

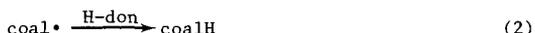
POSSIBLE HYDRIDE TRANSFER IN COAL CONVERSION PROCESSES

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INTRODUCTION

The conversion of coal to liquid fuels is usually carried out in the presence of an H-donor solvent (H-don) such as tetralin. The chemical route commonly suggested for the process is



in which there is initial thermal homolysis of sufficiently weak bonds in the coal structure yielding radical sites. These reactive sites are then "capped" by transfer of hydrogen atoms from the donor solvent. We will discuss here the chemistry of this process, including detailed consideration of the thermochemistry of Steps 1 and 2 above. We will then present some of our recent data, which suggest that there may be an ionic component in the process.

BACKGROUND

Step 1 above requires that there be bonds in coal which are weak enough to break in appropriate numbers at conversion temperatures and times. Table 1 displays some kinetic data for the cleavage of benzylic bonds in a series of increasingly aromatic compounds. In accord with expectation, an extension of the aromatic system increases the resonance stability of the thermally-formed free radical and therefore increases the ease with which the benzylic bond is broken. The phenanthrene system appears to be no more easily cleaved than the naphthalene system; however, ethyl anthracene is clearly destabilized significantly more than the other compounds in the table. The large decrease in bond-dissociation energy for the anthracene system is reflected in the three to four orders of magnitude increase in rate of scission at conversion temperatures as shown in the table.

Also pertinent to discussion of Step 1 is the material in Table 2, which includes bond dissociation energies and kinetic data at conversion temperatures for a series of C-C bonds. For the purposes of this discussion it can be assumed that substitution of -O- for -CH₂- does not change the thermochemistry. Thus, for example, the Ph-OPh bond and the Ph-CH₂Ph bond are similar in strength. Again not surprisingly, double benzylic resonance as present upon the scission of the central bond in bibenzyl results in a significant destabilization, and that compound, as well as benzyl phenyl ether, PhOCH₂Ph, are the only compounds with bonds easily broken under conversion conditions. If the full three to four orders of magnitude increase in rate shown in Table 1 for anthracene systems is applied, we see that perhaps the 1,3-diarylpropane system may also be sufficiently unstable for conversion at 400°-500°C. Thus it would seem that for coal con-

version via Steps 1 and 2, at least at 400°C, the first step can be sufficiently rapid for some structural features. We will discuss below some conversion data at 335°C, however, which suggest that thermally-promoted bond-scission is not fully consistent with experimental observation.

Next, a consideration of the kinetics for Step 2 raises some questions. The transfer of hydrogen in similar reactions has been well studied, and Table 3 presents data for the relative rates of transfer of hydrogen from a number of hydrocarbons to the free radical $\text{Cl}_3\text{C}\cdot$ at 350°C. The donor hydrocarbons are listed in order of increasing ease of H-transfer to the free radical. Tetralin is near the middle of the list. The most reactive donor in the table, 1,4-dihydronaphthalene, is about four times as active as tetralin.

The table also shows the results of experiments with the donors and coal in phenanthrene as solvent. Consistent with the transfer of hydrogen in a radical process, those donors less reactive toward $\text{Cl}_3\text{C}\cdot$ than tetralin are also less effective than tetralin in conversion of coal to a phenanthrene-soluble product. However, in contrast to the chemistry of Step 2 in the above scheme, we see that those donors which are more reactive toward $\text{Cl}_3\text{C}\cdot$ than tetralin are also less effective in their action with coal. Thus this simple conversion scheme is suspect.

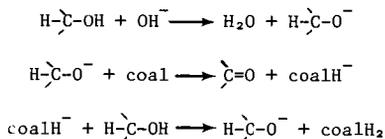
CURRENT RESULTS WITH HYDRIDE-DONORS

We have reported on the use of isopropyl alcohol as an H-donor solvent in coal conversion, and specifically on the effects of the addition of strong bases such as KOH to the system (1). We found that *i*-PrOH brought about a conversion of Illinois No. 6 coal very similar to the conversion level obtained by tetralin under the same conditions. These results are listed in Table 4, along with the results of more recent experiments using methanol as the solvent and adding KOH to the system.

Isopropanol is of course a well known reducing agent under basic conditions, reducing carbonyl compounds via hydride transfer, and becoming oxidized to acetone in the process (2). The table shows that the addition of KOH to the system significantly increases the effectiveness of the coal conversion reaction, and it would seem that such a system would have an advantage over one based on tetralin, where significant catalysis of hydrogen transfer has not been directly demonstrated. We found in our experiments with *i*-PrOH/KOH at 335°C that coal was converted to a product about 60% soluble in *i*-PrOH, that fraction having a number-average molecular weight of about 460.

In some model compound studies with the *i*-PrOH/KOH system we found that anthracene was converted to 9,10-dihydroanthracene in 64% yield. Benzyl phenyl ether was also studied and was converted to a polymeric material under the reaction conditions. There were no traces of phenol nor toluene, the expected reduction products.

We found subsequently that MeOH/KOH media at 400°C were very effective reducing systems, as the results in the table demonstrate. The methanol work yielded products with significant reductions in organic sulfur levels, and moderate reductions in nitrogen levels. We suggest the mechanism of reduction is ionic in nature, involving hydride transfer. Thus



where coalH^- and coalH_2 are an anionic intermediate and reduced coal respectively. The net reaction is

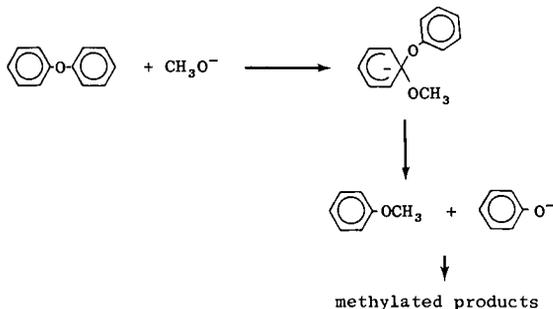


and in fact in the i -PrOH work we isolated acetone in quantities consistent with the quantities of hydrogen transferred to the coal.

The final coal product in the MeOH/KOH experiments was 20%-25% soluble in the methanol. When the methanol was removed, the resultant product was a room temperature liquid with the properties described in Table 5. The polymethylphenol fraction is apparently formed by the cleavage of phenolic ethers and subsequent methylation by the CO present in the reaction mixture as a result of methanol decomposition. The methylation reaction has been observed before for similar systems (3).

The methanol-insoluble product was also upgraded relative to the starting coal. Its H/C ratio was 0.86, its sulfur and nitrogen levels were 0.8% and 1.2% respectively, and it was fully pyridine-soluble.

Model compound studies were carried out in MeOH/KOH also, and the results are shown in Table 6. Phenanthrene and biphenyl were quantitatively recovered unchanged by the reactions, and bibenzyl was recovered in 95% yield, with small amounts of toluene observed. Anthracene and diphenyl ether, on the other hand, were converted respectively to 9,10-dihydroanthracene and a mixture of polymethylphenols similar to that observed in the work with coal. The cleavage of diphenyl ether via hydrogenolysis should yield both benzene and phenol as products; we saw no benzene in our study, and our observation of the polymethylphenols and anisoles thus indicates that nucleophilic ether cleavage is taking place. In other words, it appears that phenoxide is displaced by methoxide.



so that a favorable feature of the MeOH/KOH system in addition to its reducing power is its facility at cleaving otherwise inert ethers.

The alcohol/base chemistry observed here led logically to a system including CO/H₂O/KOH, and accordingly, a series of experiments was performed at 400°C. The COSTEAM Process is of course similar in nature, but without the purposeful addition of base. Also, it is applied primarily to lignite, though the COSTEAM chemistry has

been applied less successfully to bituminous coal also. The results we obtained with the basic system, along with the pertinent citations to earlier work by others, were recently presented (4).

To summarize our effort, we found that CO/H₂O/KOH systems converted Illinois No. 6 coal to a material which was fully pyridine soluble, 51% benzene soluble, and 18% hexane soluble. As with the basic alcoholic systems, there were significant reductions in organic sulfur levels, and moderate reductions in nitrogen levels. The chemistry here is similar to that for the basic alcoholic systems, but with formate (HCO₂⁻) as the hydride-donor, and thus the reducing agent. In control runs with H₂O/KOH or CO/H₂O little or no conversion was observed.

Model compound work with this system showed that anthracene was reduced to its 9,10-dihydro derivative (35% yield). Bibenzyl, on the other hand, was recovered unchanged with only a trace of toluene observed.

The model compound work for the three basic systems is summarized in Figure 1, in which a finding of no significant reduction in the respective system is designated by an x'ed arrow. Our criterion of successful reduction requires that significant quantities of the starting material be converted to reduced products. In the case of benzyl phenyl ether, for example, while little starting ether was recovered, most of it being converted to an intractable polymer, no phenol nor toluene was found. Thus we conclude the system was not effective in reduction of the C-O bond. Similar statements apply regarding the C-C bond in bibenzyl for the MeOH/KOH and CO/H₂O/KOH systems.

A significant conclusion to be drawn from these data is that coal is converted under conditions where the common model compounds benzyl phenyl ether and bibenzyl are not reduced. In explanation, it might be suggested that there are two conversion mechanisms. One would be the commonly considered scheme (eqs 1 and 2), taking place in tetralin-like media, involving free radical chemistry, and reducing both coal and such model compounds as bibenzyl and benzyl phenyl ether through a thermally-promoted initial bond-scission. A second mechanism would be operative in strongly basic media, involve hydride transfer, and would perhaps include the conversion of coal via chemistry related in some way to the reduction of anthracene by these systems.

However, as pointed out above, the commonly proposed free radical mechanism is not entirely consistent with the observed behavior of H-donor solvents and coal. Further, a thermally promoted C-C or C-O bond-scission is inconsistent with our observations in the *i*-PrOH work at 335°C. As also mentioned, a major fraction of the coal was converted in this system to a product with a number-average molecular weight of less than 500. If we consider that the rate constant for the unimolecular scission of the central bond in bibenzyl is expressed (5) as

$$\log k (\text{sec}^{-1}) = 14.4 - 57/2.303RT$$

then while the half-life for the reaction at 400°C is about 2 hours, and thus perhaps appropriate for considerations of conversion at those conditions, at 335°C the half-life is about 160 hours, and clearly the reaction cannot play a significant role in the conversion of coal at that temperature.

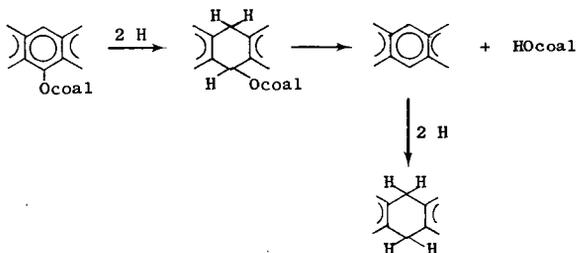
Additionally, it has been noted that tetralin operates via hydride transfer, at least in its reduction of quinones. Thus it has been shown that tetralin readily donates hydrogen to electron-poor systems such as quinones at 50°-160°C. The reaction is accelerated by electron-withdrawing substituents on the H-acceptor and polar sol-

vents, and is unaffected by free radical initiators (6). These observations are consistent with hydride transfer, as is the more recent finding of a tritium isotope effect for the reaction (7).

We propose therefore that the operative mechanisms of coal conversion in both tetralin-like media and our strongly basic systems may be the same, involving hydride donation by the H-donor solvent, followed by proton transfer. Consistent with this surmise are the results for two experiments carried out under the same conditions, utilizing tetralin on the one hand, and CO/H₂O/KOH on the other. The results are presented in Table 7, and show that the products from the two reactions have similar diagnostic characteristics, including benzene solubilities, H/C ratios, and ratios of H_{al}/H_{ar}. Further comparisons are in progress.

Since the proposed conversion process does not include a thermally promoted bond-scission step, the question arises of how the addition of hydrogen results in the bond breaking necessary for significant reduction in molecular weight. We have already noted that the nucleophilic action of the basic methanol system was sufficient to cleave diphenyl ether, and a similar route is available in the basic *i*-PrOH and CO/H₂O systems. On the other hand, we showed in control experiments that strongly basic conditions alone were not sufficient for significant conversion of coal.

Based on the data at hand, we are currently considering two possible modes of molecular weight reduction. The first involves the generation of thermally weak bonds by the initial addition of hydrogen. We suggest that the addition of hydrogen to the structures below may be a key to the cleavage of critical bonds in coal.



It can be shown thermochemically that the addition of hydrogen across structures like those above is favored under conversion conditions (1). In turn it can be suggested that the dihydroether intermediate is rapidly thermalized in the succeeding step, yielding both an oxygen-containing fragment and a rearomatized fragment that is rapidly reduced to a hydroaromatic product. The thermolysis of the intermediate is expected to be rapid at conversion temperatures, in accord with Brower's observation that, in tetralin, anthraquinone is converted all the way to anthracene (8). Moreover, it is recognized that 9-hydroxy-9,10-dihydroanthracenes readily eliminate water at ambient conditions, yielding the aromatized product (9).

The second potential conversion mode takes into consideration the recent observation that hydrogen acceptors such as benzophenone oxidatively couple phenols under

conversion conditions (10). It can thus be suggested that the major role of a reducing component in a coal conversion system is the reduction of quinones and perhaps other oxidants present in the coal rather than direct reduction of the coal. In the absence of an H-donor, then, oxidative crosslinking takes place within the coal upon heating, yielding a product even less soluble in solvents such as pyridine than was the starting coal. On the other hand, in the presence of a reducing agent, either conventional H-donors such as tetralin or our hydride-donating systems, the quinones and other oxidants should be reduced to unreactive material, and the coal then proceeds to liquefy by means of a thermal process involving no addition of hydrogen. We cannot at this time propose a route for purely thermal liquefaction (reverse Diels Alder reactions might be suggested for purposes of example) and the concept currently remains a working hypothesis.

ACKNOWLEDGEMENT

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Table 2
THERMOCHEMICAL AND KINETIC FACTORS FOR SOME BONDS IN COAL

Structure	BD ₀ ^a (kcal/mol)	t _{1/2} ^b	
		400°C (572°F)	500°C (932°F)
	> 120	∞	∞
	116	2.6x10 ¹³ yr	3.7x10 ¹⁰ yr
	82	2.7x10 ⁶ yr	10.2 yr
	81	1.3x10 ⁴ yr	5.3 yr
	69	629 days	19.7 hr
	57	2.0 hr	30 sec

^aBond dissociation energies. See S. W. Benson, *Thermochemical Kinetics*, John Wiley and Sons, New York (1968).

^bCalculated from the expressions $\log k$ (sec⁻¹) = 14.4 - BDE/4.6T, t_{1/2} = 0.7/k.

Table 1
THERMAL CLEAVAGE OF BENZYLIC BONDS IN AROMATIC SYSTEMS

Structure	BD ₀ ^a (kcal/mol)	Relative Rate	
		400°C (572°F)	500°C (932°F)
	72 (obs.)	1	1
	68 (obs.)	20	12
	68 (est.)	20	12
	60 (est.)	9x10 ⁵	3x10 ³

^aBond dissociation energies. See S. Stein and D. Golden, *J. Org. Chem.*, **42**, 839 (1977). The two observed values correspond to estimated values, and are from the unpublished work of D. Golden and D. McMillen, SR1.

Table 3

REACTIVITY OF VARIOUS H-DONOR SOLVENTS WITH CCl_4 AND COAL

Cosolvent	Relative Reactivity Toward CCl_4^a (350°C)	Relative % Dissolution ^b (2 hr/350°C)
None (Phenanthrene)	--	[33] ^c
Toluene	1.0	1
2-Methylnaphthalene	2.1	0
1-Methylnaphthalene	2.6	2
Diphenylmethane	6.0	1
Cumene	8.7	0
Fluorene	(20)	0
Tetralin	41.0	27
9-Methylanthracene	56.0	0
1,2-Dihydronaphthalene	(65)	6
9,10-Dihydroanthracene	(102)	24
9,10-Dihydrophenanthrene	(102)	22
1,4-Dihydronaphthalene	(160)	14

^aData from Hendry, D., Mill, T., Piszkiwicz, Howard, J., and Eigenman, H., J. Phys. Chem. Ref. Data, 3, 937 (1974). The values in parenthesis are estimated from other radical data available in the paper. ^bAll reactions carried out in phenanthrene as solvent with 4.0 parts solvent per part coal, and 10 wt % cosolvent. Unpublished data of D. Hendry and G. Hum, SRI. ^cValue for phenanthrene alone.

Table 4

ALCOHOLS AS H-DONOR SOLVENTS IN COAL CONVERSION

System	T(°C)/min	Pyr. Sol (%)	H/C	ZS _{org}	ZN
Untreated coal	--	13	0.73	2.1	1.7
Tetralin	335/90	48	0.81	1.8	1.6
<i>i</i> -PrOH	335/90	50	0.81	1.8	1.6
<i>i</i> -PrOH/KOH	335/90	96	0.88	1.6 ^a	1.6
MeOH/KOH	400/90	99 ⁺	0.96	0.8	1.2

^aReduced to 0.5% when product treated further.

Table 5

PROPERTIES OF THE METHANOL-SOLUBLE COAL PRODUCT

H/C	1.37	} $\xrightarrow[\text{< 0.1 torr}]{\text{distilled}}$	~40% polymethylphenols and anisoles
ZS _{org}	0.5		~40% mixture of butyrolactone and heavier materials yielding $\text{CH}_3\text{CH}_2\text{C}=\text{O}^+$ and $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{C}=\text{O}^+$ major fragments by mass spectroscopy
ZN	0.4		
H _{al} /H _{ar} ^a	5.1		~20% unidentified

^aBy nmr

