

**INVESTIGATION OF THERMOLYSIS PATHWAYS FOR DIARYLMETHANE
MODEL COMPOUNDS UNDER RESTRICTED DIFFUSION**

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

Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
1 Bethel Valley Road
P. O. Box 2008
Oak Ridge, Tennessee 37831-6197

Submitted For Publication in ACS, Division of Fuel Chemistry, Preprints

* To whom correspondence should be addressed
phone: (423) 576-2168
fax: (423) 576-5235
e-mail: buchananac@ornl.gov

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research, Corp.

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

INVESTIGATION OF THERMOLYSIS PATHWAYS FOR DIARYLMETHANE MODEL COMPOUNDS UNDER RESTRICTED DIFFUSION

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

Chemical & Analytical Sciences Division
Oak Ridge National Laboratory
1 Bethel Valley Road
P.O. Box 2008, MS-6197
Oak Ridge, Tennessee 37831-6197

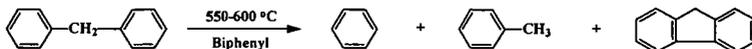
Keywords: Model compounds, pyrolysis, restricted diffusion, diphenylmethane

ABSTRACT

Diarylmethane linkages are important structural units in coals and Kraft lignins that contain only strong carbon-carbon bonds. Studies of the thermolysis of the model compound, diphenylmethane, in fluid phases have demonstrated an important retrograde cyclization pathway that forms the polycyclic aromatic hydrocarbon, fluorene, as a major product. We have now prepared a silica-immobilized form of diphenylmethane ($\approx \text{SiOC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_5$; $\approx \text{DPM}$) to investigate the influence of restricted mass transport on this retrogressive pathway. Initial studies at 425-450 °C indicate that at high surface coverages, the cyclization pathway remains the dominant thermolysis pathway. In addition, restricted diffusion leads to the production of significant quantities of triphenylmethanes (ca. 8-10 %) generated by a competing radical displacement pathway involving diphenylmethyl radicals. The impact of lower $\approx \text{DPM}$ surface coverages and the structure of neighboring spacer molecules on the retrogressive pathways is under investigation.

INTRODUCTION

The thermal decomposition of diarylmethane structures has drawn considerable attention as they are models for related linkages present in coals and Kraft lignin.¹⁻¹² These linkages are important due to their refractory nature, which makes it difficult to cleave them except at high temperatures. For example, diphenylmethane (DPM) is typically reported to be thermally stable at 400-430 °C even in the presence of a hydrogen donor solvent such as tetralin.^{8,9} Petrocelli and Klein reported that thermolysis of DPM in biphenyl solvent at 1.8-6.2 MPa (nitrogen) and 550-600 °C gave benzene, toluene, and fluorene as major products, as shown below, with fluorene yields of ca. 25-30 % and material balances of 81-85 %.¹⁰



The main products are consistent with an earlier report of Sweeting and Wilshire, who examined the thermolysis of DPM at 700 °C in the vapor phase under short contact time, flow conditions.¹¹ However, Suzuki, et. al. have reported that thermolysis of liquid DPM in the absence of solvent, catalyst, or hydrogen atmosphere can occur slowly at temperatures as low as 425 °C to produce benzene and toluene at a rate of about 1 % h⁻¹ (formation of fluorene was not reported).¹²

In our research, we have been exploring the effects of restricted mass transport on thermolysis reactions of model compounds for related structural units in fossil and renewable energy resources.¹³ Restricted mass transport, which can be important in the thermochemical processing of macromolecular energy resources, has been simulated through the use of model compounds that are covalently linked to a silica surface through a thermally robust Si-O-C_{aryl} linkage. This research has uncovered examples where product selectivities and reaction rates

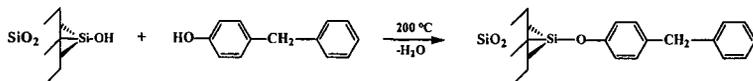
are significantly altered compared with corresponding fluid phase models. In particular, retrogressive rearrangement and cyclization pathways can be promoted under restricted mass transport conditions. In this paper, we report our first investigations of the thermolysis of a silica-immobilized diphenylmethane, indicated by \approx DPM, to examine the nature of the cyclization pathway under diffusional constraints.

Experimental

The DPM model compound was attached to the silica surface through both a *para*- and *meta*- linkage. The precursor phenol, *p*-HOC₆H₄CH₂C₆H₅, was commercially available. Purification involved elution from a silica gel column with benzene, followed by multiple recrystallizations from hot benzene:hexane (1:4) to give the desired phenol in 99.9 % purity by GC. The isomeric phenol, *m*-HOC₆H₄CH₂C₆H₅, was synthesized by the reaction of benzene with *m*-HOC₆H₄CH₂OH in the presence of AlCl₃. Following addition of water and then additional benzene, the benzene layer was separated, washed with saturated NaCl solution, dried over Na₂SO₄, filtered, and the solvent removed on a rotovap. Distillation under vacuum (135-140 °C at 0.25 torr) gave the desired phenol with a purity of 99.6 % by GC.

Chemical attachment of the precursor phenol to the surface of a nonporous silica (Cabosil M-5; 200 m² g⁻¹; ca. 1.5 mmol SiOH g⁻¹) was accomplished as described below for the *p*-DPM isomer. *p*-HOC₆H₄CH₂C₆H₅ (6.085 g; 33.0 mmol) was dissolved in dry benzene (distilled from LiAlH₄) and added to a benzene slurry of silica (9.57 g; 14.4 mmol SiOH) that had been dried at 200 °C for 4 h in an oven. Following stirring and benzene removal on a rotovap, the solid was sealed in a pyrex tube evacuated to 4 × 10⁻⁶ torr. The attachment reaction was conducted in a fluidized sand bath at 200 °C for 1 h. Unattached phenol was removed by temperature-ramped sublimation under dynamic vacuum (250-375 °C; 1 h; 0.02 torr). Surface coverage analysis was accomplished by dissolution of the solid (ca. 200 mg) in 30 mL of 1 N NaOH overnight. 4-Phenylphenol was added as an internal standard. The solution was neutralized by the addition of HCl, and extracted thoroughly with CH₂Cl₂. The solution was dried over MgSO₄, filtered, the solvent removed on a rotovap, and the resulting material silylated with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) in pyridine (2.5 M). The corresponding trimethylsilyl ether derivative was analyzed by GC (HP 5890) on a J&W Scientific 30 m × 0.25 mm i.d. (0.25 μm film thickness) methyl silicone column with flame ionization detection. GC analysis gave a surface coverage of 0.43 mmol g⁻¹ for the *para*- isomer (purity of 99.8 %), and a surface coverage of 0.29 mmol g⁻¹ for the *meta*- isomer (purity of 98.2%).

Attachment Reaction

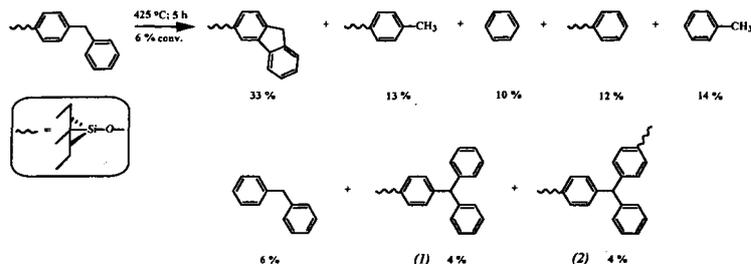


Thermolyses were conducted in sealed, evacuated (2 × 10⁻⁶ torr) T-shaped pyrex tubes in a temperature controlled furnace. Volatile products were collected as they were produced in a liquid nitrogen cold trap, and subsequently analyzed by GC and GC-MS with the use of internal calibration standards. Surface-attached products were similarly analyzed after 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.

Results and Discussion

Our initial studies of the thermolysis of the *para*-isomer of silica-immobilized diphenylmethane (\approx *p*-DPM, 0.43 mmol g⁻¹) indicate that a slow reaction occurs at 425 °C (conversion rate of ca. 1.2 % h⁻¹). The principal products are shown in the scheme below, and the selectivities are insensitive to the extent of \approx *p*-DPM conversion over the range

studied (1.8 - 18.0 %). Numerous higher molecular weight products can be detected in the GC trace, particularly at higher conversions. As expected, mass balances which are good (ca. 98% at low conversions) become progressively poorer at the higher conversions (ca. 87 % at 18 % conversion).

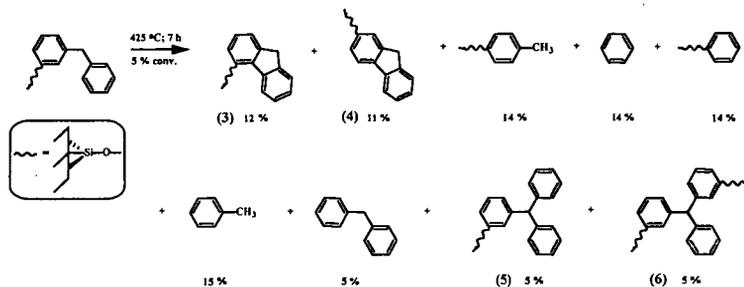


The major reaction path observed for *p*-DPM is cyclization-dehydrogenation to form silica-immobilized fluorene, which is formed in a slightly higher yield (33 mol %) than reported in the liquid phase.¹⁰ This is accompanied by hydrogenolysis of *p*-DPM to form benzene and toluene products (both gas-phase and surface-attached), which is induced by hydrogen atoms released from the cyclization step. This suggests that the dominant reaction chemistry observed in fluid-phase studies of DPM can similarly occur under restricted mass transport conditions. Hydrogen atoms are also found to induce cleavage of the $\equiv\text{SiO}-\text{PhCH}_2\text{Ph}$ bond which produces the PhCH_2Ph product. Diphenylmethyl radicals, $\approx\text{PhCH}\cdot\text{Ph}$, are thought to be the key intermediates in the cyclization to form fluorene, which are principally generated through hydrogen transfer propagation steps with gas-phase and surface-immobilized benzyl radicals. The initiation step for this radical chain process is not currently known, but a molecular disproportionation step seems most likely.^{1,2} The efficiency of this radical chain pathway should be sensitive to the *p*-DPM surface coverage as well as the structure of neighboring molecules on the surface, which is under current investigation. The formation of unexpectedly significant amounts of triphenylmethane products 1 and 2 (totaling 8 mol % of the products) is also consistent with the formation of diphenylmethyl radical intermediates, that undergo an aromatic substitution reaction on a neighboring molecule of $\approx\text{PhCH}_2\text{Ph}$ in competition with cyclization. This process appears



to be promoted compared with fluid phases as a result of the restricted mass transport. Reduced rates for radical termination on the surface as well as the close proximity of the species at high surface coverages contribute to the emergence of this pathway.

To see if the orientation of the DPM molecule on the surface would impact the pyrolysis rate and product selectivities, we have prepared the *meta*- isomer of surface-attached DPM, *m*-DPM. As we observed previously for other molecules, the *meta*- surface linkage leads to a lower saturated surface coverage (0.29 mmol g⁻¹) compared with the *para*-linkage (0.43 mmol g⁻¹) due to less efficient packing on the surface. Initial thermolyses indicate a slightly lower thermolysis rate for *m*-DPM (ca. 0.7 % h⁻¹) at 425 °C, but the principal products shown below are quite similar. Cyclization occurring through the benzylic radical, $\approx m\text{-PhCH}\cdot\text{Ph}$, can lead to two possible isomeric fluorene products, and the two isomers 3 and 4 are detected in comparable yields. The identification of 4 has been confirmed with an authentic sample of the corresponding 2-hydroxyfluorene (the product formed after detaching 4 from the silica surface) that was independently synthesized as described previously.^{13a} The combined yield of fluorene formation, 23 mol %, is somewhat less than the yield observed for the *para*- isomer. The origin of this effect remains under investigation. The radical displacement chemistry that formed the triphenylmethanes, 1 and 2, in the thermolysis of *p*-DPM occurs with similar effectiveness for the *meta*- isomer and results in significant yields of triphenylmethanes 5 and 6.



CONCLUSIONS

Thermolysis of diphenylmethane under restricted mass transport conditions has been found to occur slowly at 425 °C by an apparent radical chain process cycling through diphenylmethyl radicals. At high surface coverages, these free-radical intermediates undergo competitive cyclization to form the polycyclic aromatic hydrocarbon, fluorene (major), and radical displacement on another diphenylmethane molecule to form triphenylmethanes (minor). The selectivity for these two pathways is 4.1 for the *para*- isomer of DPM and 2.3 for the *meta*- isomer indicating some sensitivity to orientation of DPM molecules on the surface. The hydrogen liberated from these processes results, as expected, in the unselective hydrocracking of DPM to form benzene and toluene products, and both material and hydrogen balances are good at the low conversions investigated. Future studies will examine the effect of surface coverage on the pyrolysis rates and product selectivities, and will explore the impact of a co-attached hydroaromatic spacer molecule such as tetralin.

ACKNOWLEDGMENTS

The authors express appreciation to K. B. Thomas for technical support. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research, Corp.

REFERENCES

- Poutsma, M. L. *Energy & Fuels* **1990**, *4*, 113, and references therein.
- Murata, S.; Nakamura, M.; Miura, M.; Nomura, M. *Energy & Fuels* **1995**, *9*, 849.
- Futamura, S.; Koyanagi, S.; Kamiya, Y. *Fuel* **1988**, *67*, 1436.
- (a) McMillen, D. F.; Malhotra, R.; Chang, S.-J. *Fuel* **1987**, *66*, 1611. (b) Malhotra, R.; McMillen, D. F. *Energy & Fuels* **1990**, *4*, 184.
- Autrey, T.; Alborn, E. A.; Franz, J. A.; Camaioni, D. M. *Energy & Fuels* **1995**, *9*, 420.
- Mitchell, S. C.; Lafferty, C. J.; Garcia, R.; Snape, C. E.; Buchanan, III, A. C.; Britt, P. F.; Klavetter, E. *Energy & Fuels* **1993**, *7*, 331.
- Shi, B.; Ji, Y.; Guthrie, R. D.; Davis, B. H. *Energy & Fuels* **1994**, *8*, 1268.
- McMillen, D. F.; Ogier, W. C.; Ross, D. S. *J. Org. Chem.* **1981**, *46*, 3322.
- Benjamin, B. M.; Raaen, V. F.; Maupin, P. H.; Brown, L. L.; Collins, C. J. *Fuel* **1978**, *57*, 269.
- Petrocilli, F. P.; Klein, M. T. *Macromolecules* **1984**, *17*, 161.
- Sweeting, J. W.; Wilshire, J. F. K. *Aust. J. Chem.* **1962**, *15*, 89.
- Suzuki, T.; Yamada, H.; Sears, P. L.; Watanabe, Y. *Energy & Fuels* **1989**, *3*, 707.
- (a) Buchanan, III, A. C.; Britt, P. F.; Thomas, K. B.; Biggs, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2182. (b) Buchanan, III, A. C.; Britt, P. F.; Thomas, K. B. *Energy & Fuels* **1998**, in press. (c) Buchanan, III, A. C.; Biggs, C. A. *J. Org. Chem.* **1989**, *54*, 517. (d) Britt, P. F.; Buchanan, III, A. C. *J. Org. Chem.* **1991**, *56*, 6132. (e) Britt, P. F.; Buchanan, III, A. C.; Malcolm, E. A.; Biggs, C. A. *J. Anal. Appl. Pyrolysis* **1993**, *25*, 407. (f) Buchanan, III, A. C.; Britt, P. F.; Biggs, C. A. *Energy Fuels* **1990**, *4*, 415.