Thermolysis of Surface-Attached 1,4-Diphenylbutane: The Role of Hydrogen-Transfer Reactions on the Surface in Determining the Product Distribution

Phillip F. Britt* and A. C. Buchanan, III

Chemistry Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37381

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In order to probe the effects of restricted radical and substrate mobility on a complex free-radical-chain decomposition reaction, a surface-immobilized 1,4-diphenylbutane (≈DPB) has been prepared by the condensation of *p*-(4-phenylbutyl)phenol with the surface hydroxyl groups of a high-purity fumed silica. Thermolysis of ≈DPB was studied at 400 °C as a function of surface coverage (0.504–0.054 mmol g^{-1}), conversion, and coattached biphenyl (≈BP) or diphenylmethane (≈DPM). Decomposition of ≈DPB proceeds by a free-radical-chain pathway, analogous to that found for 1,4-diphenylbutane in the liquid phase, to produce as the major product pairs $PhCH_3$ plus ≈$PhCH_2CH{=}CH_2$, $PhCH_2CH_3$ plus ≈$PhCH{=}CH_2$, $PhCH{=}CH_2$ plus ≈$PhCH_2CH_3$, and $PhCH_2CH{=}CH_2$ plus ≈$PhCH_3$, whose distribution is a sensitive function of surface coverage, conversion, and structure of coattached molecules. At saturated surface coverages, bimolecular hydrogen-transfer reactions can occur on the surface to equilibrate benzylic and aliphatic radical sites such that all products are formed in nearly equal amounts. However, at lower surface coverages, the bimolecular hydrogen-transfer reactions are hindered by the spatial distribution of the molecules. At all coverages, an unusual regioselectivity is observed in the hydrogen-transfer reaction that favors the formation of the benzylic radical farthest from the surface as the proximity of ≈DPB molecules and hydrogen-abstracting radicals on the surface decrease. Coattached ≈BP is found to hinder the bimolecular hydrogen-transfer reactions on the surface, while coattached ≈DPM facilitates these reactions. These results show that radical centers can be relayed across the surface by a series of rapid hydrogen-transfer reactions to positions near unreacted ≈DPB molecules, which can lead to rapid equilibration of the benzylic and aliphatic radical sites. The implication of these results to the decomposition of aliphatic linkages connecting aromatic clusters in coal is discussed.

Introduction

Most processes for the conversion of coal into commercially useful products, such as liquid fuels or chemical feedstocks, rely on the chemical transformations that occur when coal is heated to temperatures of at least 350 °C.[1,2] On the basis of spectroscopic and chemical degradation studies, coal consists of clusters of polycyclic aromatic, hydroaromatic, and heterocyclic aromatic moieties connected by short aliphatic and ether linkages in a cross-linked, three-dimensional macromolecular array.[3] The thermal reactivity of coal results in part from the cleavage of these short linkages by bond homolysis and β-scission reactions to generate free-radical intermediates.[4] Attempts to provide a mechanistic description of the thermal decomposition of coal at the molecular level are very difficult as a consequence of its complex structure and heterogeneity. One simplifying approach has been to study the thermolysis of compounds that model structural features in coal.[5] However, extrapolation of these results to coal is difficult because of the need to account for the complicating features inherent to coal, such as structure–reactivity relationships, interaction between functional groups, restricted mass transport, and catalysis by mineral matter. Our research efforts have focused on modeling the complication of restricted translational mobility on free-radical reactions that might occur in coal as a consequence of its cross-linked macromolecular structure. The experimental approach for studying the effects of restricted diffusion on free-radical reaction mechanisms at temperatures relevant to coal thermolysis, 350–400 °C, involves the covalent attachment of model compounds to an inert silica surface.[6-8]

Previous studies on the thermal stability of surface-immobilized biphenyl (≈BP) and diphenylmethane (≈DPM) showed that the residual surface hydroxyl groups on the silica surface do not catalyze new decomposition pathways at 400 °C.[6] Moreover, the rate of C–C homolysis for 1,2-diphenylethane (≈BB) was unaffected by surface attachment. However, thermolysis studies of ≈BB showed that restricted radical and substrate mobility can cause dramatic alterations in free-radical reaction pathways in which unimolecular rearrangement and cyclization reactions are favored, while bimolecular radical–radical couplings are hindered.[6] Thermolysis of surface-immobilized 1,3-diphenylpropane (≈DPP) showed that a free-radical-chain reaction can occur efficiently under conditions of restricted diffusion, and an unexpected regioselectivity in the hydrogen abstraction process was observed.[7] We have now prepared a surface-immobilized 1,4-diphenylbutane (≈DPB) and studied its thermal decomposition as a function of conversion, surface coverage, and spacer molecules to examine the effects of restricted diffusion on a more complicated free-radical reaction pathway.[8]

Thermolysis of 1,4-Diphenylbutane. In order to delineate the effects of surface immobilization on the decomposition mechanism, the cracking of 1,4-diphenyl-

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butane (DPB or 1) in the fluid phase must be briefly reviewed.[9-12] Thermolysis of DPB at 400 °C produces four products (eq 1) whose yields depend on concentration and

$$\underset{\mathbf{1}}{PhCH_2CH_2CH_2CH_2Ph} \rightarrow PhCH_3 + PhCH_2CH{=}CH_2 + PhCH_2CH_3 + PhCH{=}CH_2 \quad (1)$$

temperature.[9] The $PhCH_2CH_3/PhCH_3$ ratio increases nonlinearly from 1.2 for the neat liquid (ca. 3.2 M) to 5.4 for the gas phase (1.8×10^{-2} M), while at 365 °C, the ratio is 0.64 (ca. 3.2 M) and 5.0 (1.1×10^{-2} M). A free-radical-chain decomposition mechanism has been proposed for the decomposition of DPB (eqs 2–7) (the 10 possible termination reactions from the four chain-carrying radicals are omitted).

$$\underset{\mathbf{1}}{PhCH_2CH_2CH_2CH_2Ph} \rightarrow PhCH_2^{\bullet} + {}^{\bullet}CH_2CH_2CH_2Ph \quad (2)$$

$$PhCH_2CH_2CH_2^{\bullet} \rightarrow PhCH_2^{\bullet} + CH_2{=}CH_2 \quad (3)$$

$$PhCH_2^{\bullet} + \mathbf{1} \rightarrow \underset{\mathbf{2}}{Ph\dot{C}HCH_2CH_2CH_2Ph} + PhCH_3 \quad (4a)$$

$$PhCH_2^{\bullet} + \mathbf{1} \rightarrow \underset{\mathbf{3}}{PhCH_2\dot{C}HCH_2CH_2Ph} + PhCH_3 \quad (4b)$$

$$\mathbf{2} \rightarrow PhCH{=}CH_2 + PhCH_2CH_2^{\bullet} \quad (5)$$

$$\mathbf{3} \rightarrow PhCH_2CH{=}CH_2 + PhCH_2^{\bullet} \quad (6)$$

$$PhCH_2CH_2^{\bullet} + \mathbf{1} \rightarrow \mathbf{2} + PhCH_2CH_3 \quad (7a)$$

$$PhCH_2CH_2^{\bullet} + \mathbf{1} \rightarrow \mathbf{3} + PhCH_2CH_3 \quad (7b)$$

In order to explain the concentration dependence of the products and the $PhCH_2CH_3/PhCH_3$ ratio near unity even though radical **2** is estimated to be more stable than **3** by 10 kcal mol^{-1},[13] a reversible intermolecular hydrogen-abstraction reaction which interconverts radicals **2** and **3** was included.[9]

$$Ph\dot{C}HCH_2CH_2CH_2Ph + DPB \rightleftharpoons DPB + PhCH_2\dot{C}HCH_2CH_2Ph \quad (8)$$

Steady-state treatment of eqs 4–8 leads to an expression (eq 9) for the dependence of the $PhCH_2CH_3/PhCH_3$ ratio on the concentration of DPB. At infinite dilution, eq 8

$$PhCH_2CH_3/PhCH_3 = [k_{4a}/(k_{4a} + k_{4b}) + (k_{-8}/k_6)[1]]/[k_{7b}/(k_{7a} + k_{7b}) + (k_8/k_5)[1]] \quad (9)$$

would cease and the product ratio would be determined by the selectivities of the hydrogen-abstraction reactions (eqs 4 and 7). At infinite concentration of DPB, eq 8 reaches equilibrium and the product ratio is determined by $(k_{-8}/k_8)(k_5/k_6)$.

Results

Surface-attached DPB (≈DPB or **4**) was prepared at saturation coverages by the condensation of p-$HOC_6H_4(CH_2)_4Ph$ (HODPB) with the surface hydroxyl groups of a high-purity fumed silica at 225 °C. The surface cov-

$$\equiv SiOH + p\text{-}HOC_6H_4(CH_2)_4Ph \rightarrow \underset{\mathbf{4}}{\equiv SiOC_6H_4(CH_2)_4Ph} + H_2O \quad (10)$$

erage, expressed as mmol of organic per gram of derivatized silica, was determined by a base hydrolysis procedure which liberates the phenol for GC analysis and quantitation. Two batches of ≈DPB were prepared with coverages of 0.504 and 0.485 mmol g^{-1} with purity of the recovered phenol of 99.8 and 99.9%, respectively. Lower coverages of ≈DPB were prepared in a similar fashion by limiting the phenol to surface hydroxyl ratio. This procedure appears to provide a random distribution of substrate on the silica surface as indicated by the results from the thermolysis of ≈DPP at lower coverages.[7] Three batches were prepared with coverages of 0.117 mmol g^{-1}, 0.084 mmol g^{-1}, and 0.054 mmol g^{-1} with purities of 99.7$_5$, 99.6, and 99.8%, respectively. Two-component surfaces were prepared in a similar fashion by condensation of a mixture of phenols (HODPB with p-HOC_6H_4Ph (HOBP) or p-$HOC_6H_4CH_2Ph$ (HODPM)) with the surface hydroxyls of a fumed silica. The surface coverage for ≈DPB/≈BP was 0.072/0.566 mmol g^{-1} and for ≈DPB/≈DPM was 0.060/0.465 mmol g^{-1} with purities of 99.9 and 99.8%, respectively.[14]

Thermolysis of ≈DPB. Surface-attached DPB was placed in a T-shape Pyrex tube, evacuated, and sealed. The tube was heated to 400 °C and the volatile organics were collected as they formed in a cold trap. The surface-attached products (designated as ≈) were removed, as the corresponding phenols, from the silica surface by base hydrolysis and silylated to the corresponding trimethylsilyl ethers. The products were analyzed by GC and GC/MS and quantitated by use of internal standards. Duplicate thermolyses were run on all batches and product distributions and rates were in good agreement (±10%) of each other.

Thermolysis of ≈DPB (0.485 mmol g^{-1}) was studied at 400 °C, and the results are presented in Table I. The numbers in the table are presented on a 100 relative mole basis. We find that the total C-16 product equivalent basis to be a more accurate measure of ≈DPB conversion than ≈DPB consumed, since the latter is calculated as a small difference of two large numbers (based on three separate analyses).

The thermolysis rate of ≈DPB could be accelerated by the addition of benzyl phenyl ether (BPE), a known free-radical initiator.[11] Thermolysis of ≈DPB (0.485 mmol g^{-1}) at 400 °C for 10 min afforded a conversion of 1.9 and 2.3%. When ≈DPB was mixed with 11 and 19 mol % BPE (the effective concentration of BPE is not known since it distills out of the heated zone into the cold trap with 88 and 64% recovered unchanged) the conversion increased to 3.3 and 4.4%, respectively.

A summary of the thermolysis results for ≈DPB at lower surface coverages and in the presence of spacer molecules, diphenylmethane and biphenyl, are presented in Table II. No new products were detected in these experiments while

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(14) (a) Previous work on ≈DPP/≈BP showed that similar thermolysis results were obtained independent of the method of synthesis of the two-component surface, suggesting that the substrates were randomly distributed on the surface. (b) Buchanan, A. C., III; Britt, P. F.; Biggs, C. A. *Energy Fuels* **1990**, *4*, 415.
(15) (a) Small quantities of ≈DPB (1–10%) are detached from the surface during the thermolysis of ≈DPB. This results from condensation of an adjacent hydroxyl group with a surface-attached phenol to eliminate the phenol and form a siloxane linkage, analogus to the dehydroxylation of silica at elevated temperatures. (b) Iler, R. K. *The Chemistry of Silica*; Wiley-Interscience: New York, 1979; Chapter 6.

Table I. Products from Thermolysis of ≈$Ph(CH_2)_4Ph$ at 0.485 mmol g^{-1} at 400 °C

time (min)[a]	5.3	10	10	20	30	40	60
charged (μmol)[b]	154	162	157	166	162	161	156
≈DPB recovered[c,d]	97.1	95.6	99.7	92.7	92.1	88.1	74.6
≈DPB consumed[c,e]	2.9	4.4	0.3	7.3	7.9	11.9	25.4
total products							
C-16 equiv, rel[f]	1.2	1.9	2.3	4.5	7.6	10.9	16.9
sum mol, rel[g]	2.3	3.9	4.5	8.8	14.6	21.1	32.6
products (mol, rel)[c]							
$PhCH_3$	0.27	0.41	0.48	0.96	1.45	2.23	3.49
$PhCH_2CH_3$	0.32	0.51	0.59	1.13	1.81	2.68	4.08
$PhCH{=}CH_2$	0.31	0.51	0.60	1.17	2.06	3.17	5.17
$PhCH_2CH{=}CH_2$	0.28	0.46	0.55	1.01	1.72	2.56	3.89
$PhC(CH_3){=}CH_2$	0.02	0.02	0.02	0.03	0.05	0.07	0.13
$PhCH{=}CHCH_3$	0.00	0.00	0.00	0.01	0.02	0.04	0.07
≈$PhCH_3$	0.27	0.49	0.52	1.13	1.96	2.98	4.37
≈$PhCH_2CH_3$	0.32	0.55	0.61	1.23	2.18	3.07	5.00
≈$PhCH{=}CH_2$	0.26	0.44	0.51	0.90	1.38	1.62	2.27
≈$PhCH_2CH{=}CH_2$	0.25	0.40	0.48	0.82	1.19	1.36	1.66
≈$PhCH_2CH_2CH_3$	0.00	0.00	0.00	0.00	0.02	0.05	0.13
≈$PhC(CH_3){=}CH_2$	0.00	0.01	0.00	0.03	0.07	0.11	0.23
≈$PhCH{=}CHCH_3$	0.03	0.04	0.05	0.14	0.32	0.51	0.92
≈DPP	0.00	0.00	0.00	0.00	0.07	0.10	0.21
≈DPP≈[h]	0.00	0.00	0.03	0.07	0.07	0.10	0.22
≈DPB≈[i]	0.00	0.00	0.00	0.02	0.06	0.11	0.23
≈$C_{24}H_{24}$≈[j]	0.00	0.00	0.00	0.11	0.14	0.25	0.36
mass balances[k]							
free C_8/≈C_8	1.10	1.03	1.04	0.98	0.98	1.09	1.09
free C_9/≈C_7	1.12	0.98	1.05	0.87	0.88	0.87	0.90
free C_7/≈C_9	0.97	0.93	0.90	0.97	0.95	1.15	1.26
selectivity							
$PhCH_2CH_3/PhCH_3$	1.19	1.24	1.23	1.18	1.25	1.20	1.17
$PhCH_2CH{=}CH_2$[l]$/PhCH_3$	1.11	1.17	1.19	1.09	1.23	1.20	1.17
$PhCH{=}CH_2/PhCH_2CH_3$	0.97	1.00	1.02	1.03	1.14	1.18	1.27

[a] Heat-up time is 1 min. [b] (Grams ≈DPB) × coverage. [c] One hundred relative mole basis. [d] HODPB found on the surface and in the trap.[15] [e] (≈DPB charged) − (≈DPB recovered). [f] Molar sum converted to a C-16 equivalent basis. [g] Molar sum of all the products detected. [h] 1,3-Bis(p-hydroxyphenyl)propane. [i] 1,4-Bis(p-hydroxyphenyl)butane. [j] Defined in text. [k] Defined in the text eqs 18–20. [l] Includes isomers $PhCH{=}CHCH_3$ and $PhC(CH_3){=}CH_2$.

Table II. Rate and Selectivity in Thermolysis of ≈DPB at 400 °C

surface composition	coverage (mmol g^{-1})	initial rate[a] (% h^{-1})	selectivity 5/6[b]	selectivity 8/5[c]
≈DPB	0.485	15.6	1.19	0.96
≈DPB[d]	0.117	9.5	2.0	1.01
≈DPB[d]	0.087	6.1	2.0	1.01
≈DPB[d]	0.054	3.3	2.07	1.08
≈DPB/≈BP[d]	0.072/0.566	7.3	2.9	1.06
≈DPB/≈DPM[d]	0.060/0.465	17.8	1.19	0.96[e]

[a] Determined from the slopes of the linear regressions of ≈DPB conversion vs time (see Figure 2). [b] Determined from the average $PhCH_2CH_3/PhCH_3$ ratio (error analysis in text). [c] Determined from the y-intercept at zero conversion from the plot of $PhCH{=}CH_2/PhCH_2CH_3$ vs conversion (see Figure 1). [d] Reactions studied from ca. 1–10% conversion (5–7 points); see supplementary material. [e] Selectivity was independent of conversion and reported as the average ±3%.

the secondary products (≈DPP, ≈DPP≈, and ≈DPB≈) were not found in the thermolysis of the two-component surfaces. The tabular data of product yields is included as supplementary material.

Discussion

Saturation Coverage. Cracking of ≈DPB at 400 °C forms eight major products in nearly equal amounts at low conversion (<4%) as shown in eq 11. This reaction is

$$\approx Ph(CH_2)_4Ph \; (\mathbf{4}) \rightarrow PhCH_3 + \approx PhCH_2CH{=}CH_2 + PhCH_2CH_3 + \approx PhCH{=}CH_2 + PhCH{=}CH_2 + \approx PhCH_2CH_3 + PhCH_2CH{=}CH_2 + \approx PhCH_3 \quad (11)$$

analogous to the thermal cracking of DPB (eq 1) except the additional product pairs result from the nonequivalence of the two ends of the molecule as a consequence of surface attachment. As conversion increases, the surface-attached olefinic products undergo secondary reactions but the gas-phase products remain relatively unchanged since they distill out of the heated zone into the cold trap.

Comparison of the rate of reaction of liquid DPB and high coverage ≈DPB at 400 °C for 10 min shows that ≈DPB reacts 10-fold faster.[9] Moreover, although the rate of decomposition of liquid DPB exhibits a mildly autocatalytic behavior, the rate of ≈DPB decomposition calculated at each point in time was independent of conversion (see below). This alteration in rate behavior could indicate that surface immobilization is hindering the bimolecular termination reactions. This hypothesis is supported by results from the thermolysis of ≈BB, where the bimolecular coupling reaction of 1,2-diphenyl-1-ethyl radicals, dominant in liquid phase, was severely hampered by surface immobilization.[6] As with DPB,[11] the rate for decomposition of ≈DPB could be accelerated by the addition of a small amount of a radical initiator. Therefore, based on the similarities in the product distribution and the effect of free-radical initiators on the rate, thermal cracking of ≈DPB seems to proceed by a free-radical-chain mechanism analogous to DPB in the liquid phase.

A reasonable free-radical-chain mechanism for the decomposition of ≈DPB is shown in eqs 12–16.

$$\approx PhCH_2CH_2CH_2CH_2Ph \; (\mathbf{4}) \rightarrow [\approx]PhCH_2^{\bullet} + [\approx]PhCH_2CH_2CH_2^{\bullet} \quad (12)$$

$$[\approx]PhCH_2CH_2CH_2^{\bullet} \rightarrow [\approx]PhCH_2^{\bullet} + CH_2{=}CH_2 \quad (13)$$

$$[\sim]PhCH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_3 + \sim Ph\dot{C}HCH_2CH_2CH_2Ph \;\; (\mathbf{5}) \quad (14a)$$

$$[\sim]PhCH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_3 + \sim PhCH_2\dot{C}HCH_2CH_2Ph \;\; (\mathbf{6}) \quad (14b)$$

$$[\sim]PhCH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_3 + \sim PhCH_2CH_2\dot{C}HCH_2Ph \;\; (\mathbf{7}) \quad (14c)$$

$$[\sim]PhCH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_3 + \sim PhCH_2CH_2CH_2\dot{C}HPh \;\; (\mathbf{8}) \quad (14d)$$

$$\mathbf{5} \rightarrow \approx PhCH{=}CH_2 + PhCH_2CH_2^{\bullet} \quad (15a)$$

$$\mathbf{6} \rightarrow \approx PhCH_2CH{=}CH_2 + PhCH_2^{\bullet} \quad (15b)$$

$$\mathbf{7} \rightarrow \approx PhCH_2^{\bullet} + PhCH_2CH{=}CH_2 \quad (15c)$$

$$\mathbf{8} \rightarrow \approx PhCH_2CH_2^{\bullet} + PhCH{=}CH_2 \quad (15d)$$

$$[\sim]PhCH_2CH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_2CH_3 + \mathbf{5} \quad (16a)$$

$$[\sim]PhCH_2CH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_2CH_3 + \mathbf{6} \quad (16b)$$

$$[\sim]PhCH_2CH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_2CH_3 + \mathbf{7} \quad (16c)$$

$$[\sim]PhCH_2CH_2^{\bullet} + \mathbf{4} \rightarrow [\sim]PhCH_2CH_3 + \mathbf{8} \quad (16d)$$

The brackets in the equations are used as a simplification to indicate that two equations could be written, one with a surface-attached species and one with a gas-phase species. The chain propagation steps are analogous to those for DPB except there are four chemically distinct radicals **5**–**8** which undergo β-scission reactions to form [≈]PhCH=CH$_2$ and [≈]PhCH$_2$CH=CH$_2$. The [≈]PhCH$_2^{\bullet}$ and [≈]-PhCH$_2$CH$_2^{\bullet}$ radicals continue the chain by hydrogen abstraction to form [≈]PhCH$_3$ and [≈]PhCH$_2$CH$_3$.

Radicals **8** and **5** are nonequivalent as a consequence of the *p*-silyloxy substituent. The effect of the *p*-silyloxy substituent on the regioselective thermal cracking of ≈DPP was modeled by the thermal decomposition of *p*-(CH$_3$)$_3$SiOC$_6$H$_4$(CH$_2$)$_3$Ph at 375 °C. The results indicate that there is a slight inherent selectivity of 1.10 ± 0.02 for formation of the benzyl radical that is para to the silyloxy substituent.[7] Therefore, in hydrogen-abstraction steps 14 and 16, benzylic radicals **8** and **5** should be formed in nearly equal amounts and should be favored over aliphatic radicals **6** and **7** since **5** is estimated to be more stable than **6** by ca. 10 kcal mol^{-1}.[13] Since these radicals undergo unique β-scission reactions, the selectivity in the hydrogen-abstraction reactions can be determined by the product yields. At low conversion (<4%), the yields of volatile and surface-attached products are, in fact, approximately equal (see Table I), indicating little or no selectivity in the hydrogen-abstraction reactions that produce **5**–**8**. The yields of PhCH$_2$CH$_3$/PhCH$_3$ (as a probe for the selectivity of formation of **5**/**6**) are dependent on surface coverage and temperature. In order to rationalize the PhCH$_2$CH$_3$/PhCH$_3$ ratio of ca. unity, an intermolecular hydrogen-transfer reaction analogous to eq 8 is included. However, as a consequence of the nonequivalence of the methylene carbons, six different reactions can be written, one of which is shown in eq 17. These reactions

$$\approx Ph\dot{C}HCH_2CH_2CH_2Ph + \mathbf{4} \rightleftharpoons \mathbf{4} + \approx PhCH_2\dot{C}HCH_2CH_2Ph \quad (17)$$

provide a pathway for benzylic and aliphatic radicals (**5**–**8**) to equilibrate before β-scission, thus altering the predicted PhCH$_2$CH$_3$/PhCH$_3$ ratio from ≫1, based on the selectivity of hydrogen-abstraction reactions in eqs 14 and 16, to approximately unity. It is interesting that in addition to equilibrating the benzylic and aliphatic radical sites, eq 17 also provides a mechanism for the migration of the radicals on the surface. Thus, the decomposition of ≈DPB at saturation coverage and at low conversion parallels the decomposition of DPB in the liquid phase indicating that the organic saturated surface approximates a two-dimensional liquid film in which the chain-carrying hydrogen-transfer reactions occur without diffusional restraints. The involvement of eq 17 on the surface in equilibrating benzylic and aliphatic radical centers is supported by studies at lower surface coverages and in the presence of spacer molecules, which are presented below.

As conversion increases, secondary products form at the expense of surface-bound olefinic products. At the highest conversion level studied (16.9%), 7.7 mol % of the products result from secondary reactions. The major secondary reaction results from the free-radical isomerization of [≈]PhCH$_2$CH=CH$_2$ to [≈]PhCH=CHCH$_3$ (3.1 mol %).[16] Although further studies are needed to determine the origin of [≈]PhC(CH$_3$)=CH$_2$ (1.1 mol %), a possible mechanism for its formation involves a 1,2-phenyl shift[16] of radical **6** or **7**, hydrogen-transfer reactions to form the 1,3-diphenyl-3-butyl radical, and β-scission.[17] Other secondary products were ≈DPP (0.6 mol %) and ≈DPP≈ (0.7 mol %) presumably from the reaction of ≈PhCH=CH$_2$ with [≈]PhCH$_2^{\bullet}$ followed by hydrogen abstraction. ≈DPB≈ (0.7 mol %) can be formed from the reaction of ≈PhCH=CH$_2$ with ≈PhCH$_2$CH$_2^{\bullet}$.[18] ≈PhCH$_2$CH$_2$CH$_3$ (0.4 mol %) apparently arises from the reduction of ≈PhCH$_2$CH=CH$_2$ since styrene and allylbenzene are known to be reduced to alkanes in the presence of hydrogen donors such as tetralin.[11,12,19] The final secondary product detected (1.1 mol %) has a *m*/*z* of 490 after silylation. This product is tentatively identified as a surface-diattached triphenylhexane (≈C$_{24}$H$_{24}$≈, *m*/*z* 490 after base hydrolysis and silylation) based on the formation of triphenylhexane from the reaction of **2** or **3** with styrene in the thermolysis of DPB.[9,18b]

Now that all the products have been identified, internal mass balances can be calculated (see Table I). The amount of products from vapor phase C$_7$, C$_8$, and C$_9$ fragments must equal the amounts of products from surface-attached C$_9$, C$_8$ and C$_7$ fragments, respectively. The ratios, defined in eqs 18–20, show no trend with conversion or with surface

$$\text{free } C_7/\text{surface } C_9 = (PhCH_3 + {\approx}DPP)/({\approx}PhCH_2CH{=}CH_2 + {\approx}PhC(CH_3){=}CH_2 + {\approx}PhCH{=}CHCH_3 + {\approx}PhCH_2CH_2CH_3) \quad (18)$$

$$\text{free } C_8/\text{surface } C_8 = (PhCH_2CH_3 + PhCH{=}CH_2)/({\approx}PhCH_2CH_3 + {\approx}PhCH{=}CH_2 + {\approx}DPP + {\approx}DPP{\approx} + {\approx}C_{24}H_{24}{\approx} + 2{\approx}DPB{\approx}) \quad (19)$$

$$\text{free } C_9/\text{surface } C_7 = (PhCH_2CH{=}CH_2 + PhCH{=}CHCH_3 + PhC(CH_3){=}CH_2)/({\approx}PhCH_3 + {\approx}DPP{\approx}) \quad (20)$$

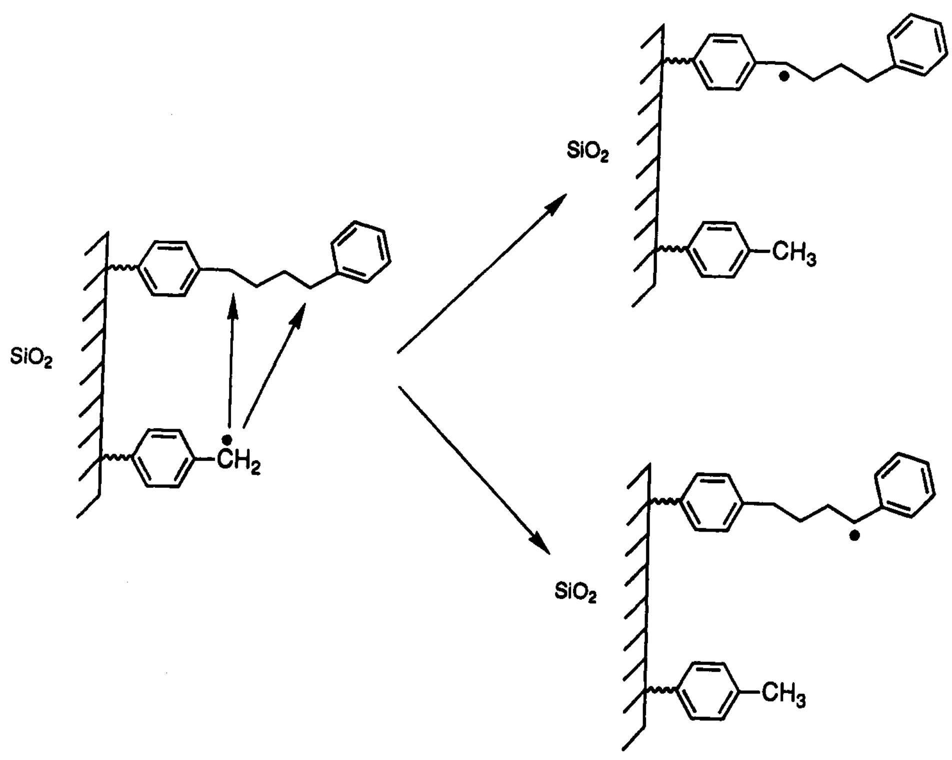
coverage. The average values from the thermolysis of ≈DPB at saturated coverages at 400 °C for C$_7$/≈C$_9$ = 1.04

(16) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8.

(17) No surface-attached 1,3-diphenylbutane was detected, but this could be a consequence of its low abundance or its thermal stability.

(18) (a) The formation of ≈DPB≈ from the reaction of ≈PhCH$_2$CH=CH$_2$ with ≈PhCH$_2^{\bullet}$ was excluded based on thermochemical kinetic data on DPB.[9] (b) This assignment will only be used in eq 19 to account for surface-attached C$_8$ fragments at high conversions.

(19) Benjamin, B. M.; Raaen, V. F.; Maupin, P. H.; Brown, L. L.; Collins, C. J. *Fuel* 1978, *57*, 269.



$\pm$ 0.05, $C_8/{\approx}C_8$ = 0.95 $\pm$ 0.09, and $C_9/{\approx}C_7$ = 1.0 $\pm$ 0.1 are within experimental error of the ideal value of unity. These results indicate that no major products have gone undetected and provide confidence in the quantitation.

In the thermolysis of DPB, the product distribution was dependent on the selectivities of the competing hydrogen abstraction reactions (eqs 4 and 7), the rates of β-scission (eqs 5 and 6), and the equilibration of the benzylic (2) and aliphatic (3) radicals (eq 8), see eq 9. Surface immobilization of the substrate and chain-carrying radicals should place restrictions on these competing processes and impact the product selectivity. In the thermolysis of ≈DPB at saturation coverages, the $PhCH_2CH_3/PhCH_3$ ratio[20] is 1.19 $\pm$ 0.05 for 1–17% conversion, indicating that the benzylic (5) and aliphatic (6) radicals are extensively equilibrated before β-scission, as in liquid DPB in which the ratio is 1.22 at <1% conversion. Ideally, the $PhCH{=}CH_2/PhCH_2CH{=}CH_2$ ratio,[20] derived from the other pair of benzylic (8) and aliphatic (7) radicals, should have a similar value but instead it is 1.03 at 1.2% conversion and 1.26 at 16.9% conversion. The difference in these ratios at low conversion can be explained by the $PhCH_2CH{=}CH_2/PhCH_3$ ratio, derived from the aliphatic radicals 7 and 6. Although there should be no thermodynamic preference in the hydrogen abstraction reactions (eqs 14b, 14c, 16b, and 16c), the $PhCH_2CH{=}CH_2/PhCH_3$ ratio is 1.16 $\pm$ 0.05 for 1–17% conversion indicating that β-scission of radical 7 is slightly faster than for radical 6 as a consequence of the *p*-silyloxy substituent which can stabilize ≈$PhCH_2^\bullet$. Since the 7/6 ratio is independent of conversion, the conversion dependence of $PhCH{=}CH_2/PhCH_2CH{=}CH_2$ ratio must result from the selective formation of styrene. A comparison of the product selectivities from the benzylic radicals 8 and 5 is shown in Figure 1 as a function of conversion for all the data at high coverage at 400 °C. A linear regression of the data gives a *y*-intercept less than unity (0.96, r^2 = 0.964), indicating a slight inherent selectivity for the formation of the benzylic radical para to the silyloxy substituent. As a result of surface immobilization, a selectivity develops with increasing conversion in the radical-chain process which favors the formation of benzylic radical 8 which produces $PhCH{=}CH_2$ and ≈ $PhCH_2CH_3$.

The conversion-dependent regioselectivity that leads to the preferential formation of 8 over 5 may be the result of spatial limitations imposed on the hydrogen-transfer reactions by surface immobilization. As conversion increases, the distance between ≈DPB molecules and the hydrogen-abstracting radicals, ≈$PhCH_2^\bullet$ and ≈ $PhCH_2CH_2^\bullet$, increases favoring hydrogen abstraction at the carbon farthest from the surface, as illustrated below. Product molecules on the surface can also play an interesting role in the selectivity of hydrogen-transfer reactions. They may act as physical barriers to hydrogen-transfer reactions or they may participate in hydrogen-exchange reactions (for example, 5 + ≈$PhCH_3$ → ≈DPB + ≈ $PhCH_2^\bullet$) to provide a mechanism for the migration of the radical center on the surface to an unreacted ≈DPB. Further insights into the origin of this unique selectivity in hydrogen-transfer reactions were gained from studies at lower surface coverages, which probed the distance dependence on product selectivity, and in the presence of spacer molecules that can act either as a barrier to hydrogen-transfer reactions or that can participate in hydrogen-transfer reactions.

Low Coverages. Three batches of ≈DPB at lower surface coverages were prepared and their thermolysis studied at 400 °C (see supplementary material). The rate of decomposition of ≈DPB was reduced as shown in Figure 2. No new products were detected, and the quantities of secondary products were reduced compared to saturation coverages. Duplicate thermolysis runs were in good agreement ($\pm$10%), although there is a little more scatter in the data at lower coverages as a consequence of the small quantities of products analyzed. However, the material and fragment balances were good with average fragment balances $C_7/{\approx}C_9$, $C_8/{\approx}C_8$, and $C_9/{\approx}C_7$ for the 0.117 mmol g^{-1} batch of 0.97 $\pm$ 0.06, 1.03 $\pm$ 0.06, and 0.9 $\pm$ 0.1; for the

(20) The gas-phase products provide a more accurate representation of the product selectivity since they distill out of the heated zone and are not consumed by secondary reactions.

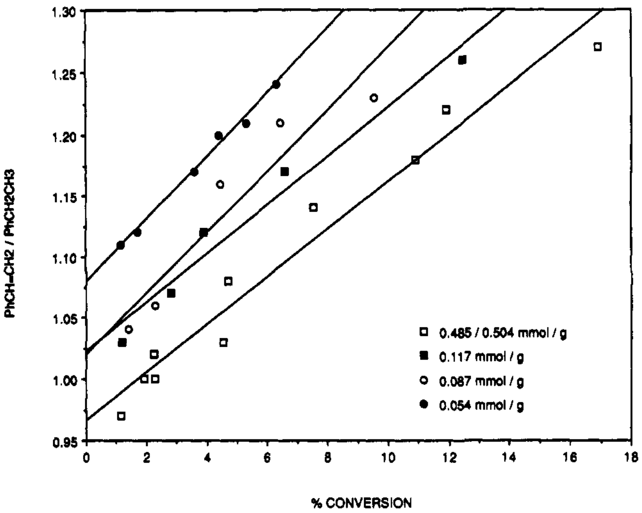


Figure 1. Styrene to ethylbenzene regioselectivity in the thermolysis of ≈DPB at 400 °C as a function of conversion and surface coverage. Linear regression gives a slope and y-intercept for the coverages of 0.485, 0.117, 0.087 and 0.054 mmol g^{-1} as 0.019, 0.96 (r^2 = 0.964); 0.020, 1.01 (r^2 = 0.967); 0.026, 1.01 (r^2 = 0.918); and 0.024, 1.08 (r^2 = 0.983).

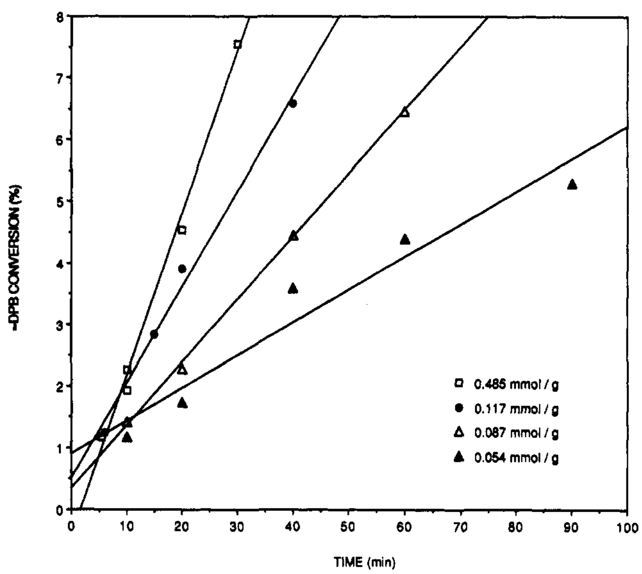


Figure 2. Rate of conversion of ≈DPB as a function of surface coverage at 400 °C.

0.087 mmol g^{-1} batch of 0.93 ± 0.08, 1.01 ± 0.09, and 0.91 ± 0.08; and for the 0.054 mmol g^{-1} batch of 0.90 ± 0.09, 0.98 ± 0.09, and 1.0 ± 0.1, respectively.

Comparison of the data in Table II shows an increase in the $PhCH_2CH_3/PhCH_3$ ratio at lower coverages. This product ratio probes the bimolecular hydrogen exchange reactions in eq 17 which equilibrate benzylic and aliphatic radicals. Increasing the separation between ≈DPB molecules by lowering the surface coverage hinders this bimolecular reaction and alters the product ratios. It is surprising that decreasing the surface coverage from 0.117 to 0.054 mmol g^{-1} does not have a greater affect on the selectivity. From the thermolysis of DPB, a plot of concentration (M) vs $PhCH_2CH_3/PhCH_3$ provided a best fit (eq 21), in the form of eq 9.[9] This equation predicts a

$$PhCH_2CH_3/PhCH_3 = (0.90 + 0.65[DPB])/(0.16 + 0.75[DPB]) \quad (21)$$

$PhCH_2CH_3/PhCH_3$ ratio of 1.16 and 1.87 for liquid DPB (3.2 M) and DPB diluted ca. 4-fold with *m*-terphenyl which is similar to the experimentally measured value of 1.22 and 2.08, respectively. Although it is difficult to equate concentration and surface coverage, analysis of the surface coverage effects on the $PhCH_2CH_3/PhCH_3$ ratio in ≈DPB with an equation analogous to eq 21 predicts values of 1.89, 2.15, and 2.65 for the surface coverage dilution factors of 4.1, 5.5, and 9.0. Hence, these substantial dilution factors predict only modest changes in this product ratio.

The $PhCH{=}CH_2/PhCH_2CH_3$ ratio (as a probe for the selectivity of formation of 8 to 5) is plotted as a function of ≈DPB conversion for all coverages in Figure 1. It is obvious, even at low conversions, that lowering the surface coverage enhances the regioselectivity in hydrogen-transfer reactions to form the radical farthest from the surface. It is difficult to determine if there is curvature in the plots or if it is scatter in the data. In either case, a trend exists in the data in which the $PhCH{=}CH_2/PhCH_2CH_3$ ratio increases with conversion. A similar coverage and conversion dependent selectivity has been reported for the thermal decomposition of a ≈DPP which favors hydrogen-transfer reactions at the carbon farthest from the surface.[7] The role that surface-attached product molecules play in this selectivity is unclear, but insights should be gained through the study of the two-component surfaces.

Reaction Rates. The rates of ≈DPB conversion at 400 °C are shown in Figure 2 for all surface coverages at low conversion (<8%) where secondary products have a minimal impact on the rate. Linear regression of the data for surface coverages of 0.485, 0.117, 0.087, and 0.054 mmol g^{-1} gives the initial rates (% conversion h^{-1}) of 15.6 (r^2 = 0.993), 9.5 (r^2 = 0.991), 6.1 (r^2 = 0.999), and 3.3 (r^2 = 0.941), respectively. At lower surface coverages, the linear regressions extrapolate to a positive conversion at time zero which could indicate a fast component exists at the very early stages of the reaction. If the ≈DPB molecules were clustered on the surface, the initial thermolysis rates would be faster than if the material were evenly distributed and the rate would decrease as these clusters are consumed. However, hydrogen-transfer reactions at these isolated sites of high local coverages of ≈DPB would proceed without restriction (eq 17) and the $PhCH_2CH_3/PhCH_3$ product ratio would be conversion dependent, contrary to what is observed at these low coverages. Therefore, the explanation above appears unlikely. In the thermolysis of ≈DPP,[7] similar deviations in the rate plots were detected. It was deduced that the initial fast component at early conversions was indigenous to the surface. Although this might not be the explanation for this system, the similarity is noted.

The data in Figure 2 show that the rate of decomposition of ≈DPB depends on the surface coverage in a nonlinear fashion. A decrease in surface coverage by a factor of 4.1, 5.5, and 9.0 lowers the rate of decomposition by a factor of 1.6, 2.6, and 4.7, respectively. The rate of decomposition of ≈DPB is more sensitive to surface coverage than DPB is to concentration. This must reflect the sensitivity in the rate of the bimolecular hydrogen-transfer reactions in eqs 14, 16, and 17 to the proximity of the ≈DPB to the surface-bound radicals. The rate depression is even more dramatic when there are no chain-carrying radicals in the gas phase which can propagate the chain without diffusional restraints. Preliminary results from the thermolysis of a doubly attached 1,4-diphenylbutane (≈DPB≈, 0.113 mmol g^{-1}), as a model for the cross-links in coal, show the rate of conversion is depressed by a factor of ca. 7 compared to ≈DPB at 0.117 mmol g^{-1} at 400 °C.[21] This

(21) Britt, P. F. Presented at the 200th National Meeting of the American Chemical Society, Washington, D.C., August 1990; poster PETR 1.

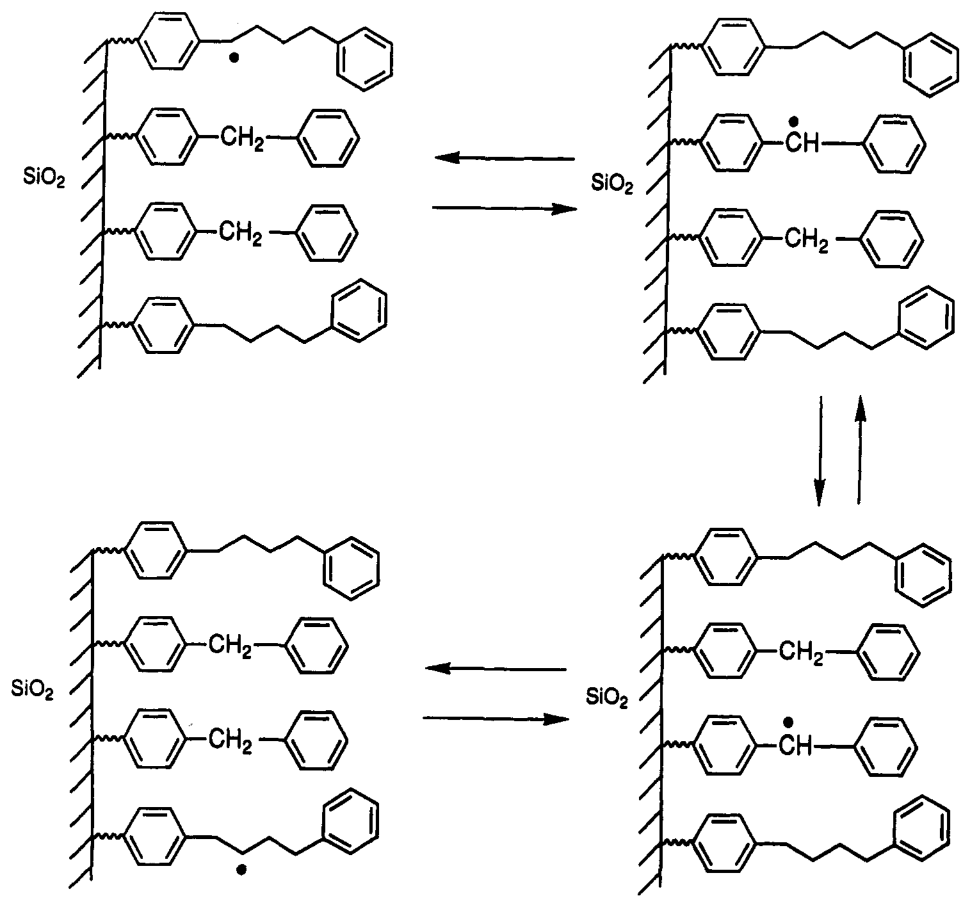


Figure 3. Pathway for equilibration of benzylic and aliphatic radicals at low ≈DPB surface coverages under conditions of restricted diffusion by radical migration involving ≈DPM.

highlights the dramatic impact that restricted radical diffusion can have on altering the rate of free-radical reactions. Under conditions of restricted diffusion, the rate constants for hydrogen-transfer reaction must be a function of the distance between radicals and substrate molecules and the conformational mobility of the species. As a consequence of the limitations placed on the free-radical reaction pathways in constrained environments, alterations in product selectivities can develop.

Spacer Molecules. In order to assess the effect of neighboring aromatic molecules on the hydrogen-transfer reactions involved in the free-radical decomposition of ≈DPB, two-component surfaces were synthesized containing a low coverage of ≈DPB with either a surface-attached biphenyl (≈BP) or a surface-attached diphenylmethane (≈DPM). Attempts were made to prepare coverages of ≈DPB close to those previously made since the rate of decomposition and product selectivities are sensitive to surface coverage. Results from the thermolysis of ≈DPB/≈BP (0.072/0.566 mmol g^{-1}) and ≈DPB/≈DPM (0.060/0.465 mmol g^{-1}) are summarized in Table II. No new products were detected, and recovered HOBP and HODPM were 96 ± 6 and 94 ± 8%, respectively.[22] The average fragment balances $C_7/{\approx}C_9$, $C_8/{\approx}C_8$, and $C_9/{\approx}C_7$ for the ≈DPB/≈BP batch were 0.8 ± 0.2, 0.98 ± 0.07, and 1.00 ± 0.08 and for the ≈DPB/≈DPM batch were 0.92 ± 0.06, 0.98 ± 0.06, and 0.91 ± 0.05, respectively. The origin of the decreased $C_7/{\approx}C_9$ for the ≈DPB/≈BP sample is unclear.

In the thermolysis ≈DPB/≈BP, it was anticipated that the rate of decomposition of ≈DPB would be reduced as a consequence of the biphenyl molecules shielding the hydrogen-abstracting radicals from the unreacted ≈DPB molecules. Interestingly, coattached biphenyl has little influence on the rate and 8/5 selectivity in the thermolysis of ≈DPB. Similar effects have been observed in the thermolysis of ≈DPP at 375 °C in which the presence of coattached biphenyl or naphthalene, as inert spacers, had virtually no effect on the rate and selectivity of the reaction.[14b] However, the 5/6 selectivity increases substantially when the spacer molecule is present. These results indicate that coattached biphenyl molecules hinder the bimolecular hydrogen-transfer reactions on the surface such as eq 17 that equilibrate benzylic and aliphatic radicals.

Coattached diphenylmethane moieties have a dramatic impact on the rate and selectivity of ≈DPB thermolysis as shown in Table II. The rate of decomposition of ≈DPB increases by a factor of 5.4 in the presence of ≈DPM compared to a similar coverage of ≈DPB without the spacer. The presence of a hydrogen donor such as tetralin had little if any effect on the rate of decomposition of liquid DPB,[9] indicating that a unique process is occurring as a consequence of restricted diffusion to accelerate the rate of decomposition of ≈DPB. The presence of ≈DPM decreased the 8/5 ratio to value similar to that found at high coverage of ≈DPB at low conversion and was independent of conversion. The 5/6 ratio was also decreased to a value similar to that found for high coverages indicating that the benzylic and aliphatic radicals were extensively equilibrated. These results confirm the hypothesis that for free-radical reactions under restricted diffusion, product selectivities arise from the conformational limitations of the hydrogen-abstracting radicals and the pool of readily available hydrogen donors.

These results indicate that rapid hydrogen-transfer reactions can occur on the surface that allow radical centers

(22) ≈BP and ≈DPM are stable at 400 °C for 4 h.[6]

to migrate across the surface. This process effectively decreases the distance between surface-bound radicals and ≈DPB moieties and overcomes the limitations imposed by restricted substrate mobility. As depicted in Figure 3, this radical mobility also provides an additional pathway to interconvert benzylic and aliphatic radical sites which impacts the product selectivity. Since the rate has dramatically increased, hydrogen-transfer reactions between the ≈DPB and ≈DPM molecules must be fast compared to β-scission. These results also suggest that similar types of bimolecular hydrogen-exchange reactions can occur with the product molecules, such as $\approx PhCH_3$, $\approx PhCH_2CH_3$, and $\approx PhCH_2CH{=}CH_2$.

Additional evidence for the involvement of ≈DPM in rapid hydrogen-transfer reactions comes from the thermolysis of ≈DPP/≈DPM (ca. 0.15/0.40 mmol g^{-1}) at 375 °C in which the rate of decomposition increased by a factor of 15–19 and the regioselectivity in hydrogen-transfer reactions was lost[14b] as in the thermolysis of ≈DPB/≈DPM. Moreover, the rate of thermolysis of ≈DPP/≈DPM-d_2 (0.16/0.36 mmol g^{-1}) at 375 °C was reduced by a factor of ca. 1.6, and gas-phase and surface-bound toluene contained deuterium.[14b] This provides evidence that hydrogen-transfer reactions occur between both chain-carrying radicals and ≈DPM molecules.

Relevance to Coal Conversion. The results presented in this study highlight the importance of the spatial distribution of hydrogen donors to the free radicals generated from the bond homolysis or β-scission reactions to the efficiency and selectivity of the decomposition reactions. In the thermal degradation of coal, radicals formed from the cracking of the short aliphatic crosslinks will be constrained by the rigid or highly viscous network structure of coal. Our work has shown that radical-chain decomposition reactions can efficiently occur under these diffusional constraints but are highly sensitive to the restraints placed on hydrogen-transfer reactions by the local environment. When the reactive groups are chemically dilute, regioselective hydrogen-transfer reactions can occur at these elevated temperatures to afford intermediates not predicted by thermochemical considerations. If hydrogen donors are present, hydrogen-transfer reactions can occur which allow radicals to migrate to a different reaction site. This hydrogen-shuttling reaction also provides a mechanism for activating the decomposition of linkages in environments that are not accessible to solvent-derived radicals such as those found in coal liquefaction and provides a route for the generation of the more reactive aliphatic radicals, which can then play a significant role in the low temperature decomposition reactions. It is evident from this work that the presence or absence of hydrogen donors in the local environment plays a significant role in the product distribution and rate of decomposition. However, mobile radicals from a hydrogen-donating solvent may remove some of the reaction dependence on the local structure of the substrate.

Experimental Section

GC analyses were performed on a Hewlett-Packard 5880A or 5890 Series II gas chromatograph equipped with a J & W Scientific 30 m × 0.25 m i.d. DB-1 capillary column (0.25-mm film thickness) and flame ionization detection. Detector response factors were experimentally determined relative to an internal standard in all cases where authentic samples were available or estimated based on carbon numbers. Mass spectra were obtained at 70 eV on a Hewlett-Packard 5995A GC/MS equipped with a capillary column identical with that used for GC analysis.

Benzene was distilled from lithium aluminum hydride before use. High-purity acetone (B & J capillary GC/GC-MS solvent), methylene chloride (Baker capillary analyzed), and water (Baker HPLC grade) were used as received. Cumene was fractionally distilled (2×) and 2,5-dimethylphenol was recrystallized (3×) from hexanes. p-(4-Phenylbutyl)phenol[23] (HODPB) and p-(2-phenylethyl)phenol[6a] (HOBB) were prepared as previously described and purified by repeated crystallizations from hexanes affording a purity of >99.9% by GC. Commercially available p-phenylphenol and p-benzylphenol were repeatedly recrystallized from benzene/hexanes until purity was >99.9% by GC.

Preparation of ≈DPB (4). Detailed procedures for the preparation, thermolysis, and analysis of surface-attached diphenylalkanes have been previously described,[6,7] and only highlights will be presented here. Saturation coverages of ≈DPB were prepared by absorbing HODPB (2.25 equiv) onto dried fumed silica (Cabosil M-5, Cabot Corp., 200 ± 25 m^2 g^{-1}, ca. 4.5 OH nm^{-2} ≡ 1.5 mmol OH g^{-1}) by solvent evaporation of a benzene slurry. Surface coverages of 0.117, 0.087, and 0.054 mmol g^{-1} were prepared by using a mole ratio of silica hydroxyl groups/phenol of 8.04, 15.3, and 25.4, respectively. Two component surfaces were prepared by solvent evaporation of a benzene slurry of silica (1 equiv of hydroxyl groups) and a mixture of phenols (2.3 equiv) with a mole ratio of HOBP or HODPM to HODPB of 21.0 or 17.2, respectively. Surface attachment was performed in an evacuated (10^{-5} Torr), sealed tube at 225 °C for 1 h in a fluidized sand bath. Excess phenol was sublimed from the sample by heating to 285–295 °C for 1 h at 5 × 10^{-3} Torr. Surface coverage was determined as follows: stirred ≈DPB (100–300 mg) in 1 N NaOH (40 mL) overnight, added HOBB in 1 N NaOH as an internal standard, acidified with HCl (pH <5), extracted with CH_2Cl_2 (3 × 7 mL), washed combined organic layers with H_2O (1 × 10 mL), dried over $MgSO_4$, removed solvent under reduced pressure, and silylated with N,O-bis(trimethylsilyl)trifluoroacetamide in pyridine (2.5 M, 0.35 mL). Multiple analyses provided surface coverages with reproducibility of ±3%.

Thermolysis Procedure. Typically, ≈DPB (0.2–1.8 g) was placed in one end of a T-shaped Pyrex tube, evacuated, and sealed at ca. 2 × 10^{-6} Torr. The sample was inserted into a preheated temperature-controlled furnace (±1.0 °C) fitted with a copper sample holder, and the other end was placed in a liquid nitrogen bath. The volatile products in the trap were dissolved in acetone (0.1–0.3 mL) containing cumene as an internal standard and analyzed by GC and GC/MS. The HODPB in the trap was determined by addition of HOBB in acetone as an internal standard, evaporation of the solvent, silylation, and analysis by GC. The surface-attached products were analyzed by a base-hydrolysis procedure analogous to that used for surface coverage assay except 2,5-dimethylphenol and HOBB were added as internal standards.

Product Assignments. Product assignments were based on comparisons of mass spectra and GC retention times of the products were authentic samples, either prepared commercially or by literature procedures, for $PhCH_3$, $PhCH_2CH_3$, $PhCH{=}CH_2$, $PhCH_2CH{=}CH_2$, $PhCH{=}CHCH_3$, $PhC(CH_3){=}CH_2$, p-cresol, p-ethylphenol, p-vinylphenol,[24] p-allylphenol,[25] p-(1-propenyl)phenol,[26] p-isopropenylphenol,[27] p-propylphenol, p-(3-phenylpropyl)phenol,[7] 1,3-bis(p-hydroxyphenyl)propane,[28] and 1,4-bis(p-hydroxyphenyl)butane[28] (phenols were also analyzed as their trimethylsilyl ethers).

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many valuable discussions.

Registry No. DPB, 1083-56-3; HODPB, 36940-99-5; BP, 92-52-4; DPM, 101-81-5; silica, 7631-86-9.

Supplementary Material Available: Tabular data of product yields, mass balances and selectivities for thermolysis of ≈DPB at 400 °C at coverages of 0.504, 0.117, 0.087, and 0.054 mmol g^{-1} and for the two component surfaces ≈DPB (0.072)/≈BP (0.566) and ≈DPB (0.060)/≈DPM (0.465) (6 pages). Ordering information is given on any current masthead page.

Excited State Selectivity in the Thermolysis of a 3,4-Diaryl-3,4-dimethyl-1,2-dioxetane

William H. Richardson,* Greg Batinica, Kasia Janota-Perret, Todd Miller, and Dongming Shen

Department of Chemistry, San Diego State University, San Diego, California 92182

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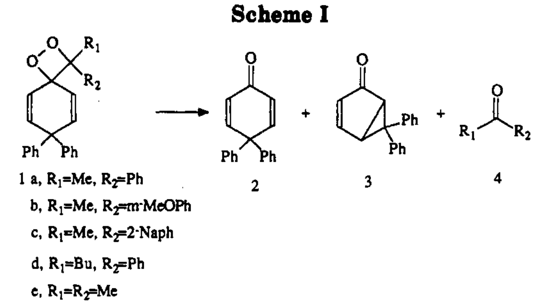
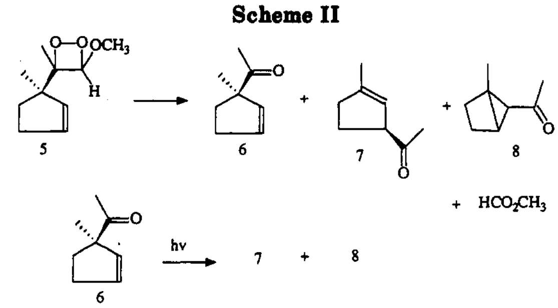
Total efficiencies for the production of triplet ketones from *cis-* and *trans*-3-(3,4-dimethylphenyl)-4-phenyl-1,2-dioxetane (11) are 14.1 ± 0.2% and 21.3 ± 0.5%, respectively. The specific efficiency for the production of triplet acetophenone from *trans*-11 was determined to be 19 ± 4% by trapping the triplet with 2-methyl-2-butene to give the oxetane. These results show that the production of triplets from the dioxetane is state selective, since the n,π* acetophenone triplet is higher in energy than the alternative π,π* triplet of 3,4-dimethylacetophenone. This state-selective production of triplet ketone is most reasonably dictated by orbital symmetry control in the thermolysis of the dioxetane. With this assumption, implications on the mechanism of dioxetane decomposition in terms of biradical intermediates or a concerted biradicaloid process are considered. Activation parameters for thermolysis of *cis-* and *trans*-11 are consistent with a biradical or biradicaloid mechanism. From these activation parameters and molecular mechanics calculations, it was concluded that the transition state was not quite half-way between the dioxetane reactant and a biradical intermediate, if the reaction proceeded through a biradical intermediate. In conjunction with earlier reported triplet efficiencies of 3,4-diaryl-3,4-dimethyl-1,2-dioxetanes and the efficiencies of *cis-* and *trans*-11, the participation of a triplet exciplex was suggested.

One of the unusual features of the thermolysis of 1,2-dioxetanes is their reported selective formation of n,π* triplet state carbonyl products, even though a π,π* state of lower energy may be available. Although there are numerous reports of the production of triplet products from dioxetanes, there are few documented examples where a higher energy n,π* state triplet is formed at the expense of a lower energy π,π* state. In the first reported example of this energy reversal, Zimmerman and co-workers[1] studied a series of dioxetanes of structures **1a–e**, where the efficiency of producing triplet **2** was monitored by the formation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**) (Scheme I). The triplet efficiencies for all these dioxetanes ranged from 11.5% to 17.1% (average 16.6 ± 3.2%). The constancy of the triplet efficiency is remarkable, since the lowest triplet energies of **4a,b,d,e** (74, 72, 74, and 82 kcal/mol, respectively)[1] are above the lowest triplet energy of **2** (68.5 kcal/mol, n,π*), while the lowest triplet energy of **4c** (59 kcal/mol, π,π*) is below that of **2**. On the basis of Boltzmann distribution of *lowest* triplet energies of the product ketones,[2] all of the triplet energy is expected to reside in 2-acetonaphthone (**4c**) and none in dienone **2**. In order to explain this observation, it was proposed that the triplet energy distribution was state selective, such that n,π* triplets were produced in preference to π,π* states. Neither the total efficiencies nor the specific triplet efficiencies of the companion ketones **4** were measured, so that it is not known if 2-acetonaphthone or the other ketones (**4**) are produced in an excited state to any extent.

Scheme I



Scheme II



State selectivity was also called upon in the comparison of the thermolysis of dioxetane **5** to the photolysis of enone **6** (Scheme II).[3] The ratios of the 1,3-acyl shift product (**7**) to the oxadi-π-methane product (**8**) for direct photolysis of enone **6**, acetone triplet-sensitized photolysis of **6**, and the thermolysis of dioxetane **5** is 2.73, 0.031, and 0.70, respectively. The 1,3-acyl shift is then favored from the S_1 state of **6** as seen from the 2.73 ratio of **7**/**8** obtained

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(2) Richardson, W. H.; Lovett, M. B.; Price, M. E.; Anderegg, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4683.
(3) Mirbach, M. J.; Henne, A.; Schaffner, K. *J. Am. Chem. Soc.* **1978**, *100*, 7127.

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