

COAL STRUCTURE AND BEHAVIOR--INTERFACIAL CHEMISTRY IN COAL

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Introduction and Background

A model for the organic phase of coal recently suggested by Shinn is shown in Figure 1 (1). This model is based on a reconstruction of the parent structure of an Illinois No. 6 coal following a thorough evaluation of reported product data from various liquefaction processes. The model structure contains 11% oxygen, with about 35% of the total O present as ether oxygen. This ether fraction is the same as the value we established in recent work on the fate of oxygen in an Illinois No. 6 coal during thermolysis and conversion (2).

Insofar as it presents an organic network of linked aromatic units, the model is similar to others presented earlier, as summarized by Davidson (3a) and Gray and Shah (3b). However, the Shinn model is closely tied to more recent evidence from liquefaction and analytical studies and as such is the most realistic picture of the organic phase available. Like earlier models, this model is limited to the organic components in coal and ignores the mineral phase. Shinn acknowledges that avoiding the heterogeneous aspect of coal structure precludes a full understanding of its structure and therefore its behavior.

This point is key to the discussion here, as is emphasized by the fact that the structure in Figure 1 is not consistent with some facts on coal behavior recently uncovered by us and others. We submit as a working hypothesis that the reactive centers in coal include and may be dominated by substantial interfacial regions common to both the organic and mineral phases. The focus of our attention is not the catalytic effects of mineral matter in coal conversion to liquids or gases, which have been investigated during the past three decades (4) or longer, but rather the chemistry at the organic/mineral boundary specifically.

While most inorganic material in coal is present in a discrete mineral phase over a range of sizes, from large crystallites to micron-size grains (5), Mraw, et al. demonstrated the presence of very small clay inclusions down to 10 nm in size (6). They speculated that the fine grain size corresponds to a very high surface area, which in turn could play a role in the chemistry of coal. More recently, Allen and VanderSande reported even smaller, ultrafine mineral material, estimating abundance of up to 15% of the full mineral assay (7). Their technique required comparison of pairs of x-ray spectra of respectively a particle and the organic matrix 1-2 particle diameters away for comparison. As is seen in Figure 2, while the particle in question clearly is rich in titanium, both spectra, in particular that from the organic matrix, show aluminum and silicon. It would thus appear that the organic phase includes clay inclusions with characteristic sizes extending below their 2 nm resolution limit, perhaps extending to collections of hundreds of atoms. The result would be an organic/mineral interface of enormous extent.

This picture of an integrated structure could be tied with the recent findings that are otherwise unreconcilable with conventional structures. Towne, et al. found that the addition of water to conventional H-donor media substantially increased the

extent of liquefaction (10). Brandes and Graff found that hydrothermal treatment activated coal for subsequent mild gasification (11a,b). Perhaps the most striking aspect of this work was the finding that their brief pretreatment changed the swelling characteristics of the coal so that water itself became a swelling agent. Bienkowski et al. have reported a beneficial effect on liquefaction (12) in line with some of our work, where aqueous pretreatment activates the coal toward subsequent liquefaction (13).

Results

In an attempt to evaluate the importance of interfacial chemistry to coal behavior, we have conducted studies at 400°C with both H₂O and D₂O, using both Illinois No. 6 coal (PSOC 1098) and pure organic compounds. We were directed to this approach through accounts in the geochemical literature, in which considerable attention is paid to kerogen/mineral interactions tied to petroleum production (14,15).

Figure 3 summarizes our effort, and virtually none of the material presented here is consistent with the organic structures depicted in Figure 1. We found that while coal recovered from simple hydrothermal treatment in D₂O/N₂ for 20 minutes under nitrogen contained more than 90% of the starting carbon, 30% of the starting hydrogen and about half the starting oxygen were lost. Our account of the anomalous O-loss has recently appeared (2). These losses could not be accounted for by CO₂ and light hydrocarbon evolution. Of the remaining protium in the product, 53% had been exchanged for deuterium. The product had been subjected to back-exchange in H₂O at mild conditions to convert the phenolic hydrogen to protium, so the large levels of exchange were strictly for hydrogen bonded to carbon.

In other runs the coal was converted to products that were 50-60% toluene soluble (TS) by replacing the N₂ with CO. The D-fractions for both TS and toluene insoluble (TI) fractions (back-exchanged) were 53% and 59% respectively, or a composite value essentially the same as that for the produce from the N₂ run. Thus, the conversion chemistry operated on the material that had undergone isotope exchange rapidly and prior to conversion to the TS fraction, a very useful finding since structural factors subsequently developed from NMR work for the TS fraction could then be tied to the original structure with some confidence.

¹H NMR studies on the TS fractions from parallel H₂O and D₂O runs revealed little exchange for the β- and γ-alkyl hydrogens in the coal. About 57% of the aromatic protium was exchanged, a result in accord with the known phenolic exchange chemistry under these conditions (16) and consistent with the known phenolic content of the coal and the structure in Figure 1. For the benzyl hydrogen, however, the result was striking. We found that fully 76% of the benzyl hydrogens in the TS fraction were replaced by deuterium in the 20-minute treatment.

These findings can be compared with those from work with work under the same conditions with pure organic materials. At 20 minutes in D₂O we found no trace of exchange for benzene, toluene, or bibenzyl. Indeed, we had to extend the period to 1200 minutes to observe the introduction of deuterium into the benzylic positions in bibenzyl and the toluene derived from it, while benzene and toluene themselves were still virtually unexchanged after this extended period.

Thus, the benzyl-protium exchange rate in coal is roughly 100 times faster than that for bibenzyl and considerably faster than that for toluene. This result can be translated to suggest that the thermal generation of free radical sites in the coal

operates at a rate two to three orders of magnitude greater than that for bibenzyl. However no feature in the organic structures proposed for coal can generate such a flux of reactive free radicals by a wide margin. Indeed, we are aware of no chemistry for structures such as that in Figure 1 which can accommodate our findings for both the H and O components of the organic phase.

Discussion

Accordingly, we are led to consider a scenario in which the chemistry involves significant reactions at the organic/mineral interface. Two accounts from areas outside coal chemistry lend support to our view. The first is geochemical work on the origins of petroleum by Hoering (17). The results and rationale are rather detailed, and they are discussed fully in Appendix A. In summary, Hoering reports anomalous incorporation of deuterium into hydrocarbons released from shale-bound kerogen upon hydrothermal pyrolysis in D_2O that we view as reconciled only through action directly at the kerogen/shale interface. The parallel to our results with coal is compelling and suggests similarity in both chemical structure and chemistry.

The second occurs in research tied to work in highway degradation, as reported by Ensley and coworkers (18a,b). Prepared bitumen/clay interface samples were studied and showed a distinct interphase volumes with a striated structure, were disrupted by water, and were most likely regions rich in H-bonding between the polar fractions of the bitumen and the mineral surface. At present, little is known about the specific chemical speciation within the region (19). The disruptive action of water seen here is that we suggest plays a role in the beneficial effects of water pretreatment observed for coal, and can act as a probe into coal structure.

Our findings could have considerable impact on both fundamental coal chemistry and the practical aspects of coal use. The potential effects on the understanding of coal behavior derive from the fact that clays are known to inhibit free radical reactions. For example, the free radical polymerization of methyl methacrylate is fully suppressed in the presence of montmorillonite, even at temperatures as high as $100^\circ C$ (20). Given the presence of a variety of clays in the mineral phase in coals, this striking factor raises the question of the significance of free radical chemistry generally in coal and supports the view put forward in this proposal that the overall structure of coal, including the nature of its reactive centers, can be viewed from a new perspective.

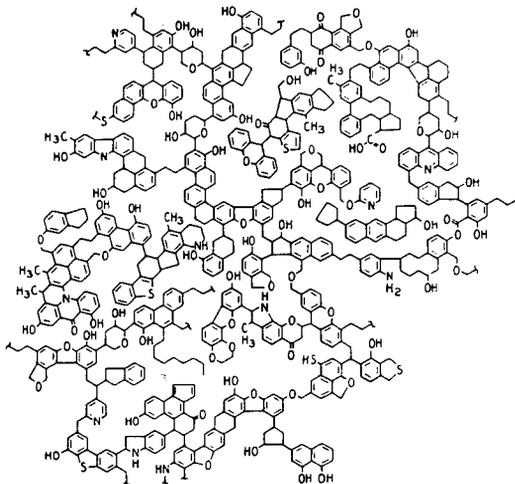
The implications for practical ends can also be noted. We can presume that the polar, heteroatom-containing portions of the organic phase migrate over geologic time to the mineral surfaces, resulting in heterogeneous distribution of the N- and S-containing components within the organic phase, concentrated around the mineral microinclusions. Just such a slanted distribution has been noted for the organic material removal from Green River shale (21). Thus, properly conducted hydrothermal pretreatment or microbial/enzymatic delamination at the mineral/organic interface could lead to separation of heteroatom components and mineral material.

Finally, geochemical studies on the role of the mineral matrix in the pyrolysis of petroleum yielding kerogen show that hydrocarbon retention and char formation correlates with the clay content of the matrix (22). Increased clay levels lead to greater carbonization. By extension, we suggest that the presence of ultrafine clay inclusions in coal contribute to the retrogressive chemistry operative during liquefaction and mild gasification and indeed may be the major factor in such action.

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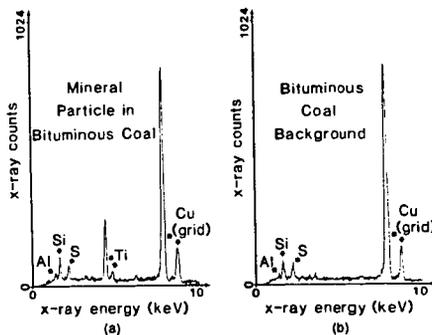
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SOURCE: J. H. Shinn, *Reactive Model of Coal Structure*, *Fuel* 63, 1190 (1984).

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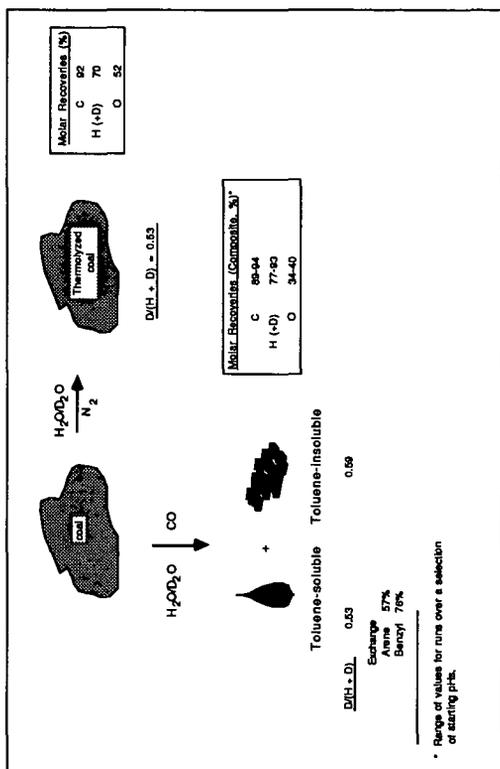
Figure 1. Model of bituminous coal structure.



SOURCE: R. M. Allen and J. B. VanderSande, *Analysis of Sub-Micron Coal Mineral Matter*, *Fuel* 63, 27 (1984)

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Figure 2. Examples of x-ray spectra from bituminous sample.



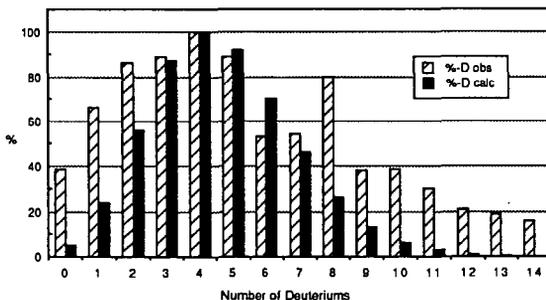
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Figure 3. Coal studies at 400°C/20 min.

APPENDIX A

GEOCHEMICAL SUPPORT FOR THE PROPOSED COAL MODEL

Our proposition of a significant and reactive mineral/organic interface in coal is supported by a somewhat parallel set of results developed in research into petroleum formation by Hoering, who reported on pyrolyses of samples of previously extracted Messel shale (1). The pyrolyses were conducted in D_2O at $330^\circ C/3$ days, and they generated a series of saturated hydrocarbons resembling natural petroleum. The hydrocarbons were extensively deuterated. A portion of the product was a series of n-alkanes in the range of 14-30 carbon atoms, with each alkane containing distributions of isomers with 0 to more than 14 deuterium atoms. The maximum deuterium substitution was in the 4-6 range as shown in Figure A-1 for the C_{18} product, a profile representative of the entire suite of isolated alkanes.



Source: T. C. Hoering, *Org. Geochem.*, 5, 267-278 (1984).

Figure A-1. Deuterium distribution.

The distribution is broad, with the D_0 case nearly 40% of the D_4 material, and significant deuteration continues out to beyond D_{14} . The author ruled out the presence of preexisting, trapped alkanes, since in that case undeuterated product would have dominated the samples. Moreover, in control experiments in which the shale was purposefully spiked with an n-alkane, it was recovered virtually entirely untagged. The purposeful addition of a terminal n-alkene resulted in the recovery of about half the corresponding alkane, a curious result suggesting the presence of reducing chemistry, but with the product containing only small quantities of deuterium.

Thus, both preexisting alkanes or olefin precursors can be eliminated as origins of the multilabeled n-alkanes. Also ruled out on the basis of the deuterium isotope

distribution is their formation from thermal production of the corresponding n-alkyl radicals through kerogen pyrolysis, followed by a successive deuterium attachment chain. The distribution expected from such a process can be estimated by numerical simulation of sequential exchange, ignoring isotope effects which would be insignificant at these temperatures. The result, adjusted so that the maximum substitution is at C₄, is presented in Figure A-1, and it is considerably more narrow than the one observed, with the bulk of the substitution falling between C₂ and C₇. The calculated D₀ level is only about 10% of that observed, and virtually no substitution is expected beyond C₁₁.

The calculated profile is firm and applies to any sequential exchange mechanism which the rate is the same for all steps. Thus the considerably broader distribution observed in Hoering's data dictates either several different mechanisms operating in parallel, an unlikely proposition, or different precursors for each isotope isomer. We adopt the latter view here.

We suggest that alkane precursors exist at the mineral surface, attached to the surface over several points. Theng has discussed a similar situation for the adsorption of linear polymers on clay (2). D₂O then engages in some chemistry yet to be uncovered, releasing the alkane and creating a C-D bond at the point of attachment. The reducing chemistry noted for the case of the consumed alkene could play a significant role.

We propose, by extension, a similar scheme for coal. We envision mineral/organic attachment at the portions of the coal structure leading to benzylic positions following hydrothermal treatment.

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