

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 CO₂ 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)



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 (=BPE, where = 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 =PhOCH•Ph, are promoted by restricted diffusion. Remarkably, the retrograde products typically account for 50 mol % of the thermolysis products.

EXPERIMENTAL

The precursor phenol, *m*-HOC₆H₄OCH₂C₆H₅ (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 Na₂SO₄, 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 m²g⁻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 LiAlH₄) 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 x 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 (=BPE) was then dried under vacuum.

Surface coverage analysis was accomplished by dissolution of the solid (ca. 130 mg) in 30 mL of 1N NaOH over night. 3,4-Dimethylphenol and 4-phenylphenol in 1N NaOH were added as internal standards. The solution was acidified with HCl (pH ~ 4) and extracted with diethyl ether (3x). The ether layer was washed with 20 mL of brine, and the emulsion separated by centrifugation. The ether phase was dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. Silylation with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) in pyridine (2.5 M) produced the corresponding trimethylsilyl ether, which was analyzed by GC (HP 5890) on a J&W Scientific 30 m x 0.25 mm i.d. (0.25 μm film thickness) methyl silicone column with flame ionization detection. GC analysis of multiple assays gave a surface coverage of 0.245 (± 1%) mmol g⁻¹ with a purity of 98.3 %.

Thermolyses were conducted at 275-325 °C (± 1 °C) in sealed, evacuated (2 x 10⁻⁶ torr), T-shaped Pyrex tubes in a temperature controlled tube furnace. Volatile products were trapped as they were produced in liquid nitrogen, and subsequently analyzed by GC and GC-MS (HP 5972A/5890 Series II) with the use of internal calibration standards. Surface-attached products were similarly analyzed after separation by digestion of the silica in aqueous base and silylation of the resulting phenols to the corresponding trimethylsilyl ethers as described above for the surface coverage analysis procedure. Independent recovery studies show that resorcinol, a major product from the thermolysis, is quantitatively recovered by this work-up procedure. The identities of nearly all the products in Table 1 were confirmed with authentic commercial materials. Two isomers of benzyl resorcinol were identified by GC-MS, and the 4-benzyl- isomer was confirmed with a commercial sample. 3-Hydroxybenzhydrol was synthesized from 3-hydroxybenzophenone by reduction with LiAlH₄ in ether. The benzylated ≈BPE isomers were identified solely by GC-MS.

RESULTS AND DISCUSSION

Thermolysis of ≈BPE proceeds readily at 275 °C to afford a complex array of products. A linear plot of conversion (%) vs. reaction time (6-runs from 2.5-13.3 % conversion) yields a rate for ≈BPE conversion of 17 x 10⁻⁴ % s⁻¹ or 6.1 % h⁻¹ (r=0.998). The principal products are shown in Table 1, and typically account for 98-99% of the products at 275 °C. Small amounts (≤ 0.2 mol % each) of bibenzyl, stilbene, and 3-hydroxydiphenylmethane are also detected. As observed from the data in Table 1, the product distributions do not exhibit a marked dependence on conversion or temperature. Mass balances are typically ≥ 97 % at 275 °C.

Typically, thermolysis of BPE in fluid phases has been reported to yield phenol, toluene, and benzylphenols as major products along with minor amounts of bibenzyl, diphenylmethane, and benzylated aromatics.⁶⁻¹¹ Clearly, for surface-immobilized BPE, a much more rich chemistry exists that produces numerous new thermolysis products. A plausible reaction scheme for the formation of these products is shown in Figure 1. Homolysis of the weak O-C bond (ca. 54 kcal mol⁻¹) generates phenoxy and benzyl radicals (Eq. 1), which can abstract hydrogen from ≈BPE to generate the ≈PhOH and PhCH₃ products (Eqs. 3-4). However, these radicals can also recouple prior to hydrogen abstraction at the ring carbons of the phenoxy radical to produce, following tautomerization, isomers of benzylphenol (Eq. 2). Benzyl radicals are also lost through addition to aromatic rings to form higher molecular weight products as illustrated in Eq. 7 for addition to ≈BPE (addition to only one ring is shown in the table and figure for convenience). In fluid phases, the retrograde radical coupling reaction analogous to Eq. 2, which generates a more refractory diphenylmethane linkage as well as a reactive phenol functionality, can account for as much as 15 mol % of the thermolysis products. However, the restricted mass transport experienced by ≈BPE (and ≈PhO•) apparently results in a substantially enhanced probability of recoupling, and the isomeric benzylphenols (analyzed as benzylresorcinols after cleavage from the surface) account for 27-31 mol % of the products.

In addition to enhanced benzylphenol production, two major new products, surface-attached benzophenone and benzhydrol, were formed in comparable amounts and totaled 21-24 % of the products. Although there are numerous studies of BPE thermolysis in fluid phases, we have found only one report of analogous compounds identified in trace amounts amongst the products.⁽⁹⁾ Formation of these products under restricted diffusion can be explained by reactions of the ≈PhOCH•Ph radical intermediate (Eq. 5), which is formed in Eqs. 3-4 by hydrogen abstraction. This radical can undergo a 1,2-phenyl shift to form ≈PhCH(Ph)O• followed by loss of hydrogen (Eq. 5a) to form the benzophenone, or hydrogen abstraction (Eq. 5b) to form the benzhydrol. The 1,2-phenyl migration from oxygen to carbon proposed in Eq. 5 has been detected previously in the thermolysis of other aryl alkyl ethers.⁽¹⁴⁾ The retrograde molecular rearrangement process shown in Eq. 5 is clearly promoted by the restrictions on molecular diffusion, and a similar rearrangement pathway was observed previously to be the dominant reaction in the thermolysis of surface-immobilized

bibenzyl ($\approx\text{PhCH}_2\text{CH}_2\text{Ph}$ - $\approx\text{PhCH}(\text{Ph})\text{CH}_3$).⁽¹²⁾ For $\approx\text{BPE}$, the benzophenone and benzhydrol products also contain reactive functional groups that can also become involved in additional retrograde reactions (reduction to diphenylmethane linkages, addition 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 $\approx\text{BPE}$ (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 $\approx\text{BPE}$ under these conditions. Radical coupling at phenolic ring positions is observed to be substantially enhanced as a consequence of restricted diffusion for $\approx\text{PhO}\cdot$ radicals compared with fluid phases. A second, kinetically competitive retrograde reaction not observed in fluid phases involves rearrangement via $\approx\text{PhOCH}\cdot\text{Ph}$ 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 $\approx\text{BPE}$ thermolysis and on the selectivity for these two retrograde pathways.

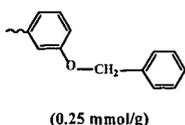
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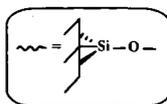
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Products From Pyrolysis of Silica-Immobilized Benzyl Phenyl Ether



where



<u>PRODUCT (mol %)</u>	<u>275 °C, 90 min</u> 9.7 % convn. 99.4 % mass bal.	<u>275 °C, 360 min</u> 25.5 % convn. 97.8 % mass bal.	<u>300 °C, 30 min</u> 17.9 % convn. 101.1 % mass bal.	<u>325 °C, 10 min</u> 22.7 % convn. 92.6 % mass bal.
	21.6	24.3	24.0	25.6
	11.0	11.1	11.0	11.9
	29.0	26.7	28.5	27.7
	12.5	12.2	10.0	10.4
	11.6	12.4	10.2	9.6
	2.6	2.4	3.0	4.0
	3.6	3.4	3.1	2.5
	1.9	1.5	1.8	2.1
	1.8	1.5	2.0	2.5
	1.5	1.3	2.0	2.5
	1.6	0.9	1.5	0.6

