

## REACTIONS OF COAL AND COAL MODEL COMPOUNDS WITH SUPERCRITICAL WATER

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### INTRODUCTION

We recently reported on the successful replacement of recycle solvent by water in conventional coal liquefaction, with and without added hydrogenation catalyst precursors (1). High coal conversions (as measured by THF solubilities) were obtained at modest temperatures (370°-385°) with the use of little or no organic recycle solvent and short reaction times (5-30 minutes).

Water has been used in the past in the liquefaction or the extraction of coal for a variety of reasons. When used in combination with carbon monoxide and a suitable catalyst, water was a source of hydrogen for the reduction of coal (2,3). Appell and co-workers frequently used an organic solvent in combination with water in these studies.

Liquefaction under carbon monoxide has also been carried out by Ross and colleagues (4,5) with slurries composed of coal and either water or aqueous base without an organic solvent. In some cases, Ross has used water to carry dissolved metal salts as homogeneous catalysts as well as a liquefaction medium (6), but still in the presence of carbon monoxide as the reducing gas.

In comparison with conventional organic liquefaction solvents, Stenberg et al. have shown water to be quite effective when used in combination with H<sub>2</sub>S, in particular under synthesis gas rather than hydrogen (7).

Aqueous liquefaction using impregnated catalysts has also been combined in a single operation with supercritical water distillation to separate the oil and asphaltene from the coal char residue (8). Barton's results clearly show that the liquids produced by hydrogenation can be extracted by supercritical water and transported away from insoluble coal residues.

Wender and co-workers have also shown that the simple treatment of coal with supercritical water in the absence of hydrogen or catalyst renders a substantial portion of the treated coal extractable by THF after the product was cooled and recovered from the autoclave (9). The amount of extract obtained depended on the density of the supercritical water. Higher yields were obtained when coal was injected into supercritical water, thus providing a rapid heat-up of the coal, than when a coal-water slurry was heated to operating temperature.

In addition to the physical role of water reported by Wender, it has also been reported that water may directly participate as a reactant in the thermolytic chemistry of certain model compounds. In the presence of water, dibenzyl ether decomposed at 400° C by both pyrolytic and hydrolytic pathways, the latter leading to the formation of benzyl alcohol (10).

The removal of nitrogen from heterocyclic compounds, such as isoquinoline, was also reported to be accelerated in the presence of supercritical water (11).

Taken together, these previous studies by other researchers indicate that under various conditions, supercritical water may act as a good liquefaction medium, dissolve or extract coal-derived liquid products, promote the cleavage of certain bonds likely to be found in coal, provide hydrogen through the water-gas shift reaction, and possibly assist the contracting of coal with catalysts or hydrogen.

Though these reports suggest a rich and varied chemistry in liquefaction with water, fundamental studies with models has received inadequate attention. The objective of this study was to initiate an investigation into the organic reaction mechanisms of coal and coal model compounds with supercritical water.

#### EXPERIMENTAL

A multireactor consisting of five individual microautoclaves, each of approximately 45-mL capacity and attached to a single yoke, was used to study these reactions (12). The entire assembly was immersed rapidly into a preheated, fluidized sand bath, allowing heat-up to reaction temperature in 4-6 minutes. Immersion in a second fluidized sand bath held at room temperature provided rapid quenching. The autoclaves were agitated by a rapid horizontal-shaking motion, assuring good mixing of heterogeneous, multiphase mixtures. Individual thermocouples allowed continuous temperature monitoring of each microautoclave. For all experiments reported here, the reactors, once pressurized, were isolated from the gas-handling manifold by a valve and a short length of tubing of negligible volume. This prevented loss of water from the reaction zone due to condensation in the unheated portion of the system. Separate experiments using different reactors, in which it was possible for water to migrate to unheated regions of the system, indicated that such water loss had a profound but erratic effect on measured values for pressure and coal conversion, and generally led to misleading data.

The pressure at reaction temperature was not measured directly in these experiments. The partial pressure of water was estimated using van der Waal's equation.

Table 1 gives the analyses of the Illinois No. 6 (River King Mine) bituminous coal and process derived solvent (SRC II). The conversion values were obtained by the centrifugation method described earlier (1).

Model compound experiments were performed in the identical reaction apparatus. Any product gases were uncollected. The reactors were washed out with dichloromethane (Fisher; ACS certified) and the aqueous layer removed. The organic layer was filtered through a sintered glass funnel, with subsequent analysis by capillary gc/ms (Hewlett Packard model 5790A gas chromatograph equipped with a Hewlett Packard model 5970A mass selective detector). Mass spectral ionization currents and gc parameters were identical in the analysis of standards and reaction products.

All model compound experiments were reacted at 385° C for 30 minutes. A 1200 psig cold charge of H<sub>2</sub> was employed in each experiment utilizing molecular hydrogen. The bibenzyl reactions used 2.5g (0.014mol) bibenzyl (Aldrich) and 1.8g (0.09 mol) deuterium oxide (Aldrich, gold label). The biphenyl experiments also employed 2.5g (0.016 mol) biphenyl (Aldrich) and 1.8g D<sub>2</sub>O. The reactions with 4-benzylphenol (Chemical Sales Co.), dibenzyl ether (Aldrich) and benzyl ethyl ether (Pfaltz & Bauer), used 0.92 (0.005 mol), 0.99g (0.005 mol), and 0.68g (0.005 mol) respectively, and 4.0g D<sub>2</sub>O in each reactor.

## RESULTS AND DISCUSSION

### I. Bituminous Coal Studies

Inverse isotope effects has been observed by Appell (13) and Ross (14) when water was replaced with  $D_2O$  in coal liquefaction. Appell observed an enhanced conversion of nearly 6% when  $D_2O$  was utilized in place of water with hexahydropyrene (HHP) as a solvent. A significant enhancement was similarly observed by Ross through substitution of water by  $D_2O$  in his use of CO/water systems without a solvent. Ross has attributed this phenomenon to a phenol-keto equilibrium followed by hydride transfer from formate to coal moieties in a Michael sense. The inverse isotope effect, in Ross' argument, results from the fact that the formate reaction with water experiences a normal isotope effect and is therefore slowed in  $D_2O$ , consequently enhancing the stability of active formate by precluding the termination reaction to  $CO_2$  and  $H_2$ , which he suggests rapidly prevails under these conditions.

Ross further contends that all coal liquefaction reactions can be viewed along similar lines. Donor solvent liquefaction, in his concept, results via hydride transfer from hydroaromatic compounds to effect reductions of quinones and/or semiquinones with subsequent elimination of substituent groups.

If the mechanism of liquefaction is indeed ionic, water may be envisioned as a polar solvent, resulting in a lowering of the transition state energy via solvation and correspondingly increased conversions. With this discussion in mind, we undertook two sets of experiments, each comparing  $H_2O$  with  $D_2O$ . The first was essentially a repeat of Appell's experiment with minor variations. Tetralin was employed as the solvent and a higher hydrogen charge was utilized. In an attempt to enhance the ionic character of these reactions, 2mmol of  $Cs_2CO_3$  was added to the water. Ross had utilized the observed catalytic effect of bases in his reactions as a major argument for his proposal of an ionic mechanism.  $Cs_2CO_3$  was chosen since Cs has been reported as the most mobile of the Group IA metals in the gasification of coals (15) and we wished to circumvent, as far as possible, any anomalies from selected ion exchange.

The conversions obtained were identical, within experimental error, as illustrated in Table 2 (68-70 wt. %). Clearly, under these conditions, no isotope effect is evident. It is significant that Appell's work, at much lower hydrogen pressure and 5 fewer minutes residence time, resulted in dramatically higher conversions (84-90 wt. %). The greater ease of hydrogen abstraction from HHP than tetralin is dramatically evidenced by these results. These results do little, however, to support the role of water as reactant in our systems, or an ionic mechanism for liquefaction in general.

If one accepts the arguments of Ross, molecular hydrogen should play no kinetic role in coal conversion. Elimination of hydrogen in favor of the polar solvent water should therefore enhance overall conversions. In this regard, we undertook four experiments, in the absence of molecular hydrogen, as illustrated in Table 3. Comparison of  $H_2O$  and  $D_2O$  with added KOH as a catalyst and tetralin as a solvent resulted in slightly lower conversions for the  $D_2O$  than  $H_2O$  experiments. More significantly, the conversions were considerably lower than those observed in Table 3 where less water, but molecular hydrogen was present. Clearly, molecular hydrogen plays a dominant role even when experimental conditions favor an ionic pathway. Since it is difficult to envision an ionic mechanism for the role of molecular hydrogen in liquefaction, such observations are inconsistent with a general ionic mechanism for

liquefaction and support the free radical hydrogenolysis mechanism proposed by Vernon (16).

Further evidence refuting not only an ionic mechanism, but the role of water as a reactant as well, can be found in comparison of Experiments 5B and 5C. Removal of the KOH catalyst and reduction of water by a factor of two resulted in no appreciable change in conversion.

A change in solvent from tetralin to SRC II, however, gave a dramatic decrease in conversion. Such an effect may be easily attributed to a lower number of hydrogen atom donors in SRC II when compared to tetralin. The significant role of such donors in water assisted liquefaction, regardless of the liquefaction mechanism, is clearly evident from these experiments.

## 2. MODEL COMPOUND STUDIES

In Appell's experiments with coal (13), the incorporation of deuterium into coal derived hydrocarbons, pyrene, and HHP was noted. Ross noted a lack of correlation between exchange and conversion in his study (14). Though his results suggested to Appell that water was a reactant under his conditions, these results could also be explained by an initial low temperature exchange of phenolic hydroxyls with  $D_2O$ , followed by higher temperature deuterium atom transfers between these now deuterated phenols and hydrocarbon radicals.

If our proposed explanation is operative, the use of O-alkylated coals could circumvent the low temperature exchange. Observation of deuterium exchange in coal products derived from such a coal may then indicate true reaction chemistry. Hydrolysis of the methyl ether of guaiacol by supercritical water was observed by Paulaitis, however. If the hydrolysis of methyl ethers is general and ionic in supercritical water, as their work with guaiacol would indicate, the formation of phenols from these hydrolysis reactions may also lead to exchange. Such an occurrence would invalidate our arguments for the experiments with O-alkylated coal.

Further, the hydrogenolysis of anisole, as reported by Friedman (17), may also indicate a reaction pathway by which phenols, protected as methyl ethers, could react in what is essentially an exchange reaction. If the phenoxyl radical initially formed from anisole is reduced to the phenoxide ion, such exchange may occur. The observation of cresols in Friedman's work, however, would tend to indicate that such is not the case.

We attempted to address both concerns via the reaction of several model compounds with  $D_2O$  in the presence and absence of molecular hydrogen.

Significant exchange between bibenzyl and  $D_2O$  was observed only upon the introduction of molecular hydrogen to the system. Exchange was not observed with biphenyl either in the absence or presence of molecular hydrogen. These results suggest that H-atoms produced from the hydrogenolysis of bibenzyl reacted with the large molar excess of  $D_2O$  to produce HD and hydroxyl radicals. Once HD was formed, incorporation of deuterium into a variety of products would be expected. The hydroxyl radical could then be capped by a variety of species, including molecular hydrogen in what would amount to a chain reaction.

There was no evidence for the observation of hydroxylated products in the total-ion-chromatograph (TIC) of the dichloromethane soluble fraction. The aqueous fraction was unanalyzed.

The TIC of the dichloromethane soluble products from the reaction of benzyl ethyl ether indicated only alcohol-d exchanged benzyl alcohol. There was no evidence in the mass spectra for incorporation of deuterium into any C-H bond. The hydrolysis appeared complete. It is important to note that molecular hydrogen was unempoyed in this experiment.

Analysis of the TIC from the organic fraction of the similar reaction with dibenzyl ether indicated only unexchanged reactant. Benzyl alcohol was not observed.

Analysis of the dichloromethane soluble products from the reaction of 4-benzyl phenol with deuterium oxide in the absence of molecular hydrogen is most intriguing. Only 4-benzyl phenol was observed in the TIC, however, massspectral analysis indicated the major product to be doubly labeled. Fragment ions clearly illustrate the incorporation of deuterium into C-H bonds.

Taken together, these results suggest electrophilic aromatic substitution between the activated phenol and a hydronium ion-d<sub>3</sub>. Activation of the aromatic ring was insufficient with the other models to effect such exchange.

Additional experiments are currently underway in our laboratory to further substantiate this hypothesis. The possibility of similar reaction between coal and water would be easy to support. Coal would be expected to possess structural units with relatively low energy as carbocation leaving groups through substitution by a proton in water. Such moieties would include carbocations with the possibility of resonance stabilization by an aromatic system (e.g., benzyl carbocation), alpha to an ether oxygen (similar to those discussed by Larsen (18)) or carbonyls (e.g., decarboxylation).

Should additional model compound studies support the feasibility of similar reactions between water and coal, the observed enhanced yields from liquefaction with water may, at least partially, be attributed to the ipso substitution of a proton for a substituent on an aromatic moiety in coal.

This suggestion in no way presupposes that electrophilic aromatic substitution is the only mechanism operating in liquefaction. It may, however, indicate a dormant reaction pathway under the traditional donor solvent liquefaction conditions, which now contributes to the overall production of liquid products, thus the apparent increase in yield. The solvation effect of supercritical water in promoting these possibly new ionic pathways in aqueous liquefaction is currently under investigation in our laboratory.

#### ACKNOWLEDGEMENTS

The expert and varied talents of Mr. Henry Davis are gratefully acknowledged in performing the mini-reactor experiments. The generous support of the DOE (DE-FG22-85PC81544) in funding this research is appreciated. Appointment by Oak Ridge Associated Universities of MAM to PETC during the summer of 1984 is also acknowledged and appreciated.

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TABLE 1. ELEMENTAL ANALYSES OF COAL AND VEHICLES.<sup>a</sup>

<u>Material</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>S</u>
Illinois No. 6 Coal, River King Mine <sup>b</sup>	73.7	5.6	1.5	14.8	4.5
SRC-II Distillate	87.1	8.0	1.4	3.0	0.4

<sup>a</sup> wt.%, daf basis, Huffman Labs, Wheatridge, Colo.

<sup>b</sup> Moisture-free ash content was determined to be 13.6 wt.% for the River King Coal. As used, the coal contained 3 wt.% water.

Table 2. Comparison of H<sub>2</sub>O and D<sub>2</sub>O as Vehicles Under Water Assisted Liquefaction Conditions<sup>1</sup>

<u>Ex. #</u>	<u>Vehicle</u>	<u>Conversion<sup>2</sup></u>
4A	H <sub>2</sub> O	68
4B	D <sub>2</sub> O	70

<sup>1</sup> Reaction Conditions: 4.00 g River King Coal; 1.70 g H<sub>2</sub>O or D<sub>2</sub>O; 1.50 g tetralin; 1200 psig H<sub>2</sub> (cold); 385°C; 20 mins. at temp.; 2 mmol Cs<sub>2</sub>CO<sub>3</sub> added via the water.

<sup>2</sup> DAF basis; average of duplicate runs; reproducibility ± 1 wt. %.

Table 3. Aqueous Liquefaction Without Molecular Hydrogen<sup>1</sup>

Ex.#	Vehicle	Solvent <sup>2</sup>	Catalyst <sup>3</sup>	Est. Reaction <sup>4</sup> Pressure	Water <sup>5</sup> Density	THF Conversion <sup>6</sup>
5A	D <sub>2</sub> O (22 mmol)	Tetralin	KOH (8 mmol)	4350	0.110	42
5B	H <sub>2</sub> O (22 mmol)	Tetralin	KOH (8 mmol)	4350	0.097	45
5C	H <sub>2</sub> O (9 mmol)	Tetralin	-----	1790	0.043	46
5D	H <sub>2</sub> O (9 mmol)	SRC II	-----	1790	0.043	26

<sup>1</sup> Reaction Conditions: 4.00 g River King Coal; 385° C; 40 minutes at temperature

<sup>2</sup> 1.50 g per reactor

<sup>3</sup> as an aqueous solution

<sup>4</sup> as calculated by van der Waal's Equation does not include solvent contributions

<sup>5</sup> g/cc

<sup>6</sup> DAF basis; average of duplicate runs; reproducibility ± 1 wt. %