

Dibenzyl ether (**2**) has previously been reported to give equal amounts of benzaldehyde and toluene in a first-order process with an activation energy of 36 kcal/mol.[6] The formation of benzaldehyde and toluene suggests a free radical process, but the reaction order and activation energy are inconsistent with this explanation. Furthermore, the low activation energy is not consistent with a concerted unimolecular reaction. However, these studies were carried out in tetralin, which is very difficult to purify and raises the possibility of initiation of a free radical process by an impurity in the tetralin. Also these authors did not purify **2** prior to use which might have resulted in peroxide-initiated reactions. Thus, the thermal chemistry of **2** is unclear.

Phenethyl phenyl ether (**3**) has been found to give phenol and styrene (eq 1) in a first-order process with



(1)

activation parameters of log A = 11 and E_A = 45 kcal/mol.[7]

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[1] Neavel, R. C. *Fuel* **1976**, *55*, 237. Whitehurst, D. D. In "Organic Chemistry of Coal"; Larsen, J. W., Ed.; American Chemical Society: Washington, DC, 1978; ACS Symp. Ser. No. 71.

[2] Benjamin, B. M.; Raaen, V. F.; Maupin, P. H.; Brown, L. L.; Collins, C. J. *Fuel* **1978**, *57*, 269.

[3] McMillen, D. F.; Ogier, W. C.; Ross, D. S. *J. Org. Chem.* **1981**, *46*, 3322.

[4] Poutsma, M. L. *Fuel* **1980**, *59*, 335.

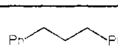
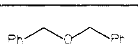
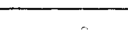
[5] Poutsma, M. L. "Symposium on Coal Liquefaction"; SRI: Menlo Park, CA, July 1980. Poutsmae, M. L., personal communication.

[6] Cronauer, D. C.; Jewell, D. M.; Shah, Y. T.; Modi, R. J. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 153. Schlosberg, R. H.; Ashe, T. R.; Pancirov, R. J.; Donaldson, M. *Fuel* **1981**, *60*, 155.

[7] Virk, P. S.; Klein, M. T.; *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1981**, *26* (3), 77, presented at New York American Chemical Society meeting, Aug 1981.

0022-3263/82/1947-4899$01.25/0

Table I. Pyrolysis of 1,3-Diphenylpropane, Dibenzyl Ether and 1-Phenoxy-2-phenylethane as Neat Liquids

								
temp, °C	log k_{obsd}	n	temp, °C	log k_{obsd}	n	temp, °C	log k_{obsd}	n
335	−5.79	1.57	310	−5.30	1.29	350	−5.24	1.22
340	−5.53	1.50	320	−4.87	1.46	370	−4.87	1.16
350	−5.41	1.57	330	−4.71	1.48	380	−4.42	1.27
365	−5.05	1.51	350	−4.15	1.53	390	−4.21	1.22
380	−4.53	1.60						

This reaction has been interpreted in terms of a retro-ene process, a concerted unimolecular reaction. The loss of the aromatic resonance energy of one ring in forming 2,4-cyclohexadienone might suggest a higher activation energy for the concerted reaction than is observed. A free radical chain process is not incompatible with the data.

Experimental Section

General Methods. Samples were pyrolyzed as neat liquids in thick-walled Pyrex ampules of 0.5-mL volume which were degassed and sealed under high vacuum. The ampules were suspended in a fluidized sand bath (Techne SLB-2) modified so that two of the heaters were controlled by a Bayley proportional temperature controller. Temperatures were measured with a Pt resistance thermometer, and temperature control was ±1 °C at 350 °C.

Samples were analyzed as 1% solutions in cyclohexane on a Varian 3700 GC equipped with an FID and a CDS-111 electronic integrator. A commercially available GC column (an 8-ft glass column of 3% Dexsil 300 on Supelcoport 100-120 available from Supelco) was temperature programmed from 60 to 230 °C. Independently determined molar calibration factors were obtained for all reactants and products. Product identification was made by comparison with authentic samples and by GC/MS. Diphenyl ether was used as an internal standard with PPE (3) and was stable to the pyrolysis conditions.

Vapor pressures were estimated from a plot of ln P vs. $1/T$ from the boiling point to the critical temperature.[8] Critical temperature and liquid densities were calculated by standard methods.[8]

1,3-Diphenylpropane (1) was prepared by Wolf-Kishner reduction of 1,3-diphenyl-2-propanone; bp 95–105 °C (0.3 mm) [lit.[9] 109–111 °C (0.5 mm)]. Samples were redistilled from sodium and stored under N_2 prior to use.

Dibenzyl ether (2) was obtained commercially (Aldrich), distilled twice from sodium, and stored under N_2 prior to use.

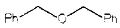
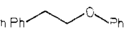
Phenethyl phenyl ether (3) was prepared from phenethyl bromide and phenol by the procedure of Gates and Allen;[10] bp 125–126 °C (1 mm) [lit.[11] bp 166 °C (14 mm)]. It was distilled from sodium and stored under N_2 prior to use.

Benzyl phenyl ether was prepared from benzyl bromide and phenol by the procedure of Gates and Allen;[10] bp 110–112 °C (1 mm); mp 36–39 °C (lit.[12] mp 40 °C).

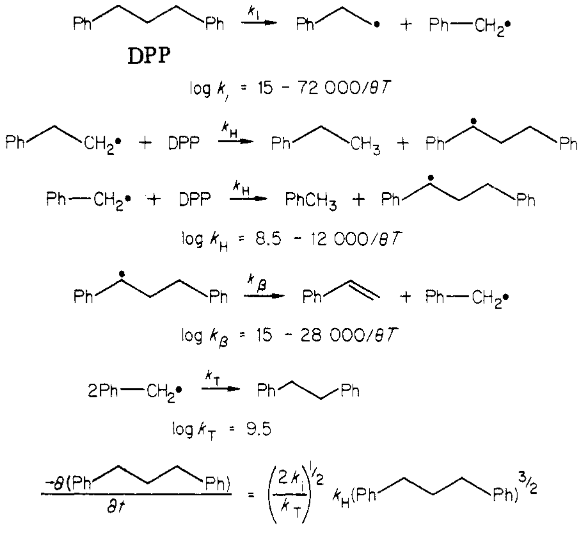
Toluene, styrene, benzaldehyde, phenol, diphenyl ether, and diphenylmethane were obtained from commercial sources and used without further purification.

Standard Kinetic Run. The desired volume of sample was transferred into an ampule, with an appropriately sized microliter syringe, degassed, and sealed under high vacuum. A minimum of four and normally eight to ten ampules were prepared for each sample at a given concentration and temperature. The samples were pyrolyzed in the sand bath for a specified time, cooled to room temperature, and then opened. In experiments involving liquid-phase pyrolyses 5-μL aliquots were removed for analysis. For gas-phase experiments the entire sample was used for analysis.

Table II. Activation Parameters and Relative Rates for 1-3

			
E_A, kcal/mol	51.4	48.0	50.3
log A (s^{-1})	12.54	12.60	12.3
n	1.55	1.43	1.21
k_{rel} (350 °C)	1	17.6	1.39

Scheme I



A least-squares plot of the concentration of starting material remaining vs. time was used to determine the concentration of starting material remaining at a specified time (normally 50 min) which was used to calculate the initial rate. Calculation of the initial rate for gas-phase experiments is straightforward. For liquid-phase experiments the percent reaction was first calculated by using eq 2, where I is the initial sample volume, X_t is the

$$\% \text{ Rxn} = \frac{I(1 - X_t)}{I - Z_g} \times 100 \qquad (2)$$

amount of starting material remaining at time t, and Z_g is the amount of sample in the gas phase. The percent reaction can then be used to calculate the initial rate.

Raoult's law was assumed to hold for mixtures of substrates with hydrogen-donating solvents.

Results and Discussion

Diphenylpropane (1) was found to give toluene and styrene in equal amounts at low conversions over the temperature range of 335–380 °C in both liquid and gas-phase reactions. A plot of log R_i vs. log C_0 (initial rate vs. concentration) over the concentration range of 0.2 (gas phase) to 3.8 M (liquid phase) at various temperatures gave straight lines with slopes (reaction orders) in the range of 1.51–1.60 with the rate constants reported in Table I. An Arrhenius plot yields the activation parameters given in Table II. All of the data are consistent with a free radical

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[8] Chilton, C. H., Perry, R., Eds. "Chemical Engineer's Handbook", 5th ed.; McGraw-Hill: New York, 1973; pp 3-226 ff.

[9] "Dictionary of Organic Compounds", 4th ed.; Oxford University Press: New York, 1965; Vol. 3, p 1291.

[10] Allen, C. F. H.; Gates, J. W., Jr. "Organic Syntheses"; Wiley: New York, 1955; Collect. vol. III, p 140.

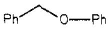
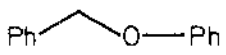
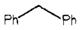
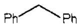
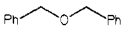
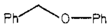
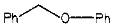
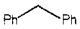
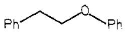
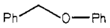
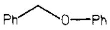
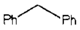
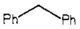
[11] "Dictionary of Organic Compounds", 4th ed.; Oxford University Press: New York, 1965; Vol. 4, p 2687.

[12] Powell, S. G.; Adams, R. *J. Am. Chem. Soc.* **1920**, *42*, 656.

[13] Wortel, T. M.; Bekkum, H. van *J. Org. Chem.* **1980**, *45*, 4763.

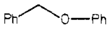
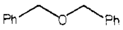
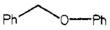
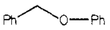
[14] Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 7.

Table III. Initial Rates in the Presence of Free Radical Initiators and Hydrogen-Donating Solvents[a]

substrate (s)	addend (A)	concn, M S	concn, M A	phase	log R_i
		0.0487	0.0025	g	−6.28
		3.61	0.185	l	−3.86
		0.025	0.030	g	−7.84
		1.91	2.23	l	−4.48
		0.037	0.0012	g	−5.93
		2.93	0.089	l	−3.24
		0.025	0.030	g	−6.87
		1.91	2.23	l	−4.01
		0.1037	0.0018	g	−6.54
		2.90	0.13	l	−3.90
		0.025	0.030	g	−7.00
		1.91	2.23	l	−4.34

[a] Temperature = 350 °C.

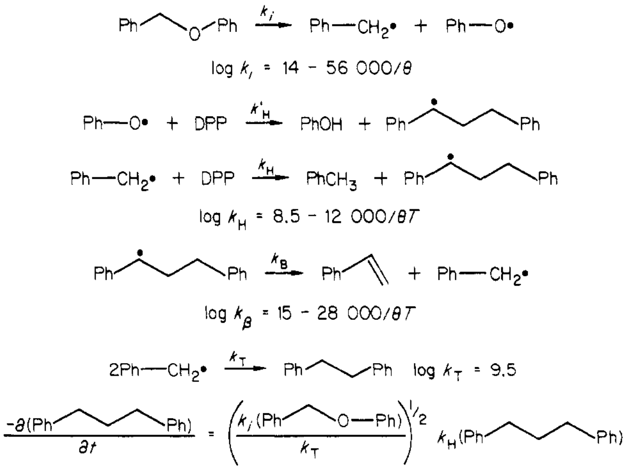
Table IV. Comparison of Calculated and Experimental Rate Constants

substrate (s)	addend (A)	concn, M S	concn, M A	log R_i exptl	log R_i calcd
		0.02 3.79		−7.77 −4.50	−7.90 −4.48
		0.049	0.0025	−6.28	−5.85
		0.05 3.79		−6.75 −3.26	−6.32 −3.50
		0.037	0.0012	−5.93	−5.64
		0.05 1.91		−6.97 −4.69	−6.92 −4.79
		0.037	0.0018	−6.54	−6.23

[a] Temperature = 350 °C.

chain process, and a mechanism is given in Scheme I. Reaction is initiated by cleavage of a C–C bond in 1 to give 2-phenethyl and benzyl radicals. These radicals can abstract hydrogen from 1 to give a 1,3-diphenyl-1-propyl radical which can undergo β scission to generate styrene and another benzyl radical,[15] thus completing the chain process (see Table III). Termination occurs by coupling two benzyl radicals to form 1,2-diphenylethane. Analysis of this reaction scheme, by using the steady-state approximation for all radicals and assuming long chains, yields the kinetic expression of Scheme I for the loss of 1. Also given in Scheme I are estimates of the rate constants for each of the individual steps.[16,17] These estimates allow calculation of the overall rate constant and activation parameters, and comparison of these with the measured quantities (Table IV) provides further support for the proposed mechanism.

Scheme II



Addition of small amounts of benzylphenyl ether to DPP results in an increased rate of loss of 1. Addition of small amounts of 1,2-diphenylethane has no effect on the rate of loss of 1. A possible reaction mechanism is given in

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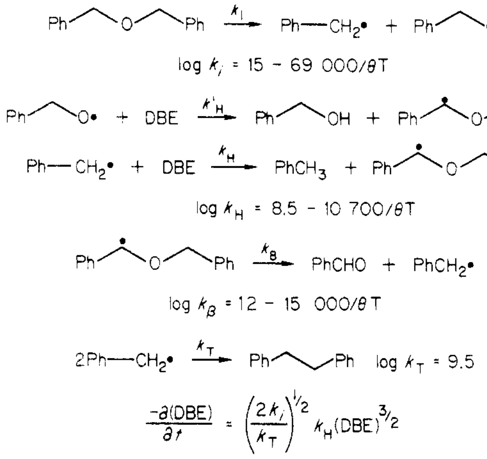
(15) The reverse reaction, addition of a benzyl radical to styrene, probably occurs but has no kinetic significance.

(16) Benson, S. "Thermochemical Kinetics"; Wiley: New York, 1976.

(17) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973, Chapter 2.

Scheme III



Scheme II. Cleavage of benzyl phenyl ether generates benzyl and phenoxy radicals which can initiate the chain process by abstracting hydrogen from 1. 1,2-Diphenylethane is not an efficient initiator of this free radical chain process because the rate of radical generation is too low to compete with radical generation by homolysis of 1 (i.e., $k_i'[\mathrm{PhCH_2CH_2Ph}] \leq k_i$ for $[\mathrm{Ph(CH_2)_3Ph}]$.

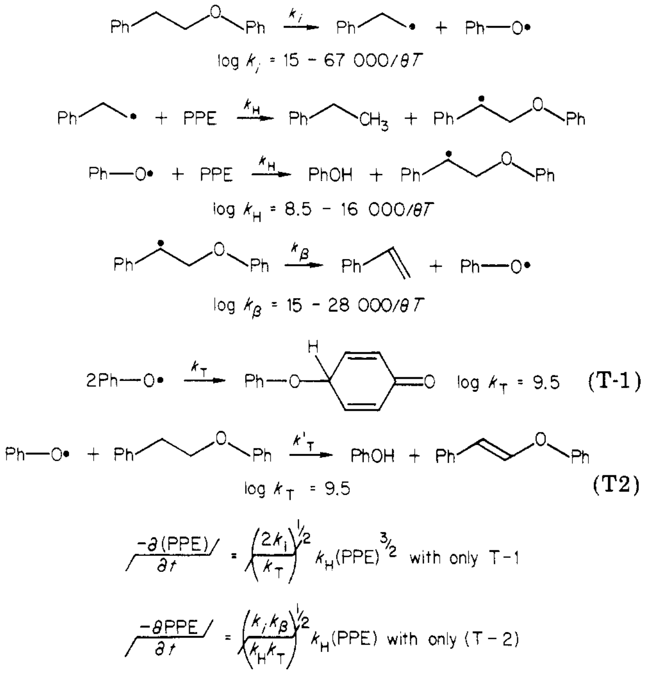
The addition of a hydrogen-donating solvent such as diphenylmethane has no effect on the products formed or the reaction rate other than a concentration effect.

Dibenzyl Ether. Dibenzyl ether (**2**) was found to give equal amounts of toluene and benzaldehyde over the temperature range of 310–350 °C in both the liquid and gas phases. The average reaction order in DBE was 1.43. The reaction rate and order were sensitive to catalysis by acid, glass surfaces, molecular sieves, and impurities present in commercial supplies of DBE. Failure to distill DBE prior to use gave the faster reaction rates and reaction orders found previously.[6] Storage of DBE over 13-X molecular sieves, in an attempt to remove peroxides,[13] resulted in a catalyzed reaction with a reaction order of 1.35, an activation energy of 28 kcal/mol, and a log *A* of 5.7. The source of catalysis is presumably dissolved (or suspended) molecular sieves. Addition of 5–10% triethylamine was necessary to eliminate catalysis by the glass surfaces of the ampules used. This procedure had no effect on the reaction rates of either 1,3-diphenylpropane or phenethyl phenyl ether. Addition of small quantities of benzyl phenyl ether resulted in a faster reaction rate but no change in the products formed. Neither 1,2-diphenylethane or diphenylmethane had any effect on the reaction.

The products formed and the reaction order observed suggest that a free radical chain process is occurring (Scheme III). That **2** reacts faster than **1** is probably due to a slightly lower activation energy for the initial bond homolysis and to a faster rate of hydrogen abstraction from **2** due to the polar effects of an α-oxygen.[14] Given the assumptions used in estimating the reaction rates for the elementary steps, the calculated overall reaction rate and activation parameters agree reasonably well with the measured quantities.

Phenethyl Phenyl Ether. Phenethyl phenyl ether (**3**) has been found to give equal amounts of phenol and styrene over the temperature range of 350–390 °C in both the liquid and gas phases. The reaction order averaged 1.2 for **3** over the temperature range with a concentration range from 0.4 to 3.7 M. The activation parameters are given in Table II. Addition of small amounts of benzyl phenyl ether increases the rate of loss of **3**. The observed reaction order and the effect of a free radical initiator suggests that a concerted retro-ene reaction[7] is not the dominant reaction path. A free radical chain mechanism consistent with the data is given in Scheme IV. The initial stages of this mechanism are similar to the mechanisms given for **1** and **2**. The major difference occurs in the termination reactions since coupling of two phenoxy radicals will not be as efficient a termination reaction as the coupling of two benzyl radicals. Unlike the coupling of two benzyl radicals to give 1,2-diphenylethane, two phenoxy radicals will not give diphenyl peroxide at this temperature. Reaction of two phenoxy radicals might occur by addition at the para position to give the quinone-type product (T-1). This product is probably not very stable at these temperatures, and termination may occur predominantly by the disproportionation reaction given in Scheme IV (T-2). Since the observed reaction order falls between first and three-halves order, both termination reactions must be contributing to the reaction mechanism. A concerted retro-ene reaction requires a first-order reaction and would not show any effect with added free radical initiators. Only a free radical chain process is consistent with all the data.

Scheme IV



Summary

The thermal chemistry of three-atom links is best described by free radical chain processes. The products are consistent with a free radical chain process involving a β-scission reaction, and the reaction orders range between first and three-halves order depending upon the nature of the chain termination reaction. Activation parameters are readily estimated from thermochemical kinetic data on the individual reactions with log $A \approx 12$ and $E_A \approx 50$ kcal/mol. Unlike the one- and two-atom linkages, reactions of the three-atom linkages are promoted by free radical initiators. The potential for inhibition of free radical chains also exists and is currently being studied.

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