

THE EFFECT OF CROSS-LINKING ON THE THERMAL DECOMPOSITION OF DIPHENYLALKANES

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ABSTRACT

In the early stages of the thermal depolymerization of coal, its cross-linked macromolecular structure may restrict the diffusion of reactive intermediates and alter the reaction pathways. In an effort to model the effects of restricted mass transport on the thermally induced free radical decomposition of polymethylene units bridging aromatic clusters in coal, a series of diphenylalkanes [$\text{Ph}(\text{CH}_2)_n\text{Ph}$] have been cross-linked to an inert silica surface by the condensation of the corresponding phenol, $\text{HOC}_6\text{H}_4(\text{CH}_2)_n\text{C}_6\text{H}_4\text{OH}$. Results from the thermolysis of the diattached substrates at 350-400 °C will be presented and compared to the thermolysis of fluid phase and mono-attached diphenylalkanes [$\approx\text{Ph}(\text{CH}_2)_n\text{Ph}$] to highlight the impact that restricted diffusion has on the reaction mechanisms.

INTRODUCTION

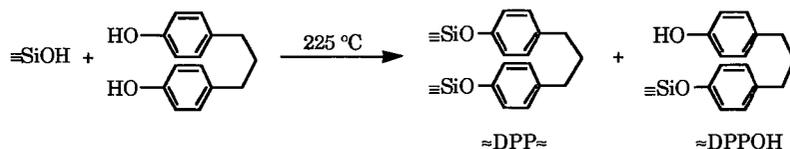
The study of the fundamental reaction mechanisms associated with the thermal decomposition of coal is hindered by its heterogeneous, cross-linked, macromolecular structure. One solution to this problem has been to investigate the thermal decomposition of model compounds representing structural features present in coal, but extrapolation of the results back to coal is difficult and sometimes unreliable.¹ In order to provide a more relevant model for exploring the reaction mechanisms associated with coal pyrolysis, some of the complexities imparted by the macromolecular network structure of coal must be taken into account.

Our research has focused on modeling the effects of restricted mass transport on thermal free radical reaction pathways.²⁻⁶ Thermolysis studies at 350-400 °C of α , ω -diphenylalkanes covalently attached to an inert silica support has provided evidence that restricted radical and substrate diffusion can alter the free radical reaction pathways as compared to their liquid or gas phase behavior. In the thermolysis of surface-immobilized 1,2-diphenylethane, unimolecular rearrangement and cyclization were favored over bimolecular coupling reactions.² Thermolysis of surface-immobilized 1,3-diphenylpropane ($\approx\text{DPP}$)³ and 1,4-diphenylbutane ($\approx\text{DPB}$)⁴ showed that a free radical chain reaction can efficiently occur under the effects of restricted diffusion, and an unexpected regioselectivity in the hydrogen abstraction process was observed. These studies have also shown that cross-linking reactions can occur under conditions of restricted diffusion. For example, in the thermolysis of $\approx\text{DPP}$ and $\approx\text{DPB}$, surface-attached benzyl radical adds to a surface-attached styrene

to form a cross-linked DPP ($\approx\text{Ph}(\text{CH}_2)_3\text{Ph}\approx$ or $\approx\text{DPP}\approx$) after hydrogen abstraction. Although the reactions responsible for cross-linking have been investigated,⁷ the effects of cross-linking on the thermal decomposition reaction pathways has not been investigated. Therefore, in this paper, we will explore the effects of cross-linking on the thermolysis of 1,3-diphenylpropane and 1,4-diphenylbutane as model compounds for coal.

EXPERIMENTAL

1,3-di(*p*-hydroxyphenyl)propane and 1,4-di(*p*-hydroxyphenyl)butane were prepared by the procedure of Richardson⁸ and purified by repeated crystallizations from benzene/hexanes until the purity was >99.9% by GC. The surface-attached materials were prepared by the condensation (225 °C for 1-4 h) of the diphenol with the surface hydroxyls of a high purity fumed silica (Cab-O-Sil, M-5, Cabot Corp.) and sublimation



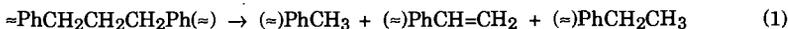
of the excess phenol under vacuum (5×10^{-3} Torr) at 275 °C, as previously described.²⁻⁴ Complete diattachment could not be obtained even at the lowest surface coverages, and the surface contains a mixture of mono- and diattached material. Surface coverages were determined by liberation of the surface-attached phenol by base hydrolysis, silylation to the corresponding trimethylsilyl ethers, and analysis by GC. Three batches of $\approx\text{DPP}\approx/\approx\text{DPPOH}$ were prepared with surface coverages of 0.465, 0.181, and 0.105 mmol of organic per gram of derivatized silica with purities of 99.9, 99.5, and 99.6%, respectively, and one batch of $\approx\text{DPB}\approx$ was prepared with surface coverage of 0.113 mmol/g and purity of 99.6%. The fraction of mono-attached substrate was determined from the quantity of HOPhCH_3 , a product from the thermolysis of $\approx\text{DPPOH}$ and $\approx\text{DPBOH}$, which distills into the cold trap.

Thermolyses were conducted in sealed, evacuated ($<5 \times 10^{-6}$ Torr) T-shaped tubes as previously described.²⁻⁴ Volatile products were collected in a cold trap and analyzed as phenols and their trimethylsilyl ethers, while surface-bound products were removed from the surface by base hydrolysis and silylated to the trimethylsilyl ethers. The samples were analyzed by GC and GC-MS with the use of internal standards.

RESULTS AND DISCUSSION

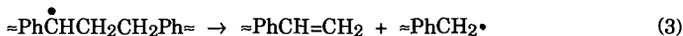
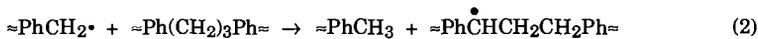
Thermolysis of $\approx\text{DPP}\approx$. In order to determine the effect of cross-linking on the thermolysis of 1,3-diphenylpropane, a series of surface-attached DPPs were synthesized in which the fraction of diattachment was varied. As shown in Table 1, the extent of diattachment increased with decreasing surface coverage, but complete diattachment could not be achieved. This is most likely a consequence of the

geometric constraints of the short aliphatic chain (see \approx DPB \approx below). Thermolysis of the high coverage \approx DPP \approx at 375 °C at low conversion produces approximately equal amounts of surface-immobilized toluene and styrene as the major products and a small amount of surface-immobilized ethylbenzene (ca.1%), eq 1. The parentheses



indicate that both a surface-immobilized species and a gas-phase species are present since the starting DPP is not completely cross-linked to the surface. At higher conversions, isomers of $\text{C}_{22}\text{H}_{22}\text{O}_3$ and $\text{C}_{23}\text{H}_{24}\text{O}_3$ (after work-up) are formed as secondary products.

The products from the thermolysis of \approx DPP \approx can be rationalized by a free radical chain reaction analogous to the one determined for \approx DPP \approx^3 and DPP.⁹ Assuming that all of the DPP is diattached to the surface, the chain propagation steps are shown in equations 2 and 3. The mono-attached DPP (\approx DPPOH) decomposes analogously, but

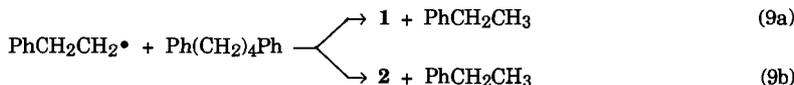
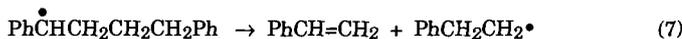
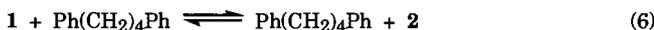
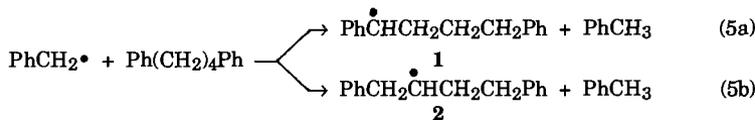


produces a mobile gas-phase (vide infra) benzyl radical (p -HOPhCH₂•). The surface-immobilized ethylbenzene could result from the initiation reaction or hydrogenation of styrene. Alkenes such as stilbene and styrene are known to be reduced to the alkane in the presence of hydrogen donors such as tetralin as well as DPP itself.^{9a} The secondary products $\text{C}_{23}\text{H}_{24}\text{O}_3$ and $\text{C}_{22}\text{H}_{22}\text{O}_3$ are formed from reaction of the diattached 1,3-diphenyl-1-propyl radical with surface-attached styrene or benzyl radical.¹⁰ Although radical addition to styrene has been observed in the thermolysis of \approx DPP and DPP, radical coupling involving a 1,3-diphenyl-1-propyl radical is a unique chain terminating reaction that has not previously been observed.

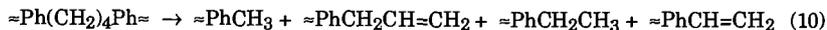
The rate of decomposition of \approx DPP \approx should be sensitive to the extent of cross-linking since the geometric constraints placed on the chain carrying benzyl radical and the neighboring DPP molecules would influence the hydrogen abstraction reaction. Comparing the rate of conversion of a high coverage \approx DPP \approx and \approx DPP (see Table 1), it is found that the small degree of cross-linking (24%) has only a modest effect on the rate. The free phenolic functionality of the mono-attached DPP is not expected to inhibit the rate of decomposition since it has been shown that in the thermolysis of DPP in the liquid phase at 350 and 400 °C, phenol and alkylated phenols have no effect on the rate of decomposition or product distribution.¹¹ Surprisingly, at lower coverages, the rate of decomposition of \approx DPP \approx is only slightly slower than that of \approx DPP. This could indicate that (1) hydrogen abstraction reactions are not more hindered by diattachment at these surface coverages, (2) gas phase HOPhCH₂•, from the decomposition of the mono-attached DPP, is an effective chain carrying radical, or (3) the rate of initiation is accelerated by strain introduced into the aliphatic chain by cross-linking. The effects of cross-linking on the rate of decomposition is under further investigation.

No new products are observed from the thermolysis of \approx DPP \approx as the fraction of cross-linking increases. However, retrogressive reactions dramatically increase as a consequence of cross-linking. A comparison of the mole % secondary products from the thermolysis \approx DPP \approx and \approx DPB \approx at similar coverages and conversions reveals that as cross-linking increases, retrogressive reactions increase over 100-fold at the lowest surface coverage as shown in Table 2. Additionally, the mole % of \approx PhCH₂CH₃ increases with decreasing surface coverage and is approximately independent of conversion. If the ethylbenzene is formed from the reduction of styrene, the yields would likely be conversion dependent.³

Thermolysis of \approx DPB \approx . The thermolysis of a diattached 1,4-diphenylbutane (\approx DPB \approx) was used to study the effects of cross-linking on the selectivity of hydrogen abstraction. In thermolysis of 1,4-diphenylbutane (DPB), four products are formed (eq 4) by a free radical chain mechanism in which the chain propagation steps are shown in equations 5-9.



A \approx DPB \approx was prepared with a surface coverage of 0.113 mmol/g with 94% of the material cross-linked. The fraction of diattachment is larger than that found for \approx DPP \approx (82%) and must be a result of the longer aliphatic chain. Thermolysis of \approx DPB \approx at 400 °C produced the four products shown in eq 10. A mechanism similar



to that proposed for the thermolysis of DPB can be invoked for the cross-linked DPB. The selectivity of formation of 1 to 2 as determined by the PhCH₂CH₃/PhCH₃ ratio is dramatically altered compared to selectivity found for \approx DPB (see Table 3), and favors

the thermodynamically less stable aliphatic radical 2. This perturbation of selectivity could result from the geometric constraints placed on the hydrogen abstraction reaction by restricted mass transport. Additionally, the rate of decomposition is significantly reduced as a consequence of cross-linking. The impact of cross-linking on the selectivity will be studied further.

CONCLUSION

This paper presents the preliminary results from the study of the effects of cross-links on the thermolysis of coal model compounds. Our previous studies have shown that restricting mass transport can alter reaction pathways. Results from this study indicate that cross-linking can dramatically increase retrograde reactions, alter the selectivity of hydrogen abstraction reactions and reduce the rate of decomposition. Additional studies are in progress to probe the impact of restricted mass transport on retrograde reactions.

ACKNOWLEDGEMENTS

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Table 1. Rate of Conversion of \approx DPP \approx and \approx DPP as a Function of Surface Coverage.

Compound	Coverage (mmol/g)	% Diattachment	Rate ^a (% h ⁻¹)
\approx DPP \approx	0.465	24	3.5
	0.181	60	0.56
	0.105	82	0.096
\approx DPP	0.57	-	7.0
	0.14	-	0.40
	0.10	-	0.26

^aDetermined from the slopes of the linear regression of conversion vs time

Table 2. Yield of Secondary Products as a Function of Surface Coverage.

Coverage (mmol/g)	Secondary Products: \approx DPP \approx / \approx DPP ^a	\approx PhCH ₂ CH ₃ ^c (mole %)
0.465	2.8	1.2
0.181	22	5.3
0.105	>120 ^b	8.5

^aRatio of the mole % secondary products from thermolysis of \approx DPP \approx and \approx DPP compared at similar coverages and conversion.

^bSecondary products for 0.10 mmol/g \approx DPP below detection limit of 0.05 mole %. ^cIndependent of conversion.

Table 3. Selectivity and Rate of Decomposition of \approx DPB \approx and \approx DPB.

Compound	Coverage (mmol/g)	1/2 Selectivity ^a	Rate (% h ⁻¹) ^b
\approx DPB \approx	0.113	0.60	1.1%
\approx DPB	0.117	2.0	9.5%

^aPhCH₂CH₃/PhCH₃ product ratio. ^bRate determined from the slope of a conversion vs time plot.