

# DETERMINATION OF HYDROGEN DONATING PROPERTIES OF COAL LIQUEFACTION PROCESS SOLVENTS

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## INTRODUCTION

The hydrogen donating properties of solvents used in direct coal liquefaction processes are of key importance in determining conversion efficiencies and overall product qualities. The reduction of fluorenone to fluorene at 400°C has recently been used in this laboratory to study the hydrogen donating properties of process solvents from different direct liquefaction technologies. Choi and Stock [1,2] have elucidated the mechanism of the reduction of fluorenone by hydrogen donating compounds and have demonstrated the utility of this reduction for evaluating the hydrogen atom transfer properties of coal and coal macerals.

The reduction reaction for fluorenone occurs in three stages [1]. Stage 1 is a radical process which produces 9-hydroxyfluorene as the intermediate product. In stage 2, this intermediate is transformed into bis(9-fluorenyl) ether by a non-radical process. The ether decomposes in stage 3 to produce fluorene and fluorenone via a radical process. In the study by Choi and Stock, it was shown that radical initiators, such as benzyl phenyl thioether or coal, accelerate the reactions of stages 1 and 3. The mechanisms of stages 1 and 3 are formulated in Scheme 1. In the absence of initiator, a bimolecular molecule-assisted homolysis reaction [3-5] between fluorenone and donor initiates the reduction reaction:



Reductions conducted in the absence of added initiators measure the ability of the solvent to both initiate the reduction and transfer hydrogen to radicals, whereas reductions carried out in the presence of initiators serve to measure the hydrogen donor ability of the solvent. Thus, the fluorenone reduction reaction provides a simple procedure to assess the relative abilities of process solvents and solvent components to participate in these radical initiating and hydrogen transfer reactions which are important to coal liquefaction.

## EXPERIMENTAL

### SAMPLES

Fluorenone was prepared by air oxidation [6] of fluorene (Aldrich Chemical) and was recrystallized from methanol to yield material >99% pure as determined by capillary column gas chromatography (GC). Process solvents from two direct coal liquefaction technologies were used in these experiments: (1) a Solvent Refined Coal (SRC)-I process solvent; and (2) a recycle pasting solvent from the Wilsonville, AL integrated two-stage liquefaction (ITSL) process. The physical and chemical properties of these materials are discussed in detail elsewhere [7,8]. Briefly, the SRC-I solvent had a boiling range of 480-850°F and the ITSL pasting solvent was a 650°F+/solid resids material. These liquefaction materials are from

developmental processes and should not necessarily be considered representative of future commercial coal liquefaction products.

The crude solvents were each tested individually for fluorenone conversion efficiency. In addition, chemical class fractions of these materials were obtained by alumina adsorption chromatography. Details of this procedure have been previously reported [9]. Briefly, the crude coal liquefaction materials were separated into four chemical classes: (1) aliphatic hydrocarbons, (2) neutral polycyclic aromatic hydrocarbons (PAH), (3) nitrogen-containing polycyclic aromatic compounds (N-PAC) and (4) hydroxylated PAH (Hydroxy-PAH).

### Fluorenone Reduction Reactions

Fluorenone reductions were conducted at 400°C for 1 hr in sealed evacuated quartz tubes. Generally, benzene solutions of reactants were prepared and aliquots were transferred by microliter syringes to 6 mm o.d. quartz tubes (1 mm wall thickness), so as to provide 50  $\mu$ L total volume containing approximately 5 mg donor and 0.025 mmol fluorenone. Reactions with the ITSL crude process solvent necessitated weighing the material directly into the tubes due to its insolubility in benzene. Loaded reaction tubes were freeze-thaw degassed on a vacuum line prior to flame sealing and thermostating in a Tecam SB-4 fluidized sandbath with TC4D temperature controller.

### Quantitative Analyses

Quantitative analyses of the fluorenone reaction products were performed by capillary column GC. A Hewlett-Packard (HP) model 5880A gas chromatograph equipped with a 30 m x 0.25 mm i.d. fused silica DB-5 (J&W Scientific) capillary column was used. The splitless injection technique was used for sample introduction in conjunction with an HP7671A auto sampling device. Each sample was analyzed in triplicate using a flame ionization detector with peak response information stored and manipulated by the HP5880 microprocessor-controlled integrator. 2-Chloroanthracene was added to all reaction products at a concentration of 100 ng/ $\mu$ L and was used as internal standard for all GC quantitative analyses. Calculations for the conversion of fluorenone to fluorene were done on a mole basis with the conversion amounts reported for fluorene as a percentage of the initial fluorenone present in the reaction. This value was then adjusted to reflect a weight-normalized conversion based on a 5 mg quantity of coal liquid used in the fluorenone reduction reaction. Replicate analyses were performed with the mean and standard deviation reported in Table 1. Recovery percentages were also calculated and reported.

## RESULTS AND DISCUSSION

The conversion yields for the reduction of fluorenone to fluorene by the crude process solvents and their chemical class fractions are presented in Table 1. For comparison, 9,10-dihydroanthracene was run and was observed to produce a 21 $\pm$ 2% conversion of fluorenone; this is in close agreement with the results of Choi and Stock for the same compound [1,2]. Recoveries of fluorenone plus fluorene were greater than 90% for the unfractionated process solvents indicating that little adduction of intermediate fluorene-based radicals with solvent constituents had occurred. The aliphatic hydrocarbon and neutral PAH fractions showed recoveries similar to the crudes; greater than 85%. But, the more polar constituents exhibited lower recoveries (70-80%), which suggests that adduction of fluorenone reduction intermediates with N-PAC ( $A_3$ ) and hydroxy-PAH ( $A_4$ ) components occurred under these reaction conditions. Ionic reactions of the 9-hydroxyfluorene with these polar fractions likely divert the reduction reaction producing fluorenyl adducts to the

activated aromatic rings. Choi and Stock [1] observed that reductions of benzophenone in the presence of phenol lead to diphenylmethylphenols and other side products.

The SRC-I solvent showed lower conversion (38%) than the ITSL process solvent (88%) from the new generation two-stage liquefaction technology. The chemical composition of the process solvents investigated in these experiments have been characterized and compared previously [7]. Table 2 provides information regarding their relative chemical class compositions. The ITSL material contained a wide range of high boiling, high molecular weight constituents while the SRC-I process solvent had intermediate boiling point and molecular weight ranges. The ITSL recycle pasting solvent contained the highest levels of aliphatic hydrocarbons and had the lowest combined levels of nitrogen and oxygen heteroatomic PAH. Furthermore, from detailed chemical analyses by GC and GCMS [7,8], hydroaromatic compounds such as dihydropyrene, which are known to be excellent hydrogen-donating compounds, were major constituents of the ITSL process solvents.

If the relative conversion yields for the different chemical classes are compared for a given coal liquefaction solvent (see Table 1), the chemical class producing the lowest conversion was the aliphatic hydrocarbon fraction ( $A_1$ ), followed by the neutral PAH isolate ( $A_2$ ). The N-PAC ( $A_3$ ) and hydroxy-PAH ( $A_4$ ) classes provided the highest yields for the conversion of fluorenone to fluorene. Hence, it is apparent that the polar constituent of coal liquefaction process solvents participate well in both the radical initiating and hydrogen donating steps shown in Scheme I. This observation is consistent with model studies which showed that 1,2,3,4-tetrahydroquinoline produced higher conversions to fluorene than tetralin or 9,10-dihydroanthracene [1,2]. Thus, the reduced levels of N-PAC in the SRC I versus the ITSL process solvent is one possible reason for the relatively lower conversion yields observed for the SRC I material.

Considerable variability in the conversion yields of the neutral PAH fractions ( $A_2$ ) of these two process solvents was observed. It was therefore of interest to compare the chemical/physical properties of these isolates. The neutral PAH isolates of the SRC-I process material displayed only a 7% conversion yield. This isolate was mostly 2- to 5-ring parent PAH with relatively low levels of alkylated and hydroaromatic PAH [9]. The neutral PAH isolate ( $A_2$ ) from the ITSL recycle pasting solvent had a higher fluorenone conversion yield, 44%, and was characterized by high levels of alkylated PAH and hydroaromatic compounds. The mean molecular weight of this isolate was much higher than the SRC I process solvent [7]. The presence of significant levels of greater than 5-ring PAH in this isolate was responsible for the shift to higher average molecular weight. Larger aromatic ring systems provide greater resonance stabilization of radicals derived from PAH components of this fraction. Greater resonance stabilization energies of radicals cause lower energies of activation ( $E_a$ ) for initiation and hydrogen transfer reactions which equates with increased reaction rates and higher conversions.

#### SUMMARY

In summary, it is evident from the data presented in this paper using the fluorenone-fluorene conversion model system that comparative assessments of recycle solvents with different chemical and physical properties are possible. The polar constituents of these process materials, the N-PAC and hydroxy-PAH, appeared to be the most efficient radical initiators and hydrogen donors. The effectiveness of neutral PAH chemical fractions as reductants was dependent on the amounts of alkylated and hydroaromatic compounds present, as well as the size distribution of aromatic ring systems which make up the fraction. The ITSL neutral PAH fraction showed a better conversion efficiency than the analogous SRC-I fraction. The addition of a radical initiating agent, such as coal, is expected to alter the net

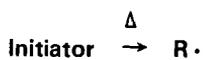
fluorenone conversion efficiencies of these crude solvents and solvent fractions, presumably to reflect relative hydrogen donating abilities.

#### ACKNOWLEDGEMENTS

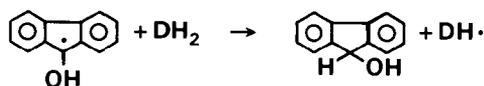
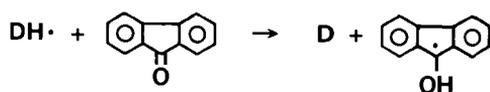
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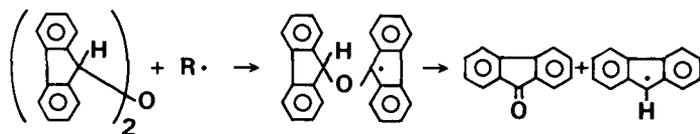
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Stage 1:



Stage 3:



Scheme I. Radical Mechanism for the Reduction of Fluorenone by Hydrogen Donors

**TABLE 1.** Conversion of Fluorenone to Fluorene by Two Coal Liquids and Their Chemical Fractions

| Sample                        | Fraction <sup>(a)</sup> | % Conversion <sup>(b)</sup> | % Recovery <sup>(c)</sup> |
|-------------------------------|-------------------------|-----------------------------|---------------------------|
| SRC-I Process Solvent:        | Crude                   | 38 ± 2                      | 91                        |
|                               | A <sub>1</sub>          | 1 ± 1                       | 89                        |
|                               | A <sub>2</sub>          | 7 ± 1                       | 95                        |
|                               | A <sub>3</sub>          | 45 ± 4                      | 78                        |
|                               | A <sub>4</sub>          | 43*                         | 81*                       |
| ITSL Recycle Pasting Solvent: | Crude                   | 88 ± 1                      | 97                        |
|                               | A <sub>1</sub>          | 9 ± 3                       | 86                        |
|                               | A <sub>2</sub>          | 44 ± 11                     | 91                        |
|                               | A <sub>3</sub>          | 65*                         | 82*                       |
|                               | A <sub>4</sub>          | 57 ± 1                      | 78                        |
| Fluorenone Only               | ---                     | 0                           | 85                        |

- (a) Key: A<sub>1</sub> = aliphatic hydrocarbons; A<sub>2</sub> = neutral PAH; A<sub>3</sub> = N-PAC; and A<sub>4</sub> = hydroxy-PAH.  
 (b) % conversion is quantity of fluorene in moles versus the initial fluorenone quantity normalized to 5 mg of sample.  
 (c) % recovery is the sum of both fluorene and fluorenone as compared with the initial fluorenone quantity.  
 \* Single point determination.

**TABLE 2.** Comparative Chemical Class Composition of Process Solvents from Two Different Direct Coal Liquefaction Technologies

|                              | Aliphatic Hydrocarbons | Neutral PAH/ Hydroaromatic | N-PAC | Hydroxy-PAH |
|------------------------------|------------------------|----------------------------|-------|-------------|
| SRC-I Process Solvent        | 13.9                   | 47.5                       | 13.5  | 25.1        |
| ITSL Recycle Pasting Solvent | 25.9                   | 41.0                       | 21.1  | 12.0        |