

HYDROGEN TRANSFER PATHWAYS UNDER RESTRICTED DIFFUSION

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ABSTRACT

The impact of restricted mass transport on the thermal processing of coal is being explored through the study of organic model compounds that are covalently anchored to an inert silica surface. Two-component surfaces are being prepared and pyrolyzed at 375 °C that contain a thermally reactive component [$\text{Ph}(\text{CH}_2)_n\text{Ph}$, $n=2-4$] in the presence of a second component that is either thermally inert [biphenyl or naphthalene] or contains reactive C-H bonds [diphenylmethane (DPM) or 9,10-dihydrophenanthrene (DHP)]. Reactions are found to be highly sensitive to the spatial distribution of hydrogen donors and nondonors that surround immobilized free-radical intermediates. In the presence of DPM or DHP, rapid serial hydrogen transfer steps allow radical intermediates to migrate across the surface overcoming normal diffusional limitations. Studies with DHP also reveal a minor reaction channel in which strong bond cleavage reactions occur via hydrogen transfer in these diffusionaly constrained environments.

INTRODUCTION

Our research has been concerned with the development of model systems¹⁻⁴ that probe the potential perturbations in free-radical reaction pathways that may arise in coal as a result of its cross-linked, network structure.⁵ This effect may be particularly important in thermal conversions of coals at low temperatures, e.g., 350-400°C, where bonds begin to break but most of the residual framework is retained.⁶ Important mechanistic insights have now been gained through the study of representative organic compounds that are covalently immobilized on an inert silica surface through Si-O-C_{org} linkages.

In order to maximize the production of hydrogen-rich products during liquefaction or pyrolysis of coal, it is important to understand and potentially control the reactions of native, reactive hydrogen-containing molecules. Our current studies employ two-component surfaces to address the influence of the structure and distribution of neighboring molecules on pyrolysis decay pathways in diffusionaly restricted environments, particularly with respect to key hydrogen transfer steps. We have focused on the thermolysis of surface-immobilized diphenylalkanes, $\text{-Ph}(\text{CH}_2)_n\text{Ph}$ [$n=2-4$], in the presence of the surface-immobilized spacer molecules, biphenyl, naphthalene, diphenylmethane, and 9,10-dihydrophenanthrene.

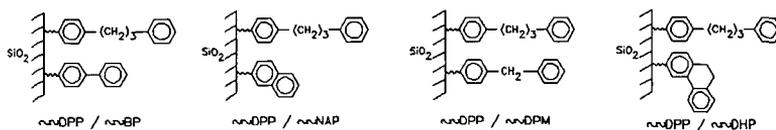
EXPERIMENTAL

The surface immobilization, pyrolysis, and product analysis procedures have been described in detail previously.^{1,2} The syntheses of $p\text{-HOC}_6\text{H}_4(\text{CH}_2)_n\text{C}_6\text{H}_5$, $n=2^1$, 3^2 , and 4^3 have also been described.

The starting materials, *p*-HOC₆H₄C₆H₅, *p*-HOC₆H₄CH₂C₆H₅, and 2-HOC₁₀H₇, were commercially available, and were purified to >99.9%. A multistep synthesis was employed to prepare 3-hydroxy-9,10-dihydrophenanthrene,⁷ which contained about 0.5% of the 3-hydroxyphenanthrene as impurity. The two-component surfaces were prepared by co-attachment in a single step, and had final purities >99.5%. Gas-phase pyrolysis products were collected in a cold trap (77K) as they formed and were analyzed by GC and GC-MS with the use of internal calibration standards. Surface-attached products were liberated as phenols following digestion of the silica in base, silylated to the corresponding trimethylsilyl ethers, and analyzed as above.

RESULTS AND DISCUSSION

Surface-Immobilized 1,3-Diphenylpropane (=DPP). Our most detailed results come from studies of the free-radical chain decomposition pathway for =DPP in the presence of the surface spacer molecules shown below. Pyrolysis of =DPP alone in sealed, evacuated (2x10⁻⁶ torr) tubes at 375°C and low conversions produces the cracking products shown in Eq. 1.² No new products are detected



in the presence of the co-attached =BP, =NAP, or =DPM, while a minor new reaction channel is observed in the presence of =DHP (vide infra). The long chain, free-radical decay pathway (propagation steps shown in Eqs. 2-4) cycles through the two distinct benzylic radicals, =PhCH•CH₂CH₂Ph (1) and =PhCH₂CH₂CH•Ph (2) that undergo subsequent rapid unimolecular



decay via β -scission (Eqs. 2-3).² Selectivity in the product distribution is determined by the relative concentrations of the two benzylic radicals, [2]/[1], and is experimentally monitored by the PhCH=CH₂/PhCH₃ yield ratio, S. In related fluid phase studies of *p*-Me₃SiOPh(CH₂)₃Ph at 375 °C,

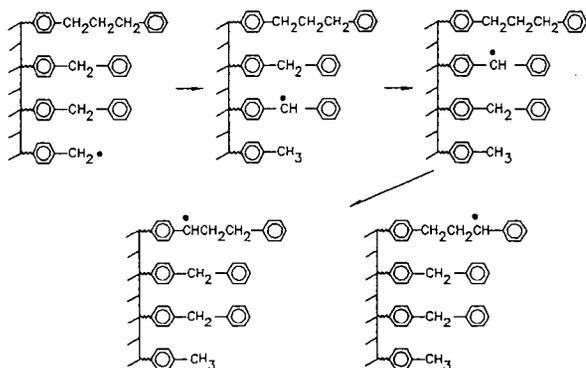


a substituent effect, S=0.91, was observed indicating a slight inherent stabilization of the benzylic radical para to the siloxy substituent.²

The initial rates and selectivities for thermolysis of =DPP at 375°C as a function of surface coverage and co-attached aromatic are given in Table 1.⁴ For surfaces containing only =DPP, the thermolysis rate decreases dramatically with decreasing surface coverage, while S increases indicating an increasing preference for abstracting the more accessible benzylic hydrogen farthest from the surface. As shown in Table 1, the presence of =BP or =NAP results in reaction rates and selectivity values comparable with surfaces containing only =DPP at similar =DPP surface coverages. On the other hand, the

presence of \sim DPM leads to a dramatic rate acceleration compared with the \sim BP or \sim NAP spacers, and gives rate and selectivity values more typical of saturated coverages of \sim DPP (see Table 1).

These results suggest that rapid hydrogen transfer steps involving \sim DPM are occurring that allow radical centers to "migrate" on the surface as illustrated below. The result of this process is to effectively decrease the distance between a \sim DPP molecule and a radical center on the surface. This



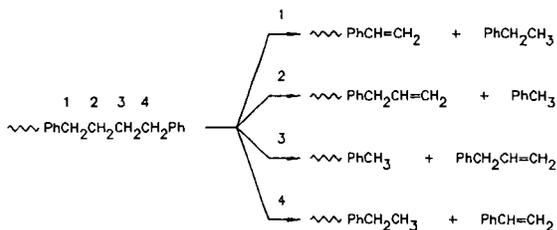
enhances the rate at which \sim DPP reacts by increasing the rate of the hydrogen transfer propagation step, which probably contains a distance dependence in the rate constant when the hydrogen abstracting radical is also surface attached. In contrast, the presence of a hydrogen donor such as tetralin⁸ or diphenylmethane⁹ had essentially no effect on the pyrolysis rate of liquid-phase DPP at ca. 350 °C at similar dilutions, and behaved similarly to liquid biphenyl⁸ as diluent. The values of $S < 1.0$ for \sim DPP/ \sim DPM surfaces are also consistent with a reduced separation between \sim DPP molecules and radical centers on the surface. Radical migration effectively removes the distance dependent conformational constraints on the hydrogen abstraction reactions from \sim DPP that resulted in the unexpected regioselectivity in product formation at lower coverages.

Supporting evidence for the involvement of \sim DPM in the radical relay mechanism depicted above comes from studies of surfaces containing \sim DPP/ \sim DPM- d_2 .⁴ Consistent with the results for \sim DPM, we find $S < 1.0$ and a substantial rate enhancement, although the rate enhancement is slightly less than the protium analog perhaps due to a small kinetic isotope effect. Furthermore both the gas-phase and surface-attached toluene products show substantial deuterium incorporation providing direct evidence for the involvement of H(D) transfer between \sim DPM- $h_2(d_2)$ and both chain carrying gas-phase and surface-attached benzyl radicals.

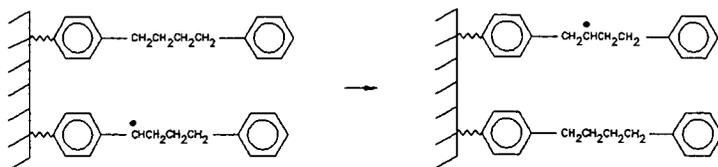
As evidenced by the rate and selectivity parameters in Table 1, the hydroaromatic \sim DHP is also very effective in promoting the radical relay pathway even for an extremely low surface coverage of \sim DPP. In addition, a second reaction channel is observed (accounting for about 2.5% of the \sim DPP reacted) that results in hydrodealkylation of \sim DPP to form \sim PhH + PhC₃H₇, and \sim PhC₃H₇ + PhH in comparable amounts. This strong bond cleavage likely results from transfer of hydrogen atoms from intermediate surface-immobilized hydrophenanthryl radicals which, as opposed to diphenylmethyl

radicals, are known to possess hydrogenolysis activity.¹⁰ Additional studies are in progress that examine the influence of α -DHP/ α -DPP surface coverage and reaction temperature on the selectivity for this reaction channel.

Surface-Immobilized 1,4-Diphenylbutane (α -DPB). A detailed analysis of the influence of restricted mobility on the pyrolysis of α -DPB at 400 °C has been recently reported.³ At low conversions α -DPB cracks to form four main sets of products, as shown below, resulting from a long chain radical decay pathway analogous to that for α -DPP that cycles through both benzylic and nonbenzylic radicals at positions 1-4.



Data for initial rates and selectivities as a function of surface coverage and co-attached spacer molecule are summarized in Table 2. The selectivities again depend on the relative concentrations of the radicals centered on carbons 1-4. The benzylic selectivity, C_4/C_1 , shows the same trend with decreasing surface coverage and the type of spacer present as did the related selectivity for α -DPP. The lack of selectivity between benzylic and nonbenzylic sites at high coverage (as typified by the values for C_1/C_2), and the increase in this selectivity with decreasing surface coverage, necessitates a rapid hydrogen transfer step that interconverts benzylic and nonbenzylic radical sites prior to β -scission as illustrated below. This interconversion step is most efficient at high surface coverages.



The C_1/C_2 product selectivity is found to be quite sensitive to the nature of the co-attached spacer present. The presence of α -BP provides a barrier that inhibits the hydrogen transfer step that interconverts benzylic and nonbenzylic radicals on the surface and results in a substantially increased value of C_1/C_2 . On the other hand, as in the case of α -DPP, the presence of α -DPM enhances the rate of radical interconversion and leads to a decreased value of C_1/C_2 identical with that of a high surface coverage of α -DPB alone.

SUMMARY

Investigations of pyrolysis reactions employing two-component surfaces have provided fundamental insights into the influence of the structure of neighboring molecules on free-radical decay pathways in diffusionally constrained environments. The rates and selectivities of key hydrogen transfer steps can be profoundly effected by the structure and spatial distribution of hydrogen donors surrounding immobilized free-radical intermediates. The results give dramatic evidence that intervening molecules containing reactive C-H bonds can act as "relay catalysts" for radical intermediates allowing them to "migrate" under conditions where classical diffusion is prohibited. Diffusional limitations for similar intermediates in coal may also be overcome by similar processes. Related studies are now in progress for α -BB, which has been found to primarily undergo retrogressive rearrangement and cyclization reactions when pyrolyzed under conditions of restricted mass transport.¹

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Table 1. Rate and Selectivity in Pyrolysis of α -Ph(CH ₂) ₃ Ph at 375 °C			
Surface Composition	Coverage (mmol/g)	Rate x 10 ⁴ (% s ⁻¹)	S ^a
α -DPP	0.57	18	0.96
	0.14	1.1	1.09
	0.10	0.72	1.21
α -DPP / α -NAP	0.12 / 0.44	1.9	1.08
α -DPP / α -BP	0.13 / 0.51	2.3	1.14
	0.10 / 0.51	1.2	1.18
α -DPP / α -DPM	0.17 / 0.42	21	0.82
	0.13 / 0.37	16	0.93
α -DPP / α -DPM-d ₂	0.16 / 0.36	13	0.98
α -DPP / α -DHP	0.065 / 0.47	13	0.89

^a Measured by PhCH=CH₂ / PhCH₃ yield ratio.

Table 2. Rate and Selectivity in Pyrolysis of α -Ph(CH ₂) ₄ Ph at 400 °C				
Surface Composition	Coverage (mmol/g)	Rate x 10 ⁴ (% s ⁻¹)	S ^a (C ₁ /C ₂)	S ^b (C ₄ /C ₁)
α -DPB	0.485	43	1.19	0.96
	0.087	17	2.0	1.01
	0.054	9.2	2.07	1.08
α -DPB / α -BP	0.072 / 0.566	20	2.9	1.06
α -DPB / α -DPM	0.060 / 0.465	49	1.19	0.96

^a Measured from PhCH₂CH₃ / PhCH₃ yield ratio.

^b Measured from PhCH=CH₂ / PhCH₂CH₃ yield ratio.