

## ADDITION IN DONOR SOLVENT CONVERSION OF EASTERN SHALE

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### INTRODUCTION

Rich deposits of Devonian oil shale are found east of the Mississippi. The carbon in oil shales from Kentucky have been shown to have a higher aromatic carbon content (~54% aromatic carbon) than oil shales from the Green River formation (~22% aromatic carbon).<sup>(1)</sup> This, along with the low H/C atomic ratio of 1.0-1.2 in eastern shales, suggests that these shales have a structure similar to that of coal. During coal liquefaction, as with eastern oil shale conversion, one objective is to decrease the extent of recombination of thermally produced free radicals through the use of a donor solvent. The donor solvent donates hydrogen to the substrate and, therefore, becomes more aromatic. In addition to donating hydrogen, the solvent can isomerize and/or be adducted. The objective of this work is to identify the types of adduction of donor solvents tetralin, octahydrophenanthrene, and mesitylene in eastern oil shale runs.

### EXPERIMENTAL

The shale sample was provided by IMMR (Lexington, KY). It was taken from the Hilpat site (Fleming Co., KY) and it is classified as a Cleveland member, Ohio shale. It has a Fischer assay of 10.1 g/ton and a carbon content of 12.2 wt% (MF). The unlabeled solvents were obtained from Fisher Scientific and were used as received. The labeled solvents (see Figure 1) were prepared by E. J. Eisenbraun of Oklahoma State University.

Batch conversion experiments were made using equal charges of shale and solvent to a small microreactor which was lowered into a preheated sand-batch to bring its contents quickly to reaction temperature. The experiments were made at a temperature of 450°C and reaction times between 0 (allowing 2.5 min. for heating) and 30 min. Mixing was provided by up-and-down agitation at about 800 strokes/min. Further details are given in Reference 2.

The total reaction product was transferred to a small test tube and the solvent was stripped with a nitrogen flow to ensure a minimum of cosolvent effects during extraction. The product was then sequentially Soxhlet extracted to give pentane and toluene solubles. Percent solubles is defined as 100% minus Soxhlet residue. Selected samples of the toluene insolubles were also extracted with tetrahydrofuran (THF). The THF Soxhlet extract was stripped with a nitrogen flow at 80°C overnight to remove solvent and recover a sample of preasphaltenes for analysis.

$^{13}\text{C}$  NMR spectra were obtained at 50.3 MHz on a Varian associates XL-200 spectrometer. Samples were made up in  $\text{CDCl}_3$  with  $\text{Cr}(\text{acac})_3$  added at a level of 0.05 M. Spectra were obtained with  $90^\circ$  pulses, 0.4 second acquisition time, 2 second delay between pulses and gated decoupling. Spectra were referenced internally to TMS. In some cases, only 10-20 mg of each fraction were available so spectra were accumulated for 50-61 hours. In some cases, the spectral quality even then was poor, so only major types of adduction are discernable. A reference spectrum of the run made with unlabeled donor solvent was obtained for each labeled donor solvent run.

## DISCUSSION

### Tetralin Adduction

Tetralin can be adducted as tetralin, naphthalene, or isomerized tetralin, e.g., methylindane or butylbenzene. The possible fates of tetralin are given in Figure 2.

### Pentane Solubles

The spectra from this fraction are shown in Figure 3.

Adduction of tetralin can occur in either the aromatic or aliphatic portion of the molecule. Adduction through the aromatic portion is difficult to identify because it does not perturb the chemical shift of the labeled carbon. Attachment at the aliphatic portion can occur in any of the four positions, but two of them are equivalent. Attachment at the labeled position, which is  $\alpha$  to the aromatic ring, will move the chemical shift from its normal position of 29.9 ppm to 37.2 ppm or 42-46 ppm, depending on whether the attachment is by an aliphatic or aromatic structure. There are two signals at 45.4 ppm and 45.9 ppm, indicating attachment at the labeled carbon by an aromatic structure. In addition, there is a small amount of signal intensity at 41-42 ppm, also indicating attachment of the tetralin at the labeled position by an aromatic structure. The signal at 37.8 ppm can be due to attachment at the labeled position of tetralin by an alkyl group or attachment at the tetralin position  $\beta$  to the aromatic ring by an aromatic substituent. Because the  $\alpha$  to aromatic position is the most active, it is assumed that this signal is due to attachment at that position by an alkyl substituent. The large signal at 29.9 ppm is due both to long chain material from shale and to tetralin adducted through a position which does not perturb the chemical shift of the labeled carbon, i.e., through the aromatic ring. This represents the largest amount of adducted tetralin.

The amount of each type of adducted tetralin is given in Table 1. They were estimated based on a comparison of signals in the spectra of the labeled and unlabeled runs.

### Butyl Benzene Adduction

Tetralin can open to form n-butyl benzene with the label either in the position  $\alpha$  to the aromatic ring or at the terminal methyl. The signals due to the label would then be at 36 ppm or 14 ppm, respectively, unless

adduction occurred through the alkyl chain. There is a signal at 36 ppm that is not present in the spectrum from the unlabeled run. This signal is due to butyl benzene with the label in the  $\alpha$  position. The relative intensities of the signal at 22.4 and 14 ppm in both the labeled and unlabeled runs are the same. This indicates that there is little contribution to the signal at 14 ppm from n-butyl benzene. However, there is a signal at 36 ppm which indicates that n-butyl benzene is present and the label is in the  $\alpha$  position. The amount of tetralin present as n-butyl benzene is given in Table 1.

Tetralin can also open to form 1-phenyl 1-methyl propane. In this case, the label would be present in the methyl group and would have its signal at 22.5-23 ppm. There is a signal present in both the labeled and unlabeled spectra at this position. However, it is present in the same amount relative to the signal at 22.4 in both spectra, indicating that it is due to the unlabeled  $\beta$  carbon of tetralin rather than the propane derivative.

#### Methyl Indane/Methyl Propyl Benzene Adduction

Tetralin can rearrange to form methyl indane or open to form ortho methyl propyl benzene. In either case, the label would be present on the methyl group and would have its signal at 20 ppm. One or both of these isomers is present as indicated by the signal at 20 ppm in the labeled run. Adduction of these isomers has probably occurred through the aromatic ring. The amount of these isomers is given in Table 1.

#### Naphthalene Adduction

Tetralin converted to naphthalene can be adducted at either of two equivalent positions. The labeled carbon has its signal at 127.9 ppm. The aromatic region of the spectrum has a large amount of signal intensity in this region, indicating that naphthalene has been adducted through the unlabeled ring. In addition, there are signals at 126 and 125.5 ppm, indicating adduction ortho to the label by either aromatic or short alkyl chain substituents. There is a signal at 131.2 ppm that only can be due to adduction para to the label and the labeled carbon must also contain a methyl group. The signal at 134.2 is indicative of naphthalene with an attached methyl group. In this case, adduction must be through the unlabeled ring. There are two signals at 137 and 138.4 ppm that are due to naphthalene adducted through the position para to the label and the labeled carbon must contain a short ( $C_{2-3}$ ) alkyl group. There are also signals present at 140.1 and 140.4 ppm that are due to naphthalene adduction by an aromatic group.

#### Asphaltene Fraction

The aromaticity of the asphaltene fraction obtained from the unlabeled tetralin run of 5 min. was 70.7%. There are sharp signals in the spectrum at the classic positions for long alkyl chain material. The aromatic region is broad and featureless. The asphaltene fraction obtained from the  $^{13}C$  labeled tetralin run of 5 min. has an aromaticity of 81.5%. The aliphatic region has the same classic signals for long chain material that were present in the unlabeled run.

There are two small signals at 32.5-33 ppm and at 36 ppm in the labeled asphaltene spectrum. These are due to small amounts of attachment of the hydroaromatic ring to the asphaltenes. The hydroaromatic ring is not attached at the labeled position. Otherwise, a signal would be present at either 37.2 ppm or 48 ppm for an alkyl or aryl aromatic attachment, respectively. The tetralin is probably attached at the position alpha to the label. Attachment at this position would move the chemical shift of the labeled carbon to 33.9 for attachment through an alkyl substituent or 36.9 ppm for attachment through an aromatic substituent. Both the positions  $\alpha$  and  $\beta$  to the labeled carbon should be substituted to the same extent. However, some types of substitution at the  $\beta$  position would shift the signal under signals present from long alkyl chain material and hence would not be seen.

In addition to the aliphatic signals, there are several sharp signals present in the aromatic region at 126.0, 127.7, and 128.3 ppm. These indicate that some of the tetralin has been converted to naphthalene. The unperturbed chemical shift of the labeled carbon would be at 127.9 ppm. Attachment at the labeled carbon would move the chemical shift into the range of 134-148 ppm. Since there are no sharp signals in this region, the naphthalene must not be adducted at this position. Attachment ortho to the label would move the chemical shift of the labeled carbon upfield into the region of 124.8-128.8 ppm. The signal at 126.0 ppm can be due to alkyl attachment at this position. Attachment at the position meta to the label moves the signal only slightly for alkyl attachments but down to 128.3 ppm for an aryl substituent. There is a signal at 128.3 ppm which may be due to aromatic attachment of naphthalene to asphaltenes at the 3-position. Attachment para to the label would move the labeled carbon signal upfield into the region of 125.0-125.5 ppm or 126.9 for an alkyl or aryl attachment, respectively. Since no attachment was seen at the labeled position, it is unlikely that there will be any attachment at the position para to it.

Attachment in the ring without the labeled carbon will not significantly perturb the chemical shift of the labeled carbon. The signal at 127.7 ppm is due to unperturbed label indicating attachment to the unlabeled ring.

#### Adduction of Mesitylene

##### Asphaltene Fraction

The  $^{13}\text{C}$  NMR spectrum of asphaltenes recovered from the run with unlabeled mesitylene shows an aromaticity of 88.5%. The sharpest signal in the spectrum is at 29.0 ppm. The spectrum of the asphaltene fraction obtained from the run with  $^{13}\text{C}$  labeled mesitylene has an aromaticity of 75.9%. The decrease in aromaticity is due to an increase in aliphatic structure which comes from the  $^{13}\text{C}$  label on one of the methyls of mesitylene.

The aliphatic region of the spectrum has two sharp signals at 29.4 ppm and 21.1 ppm. The signal at 21.1 ppm is due to the labeled methyl group on mesitylene. Adduction of mesitylene has not taken place through this

methyl group since its original chemical shift of 21.0 ppm is not significantly perturbed. Had adduction occurred through this methyl group, the chemical shift would move to 42 ppm if the attached group were aromatic, 29-36 ppm if the attached group were an alkyl chain, and 43-48 ppm if more than one alkyl group were attached. Adduction of the mesitylene on the aromatic carbon ortho to the labeled methyl group by an alkyl group would move the chemical shift of the labeled methyl group upfield by 2-3 ppm. Adduction at the aromatic carbon para to the labeled methyl group would have little effect on the chemical shift of the labeled methyl group. Similarly, adduction through one of the meta methyl groups would have little effect on the chemical shift of the labeled methyl group. It, therefore, appears that the mesitylene has been adducted through either the unlabeled methyl groups or the aromatic carbon para to the labeled methyl group.

#### Preasphaltene Fraction

The  $^{13}\text{C}$  NMR spectrum of this fraction obtained from the run with unlabeled mesitylene shows an aromaticity of 84.7%. The most defined signal in the spectrum is at 29.6 ppm. The spectrum of the preasphaltene from the run with  $^{13}\text{C}$  labeled mesitylene has an aromaticity of 81.0%. This decrease again is due to incorporation of the labeled methyl group from mesitylene. The most predominant signals in the spectrum are at 29.7 ppm and 21.5 ppm, the latter due to the labeled methyl group of mesitylene. It again appears that the mesitylene is not adducted through the labeled methyl group nor through the aromatic carbon ortho to the methyl group.

#### Adduction of Octahydrophenanthrene

##### Preasphaltene Run

The aromaticity of the preasphaltenes obtained from the run made without the labeled octahydrophenanthrene was 75.3%. The only sharp signal in the spectrum was at 29.6 ppm. The aromaticity of the preasphaltenes obtained from the run made with  $^{13}\text{C}$  labeled octahydrophenanthrene was 77%. There are two sharp signals in the spectrum of the fraction. The signal at 128.4 ppm is the unperturbed chemical shift of carbon 1 in phenanthrene. This indicates that at least some of the adducted octahydrophenanthrene has been dehydrogenated to phenanthrene. The point of attachment of the phenanthrene to the preasphaltenes is not on the labeled carbon. Such attachment would move the chemical shift into the region of 137.6-150.7 ppm, depending on the nature of attached groups. It also is not attached at the carbon para to the label which moves the signal to 119.5-120 ppm for an alkyl attachment and 127.3 ppm for an aromatic attachment. Attachment of the phenanthrene at the ring position ortho to the label by some groups, some types of alkyl attachments, attachment at the position meta to the label, and attachment at one of the unlabeled rings will not be seen in the chemical shift position of the labeled carbon. Since the sharp signal is in a virtually unperturbed position, the phenanthrene must be adducted at one of the unlabeled rings or at the position ortho or meta to the labeled carbon.

Some phenanthrene is also attached as octahydrophenanthrene. There are sharp signals at 29.6 ppm in both the unlabeled and labeled runs.

However, in the labeled run, the ratio of aromatic carbon area, corrected for the sharp signal at 128.4 ppm to the area of the signal at 29.6 ppm is less by a factor of 7 than the same ratio in the unlabeled run. This indicates that there is substantially more area in this region in the labeled run. The chemical shift of the labeled carbon in octahydrophenanthrene is 30.3 ppm, which could overlap with the signal at 29.6 ppm under conditions where  $\text{Cr}(\text{acac})_3$  is added to the spectrum. In fact, there appears to be a downfield shoulder on the peak at 29.6 ppm in the labeled run. This indicates that there is some labeled octahydrophenanthrene adducted. The fact that the chemical shift of the labeled carbon is not moved substantially from its unadducted position indicates that it is adducted at either of the two aromatic rings or at the  $\gamma$  aliphatic carbon in the saturated ring. By analogy with tetralin, if it were attached at the labeled carbon, the chemical shift would be at 38.4 ppm. If it were attached at the aliphatic carbon  $\alpha$  or  $\beta$  to the labeled carbon, the chemical shift of the labeled carbon would be 34.3 ppm or 26.8 ppm, respectively. Attachment in the  $\gamma$  position would not perturb the chemical shift of the labeled carbon. Since the chemical shift is virtually unperturbed, the point of attachment must be at the  $\gamma$  aliphatic carbon or on the two aromatic rings.

#### CONCLUSIONS

Adduction of donor solvents occurs during eastern shale conversion. Tetralin is adducted as tetralin, naphthalene, and isomerized tetralin. Mesitylene is adducted through the aromatic ring or unlabeled methyl groups rather than the labeled methyl group. Octahydrophenanthrene is adducted both as octahydrophenanthrene and phenanthrene.

#### REFERENCES

1. Miknis, F. D. and Maciel, G. E., Atomic and Nuclear Methods in Fossil Energy Research, Filby, R. H., ed., Plenum, NY, 1982, pg. 349.
2. Cronauer, D. C., McNeil, R. I., Young, D. C., and Ruberto, R. G., Fuel (1982), 61, 610.

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Table 1  
<sup>13</sup>C NMR Analysis of Naphthalene/Tetralin  
 Adduction in Pentane Solubles

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Shale Derived Material	81.6%
Adducted Tetralin	9.6%
at $\alpha$ position by aromatics	1.6%
at $\alpha$ position by alkyls	1.4%
not in aliphatic ring	6.6%
Adducted n-Butyl Benzene	1.0%
Adducted Methyl Indane/Methyl Propyl Benzene	1.0%
Adducted Naphthalene	6.8%
at $\alpha$ position by aromatics	0.7%
at para position with alkyl and methyl	0.3%
at $\alpha$ position by methyl	0.2%
at m position or in unlabeled ring	4.7%
at $\alpha$ by short alkyl with para alkyl	0.3%
0 to label by aromatics	0.5%

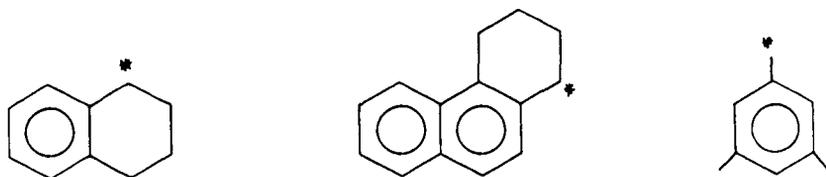


FIGURE 1.  $^{13}\text{C}$  LABELED (\*) COMPOUNDS USED IN ADDUCTION STUDY

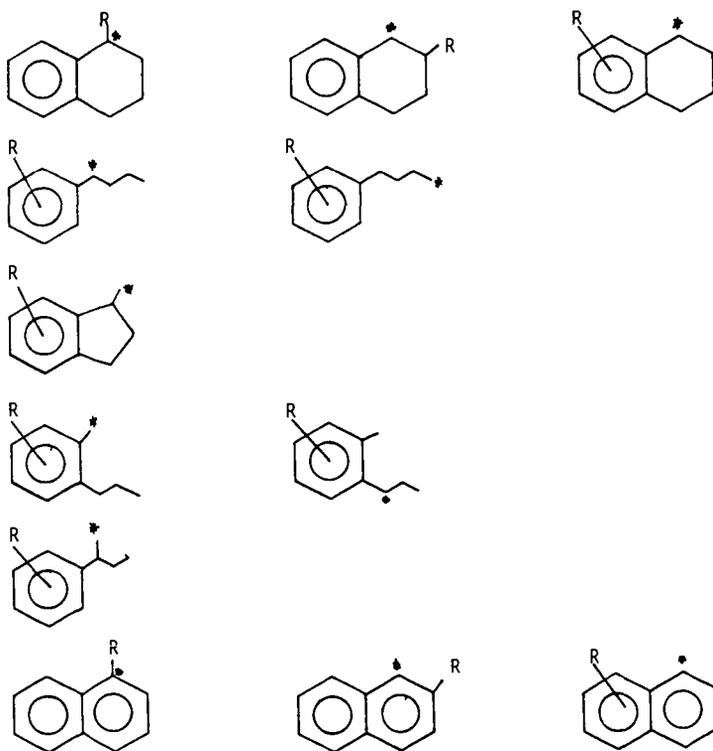


FIGURE 2. POSSIBLE FATES OF TETRALIN DURING ADDUCTION

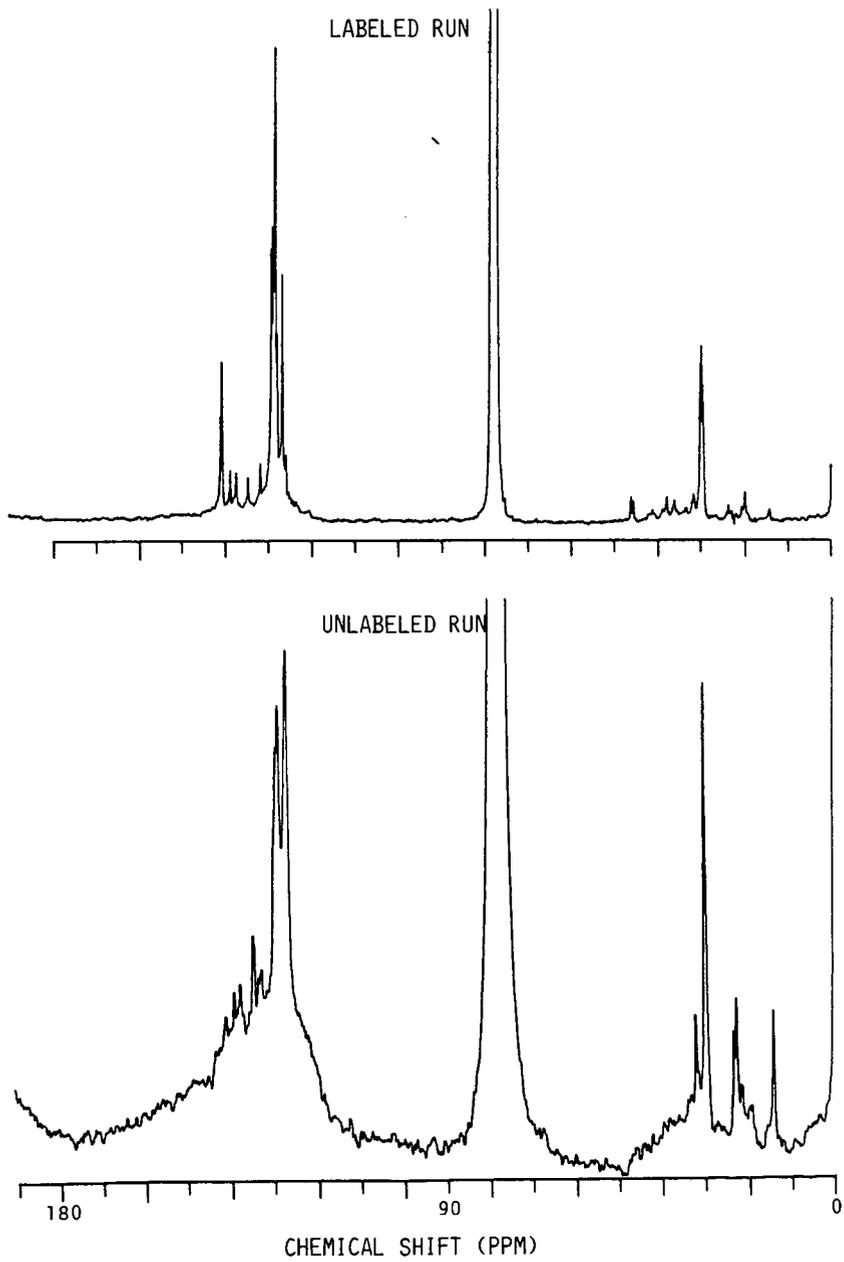


FIGURE 3.  $^{13}\text{C}$  NMR SPECTRA OF PENTANE SOLUBLES FROM TETRALIN RUN