Thermolysis Pathways for Surface-Immobilized Diary1methanes

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ABSTRACT

Diarylmethane linkages are important structural units in coals and Kraft lignins that contain thermally robust carbon-carbon bonds. Studies of the thermolysis of the model compound, diphenylmethane, in fluid phases 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 ($=SiO_6H_4CH_2C_6H_5$) to investigate the influence of restricted mass transport on this PAH-forming pathway that involves free radical intermediates. Initial studies at 425-450'C indicate that, at high surface coverages, the cyclization pathway remaim, the dominant thermolysis pathway. However, restricted diffusion leads to a new competing radical displacement pathway, involving diphenylmethyI radicals, which produces significant quantities of triphenylmethanes (ca. 8-10 %). The generality of these thermolysis pathways for other diarylinethanes, and the influence of neighboring hydroaromatic spacer molecules on the surface is under current investigation. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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