

INVESTIGATION OF LIQUEFACTION MECHANISMS USING MOLECULAR PROBES

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INTRODUCTION

The mechanisms of coal liquefaction have been investigated using 1,3-dimethylnaphthalene and decalin as molecular probes. These two pure compounds have been added to various mixtures composed of a coal, a liquefaction solvent, and a high molecular weight alkane. In all cases, the amount of the probes added to the reaction mixture of coal, solvent, and alkane is small enough that the probes themselves are unlikely to perturb the reaction chemistry to a measurable degree.

The mixtures were heated in small autoclaves to liquefaction conditions, and the products recovered for analysis by quantitative gas chromatography. From the analysis of the products from the added probes, it is possible to draw conclusions about the relative amount and kind of intermediates that were created by the liquefaction conditions. For example, cis-decalin is transformed to the equilibrium mixture of the cis-and trans-isomers by the abstraction of hydrogen from either tertiary position by a free radical (1,2). The extent to which the equilibrium has gone to completion is then a measure of the exposure of decalin to radicals of sufficient reactivity to abstract the tertiary hydrogen. In the case of 1,3-dimethylnaphthalene, it is the monomethyl products that are of particular interest. Dealkylation of aromatic compounds is known to proceed under liquefaction conditions by the attack of free hydrogen atoms (3,4) or by the transfer of a hydrogen atom from a reactive donor (5). The total amount of demethylation is then a measure of the exposure of 1,3-dimethylnaphthalene to the total of free hydrogen atoms plus hydrogen atom donors. The use of the 1,3-isomer also allows the selectivity of the attack of hydrogen atoms to be measured. Loss of the methyl group from the 1-position leaves 2-methylnaphthalene as the product, whereas loss of the methyl group from the 3-position leaves the 1-methylnaphthalene as the product. The ratio of these easily separated isomers is then a measure of the weighted average of the selectivities of the entire population of hydrogen atom donors to which the probe is exposed.

In the present application of this approach, it is of particular interest to probe the effect of using petroleum residua as the liquefaction solvent in conjunction with coal. A combination of coal and resid was selected that has previously been used at the Pittsburgh Energy Technology Center for detailed evaluation of coprocessing schemes (6). The results

described below show that the interaction of coal and residua may lead to a reaction environment wherein the exposure of the probes to free radicals is enhanced over that expected based on additive behavior alone. The addition of coal, in particular, also has a very large influence on the selectivity of demethylation of dimethylnaphthalene.

EXPERIMENTAL

The 8-gram reaction mixtures contained 2.5% cis-decalin, 2.5% 1,3-dimethylnaphthalene, 0-20% Illinois No. 6 coal, 0-20% Maya atmospheric tower bottoms (ATB), and 57-95% n-octacosane or n-dotriacontane as solvent. The 40-mL reactors were pressurized to 1200 psig with hydrogen, heated to 425°C within 5-6 minutes by plunging them into a preheated fluidized sand bath, and held at temperature for 15, 60, or 180 minutes. The reaction products were washed from the reactors with tetrahydrofuran, and the soluble products were analyzed by quantitative capillary gas chromatography using internal standards. Selected samples were analyzed by GC/MS. The proximate and ultimate analyses of the coal and ATB are given in Table 1.

RESULTS AND DISCUSSION

The isomerization of cis-decalin is initiated by the free radical abstraction of the tertiary bridgehead hydrogen. Subsequent hydrogen transfer to the near planar radical intermediate leads to a mixture of cis- and trans-decalin. Thus, decalin can be used as a probe for radical activity in general, since its isomerization is initiated by any radical capable of abstracting the tertiary hydrogen. Since the isomerization is reversible, the ratio of decalin isomers eventually approaches its equilibrium value. If the rates of isomerization are constant over time, the rate of approach to equilibrium can be described by the expression for first-order reversible reactions

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = kt \quad (1)$$

where A_0 is the initial mole percent of cis-decalin, A_e is the equilibrium mole percent, A is the mole percent at time t , and k is the pseudo-first-order rate constant. Added radical sources will increase the pseudo-first-order rate constant and thus increase the rate of equilibration. Furthermore, if the added source provides over time a stable concentration of radicals of constant reactivity, the rate of equilibration should be well fit by Equation 1. To test this supposition, the extent of equilibration was measured after 15, 60, and 180 minutes without an additive and with either coal or petroleum residuum.

The time dependence of the decalin isomerizations is shown in Figure 1. The linear regression results are given in Table 2. The value of A_e was calculated by extrapolating the results of Schucker (7) to 425°C. The expected equilibrium ratio is 5.0, or about 83% trans-decalin. The large effect of added Illinois No. 6 coal is evident even at 15 minutes. The increase in the rate constant is striking; it becomes 50% larger when 10% coal is added. Both the ATB and the coal give good straight-line relationships. Thus, first-order reversible kinetics is a good approxima-

tion to the actual rate, and the efficiency of the hydrogen abstraction is not changing appreciably with time. This indicates that a steady-state radical activity is reached early in the reaction and maintained.

Of the benefits claimed for coprocessing, the synergism between the coal and residua leading to higher conversions for the mixtures than for either alone is especially intriguing (6). A chemical basis for this activity was sought in the total radical activity as measured by the cis-decalin isomerization. To accurately predict the expected activity of mixtures of coal and residua, the influences of coal concentration and ATB concentration on the extent of equilibration at 60 minutes were determined independently. These results, plotted as a function of the weight fraction squared, are shown in Figure 2. The dependence on concentration squared was determined empirically; considerable curvature was apparent when linear correlations with concentration were attempted. Linear regression analysis for the coal data gave

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = 0.32 + 24.9 [\text{Coal}]^2 \quad (2)$$

where A_0 , A_e , and A are as defined in Equation 1. The regression analysis of the ATB data gives

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = 0.30 + 13.1 [\text{ATB}]^2 \quad (3)$$

Both sets of data should, and do, share a common intercept.

Equations 2 and 3 define the dependence of the extent of decalin equilibration in the presence of only ATB or only coal. If there is no interaction between the coal and ATB, then the total isomerization will be given by the sum of the contributions of the coal, ATB, and background. Thus, Equation 4 should predict the extent of decalin isomerization after 60 minutes if no synergism or inhibition is present.

$$\ln \left(\frac{A_0 - A_e}{A - A_e} \right) = 0.31 + 13.1 [\text{ATB}]^2 + 24.9 [\text{Coal}]^2 \quad (4)$$

The 0.31 in this equation is the average of the intercepts of Equations 2 and 3.

A parity plot of experimental data and the predicted results is shown in Figure 3. The open circles represent the data already presented in Figure 2 for the ATB and coal in the absence of one another, which were used to derive the Equation 4. The solid circles represent the data obtained from experiments using mixtures of coal and ATB. At low total concentrations, no difference between the experimental and the predicted extent of isomerization is seen. At moderate concentrations, a significant increase in the extent of isomerization above that predicted by the sum of individual effects becomes apparent. An enhanced steady-state activity is attained for these mixtures of Maya ATB and Illinois coal. The synergism observed in the conversion of the coal and ATB (6) may be related to the enhanced radical activity displayed by these mixtures.

The isomerization of decalin is a non-specific indicator of free radical activity, since any radical of sufficient energy can abstract the tertiary hydrogen. In contrast to this probe for overall activity, the demethylation of 1,3-dimethylnaphthalene is specific for hydrogen atom activity.

The free radical hydrocracking of 1,3-dimethylnaphthalene (DMN) proceeds via the attachment of a hydrogen atom to the position ipso to a methyl group. Subsequent loss of methyl radical leads to either 1- or 2-methylnaphthalene. The yield of the monomethylnaphthalenes is an indicator of the extent of hydrocracking activity. Additionally, the ratio of the products is a measure of the selectivity of the ipso substitution.

In the presence of added coal or ATB, the percent yield of methyl-naphthalenes increases. The change in the 1-methylnaphthalene (1-MN) yield with increasing additive is small at most, while the yield of 2-methylnaphthalene (2-MN) increases with added ATB or coal. The net effect on the selectivity of DMN hydrocracking is shown in Figure 4.

While the total yields of monomethylnaphthalenes provide an estimation of the hydrocracking activity, the ratio of the 2-MN to the 1-MN provides a sensitive measure of the selectivity of the hydrocracking reactions. Selectivity differences indicate a common intermediate does not predominate in all cases. McMillen et al. (5) have shown in studies of model compounds that the selectivity of attack at the 1- and 2-positions of naphthalene may vary according to the hydrogen atom donor responsible for the attack. The most reactive and least selective intermediate is the hydrogen atom itself. Hydrogen atoms are formed as the result of radical hydrogen abstraction from gas phase hydrogen (3). Hydrogen atoms react with suitable acceptors, such as aromatic hydrocarbons, to form sigma complexes. Hydrogen transfer from these complexes is less exothermic and hence more selective than direct attack by hydrogen atoms. In the present experiments, hydrogen atoms may form more selective hydrogen atom donors by attachment to aromatic species in the coal or ATB. In addition to providing hydrogen atom acceptors, the aromatic and hydroaromatic species in the coal and ATB could interact to form the intermediate sigma complexes directly. The disproportionation of dihydroanthracene and anthracene to form hydroanthracenyl radicals is an example of this type of reaction (8). Thus, the selectivity of the hydrocracking reactions can be altered by several means in the presence of coal or ATB.

The results in Figure 4 are particularly interesting for the case of mixtures of coal and ATB. The bottom two curves show the effect of each additive in the absence of the other. The top two curves show the effect of increasing either coal or ATB in the presence of a constant amount of the other. As the concentration of ATB is increased in the absence of coal (bottom curve), the selectivity increases in a nearly linear fashion. This effect is more pronounced in the presence of coal. The efficiency of the coal in altering the selectivity of the hydrocracking is much greater than that of the ATB. Only 5% coal is needed to achieve the same selectivity as 20% ATB.

Surprisingly, selectivities in the mixtures are higher than in either component separately. A limiting value around 7.5 is approached at the highest levels of addition. These preliminary data are insufficient to determine whether the selectivity produced by addition of still higher levels of coal by itself would approach the same limiting value. However, it now appears that the combination of the ATB with the coal enhances the approach of the selectivity to this value. Thus, as revealed by this probe, the nature of the hydrogen atom intermediates becomes more dominated by coal or coal products as ATB is mixed into the systems.

CONCLUSIONS

Selected organic compounds can be used to probe the types of reactions occurring during the coprocessing of coal with petroleum residua. By combining the results from both the decalin isomerization and the dimethylnaphthalene cracking, a fuller description of the nature of the free radical activity during coprocessing can be achieved. As measured by the equilibration of decalin, the total radical activity remains fairly constant with time. This total activity is increased with added coal or ATB, and thus these additives can be viewed as functioning as free radical initiators. Some portion of this total activity results in hydrocracking reactions. The selectivity of these hydrogen atom or mediated hydrogen atom reactions is strongly influenced by coal and to a lesser degree by ATB. The total radical activity is greater than expected from a simple additivity of effects, while the selectivity of the demethylation of dimethylnaphthalene is more strongly mediated by coal when ATB is also present. Work to determine if these effects can be seen for other coals and resids is under way.

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Table 1. Analyses of Coal and Residua

	<u>Illinois No. 6</u>	<u>Maya ATB</u>
<u>Proximate Analysis, wt%</u> (As Received)		
Moisture	11.52	<0.03
Volatile Matter	34.04	----
Fixed Carbon	44.78	----
Ash	9.66	0.06
<u>Ultimate Analysis, wt%</u> (As Received)		
Carbon	61.57	84.2
Hydrogen	5.53	11.9
Nitrogen	0.83	0.29
Sulfur	2.47	3.0
Oxygen (Indirect)	19.94	0.55
Ash	9.66	0.06

Table 2. Linear Regression Results for the Time Dependence of the Decalin Isomerization

<u>Additive</u>	<u>Slope x 1000</u> <u>(Min.⁻¹)</u>	<u>Y-Intercept</u>	<u>R²</u>
None	6.87	-0.09	0.991
10% Maya ATB	6.98	0.00	0.999
10% Illinois No. 6 Coal	10.66	0.01	0.990

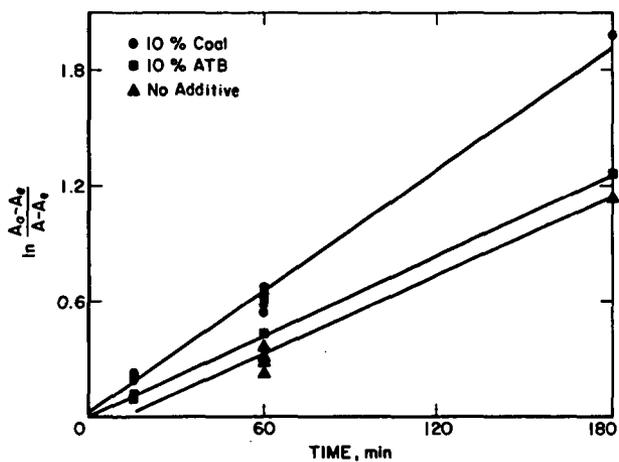


Figure 1. First Order Reversible Kinetics for the Decalin Isomerization.

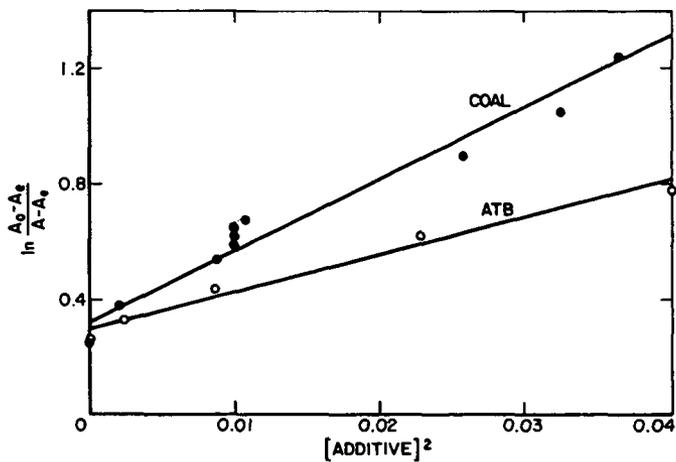


Figure 2. Effect of Coal and ATB on the Rate of the Isomerization of Decalin.

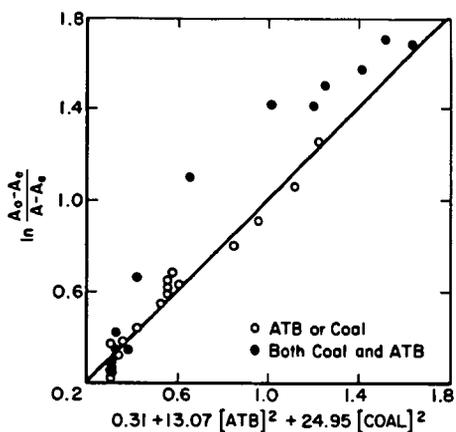


Figure 3. Parity Plot for the isomerization of Decalin.

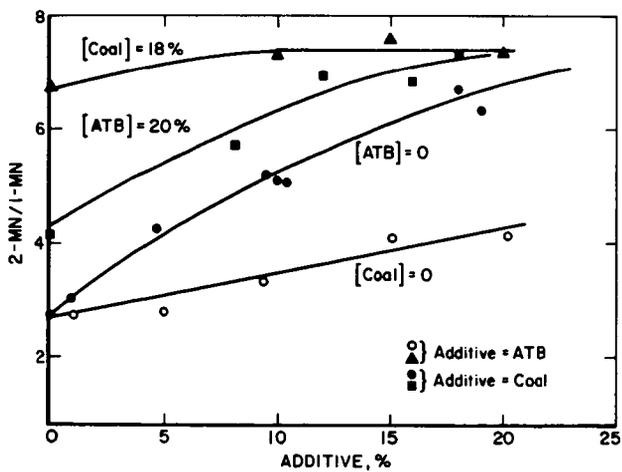


Figure 4. Effects of Coal and ATB on the Hydrocracking Selectivity.