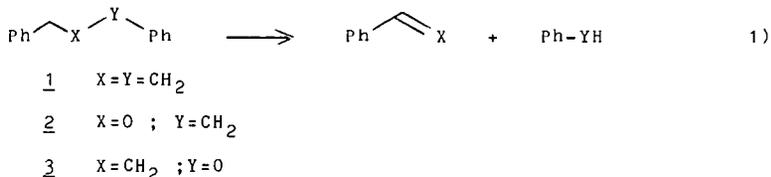


Radical Initiation and Phenol Inhibition in the Thermal, Free Radical Decomposition of 1,3-Diphenylpropane(1), Dibenzylether(2) and Phenethylphenylether (3). Coal Liquefaction Model Studies

K.E. Gilbert

Department of Chemistry  
Indiana University  
Bloomington, IN 47405

Current thought on the structure of coal and the chemistry of coal liquefaction suggests that coal consists of large polycyclic clusters joined by short aliphatic links and that liquefaction reactions occur at these links. Much research has gone into the two atom links. We have been interested in the three atom links because in addition to the cleavage-abstraction reactions available to the two atom links, the three atom links may also react by radical chain reactions. These radical chain reactions can occur over a much wider temperature range than the cleavage-abstraction reactions and thus offer the possibility of a low temperature liquefaction process. Previous work has shown that 1, 2 and 3 decompose by free radical chain reactions as neat liquids or as solutions in hydrogen donating solvents in the temperature range of 300 to 400°C.(1)(Equation 1) Initiation of the radical chain process by benzylphenylether at 350° was demonstrated, but inhibition of the chain reactions by standard inhibitors, such as hindered phenols, was not studied. Herein we report on the effect of hindered phenols on the decomposition of 1, 2 and 3 at 350°, the development of methods for initiating these reactions at temperatures as low as 138°, the effect of hindered phenols on these reactions at lower temperatures and on the kinetic and thermodynamic barriers to these radical chain reactions.



A large number of phenols, including 2,6-di-*tert*-butyl-4-methylphenol, have no effect on the decomposition of 1 at 350°. Stock has found that phenols catalyze the decomposition of 2 at 400°.(2) In order to understand the effect hindered phenols on radical chain processes the reaction of 1, 2 and 3 have been investigated at lower temperatures.

Prior to experimental work the thermodynamics of the overall reaction of 1 to toluene and styrene, 2 to toluene and benzaldehyde and 3 the phenol and styrene were investigated using the group additivity method of Benson (Table 1).(3)

Reaction of 1 is unfavorable at temperatures below 300°, thus initiation of this reaction should not occur at lower temperatures. Replacement of a CH<sub>2</sub> group by an oxygen greatly changes the thermodynamics and the decomposition of 2 and 3 are energetically favorable over the temperature range of interest.

The decomposition of 1 could not be effected by any of the low temperature initiators in accord with the thermodynamic calculations (Table 2). Reaction of 2 could be initiated by all of the low temperature initiators except AIBN, though this may not be a good experiment since AIBN is not very effective at hydrogen abstraction.(4) Reaction of 3 could be effected by di-tert-butyldiazene (TBD) at 180° but not by di-tert-butylperoxide (TPO) at 138° reflecting a kinetic barrier to reaction. In all cases the products were those expected from a radical chain reaction.

Reaction of 2 with TPO was found to be 0.68 order in 2 and 0.62 order in TPO (Table 3). The products were toluene, benzaldehyde and 1,2-diphenylethane(4) in the ratio of 1.1:2:0.65. The chain length, given by the ratio of benzaldehyde to 4, is 1.5. A mechanism consistent with this data is given in Scheme 1. Since the chain length is short both terms in the kinetic expression, derived using the steady state approximation, contribute thus accounting for the non-integral order in 2. The large amount of 4 formed suggests that hydrogen transfer from 2 to benzyl radical is slow at this temperature and controls the reaction path.

Addition of 2,6-di-tert-4-methylphenol to a mixture of 2 and TPO decreases the rate of reaction and suppresses the formation of 4. Toluene and benzaldehyde are the major products. The reaction order in 2 is 0.67 and -0.53 in phenol. A mechanism consistent with this data is given in Scheme 2. This is a general reaction scheme and under these experimental conditions  $k_5$  and  $k_7$  are small. The rate expression, using the steady state approximation, involves only first term under these conditions. Since  $k_3 > k_2$  (5) while  $[2] > [ArOH]$  the two terms in the denominator are of similar magnitude. The data suggests that phenols function as inhibitors in this reaction by effectively competing with the substrate for initiator radicals, and by scavenging the chain carrying benzyl radicals.

Reaction of 2 with TBD at 180° to 200° was found to be 0.93 order in 2, 0.5 order in TBD with the products being toluene, benzaldehyde and 4 in a 6:8:1 ratio. The reaction mechanism of Scheme 1 accounts for this data with the recognition that the second term in the kinetic expression becomes more important at longer chain lengths. The increased temperature favors hydrogen transfer from 2 to benzyl radical at the expense of termination.

Addition of a 2,6-di-tert-butyl-4-methylphenol to the reaction of 2 and TBD decreases the reaction rate and suppresses the formation of 4 while still giving toluene and benzaldehyde. The reaction is first order in 2 and inverse first order in

phenol. The mechanism in Scheme 2 applies, except under these conditions  $k_5$  is significant. This results in a two term rate expression. Phenol competes with 2 for initiator radicals and also for benzyl radicals. Reaction 7 is not yet important and hindered phenols continue to function as inhibitors at 180°C.

Reaction of 2 with 1,1,2,2-tetraphenylethane at 250° gives toluene and benzaldehyde in a reaction that is first order in 2. Addition of a hindered phenol has no effect on the reaction. Thus on going from 180° to 250° hindered phenols go from being inhibitors to being chain transfer agents.

In summary it should be noted that 2 is an excellent model compound. It decomposes over a wide temperature range to give stable products, can be initiated with a wide variety of initiators and allows the study of kinetic barriers to radical chain reactions. Finally the wide temperature range permits investigation of the temperature dependence of inhibition by phenols.

Conversely the all carbon system, 1, demonstrates a thermodynamic barrier to reaction with no reaction observed below 300°. This suggests that all carbon systems will not cleave to toluene and styrene by any process below 300° and that attempts to construct lower temperature coal liquefaction processes based on the thermal chemistry of all carbon systems will not be successful. That is the reactions of one and two atom links are limited to high temperatures by the energy required to cleave a C-C bond, while the three atom and higher number links are thermodynamically limited and would require higher temperatures to drive the reactions towards product formation. This might be circumvented by hydrogenating the alkenes formed, however this would probably require the use of catalysts and gets into subjects more complex than we wish to discuss here. This also suggests that free radical initiators will have no effect on coal liquefaction processes.

Acknowledgement This work was supported by the DOE office of Basic Energy Sciences under contract DEA C02-10721A.

#### References

1. Gilbert, K.E. and Gajewski, J.J., J Org Chem, (1982), 47, 4899.
2. Stock, L.M. and King, H-H., Fuel, (1982), 61, 1172.
3. Benson, S.W., "Thermochemical Kinetics", Wiley-Interscience: New York, 1976.
4. Bartlett, P.D.; Fickes, G.N.; Haupt, F.C.; Hegelson, R., Accts Chem Res, (1970), 3, 177.
5. Howard, J.A.; Ingold, K.U., Can J Chem, (1964), 42, 2324.

Table 1 Thermodynamics of the Reactions of 1, 2 and 3

		<u>Δ G kcal/mol</u>						
		<u>Δ H</u>	<u>Δ S</u>	<u>100</u>	<u>200</u>	<u>300</u>	<u>400</u>	
<u>1</u>	→ Ph-CH <sub>3</sub> + Ph $\text{C}\equiv\text{C}$	17.66	32.5	5.5	2.3	-0.96	-4.2	
<u>2</u>	→ Ph-CH <sub>3</sub> + Ph-CHO	1.23	53.0	-18	-24	-29	-34	
<u>3</u>	→ Ph-OH + Ph $\text{C}\equiv\text{C}$	10.30	33.9	-2.3	-5.7	-9.1	-12.5	

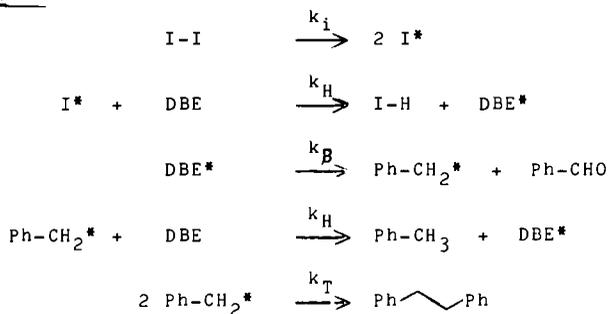
Table 2. Reaction of 1, 2 and 3 with Various Initiators

<u>Initiator/Temperature</u>	<u>1</u>	<u>2</u>	<u>3</u>
AIBN/80 <sup>0</sup>	NR	NR	NR
TPO/138 <sup>0</sup>	NR	+	NR
TBD/180-200 <sup>0</sup>	NR	+	+
(Ph) <sub>2</sub> CHCH(Ph) <sub>2</sub> /250 <sup>0</sup>	NR	+	+
Ph $\text{C}\equiv\text{C}$ -O-Ph/350 <sup>0</sup>	+	+	+

Table 3 Reaction of 2 with TPO and TBD

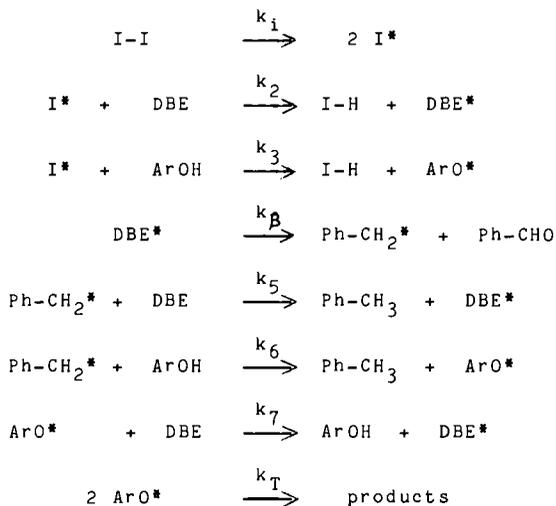
<u>[DBE]</u>	<u>[I]</u>	<u>[ArOH]</u>	<u>log R<sub>i</sub></u>	<u>Rxn Order</u>
3.07	TPO/1.12	-	-4.07	
2.38		-	-4.15	
1.77		-	-4.19	.68
1.46		-	-4.29	
1.15		-	-4.37	
1.77	1.55	-	-4.11	
	1.12	-	-4.19	.62
	.61	-	-4.36	
1.77	1.12	.87	-4.85	
		.58	-4.68	
		.37	-4.52	-.61
		.29	-4.49	
		.14	-4.36	
2.38	1.12	.29	-4.41	
1.77			-4.49	.67
1.15			-4.62	
3.1	TBD/.51	-	-3.97	
2.0		-	-4.19	.93
1.3		-	-4.32	
2.0	.82	-	-3.95	
	.51	-	-4.19	.5
	.36	-	-4.27	
2.0	.51	1.15	-4.82	
		.89	-4.69	-1.10
		.57	-4.47	
		.29	-4.16	

Scheme 1



$$-\frac{\partial [\text{DBE}]}{\partial t} = ek_i[\text{I}] + \left(\frac{ek_i[\text{I}]}{k_t}\right)^{1/2} k_H[\text{DBE}]$$

Scheme 2



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