CONTRASTING RETROGRESSIVE REARRANGEMENT PATHWAYS DURING THERMOLYSIS OF SILICA-IMMOBILIZED BENZYL PHENYL ETHER*

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INTRODUCTION

Many coal model compound studies have focused on the mechanisms of bond *cleavage* reactions, and the means to alter reaction conditions to promote such reactions. However, there has become increasing interest in elucidating mechanisms associated with retrogressive or retrograde reactions in coal processing, which involve the *formation* of refractory bonds.[1-3] Retrograde reactions inhibit efficient thermochemical processing of coals into liquid fuels, which has been particularly well-documented for low rank coals where abundant oxygen-containing functional groups are thought to play a key role in the chemistry. For example, the decarboxylation mechanism of carboxylic acids is being investigated because of the correlation between CO_2 evolution and cross-linking in low rank coals.[4,5] In addition, phenols have been investigated because of their ability to undergo condensation reactions.[6,7]

Much less is known about retrogressive reactions for ether-containing model compounds. Radical recombination through ring coupling of phenoxy radicals in benzyl phenyl ether (BPE) is known to lead to more refractory diphenylmethane linkages to a limited extent.[2,8-11].

$$PhOCH_2Ph \rightarrow PhO\bullet + \bullet CH_2Ph \rightarrow o\text{-}, p\text{-}HOPhCH_2Ph$$
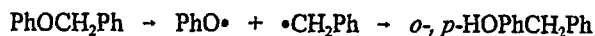
Since this chemistry may be attributed at least in part to cage recombination, it could be promoted in a diffusionally constrained environment such as in the coal macromolecule. Using silica-immobilization to simulate restricted diffusion in coal, we have found that retrogressive reactions can be promoted for certain hydrocarbon model compounds.[12,13] We have now begun an examination of the thermolysis behavior of silica-immobilized benzyl phenyl ether ($\approx$BPE, where $\approx$ represents the Si-O-C linkage to the surface as shown in Table 1) at 275-325 °C. Our initial results indicate that *two retrogressive reaction pathways*, radical recombination as shown above and molecular rearrangement through $\approx$PhOCH$\bullet$Ph, are promoted by restricted diffusion. Remarkably, the retrograde products typically account for 50 mol % of the thermolysis products.

EXPERIMENTAL

The precursor phenol, $m\text{-}HOC_6H_4OCH_2C_6H_5$ (HOBPE), was synthesized by the reaction of benzyl bromide with the sodium salt of resorcinol (NaH in DMF). Following addition of water and acidification, the organics were extracted into toluene. Ether was added to the toluene solution, and the desired phenol was separated from the dibenzylated byproduct by extraction with 2 M NaOH. The basic layer was acidified and extracted with diethyl ether, which was then washed with brine, dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure to produce a brown oil. The product was eluted twice from silica gel columns, once with toluene and then with toluene:hexane (75:25). Multiple recrystallizations from hot toluene:hexane (1:1) gave the desired phenol in 99.9 % purity by GC.

Chemical attachment of the precursor phenol to the surface of a nonporous silica (Cabosil M-5, Cabot Corp.; 200 m^2g^{-1}; ca. 1.5 mmol SiOH per g) was accomplished as described below. HOBPE (2.715g; 13.6 mmol) was dissolved in dry benzene (distilled from $LiAlH_4$) and added to a benzene slurry of silica (9.00g; 13.5 mmol SiOH) that had been dried at 225 °C for 4 h under vacuum. Following stirring and benzene removal on a rotovap, the solid was added to a Pyrex tube which was evacuated to 2×10^{-6} torr and flame sealed. The attachment reaction was performed at 200 °C for 1 h. Unattached HOBPE was removed by Soxhlet extraction (6h) with dry benzene under argon. The silica-attached BPE ($\approx$BPE) was then dried under vacuum.

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...ously to be the dominant reaction in the thermolysis of ...f...i...ment pathway

bibenzyl {≈PhCH$_2$CH$_2$Ph → ≈PhCH(Ph)CH$_3$}.[12] For ≈BPE, the benzophenone and benzhydrol products also contain reactive functional groups that can also become involved in additional retrograde reactions (reduction to diphenylmethane linkages, adduction to aromatics, formation of complex cyclic ethers, etc.) under coal processing conditions.[6,7,15] Finally, the hydrogen required for formation of the unexpected hydrocracked products (Eq. 6) likely arises from the formation of the aldehyde and ketone products (principally the benzophenone (Eq. 5a)) and the benzylation of aromatics such as ≈BPE (Eq. 7).

CONCLUSIONS

Thermolysis of benzyl phenyl ether under conditions of restricted mass transport has been found to produce a dramatically different product distribution compared with fluid phases. Two significant retrograde, free-radical reaction pathways are found to be promoted for ≈BPE under these conditions. Radical coupling at phenolic ring positions is observed to be substantially enhanced as a consequence of restricted diffusion for ≈PhO• radicals compared with fluid phases. A second, kinetically competitive retrograde reaction not observed in fluid phases involves rearrangement *via* ≈PhOCH•Ph intermediates to form benzophenone and benzhydrol products in significant yields. The sum of these two retrograde processes accounts for a remarkable 50-54 mol % of the products at 275 °C. In addition to forming more stable diphenylmethyl-type bridges, these two processes also generate reactive hydroxyl and keto functionalities that can be involved in secondary retrograde reactions. Current research is exploring the effect of surface coverage and reaction temperature on the rate of ≈BPE thermolysis and on the selectivity for these two retrograde pathways.

## ACKNOWLEDGEMENTS

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Products From Pyrolysis of Silica-Immobilized Benzyl Phenyl Ether

(structure: immobilized phenyl ether) $\sim\!\!\!-C_6H_4-O-CH_2-C_6H_5$

(0.25 mmol/g)

where $\sim\sim = $ Si$-$O$-$
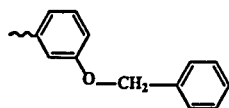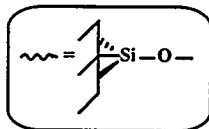
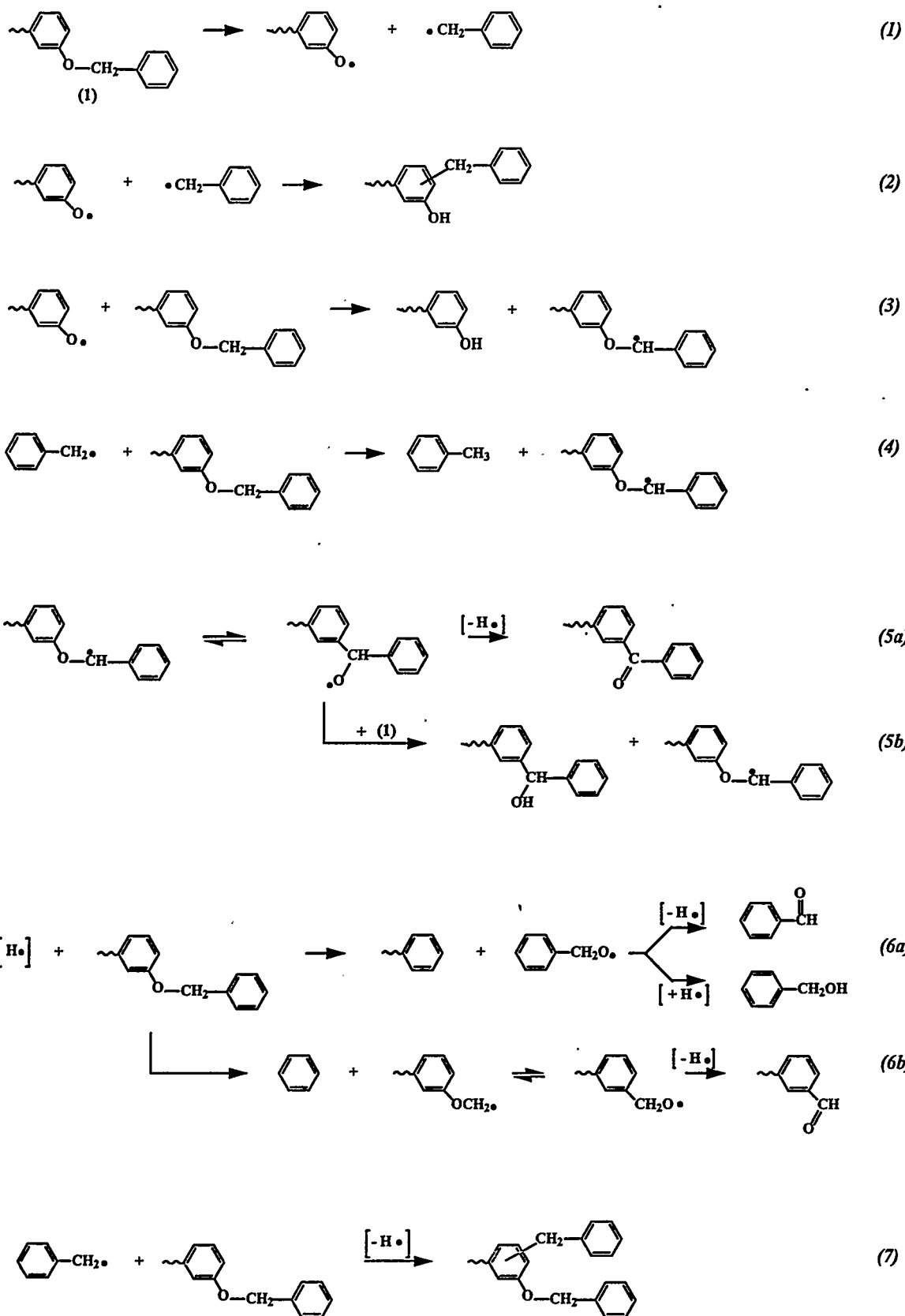| PRODUCT (mol %)	275 °C, 90 min 9.7 % convn. 99.4 % mass bal.	275 °C, 360 min 25.5 % convn. 97.8 % mass bal.	300 °C, 30 min 17.9 % convn. 101.1 % mass bal.	325 °C, 10 min 22.7 % convn. 92.6 % mass bal.
phenol (immobilized) –OH	21.6	24.3	24.0	25.6
toluene –CH₃	11.0	11.1	11.0	11.9
benzyl phenol (immobilized) –CH₂– / OH	29.0	26.7	28.5	27.7
hydroxy diphenylmethane (immobilized) CH / OH	12.5	12.2	10.0	10.4
hydroxy benzophenone (immobilized) C=O	11.6	12.4	10.2	9.6
benzene (immobilized)	2.6	2.4	3.0	4.0
benzyl alcohol –CH₂OH	3.6	3.4	3.1	2.5
benzaldehyde (C=O)H	1.9	1.5	1.8	2.1
benzene	1.8	1.5	2.0	2.5
benzaldehyde (immobilized) CH / O	1.5	1.3	2.0	2.5
dibenzyl ether (immobilized) –CH₂– / O–CH₂–	1.6	0.9	1.5	0.6

Figure 1. Proposed Reaction Mechanism For Principal Product Formation