CONF-950963--3

PNL-SA-26306

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September 1995

Presented at the
International Energy Agency 8th International
Conference on Coal Science
September 10-15, 1995
Oviedo, Spain

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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# Hydrogen Shuttling Pathways in Thermal Hydroliquefaction: Solvent-Induced Scission of Coal Model Compound Structures.

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**1. INTRODUCTION.** It has been demonstrated that donor solvents play a key role in the scission of "thermal stable" bonds in coal model compounds and therefore it has been speculated that they will improve liquefaction efficiencies.[1-8] We have been studying the transfer of hydrogen from dihydroarene donor solvents to arene model compounds to quantify the barriers of competing hydrogen transfer mechanisms.[9-16]. Hydrogen can be transferred between arene rings by a variety of pathways. The specific hydrogen transfer pathway or pathways can be predicted given an understanding of the thermochemistry of the reactants intermediates and products. The individual pathways that contribute to strong bond scission have been shown to be dependent on the dihydroarene donor and the arene acceptor.

In this paper we quantify the hydrogen pathways between the solvent components anthracene and phenanthrene. In addition, we describe reaction conditions requiring consideration of an additional hydrogen transfer pathway: a multi-step nonipso hydrogen transfer to coal model compounds to evaluate the hydrogen transfer steps to cleave strong diarylmethane bonds in coal structures.

**2. EXPERIMENTAL.** Anthracene was sublimed, dihydroanthracene and phenanthrene recrystallized from ethanol, and dihydrophenanthrene recrystallized from methanol. Thermolysis experiments of mixtures containing arene and dihydroarene were prepared in Pyrex tubes degassed and sealed under vacuum. Stock mixtures of different ratios of arene/dihydroarene were prepared in bulk by grinding the pure compounds together with a roller ball mixer. A fluidized sand bath was used in the thermolysis studies. A Hewlett Packard 5890 GC equipped with an FID and/or a mass detector (HP 5971) and a J&W DB17, 15 or 30m capillary column was used for product analysis. An internal standard was added for quantitative analysis. 9,10-Dihydroanthracene-$d_4$ was prepared by the catalytic exchange with DMSO-$d_6$ and sodium hydride and the reaction mixture was heated to 70 °C for 3 h. After cooling to room temperature, the mixture was quenched with $D_2O$, then ammonium chloride, extracted with diethyl ether, and dried over sodium carbonate. The process was repeated three times, recrystallized from methanol to yield > 99 % (d4) isomer. $^1$H-NMR and $^2$H-NMR were recorded on a Varian VXR 300 spectrometer. 9,10-dihydroanthracene-$d_{12}$ was prepared by reduction of anthracene-$d_{10}$, sodium in EtOD. Acuchem [17] uses a variable step integrator to solve stiff integration problems. Temperature-dependent molar densities of anthracene were obtain from the American Petroleum Institute Reference Guide available through Chemical Abstracts online service in the file DIPPR.

## 3. RESULTS & DISCUSSION.

**3.1** Hydrogen transfer between $AnH_2$ and An. Addition of arenes to hydrogen donor solvents may have beneficial effects: (1) lowers the barrier, required energy, for initiation events to generate hydrogen atom carriers and precursors, and (2) serves as a trap for hydrogen atoms, engendered bond scission of diarylmethanes. Hydrogen transfer to the ipso position of the 1-substituted ring yields 2-methylnaphthalene and naphthalene, while hydrogen transfer to the ipso position of the 2-substituted ring yields 1-methylnaphthalene and naphthalene. Because the radical adduct formed by addition of a hydrogen atom to the 1-position of naphthalene is ca. 3 kcal/mol more stable than the adduct formed by addition to the 2-position, the ratio of 2-methylnaphthalene/1-methylnaphthalene has been used to probe the mechanism of hydrogen transfer. Two different competing hydrogen transfer pathways have been proposed to explain the selectivity differences in bond scission as a function of donor concentration. However, we believe a third pathway must be considered to explain the selectivity at high donor concentrations. Analogous to the above observations for the formation of tetrahydroanthracene, the adduct formed by hydrogen transfer to a nonipso position of 1,2'-DNM, specifically the 1-position of the 2-substituted ring, can be trapped at high donor concentrations to yield a thermally labile adduct that yields 1-methylnaphthalene. Further support for these suggestions comes from deuterium labeling studies. Thermolysis of 9,10-dihydroanthrancene-$d_4$ in anthracene at 400 °C for 60 minutes yields extensive scrambling of the deuterium label into the anthracene 1,2, 9, and 10-positions. The amount of deuterium incorporated into the naphthalene formed in the thermolysis of 1,2'-DNM in a perdeuterated mixture of 9,10-dihydroanthracene-$d_{12}$ and anthracene-$d_{10}$ is dependent on the ratio of arene to dihydroarene. At high arene concentrations we detect ca. 1 deuterium per naphthalene, presumably through an ipso displacement. At high dihydroarene concentrations we detect ca. > 1.5 deuterium incorporated per naphthalene. This suggests that multiple hydrogen transfers occur between the substrate and the solvent and that at higher donor concentrations, nonipso reduction pathways may become important.

Hydrogen transfer from 9,10-dihydrophenanthrene to 1,2'-DNM results in both a lower observed selectivity and observed rate of bond scission. As discussed above, this the lower rate is due in part to the increase in the activation barrier for hydrogen transfer. However, this is partially compensated for by the operation of a free radical hydrogen atom chain pathway.

**4. CONCLUSIONS.** Hydrogen from donor solvent is transfered several times between other donor solvent components and coal model compounds before engendering bond scission by an ipso displacement mechanism. At sufficient donor concentrations, nonipso hydrogen addition yields bond scission. Addition of an anthracene to donor solvent mixtures will help minimize the formation of $H_2$ gas due to the competing addition reaction. The anthracene-solvent radical adduct becomes a less reactive hydrogenating agent than free hydrogen atoms. It can either (1) be reduced in a subsequent disproportionation step to regenerate a donor or (2) act as a shuttler of hydrogen atoms.

Although dihydrophenanthrene is less selective and slower to promote bond scission than dihydroanthracene in the model compound 1,2'-DNM, it is in general a better coal liquefaction solvent. This may be due in part to some physical solvenacy properties, but thermodynamic arguments suggest that a free radical chain pathway generating hydrogen atoms may compensate for the higher initial activation barrier initiating the hydrogen transfer pathways. In addition, while 9,10-dihydroanthracene, a good donor for capping thermally generated free radicals, yields anthracene as a product, and anthracene is a very good hydrogen atom acceptor and will compete with coal substrates for hydrogen in the liquefaction process.

**5. ACKNOWLEDGMENT.** This work was supported by the U.S. Department of Energy, Office of Basic Energy Research, Chemical Sciences Division, Process and Techniques Branch. The work was conducted at Pacific Northwest Laboratory, which is operated by Battelle Memorial Institute for the U. S. Department of Energy under Contract DE-ACO6-76RL0 1830. We thank the Chemical Kinetics Data Center at NIST for providing the modeling program, Acuchem. Support for EAA and TRP was provided through AWU-NW under grant DE-FG06-89ER-75522 with the U.S. Department of Energy.

## 6. GLOSSARY OF ACRONYMS.

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| Phen | phenanthrene |
| PhenH$_2$ | 9,10-dihydrophenanthrene |
| An | anthracene |
| AnH$_2$ | 9,10-dihydroanthracene |
| AnH | 9-hydroanthryl |
| HAn | 1-hydroanthryl |
| H$_2$An | 1,2-dihydroanthracene |
| H$_3$An | 1,2,3-trihydro-4-anthryl |
| H$_4$An | 1,2,3,4-tetrahydroanthracene |
| 1,2'-DNM | 1,2'-dinaphthylmethane |

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