

# AN ISOTOPIC STUDY OF THE ROLE OF A DONOR SOLVENT IN COAL LIQUEFACTION

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## INTRODUCTION

For a number of years, laboratory and pilot-scale studies have been conducted in the area of coal liquefaction with hydrogen donor solvents<sup>(1-4)</sup>. The kinetics of these processes and the composition of the coal products have been studied; however, the mechanism of hydrogen transfer from donor solvent to coal is still not well understood.

Recently we reported on a deuterium tracer method for the investigation of coal hydrogenation<sup>(5)</sup>. The work involved the use of deuterium gas as a tracer to follow the incorporation of hydrogen into coal during liquefaction. No donor solvent or catalyst was added to the coal in those experiments. Using an isotopic tracer, it was possible to follow the reaction mechanism more closely and to determine the fate of the reactants, without altering the course of the reaction. Two significant results were obtained in that investigation. Deuterium incorporation in solvent-fractionated coal products was found to vary with product fraction and structural type. Deuterium uptake increased from the most soluble oil fraction to the insoluble residue. In each of the three soluble fractions as determined by NMR spectrometry, selective incorporation of deuterium was found in the  $\alpha$ -alkyl functional region.

The present work examines the donor solvent process during coal liquefaction. A deuterium labeled donor solvent (tetralin- $d_{12}$ ) was prepared to study the chemistry of the solvent during liquefaction. In a separate experiment, naphthalene- $d_8$  was used to investigate the chemistry of hydrogen transfer between coal and a solvent. In each experiment, the coal products and spent solvent were analyzed for total deuterium content and for deuterium content by structural position.

## EXPERIMENTAL

### Materials and Apparatus

High volatile A bituminous coal (81.8% C, 5.1% H, dmmf basis), -200 mesh, from the Loveridge Mine, Pittsburgh Seam, was dried at 115°C for 4 hours before use in each experiment. Technical grade deuterium (>98 atom % deuterium and total hydrocarbons <1 ppm) and high-purity nitrogen were utilized. Naphthalene- $d_8$  was purchased from the Aldrich Chemical Co., and tetralin- $d_{12}$  was prepared in this laboratory<sup>(6)</sup>. The isotopic purity of tetralin- $d_{12}$  and naphthalene- $d_8$  were determined by NMR spectrometry. Batch experiments were performed in a 1-liter stirred autoclave (Autoclave Engineers) and a 0.25-liter rocking autoclave (Parr).

### Experimental Procedure

In a typical liquefaction experiment, the autoclave was charged at room temperature with tetralin- $d_{12}$ , coal and deuterium gas. The autoclave was heated to 400°C, the reaction was conducted for 1 hour, then the autoclave was cooled to room temperature.

Gaseous products were removed for analysis by GC-MS. The reaction products were distilled at reduced pressure to remove spent donor solvent mixture, and the remaining coal products were solvent-fractionated. The naphthalene extraction experiment was carried out under similar conditions except that nitrogen cover gas was used instead of deuterium.

### Product Analyses

The spent solvent mixture was distilled from the coal products, separated by gas chromatography (GC) and analyzed by NMR spectrometry. The solid and liquid coal products were solvent-fractionated into oil (hexane soluble, HS), asphaltene (benzene soluble, BS), benzene-methanol soluble (BMS) and insoluble residue (benzene-methanol insoluble, BMI) fractions. The liquefaction products were solvent-fractionated using three ACS reagent grade solvents: hexane isomer mixture, benzene and methanol. Samples of fractions were combusted, and the resulting water was analyzed by mass spectrometry (Shrader Analytical Labs) to determine the deuterium and protium atom % distribution. Elemental analysis of product fractions was conducted by Galbraith Laboratories.

Proton and deuterium NMR spectra of soluble fractions and spent solvent mixtures were obtained using a JEOL FX60Q FT NMR Spectrometer. A flip angle of  $45^\circ$  was used which corresponds to  $14 \mu\text{s}$  for proton and  $75 \mu\text{s}$  for deuterium NMR spectra. The pulse repetition times were 6.0 and 9.0 s, respectively. Chloroform-d was used as the proton NMR solvent, and chloroform was used as the deuterium NMR solvent.

### RESULTS AND DISCUSSION

The results of two donor solvent hydrogenation experiments and a coal extraction experiment are presented in this paper. The experimental conditions and product yields of the two donor solvent liquefaction experiments (E10 and E19) are summarized in Table 1. These two experiments were conducted under similar conditions except for differences in the type of autoclave and applied pressure. The experiments were designed to investigate hydrogen transfer from a donor solvent to coal. The atom %  $^2\text{H}$  values are also shown in Table 1. While in previous hydrogenation experiments made without the use of a donor solvent<sup>(5)</sup>, it was found that deuterium incorporation increased from the most soluble oil fraction to the insoluble residue, no similar trend was observed in these experiments.

The solvent-fractionated coal products from E10 and E19 were analyzed by proton and deuterium NMR spectrometry. Table 2 lists the integration percentages of the three soluble fractions by functional region. The selective incorporation of deuterium by functional region is demonstrated by taking the ratio of deuterium incorporation over protium incorporation. For example, the E10 HS  $^2\text{H}$  percentage of 7% listed in Table 2 is the  $^2\text{H}_x/^2\text{H}$  ratio, and the E10 HS  $^1\text{H}$  percentage of 11% is the  $^1\text{H}_x/^1\text{H}$  ratio. The value 7% represents the number of deuterium atoms in that functional region normalized to a  $^2\text{H}$  value of 100%. The  $(^2\text{H}_x/^2\text{H})/(^1\text{H}_x/^1\text{H})$  ratios are shown in Table 3. A ratio of unity means that the normalized fraction of protium and deuterium contained in that functional region are equal. Since the ratio is much greater than unity in all of the  $\alpha$ -alkyl regions, indications are that in liquefaction experiments conducted with a donor solvent, as well as in liquefaction experiments conducted without a donor solvent or catalyst as was shown in our previous presentation<sup>(5)</sup>, significant specific incorporation occurs in the  $\alpha$ -alkyl position.

One can utilize the isotopic composition and deuterium incorporation by structural position of the spent donor solvent to develop a mechanistic pathway of hydrogen transfer. Attention was focused on two major processes which can occur simultaneously in donor solvent liquefaction. Tetralin- $d_{12}$  can donate four of its transferable deuterium atoms to coal with the formation of naphthalene- $d_8$ ; tetralin- $d_{12}$  can participate in isotopic exchange of its deuterium with protium in the coal. It is worthwhile to examine the reaction pathways of the donor solvent to assess the importance of each process.

Figure 1 is a summary of the most probable chemical reactions of the donor solvent, tetralin, under liquefaction conditions. Tetralin can be hydrogenated to form decalins, dehydrogenated to form naphthalene, or rearranged to form methylindan. All of the compounds shown in Figure 1 except methylindan were detected in the spent solvent from E10. Figure 2 is the proton NMR spectrum of the spent solvent. Tetralin, naphthalene, and decalin absorption peaks are evident.

In a hydrogen donor reaction, the liquefaction process is generally assumed to occur with the formation of solvent radical intermediates which can accept or donate hydrogen atoms; therefore, in Figure 1 each reversible reaction can be divided into a number of stepwise additions or removals of hydrogen radicals. The initial stage of the dehydrogenation of tetralin to naphthalene is expanded in Figure 3 to include each hydrogen atom transfer pathway. The dihydronaphthalenes are shown as possible intermediates in the formation of naphthalene. The pathway of donation of hydrogen by tetralin requires the abstraction of  $\alpha$ - and  $\beta$ -hydrogens by coal or gas phase products, and Reactions 1 and 2 in Figure 2 show the main pathways of hydrogen abstraction. The quantities of hydrogen in the spent solvent can be subtracted from the hydrogen in the starting solvent to determine the net donation.

Table 4 summarizes the composition of the donor solvent before and after completion of E10 and E19. These data have been examined to formulate a mechanism of isotopic exchange. The distilled spent solvent was separated by GC, and the isotopic composition and incorporation by structural position was determined by NMR spectrometry with an internal quantitative standard. In E10, the extent of hydrogen donation to the coal can be calculated from the formation of naphthalene corrected by the amount of hydrogen used in the formation of decalins (Table 4). It is also shown in Table 4 that in addition to the donor mechanism, considerable isotopic exchange occurred between the tetralin- $d_{12}$  and coal; 17.2 atom % of the deuterium in the solvent was exchanged. Tetralin contains four hydrogen atoms in each of three chemically different positions: aromatic ( $H_{ar}$ ), alpha ( $H_{\alpha}$ ) and beta ( $H_{\beta}$ ) hydrogens. Of the 17.2 atom % replaced by protium, 66% of the protium resided in the  $H_{\alpha}$ , 23% in  $H_{\beta}$  and 11% in  $H_{ar}$  position. E19 shows a similar effect. Specific protium incorporation occurs in the  $H_{\alpha}$  position of tetralin- $d_{12}$ , and this indicates the predominant pathway of hydrogen exchange is Reaction 1. The fact that the  $\alpha$ -radical has greater resonance stabilization than the  $\beta$ -radical also supports the choice of Reaction 1 as the predominant pathway. It should be noted that the  $\beta$ -radical can interconvert to the  $\alpha$ -radical by a 1,2-hydrogen shift.

An evaluation of the data on the formation of naphthalene- $d_8$  from tetralin- $d_{12}$  (donation) and protium incorporation into tetralin- $d_{12}$  (exchange) showed that in experiment E10 donation took place to approximately the same extent as did exchange. According to the indicated mechanism (Figure 3) not only hydrogen donation but also hydrogen exchange via the  $\alpha$ -radical of the tetralin can have a significant role in stabilizing the primary free radical structures which form by thermal decomposition of the coal.

Table 1 includes the data of an extraction experiment (E21) conducted with naphthalene- $d_8$  and nitrogen as cover gas. This experiment investigated the transfer of hydrogen taking place during a solvent extraction experiment in the absence of a donor solvent. In the experiment, coal and naphthalene- $d_8$  with a cover gas of nitrogen were heated at 380°C for 1 hour. The solvent and coal products were analyzed for deuterium loss and incorporation, respectively. The isotopic composition of the starting and spent naphthalene- $d_8$  is shown in Table 5. The starting naphthalene lost 4 atom %  $^2H$ , and the combined coal products gained 11 atom %  $^2H$ . It is interesting to note that the  $H_{\alpha}$  position of naphthalene exchanged more of its deuterium with the coal than the  $H_{\beta}$  position. This experiment will be discussed in terms of the chemistry of hydrogen transfer between solvent and coal.

In summary, coal hydrogenation and extraction experiments conducted with deuterated tetralin and naphthalene have been discussed. With the use of the deuterium tracer

method, deuterium incorporation was found in specific structural positions of the solvent and soluble coal products. The method has provided insight into the mechanism of hydrogen transfer.

#### ACKNOWLEDGMENT

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TABLE 1  
SUMMARY OF EXPERIMENTAL CONDITIONS AND PRODUCT YIELDS

EXPERIMENTAL CONDITIONS			
Parameter	E10	E19	E21
Cover Gas	D <sub>2</sub>	D <sub>2</sub>	N <sub>2</sub>
Solvent	tetralin-d <sub>12</sub>	tetralin-d <sub>12</sub>	naphthalene-d <sub>8</sub>
Coal Weight (g)	25	25	25
Solvent Weight (g)	25	25	25
Reactor Volume (liter)	0.25	1.0	1.0
Stirring Rate or Rocking Rate	100 osc/min	100 rpm	100 rpm
Reaction Time (h)	1.0	1.0	1.0
Cold Pressure <sup>2</sup> H <sub>2</sub> or N <sub>2</sub> (psi)	1200	1000	1000
Operating Pressure (psi)	3000	2200	2200
Temperature (°C)	400	400	400

SOLVENT-FRACTIONATION PRODUCTS					
Products	Weight %		Atom % <sup>2</sup> H		
	E10	E19	E10	E19	E21
Oil (HS)	16	17	38	52	11*
Asphaltene (BS)	32	10	45	43	
Benzene-methanol Soluble (BMS)	8	2	35	38	
Benzene-methanol Insoluble (BMI)	44	71	37	61	

\* An average value of the combined coal products.

TABLE 2  
 $^1\text{H}$  AND  $^2\text{H}$  NMR ANALYSES OF PRODUCT FRACTIONS

E-10						
Functional Region	$\% ^1\text{H}$			$\% ^2\text{H}$		
	HS	BS	BMS	HS	BS	BMS
$\gamma$ -Alkyl	11	12	6	7	8	7
$\beta$ -Alkyl	40	23	20	20	14	16
$\alpha$ -Alkyl	26	25	26	44	42	41
Aromatic <sup>+</sup>	23	40	48	29	36	36

E-19						
Functional Region	$\% ^1\text{H}$			$\% ^2\text{H}$		
	HS	BS	BMS	HS	BS*	BMS
$\gamma$ -Alkyl	9	17	8	5	-	4
$\beta$ -Alkyl	31	33	15	17	-	15
$\alpha$ -Alkyl	20	16	33	40	-	50
Aromatic <sup>+</sup>	40	34	44	38	-	31

\* Sample size was too small for analysis.

<sup>+</sup> Aromatic region contains phenolic absorbances.

TABLE 3  
COMPARISON OF DEUTERIUM AND PROTIIUM DISTRIBUTION  
IN E10 AND E19 LIQUEFACTION PRODUCTS

Functional Region	$(^2\text{H}_x/^2\text{H})/(^1\text{H}_x/^1\text{H})$ Ratio†					
	HS	E10 BS	BMS	HS	E19 BS††	BMS
$\gamma$ - Alkyl	0.6	0.7	1.2	0.6	-	0.5
$\beta$ - Alkyl	0.5	0.6	0.8	0.5	-	1.0
$\alpha$ - Alkyl*	1.7	1.7	1.6	2.0	-	1.5
Aromatic**	1.3	0.9	0.5	1.0	-	0.7

\*Includes  $\alpha^2$ -alkyl region  
\*\*Includes phenolic region

†Estimated error:  $\pm 0.1$   
††Sample size was too small for analysis

TABLE 5  
ISOTOPIC COMPOSITION OF HYDROGEN TRANSFER SOLVENT

<u>STARTING SOLVENT</u>	<u>SPENT SOLVENT</u>
Naphthalene- $d_8$	Naphthalene- $d_8$
98.5 atom % D	94.6 atom % D
$H_\alpha$ 59%	$H_\alpha$ 78%
$H_\beta$ 41%	$H_\beta$ 22%

TABLE 4  
ISOTOPIC COMPOSITION OF DONOR SOLVENTS FROM E10 AND E19

<u>STARTING SOLVENT</u>		<u>E10 COMPOSITION</u>	<u>SPENT SOLVENT</u>	
Tetralin	94 mole %	→	Tetralin	70 mole %
Naphthalene	6 mole %		Naphthalene	28 mole %
			<u>Trans</u> -decalin	1 mole %
			<u>Cis</u> -decalin	1 mole %

<u>STARTING SOLVENT</u>		<u>E10 ISOTOPIC DISTRIBUTION</u>	<u>SPENT SOLVENT</u>	
Tetralin-d <sub>12</sub>	97.2 atom % D	→	Tetralin-d <sub>12</sub>	H <sub>α</sub> 66% <sup>1</sup> H
			80.0 atom % D	H <sub>β</sub> 23% <sup>1</sup> H
				H <sub>ar</sub> 11% <sup>1</sup> H

<u>STARTING SOLVENT</u>		<u>E19 COMPOSITION</u>	<u>SPENT SOLVENT</u>	
Tetralin	99 mole %	→	Tetralin	58 mole %
			Naphthalene	22 mole %
			<u>Trans</u> -decalin	4 mole %
			<u>Cis</u> -decalin	16 mole %

<u>STARTING SOLVENT</u>		<u>E19 ISOTOPIC DISTRIBUTION</u>	<u>SPENT SOLVENT</u>	
Tetralin-d <sub>12</sub>	99.0 atom % D	→	Tetralin-d <sub>12</sub>	H <sub>α</sub> 64% <sup>1</sup> H
			91.6 atom % D	H <sub>β</sub> 24% <sup>1</sup> H
				H <sub>ar</sub> 12% <sup>1</sup> H

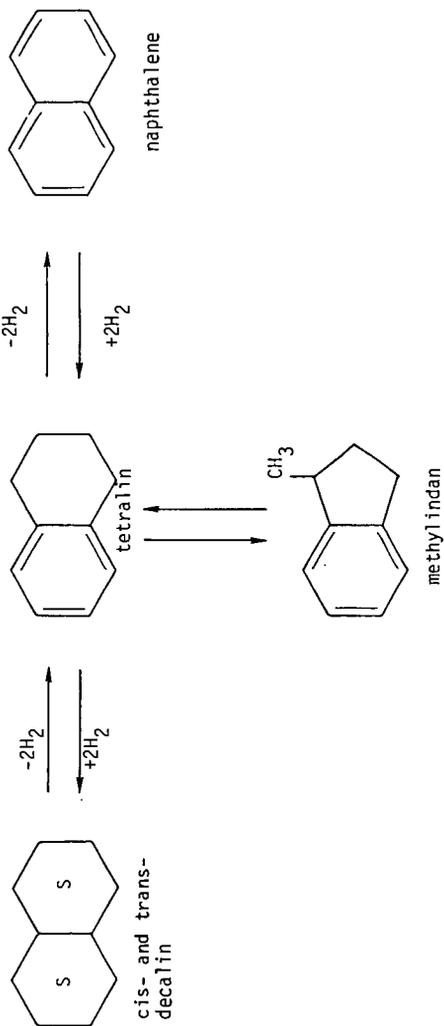


FIGURE 1. REACTION PATHWAYS OF A DONOR SOLVENT DURING LIQUEFACTION

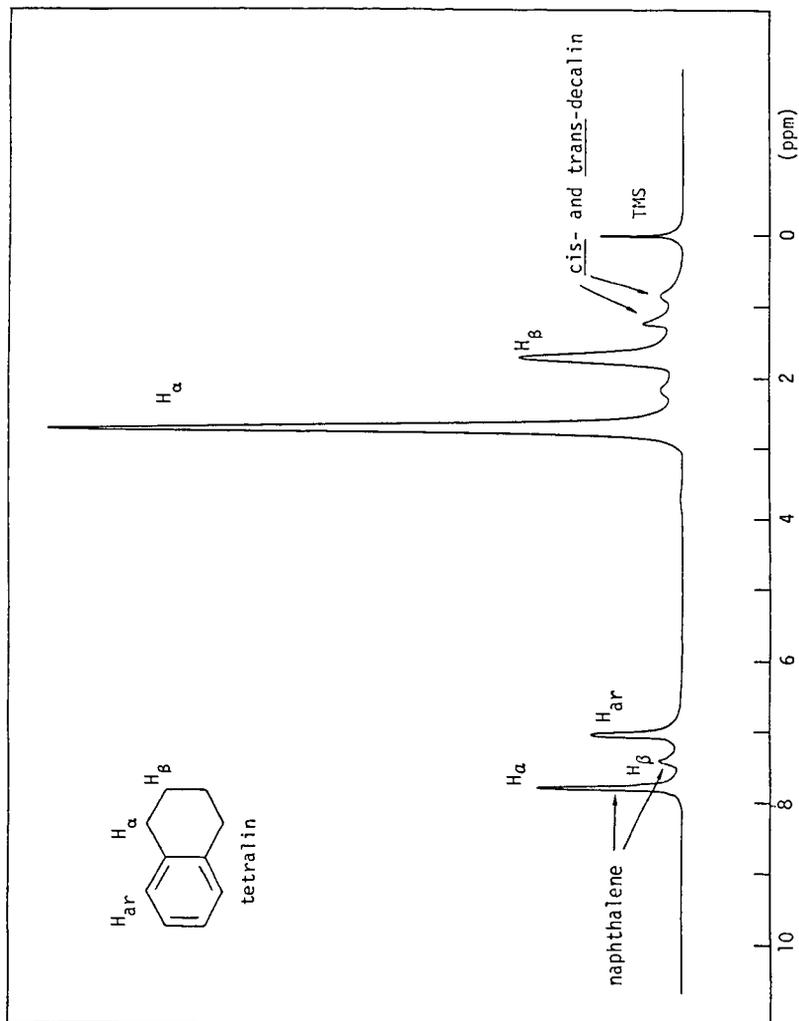


FIGURE 2. PROTON NMR SPECTRUM OF PRODUCT DONOR SOLVENT FROM E10

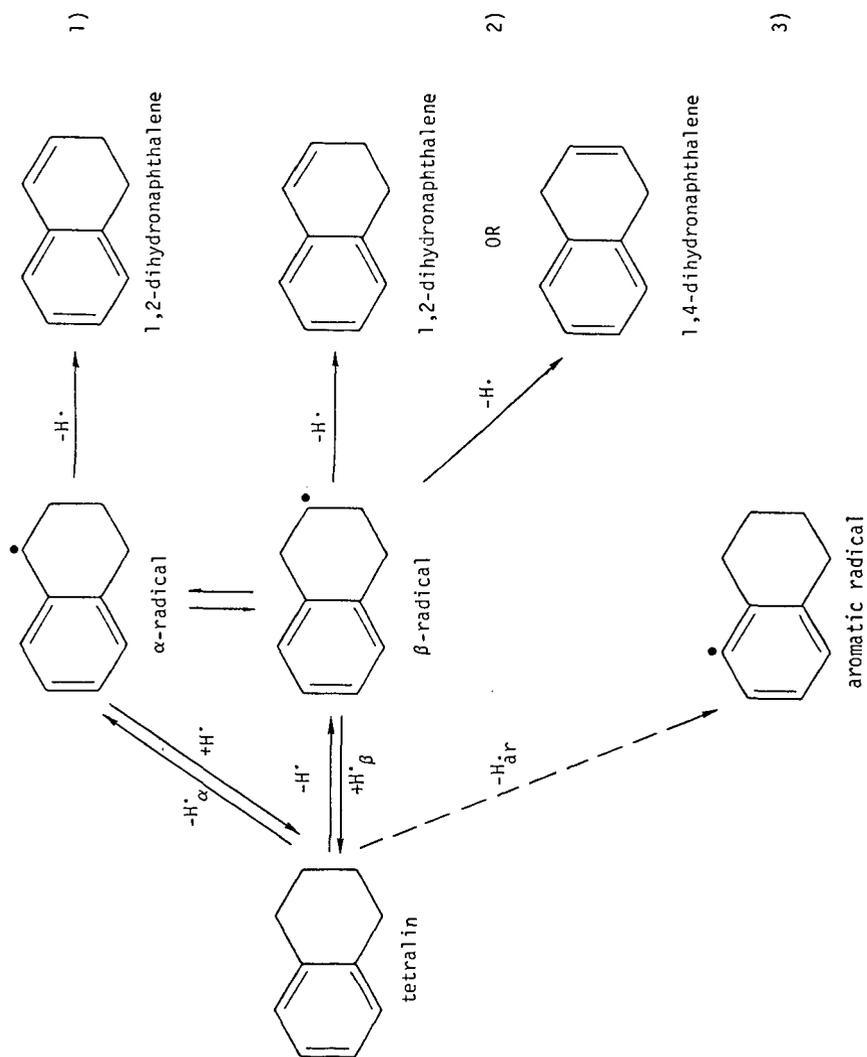


FIGURE 3. STEP-WISE HYDROGEN ATOM TRANSFER FROM TETRALIN