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Presenter: A. C. Buchanan, III

Phone: (865) 576-2168

FAX (865) 574-4902

E-mail: buchananac@ornl.gov

Free-Radical Reactions Under Diffusional Constraints: Impact of Oriented Hydrogen Transfers

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

Oak Ridge National Laboratory

Chemical and Analytical Sciences Division

P. O. Box 2008, 4500S, MS-6130

Oak Ridge, Tennessee 37831-6130

The thermal decomposition of coal (pyrolysis, liquefaction, etc.) is recognized to be influenced by mass transport limitations, which impact the reaction kinetics as well as product yield and quality. We have been exploring the molecular-level details of restricted mass transport on high temperature (350-450°C) free-radical reactions. Restricted mass transport has been simulated through covalent immobilization of coal model compounds on the surface of non-porous, silica nanoparticles. These studies have provided considerable insight into the origins of altered pyrolysis rates and product distributions in the free radical decomposition of these model compounds. In studies of the pyrolysis of silica-immobilized diphenylalkanes, results suggested that oriented hydrogen transfer steps under diffusional constraints are critical in determining the efficiency of free-radical chain processes. We are now examining the details of these hydrogen transfer steps through pyrolysis of two-component surfaces containing immobilized 1,3-diphenylpropane as the probe molecule in the presence of immobilized hydrogen donor molecules (tetralin, fluorene, and dihydrophenanthrene). These hydrogen donor molecules not only vary in their hydrogen donating ability, but they can also be synthesized (via the phenol precursors) to vary the orientation of attachment of the molecule to the surface. We will examine how orientational effects on

hydrogen transfer steps impact the free radical decomposition mechanism for the diarylalkane model. Implications for depolymerization and retrogressive reaction pathways in coal pyrolysis will also be discussed.

Key Words: Free Radical, Restricted Diffusion, Mechanisms, Model Compound

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