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INFLUENCE OF RESTRICTED DIFFUSION ON RETROGRESSIVE FREE RADICAL REACTIONS

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INTRODUCTION

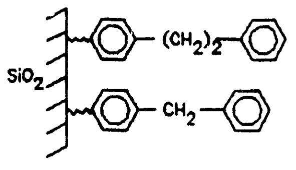
A major emphasis in current research on coal processing is the development of reaction conditions and dispersed catalysts that will avert retrogressive chemical reactions *(1,2)*. These reactions contribute to lower yields of tars (pyrolysis) and oils (liquefaction) as well as to a deterioration in product quality. Retrogressive reactions are generally considered to be associated with reactions that establish new cross-links in the network. For example, in the pyrolysis of low rank coals, low-temperature cross-linking events have been associated with CO_2 and H_2O loss, which could involve decarboxylation of carboxylic acids and condensation of phenols *(3-5)*.

Another potential retrogressive reaction type that has received less attention is the conversion of a labile bridge into a more refractory bridge *(6)*. Although no new cross links are created, the production of more refractory bridges will lead to increased difficulty in depolymerizing the coal network. The cross-linked, network structure of coal may substantially impact reaction pathways during thermal or catalytic processing as a consequence of restricted mass transport. Such constraints on mobility could enhance these retrogressive reaction processes.

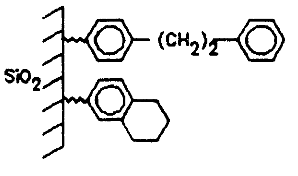
We have found that the study of model compounds immobilized on silica surfaces provides insights into the effects of restricted mass transport on free-radical reaction pathways *(7)*. We have also found certain conditions under which the perturbations induced by restricted diffusion can be mitigated by facile radical relay processes *(8)*. In an earlier study of silica-immobilized bibenzyl, $\approx PhCH_2CH_2Ph$ ($\approx$BB), restricted diffusion was found to substantially promote retrogressive chemistry via free-radical chain processes *(9)*. The dominant reaction pathway to emerge was rearrangement to form $\approx Ph(Ph)CHCH_3$, which results in the conversion of a thermally labile bibenzylic bridge to a more stable diphenylmethane-type bridge. In addition, a second retrogressive pathway, cyclization/dehydrogenation to form silica-immobilized phenanthrene, was promoted to a lesser extent (this process does potentially create an additional cross link). In the current study, we have prepared samples of immobilized bibenzyl that contain a second immobilized component that is either thermally inert (naphthalene, $\approx$NAP), contains reactive benzylic C-H bonds (diphenylmethane, $\approx$DPM), or is a donor hydroaromatic (tetralin, $\approx$TET). These studies are designed to probe the sensitivity of the retrogressive radical chain processes for $\approx$BB to the structure of neighboring molecules in the matrix.

EXPERIMENTAL

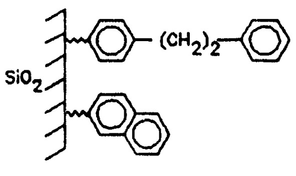
The synthesis and purification of *p*-(2-phenylethyl)phenol (or *p*-hydroxybibenzyl) have been previously described *(9)*. *p*-Benzylphenol, 2-naphthol, and 5,6,7,8-tetrahydro-2-naphthol were commercially available and were purified to >99.9% by GC. The two-component surfaces were prepared in a single step, as previously described, by the condensation of the phenols with the surface hydroxyls of a high purity, fumed silica *(9)*. The resulting silica-immobilized materials shown below ($Si\text{-}O\text{-}C_{aryl}$ linkages) had final purities of >99.4%.



∿BB / ∿DPM



∿BB / ∿TET



∿BB / ∿NAP

Pyrolyses were performed at 400°C under vacuum (2×10^{-6} torr) in a tube furnace as previously described *(9)*. Volatile products were collected as they formed in a liquid nitrogen cold trap, 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 aqueous base, silylated to the corresponding trimethylsilyl ethers, and analyzed as above.

RESULTS AND DISCUSSION

Pyrolysis of silica-immobilized bibenzyl generates a very complicated product mixture, which has been described in detail *(9)*. The major initial product classes in order of decreasing amounts were found to be (surface-attached products are indicated by a "≈"): *(a)* rearrangement to form $\approx Ph(Ph)CHCH_3$; *(b)* cyclization-dehydrogenation to form surface-attached 9,10-dihydrophenanthrene and phenanthrene; *(c)* homolysis to form $\approx PhCH_3$ and $PhCH_3$; *(d)* dehydrogenation to form $\approx PhCH{=}CHPh$; and *(e)* hydrodealkylation to form $\approx PhH$ plus PhC_2H_5 and $\approx PhC_2H_5$ plus PhH. The retrogressive rearrangement and cyclization paths were attributed to free-radical chain processes on the surface that were promoted in this diffusionally constrained environment as a result of restrictions on radical termination events for $\approx PhCH{\bullet}CH_2Ph$. The propagation steps for the rearrangement path are shown in Equations 1 and 2.

$$\approx PhCH{\bullet}CH_2Ph \rightleftarrows \approx Ph(Ph)CHCH_2{\bullet} \tag{1}$$

$$\approx Ph(Ph)CHCH_2{\bullet} + \approx PhCH_2CH_2Ph \rightarrow \approx Ph(Ph)CHCH_3 + \approx PhCH{\bullet}CH_2Ph \tag{2}$$

The selectivity for the rearrangement path is reduced at lower surface coverages (see Table below) as the key hydrogen atom transfer step (Eq. 2) becomes hindered by the increased spatial separation on the silica surface.

Pyrolyses have been conducted on samples that contained low surface coverages of immobilized bibenzyl in the presence of immobilized diphenylmethane, tetralin or naphthalene. Preliminary results at 400 °C, shown in the table below, indicate that both the overall rate for ≈BB thermolysis and the product distribution are very sensitive to the chemical structure of neighboring molecules surrounding the immobilized free-radical intermediates.

Thermolysis of $\approx PhCH_2CH_2Ph$ at 400°C With Spacer Molecules

Surface Comp.	Coverage (mmol g^{-1})	Rate x 10^4 (% s^{-1})	k_{homol} x 10^6 (s^{-1})	Rearr. Prod. (mol %)
≈BB	0.57	68	8.4	51
	0.083	27	8.8	22
≈BB/≈DPM	0.089/0.38	42	9.1	34
≈BB/≈TET	0.10/0.34	21	8.3	30
≈BB/≈NAP	0.073/0.33	12	6.7	8

In contrast, the rate constant for initial homolysis of the weak central C-C bond to form $\approx PhCH_2\bullet$ and $PhCH_2\bullet$ is relatively insensitive to the structure of neighboring molecules on the surface. The measured homolysis rate constants are also comparable to the value of 8.1 x 10^{-6} s^{-1} measured by Stein for fluid-phase bibenzyl in tetralin (10).

As indicated in the table, the decrease in the overall decomposition rate for ≈BB generally correlates with a decrease in selectivity for the rearrangement product. A more detailed description of the impact on the other product classes is beyond the scope of this paper. Interestingly, tetralin appears to be only slightly more effective at inhibiting this retrogressive pathway than is diphenylmethane. Furthermore, the aromatic non hydrogen donor, naphthalene, is the most effective at inhibiting the rearrangement path. An explanation for the effect of these spacer molecules on the rearrangement process may lie in their effect on the rate-limiting hydrogen transfer step (Eq. 2). The naphthalene spacer may inhibit the process by acting as a barrier for this hydrogen transfer step. We have previously shown that biphenyl spacer molecules can hinder related hydrogen atom transfers in the pyrolysis of silica-immobilized 1,4-diphenylbutane (11). On the other hand the diphenylmethane spacer can actually assist hydrogen atom transfers by acting as a radical relay catalyst (8,11), as illustrated in general in Eqs. 3 and 4. This type of relay process is a likely contributor to the fact that the ≈BB decomposition rate and the rearrangement selectivity for the ≈BB/≈DPM system are greater than for similar low surface coverages of ≈BB alone.

$$\approx PhCH{\bullet}R^1 + \approx PhCH_2Ph \rightleftharpoons \approx PhCH_2R^1 + \approx PhCH{\bullet}Ph \qquad [3]$$

$$\approx PhCH{\bullet}Ph + \approx PhCH_2R^2 \rightleftharpoons \approx PhCH_2Ph + \approx PhCH{\bullet}R^2 \qquad [4]$$

SUMMARY

The effects of restricted mass transport on retrogressive reaction pathways can be probed through the study of model compounds immobilized on silica surfaces. Silica-immobilized bibenzyl undergoes a free radical chain rearrangement reaction that converts the thermally labile bibenzylic linkage into a more refractory diphenylmethane-type linkage. The efficiency of this process was found to be quite sensitive to the structure of neighboring molecules on the surface. Co-immobilized naphthalene was more effective that co-immobilized tetralin (a hydrogen donor) in inhibiting the process, apparently by retarding the key hydrogen atom transfer step. The effect of the co-attached molecules on the retrogressive cyclization-dehydrogenation path as well as other reaction pathways for this complex system remain under investigation.

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