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EXPLORATORY STUDY OF COAL CONVERSION CHEMISTRY

Quarterly Report No. 10 for August 19—November 18, 1983

By
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December 1983

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SRI International
Menlo Park, California

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Georgina P. Hum, Thomas K. Green, and Ripudaman Malhotra

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ABSTRACT

Work has continued in Task A to focus this quarter on Subtask A.3, "Derivation of an Improved Correlation Between Coal-Conversion Effectiveness and Donor-Solvent Structure." We are taking two new approaches to test the hypothesis that the critical class of reactions, which distinguishes between good donor and poor donor solvents, is bimolecular transfer of hydrogen atoms from solvent radicals to the ipso positions of substituted aromatics Ar-X, resulting in "solvent-mediated hydrogenolysis."

In the first approach, experiments in which real coal liquefaction mixtures were doped with specific model compounds showed that hydrogen-transfer reactions promoted by the coal do engender bond scission in the dinaphthylmethane to an extent that the half-life for cleavage at 400°C in tetralin is decreased from 200 hours to about 4 hours. This result greatly strengthens our suggestion that the cleavage of phenyl-alkyl bonds, formerly considered to be very refractory under liquefaction conditions, may play an important role in coal liquefaction. Further experiments of this type surprisingly did <u>not</u> show pyrene to be a better solvent (at least under these conditions) for shuttling hydrogen from coal structures to the dinaphthylmethane.

In the second approach to testing our liquefaction mechanism hypothesis, we have constructed a "simplified" numerical model for "liquefaction" of some coal-like structures, incorporating some of the rate constants for bond cleavage measured in this work to determine whether the calculated relative bond cleavage rate with various hydroaromatic contents successfully mimics the relative model compound and coal conversion rates measured in the laboratory. In several respects, this model does mimic the actual experiments, but in at least one important respect, agreement is not complete.

Our efforts in Task B, "Conversion in CO/H_2O Systems," were concentrated on Subtask B.1 this quarter. The study of conversion behavior of an Illinois No. 6 coal was extended to different reaction times and lower pH's. The results reveal that significant conversion to soluble products can be achieved even under neutral conditions, providing that the reaction time is extended to allow significant conversion of CO to CO_2 via the water-gas-shift reaction (WGSR). The amount of toluene-soluble material produced in any given run follows the CO disappearance, irrespective of the initial pH or reaction time. Thus, the primary reaction parameter that controls coal conversion at 400°C is the amount of CO that is allowed to enter the reaction pathway.

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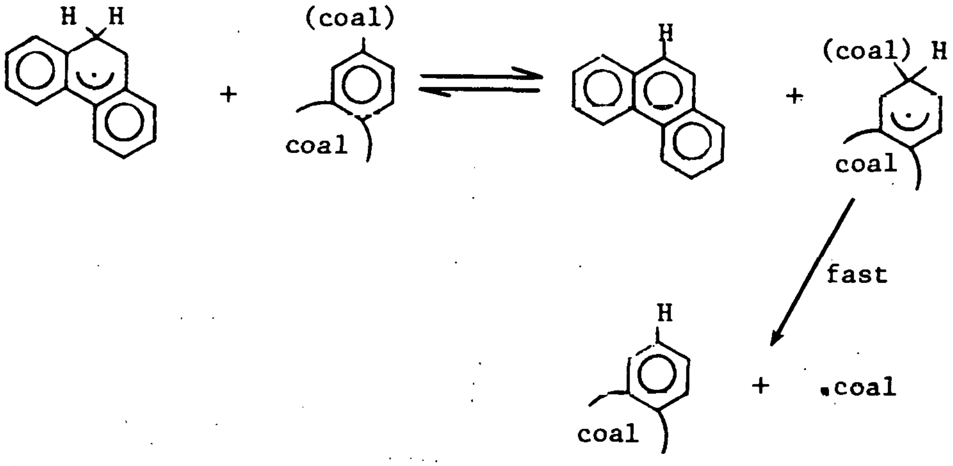
SUBTASK A.3: IMPROVED CORRELATION BETWEEN DONOR-SOLVENT STRUCTURE AND COAL CONVERSION EFFECTIVENESS

Donald F. McMillen, Ripudaman Malhotra,
Georgina P. Hum and Sou-Jen Chang

Introduction

In this quarter, work has continued on Subtask A.3, "Improved Correlation Between Donor-Solvent Structure and Coal Conversion Effectiveness." In this subtask, we hope to extend the insight gained with model coal structures to the chemistry of fragmentation of real coal structures. The current effort involves (1) reactions of mixtures of model compounds and real coals, and (2) numerical integration of a "simple" coal liquefaction model based on the results of the model compound studies.

Efforts were continued in this quarter to test our hypothesis that the specific reactions by which donor-solvents promote coal liquefaction, and which distinguish the good solvents from the poor solvents, all involve hydrogen transfer from a solvent radical to the ipso position of a substituted aromatic.



(1a)

(1b)

These reactions result in what is formally equivalent to hydrogenolysis resulting from addition of free hydrogen atoms to substituted aromatics, but in this case, it occurs where substantial concentrations of free hydrogen atoms are not expected and has indeed been shown[1(a)-(c)] to take place without the intervention of free hydrogen atoms.

Two parallel approaches are being taken to test the hypothesis that this class of reactions contributes significantly to donor-solvent coal liquefaction. The first approach is to determine the rate of bond cleavage for model coal linkages in the presence of real coals and various solvents to test not only the capabilities of the coals to promote, by hydrogen transfer, the cleavage of specific bonds, but also the capabilities of the various solvents to shuttle the hydrogens made available by the coals.

The second approach consists of two parts. The first part is to construct a numerical model containing the chemical and rate equations for the various reactions postulated as important in the hydrogen-shuttling process. The second part is to compare the predicted and the observed effectiveness for these "solvent-mediated hydrogenolysis," using various solvents, for bond scission in model compounds and for liquefaction of real coals. The latter results come both from the present work and from the recent work of other groups, in particular those of Davies et al.,[2] Guin and coworkers,[3] Burke and Winschel,[4] and earlier work by Orchin et al.[5] The bond scission effectiveness with coal models and real coals is also compared with the relative effectiveness of various donor-solvents as radical scavengers, as carefully determined by Bockrath and coworkers[6(a),(b)] and Franz and Caimioni.[7] All of these comparisons tend to support our general hypothesis that such solvent-mediated hydrogenolysis are, in fact, the major determining factor in donor-solvent effectiveness. However, there is not a complete quantitative correspondence between predictions of relative effectiveness from the numerical model and experimental observations. Because of the uncertain coupling between chemical and mass transport factors in real coals (and the uncertainty in thermochemical estimates for various solvent species), it is not yet clear whether the chemical model should be modified. This question is being addressed in the work now in progress.

Inadequacy of the Thermal Bond-Scission, Radical-Capping Mechanism

The sequence of thermal scission of critical linkages in the coal structure, followed by "capping" of the thermally produced coal radicals, has been the most widely assumed and quoted coal liquefaction mechanism for the last 30 years. This mechanism has been implicitly extended to cover coal dissolution with nondonor solvents, where the hydrogen required must originally come by disproportionation of the coal structure. It has been commonly assumed that the solvents that function most effectively as hydrogen shuttlers in this dissolution do so because of in-situ production of donor molecules (ArH_2, ArH_4, and so forth) which then function as radical scavengers or "capping" agents. However, as discussed in previous reports,[1(a)-(c)] invoking the traditional scavenging function as the most important role that the solvent plays does not explain the relative coal liquefaction effectiveness of various solvents. This inadequacy is most evident for conversion in solvents with low or zero hydroaromatic content. That is, from results in the literature,[2-5] it is abundantly clear that the solvents in which it is expected that both the highest concentrations and the most effective radical scavengers would be generated by hydrogen transfer from the coal are not the most effective liquefaction agents.

Of all the commonly used aromatics solvents, anthracene is the one with which the highest concentration of the dihydrocompound should be obtained,[8] and also the system in which the dihydrocompound thus produced should be the most effective scavenger (on a molar basis).[6(a),(b),7] Nevertheless, anthracene has been repeatedly found to be a much poorer liquefaction solvent than either phenanthrene or pyrene. Results of this type, together with our own results, led us to invoke reactions of the type shown above (equation (1)] as being responsible for a substantial fraction of the bond scissions in coal liquefaction. In work performed under this contract, linkages too strong to break by thermal scission (e.g., the central bond in 1,2'-dinaphthylmethane with a thermal scission half-life $>10^7$ h) undergo central bond scission in various hydroaromatic solvents with a half-life ranging from 10 to 200 hours, thus supporting our speculation that they may be important in coal liquefaction. In any case, it is clear that the solvent is actually engendering bond scission, not merely capping thermally generated radicals.

Bond Cleavage as a Result of Hydrogen Transfer from Coal Radicals

Solvent-mediated hydrogenolysis, such as that shown in equation (1), are clearly good candidates for explaining the active role of solvents in coal structure fragmentation (liquefaction). The major questions to be answered are the following:

(1) Is the hydrogen transfer actually bimolecular, as shown in equation (1a), or does it involve elimination of hydrogen atom, followed by addition of free hydrogen atom to the substrate?

(2) How is the solvent radical (ArH•) generated, and what will be the relative concentrations of ArH• in various aromatic and hydroaromatic solvents?

(3) How "should" the presence of coals affect the ArH• concentration?

(4) How will the rates of hydrogen transfer fromn ArH• differ for different aromatic systems and different hydrogenolysis substrates?

(5) How does the presence of coal(s) affect the observed cleavage rate of diarylmethane model compounds?

(6) When the answers to (1)-(5) are incorporated into a numerical chemical model of model compound conversion and coal-conversion systems, how well can such a model reproduce experimental observations with real coals?

The answer to question (1) and partial answeres to questions (2), (3), and (4) were determined in previous quarters.[1(a)-(c)] This work showed that in solvents such as phenanthrene and anthracene, the hydrogen transfer is clearly a single, bimolecular step as suggested in equation (1a). More complete answers to questions (2) through (4) and the answer to (6) will require numerical integration of the model described in question (6), using a judicious choice of rate parameters for the various reactions. Determination of the answers to (6) will help test the mechanism in the numerical model. Progress to date is described below.

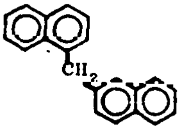
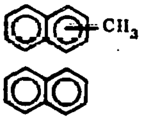
Effect of Addition of Real Coals on Diarylmethane Hydrogenolysis Rates

It has been repeatedly determined[9] from deuterium scrambling reactions that coals are very good promoters of hydrogen exchange, even better than radical initiators like bibenzyl. Also, we have determined that in aromatic/hydroaromatic mixtures central bond scission in diarylmethanes is increased by some five to six orders of magnitude over the thermal bond scission rate. The determination that this cleavage results directly from the transfer of a single hydrogen atom from a cyclohexadienyl radical in the solvent system to one of the ipso positions in the diarylmethane,[1(a)-(c)] prompted the following speculation: if real coals are added to diarylmethanes in donor-solvent systems, accelerated hydrogen transfer may result in increased diarylmethane cleavage rates.

The data in Table 1 show that the above speculation is correct. Addition of coal (PSOC 1116, HV-bituminous, Sunnyside, Utah) to a 5% 1,2'-dinaphthylmethane solution in tetralin increased the dinaphthylmethane cleavage rate by a factor of ~50. More importantly, a decrease in the cleavage half-life at 400°C from ~ 200 h to ~ 5 h brings it well into the range of importance in coal liquefaction. Clearly, hydrogen transferred from the coal (or coal fragments) induces cleavage of bond types that in tetralin at 400°C otherwise cleave too slowly to be significant in coal liquefaction. This does not demonstrate that such cleavage reactions are important in coal liquefaction, only that they could be if such linkages were either in the original coal or generated during liquefaction.

Table 1

EFFECT OF COAL ON 1,2′-DINAPHTHYLMETHANE CENTRAL BOND SCISSION RATES UNDER COAL LIQUEFACTION CONDITIONS [a]

SUBSTRATE	PRODUCTS	SOLVENT	k_1 (s^{-1})	$t_{1/2}$ (h)
	None	Pyrene only	$\leq$4 x 10	$\gtrsim$ 500
"		Tetralin	1 x 10^{-6}	~200
"	"	Tetralin/PSOC 1116 (2/1)	4.6 x 10^{-5}	4

[a] 400°C, solvent:coal:dinaphthylmethane was 4:1:0.14.

From this point, we wished to test further our speculation$^{1(b)}$ that the relative effectiveness of coal liquefaction in pure aromatic solvents (zero donor content) paralleled both the relative ease of formation of solvent radicals ArH• and the relative difficulty that AH• exhibits in undergoing successful termination reactions. An explanation for the marked effectiveness of pyrene as a shuttling agent is as follows: hydrogen transfer to the one-position of pyrene is more favored than transfer to any position of any other two-, three-, or four-ring polycyclic aromatic (except the 9-position of anthracene$^{10(a)-(c)}$) but the 1-hydropyrenyl radical will be a relatively ineffective terminator because 1,2-dihydropyrene is the least stable of all the dihydroaromatics in these systems.$^{10(a)-(c)}$ The estimated ΔH^0_{298} values for hydrogen transfer and radical disproportionation (Table 2) amply illustrate this point.

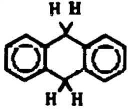
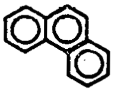
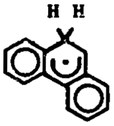
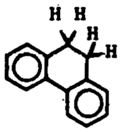
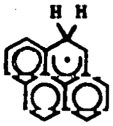
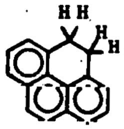
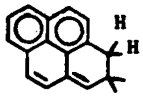
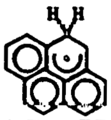
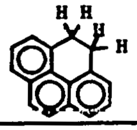
The effect of added coal on the rate of dinaphthylmethane central bond scission in several additional solvent systems is shown in Table 3. In contrast to our expectation, these results indicate that the transfer of hydrogen from this coal to the ipso positions of the substrate is no better in pyrene than in tetralin or in naphthalene. Either we are incorrect in speculating that the net transfer rate (the efficiency of hydrogen shuttling) should be increased by increasing ease of acceptance of hydrogen atoms from the coal and by decreasing ease of termination or the bulk of the effective hydrogen transfer is directly from coal fragments to dinaphthylmethane, and the shuttling "agent" in this case makes little difference. The absence of a substantial solvent effect on hydrogen transfer maximized the need for shuttling in spite of our intentional use of a low-fluidity coal. It then occurred to us, however, that our reasoning was inverted and that we should have chosen a coal with a very high maximum fluidity: it is only for high-fluidity coals that previous workers^{11} have found that a good hydrogen shuttler (e.g., pyrene) can be substituted for a good hydrogen donor (e.g., 4,5-dihydropyrene) and result in an extent of liquefaction that is well beyond that provided by solvents that are neither donors nor shuttlers (e.g., decalin or biphenyl).

Table 2

ESTIMATED THERMOCHEMISTRY OF HYDROGEN TRANSFER AND RADICAL DISPROPORTIONATION FOR POLYCYCLIC AROMATIC SOLVENTS[a]

Reaction 2:

Reaction 3: $ArH^{\cdot} + ArH'^{\cdot} \rightleftharpoons Ar + ArH_2$

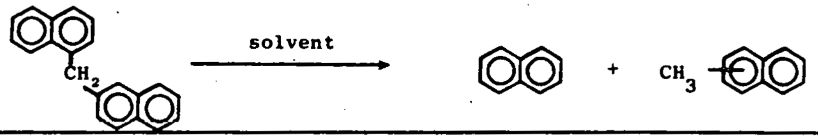
Aromatic Solvent	ArH·	ArH'·[b]	ArH$_2$	ΔH_2^o	ΔH_3^o
		--		+15.3	-31.2
		—		+ 6.8	-50.0
		—		+ 3.9	-46.9
"		—		+13.3	- 8.3
"				+13.3	-37.4

[a] From 8 and 9.

[b] If different than ArH.

Table 3

EFFECT OF SOLVENT SYSTEM ON ACCELERATION BY COAL OF 1,2′-DINAPHTHYLMETHANE CLEAVAGE



Solvent[a]	Coal	k_1 (s^{-1})	$t_{1/2}$ (h)
Tetralin	PSOC 1116	4.6×10^{-5}	4
Tetralin/Pyrene (1/1)	PSOC 1116	3.3×10^{-5}	6
Pyrene	PSOC 1116	1.5×10^{-5}	13
Pyrene/4,5-Dihydropyrene (1/1)	PSOC 1116	1.4×10^{-5}	14
Naphthalene	PSOC 1116	4.1×10^{-5}	5
Pyrene	PSOC 1099	1.7×10^{-5}	11
Anthracene	PSOC 1116	1.2×10^{-5}	16

[a] 400°C, solvent:coal:dinaphtylmethane was 4:1:0:14.

However, repeating the PSOC 1116 in pyrene with PSOC 1099 (HVA bituminous, Pittsburgh seam, maximum fluidity, 14,700, Gieseler dial divisions/min) did not indicate that pyrene was a better shuttler of hydrogen from the coals to the dinaphthylmethane than naphthalene. It may be that the system benefits significantly from good shuttling capabilities only when both the source and the acceptor of the shuttled hydrogen are in imiscible phases. To determine whether this was the case, we began the next step necessary to understand in a more quantitative way the combined effect of the various hydrogen-transfer processes now believed to operate in these systems. Results to date from the numerical modeling of the important chemical reactions in these solvent-substrate systems are discussed below.

Numerical Integration of the Solvent-Mediated-Hydrogenolysis Coal-Liquefaction Model

At present, the model for testing the mechanism of coal liquefaction by hydrogen transfer from ArH• includes 14 species and 33 reactions. For shorthand purposes, the species are designated in the computer input and output by names of up to four characters. Because the identities of some of these are not self-evident, they are all shown in Table 4.

Table 5 is the list of reactions for the case of liquefaction in pyrene, arranged as required for the numerical integration computer program input. For the cases of phenanthrene and anthracene at this same level of detail, there are fewer reactions because hydrogen-atom transfer occurs almost exclusively to the 9-position for both solvents. The numerical integration program is based upon the GEAR Algorithm. An example of the tabular output is shown in Table 6 where, for all 14 species, concentrations and net rates are listed at a particular reaction time (500 s). Also listed are the rates for each of the 33 individual reactions. The validity of the present hypothesis will be judged in large part by the ability of the model to reproduce the repeatedly observed, but not yet explained, relative effectiveness of various aromatic and hydroaromatic liquefaction solvents.

Table 4

SYMBOLS USED IN THE MODELING OF COAL LIQUEFACTION
BY RADICAL HYDROGEN TRANSFER

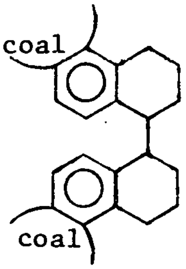
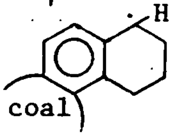
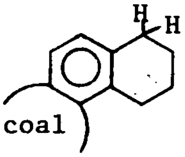
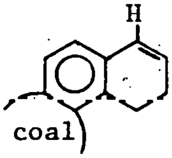
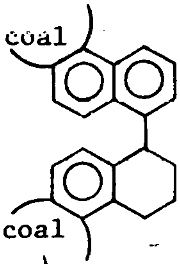
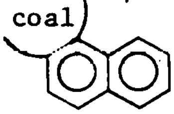
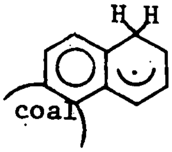
Symbol	Identity	Structural Example
CO	"Coal zero" (starting coal)	
CO2	Starting coal cleaved	
CO2H	Cleaved, capped coal	
CO2=	Cleaved coal minus 1 hydrogen	
BC	"Coal zero"(starting coal not subject to cleavage by homolysis)	
BC2	Fragment of "coal zero "	
	Cleaved coal minus 2 hydrogens	

Table 4 (continued)

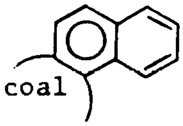
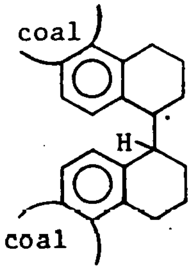
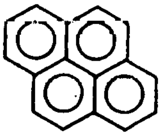
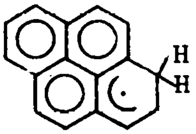
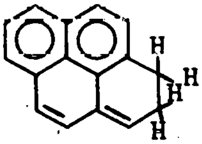
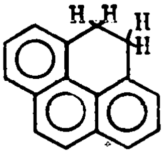
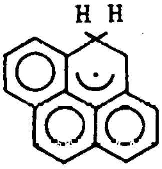
CO2N	Cleaved coal minus 3 hydrogens	
CO-H	Unfragmented coal minus 1 hydrogen	
PO	Pyrene	
P1	1-Hydropyrenyl radical	
P2H	1,2-Dihydropyrene	
P5H	4,5-Dihydropyrene	
P4	4-Hydropyrenyl radical	

Table 5

REACTIONS USED IN THE MODELING OF COAL LIQUEFACTION BY RADICAL HYDROGEN TRANSFER USING PYRENE AS THE SOLVENT

	Reactions						A-Factor	Ea (K)
1	C0		=	C02	C02		2.510E+16	2.997E+04
2	C02	C02	=	C0			3.160E+08	0.000E-01
3	C02H	C02=	=	C02	C02		1.000E+08	2.026E+04
4	C02	C02	=	C02H	C02=		1.000E+08	0.000E-01
5	C02	P5H	=	C02H	P4		3.160E+08	6.366E+03
6	C02	P2H	=	C02H	P1		3.160E+08	1.007E+03
7	C02	P1	=	C02H	P0		3.160E+08	0.000E-01
8	C02H	P0	=	C02	P1		3.160E+08	2.114E+04
9	C02=	C02=	=	C02	C02N		3.160E+07	1.726E+04
10	C02N	C02=	=	C02S	C02		3.160E+07	3.762E+03
11	C02	C02=	=	C02H	C02N		3.160E+07	6.039E+03
12	P1	P1	=	P0	P2H		3.160E+08	1.510E+03
13	P0	P2H	=	P1	P1		3.160E+08	9.640E+03
14	P4	P4	=	P0	P5H		3.160E+08	0.000E-01
15	P0	P5H	=	P4	P4		3.160E+08	2.360E+04
16	P1	P4	=	P0	P5H		3.160E+08	0.000E-01
17	P0	P5H	=	P1	P4		3.160E+08	1.882E+04
18	P1	BC	=	P0	BC2	C02	3.160E+08	1.090E+04
19	P4	BC	=	P0	BC2	C02	3.160E+08	8.505E+03
20	C02	P0	=	C02=	P4		3.160E+08	1.039E+04
21	C02	P0	=	C02=	P1		3.160E+08	8.002E+03
22	C02	P4	=	C02H	P0		3.160E+08	0.000E-01
23	C02H	P0	=	C02	P4		3.160E+08	2.592E+04
24	C02H	P4	=	C02	P5H		3.160E+08	8.731E+03
25	C0	P0	=	C0-H	P1		3.160E+08	1.963E+04
26	C0	P0	=	C0-H	P4		3.160E+08	2.441E+04
27	C0-H	P1	=	C0	P0		3.160E+08	0.000E-01
28	C0-H	P4	=	C0	P0		3.160E+08	0.000E-01
29	C02	C02N	=	C02=	C02=		3.160E+07	0.000E-01
30	C02=	P1	=	C02	P0		3.160E+08	7.096E+03
31	C02=	P4	=	C02	P0		3.160E+08	4.706E+03
32	P1	P0	=	P0	P4		3.160E+08	9.940E+03
33	P4	P0	=	P0	P1		3.160E+08	2.391E+03

Table 6

EXAMPLE OF NUMERICAL INTEGRATION OUTPUT FOR LIQUEFACTION IN PYRENE: SPECIES CONCENTRATIONS, NET RATES, AND SPECIFIC REACTION RATES AS A FUNCTION OF TIME

```
TIME =  0.000E-01                    INTERVAL =  1.000E-16
    CO          CO2         CO2H        CO2=       P5H         P4          P2H         P1          PO          CO2N
   CO2S         BC          BC2         CO-H        M

  CONCENTRATIONS
  5.000E-02  0.000E-01  0.000E-01  0.000E-01  0.000E-01  0.000E-01  0.000E-01  0.000E-01  1.000E+00  0.000E-01
  0.000E-01  9.500E-01  0.000E-01  0.000E-01  2.000E+00


TIME =  5.000E+02                    INTERVAL =  1.526E+01
    CO          CO2         CO2H        CO2=       P5H         P4          P2H         P1          PO          CO2N
   CO2S         BC          BC2         CO-H        M

  CONCENTRATIONS
  2.958E-02  1.125E-07  2.455E-02  2.933E-02  1.565E-06  1.174E-11  3.307E-10  8.166E-07  1.000E+00  3.871E-09
  4.126E-03  9.328E-01  1.716E-02  7.794E-09  2.038E+00

NET RATES
 -2.994E-05  1.412E-11  4.334E-05  2.554E-05 -1.451E-09  7.276E-12 -5.457E-12 -7.349E-10  2.183E-09  1.214E-12
  1.340E-05 -2.241E-05  2.241E-05 -9.520E-13  5.234E-05

 THE REACTION RATES ARE
        3.394E-05   4.000E-06   6.099E-09   1.266E-06   4.338E-09   2.633E-09   2.903E-05   1.775E-07   1.972E-07   1.340E-05
        1.322E-05   2.235E-05   2.235E-05   4.355E-14   2.903E-13   3.029E-09   3.533E-10   2.240E-05   1.124E-08   6.995E-06
        2.438E-04   4.174E-10   1.456E-10   2.114E-10   2.010E-06   1.654E-09   2.012E-06   2.892E-11   1.376E-08   1.995E-04
        9.996E-08   9.938E-05   1.063E-04


TIME =  1.000E+03                    INTERVAL =  4.620E+01
    CO          CO2         CO2H        CO2=       P5H         P4          P2H         P1          PO          CO2N
   CO2S         BC          BC2         CO-H        M

  CONCENTRATIONS
  1.795E-02  9.428E-08  4.327E-02  3.615E-02  1.013E-08  8.538E-12  1.713E-10  3.877E-07  1.000E+00  3.267E 09
  1.122E-02  9.235E-01  2.653E-02  6.573E-09  2.059E+00

 NET RATES
 -1.778E-05 -1.677E-10  3.173E-05  5.866E-06 -7.246E-10  0.000E-01  2.092E-11 -1.746E-10  8.658E-10  1.449E 11
  1.394E-05 -1.596E-05  1.596E-05 -2.614E-12  3.375E-05

 THE REACTION RATES ARE
        2.059E-03   2.809E-06   1.325E 00   0.009E 07   2.362E-09   1.142E-09   1.751E-05   3.128E-07   2.994E-07   1.394E-05
        1.365E-05   1.158E-05   1.157E-05   2.304E-14   1.879E-13   1.586E-09   2.286E-10   1.596E-05   8.093E-09   5.862E-06
        2.043E-04   2.544E-10   2.567E-10   2.710E-10   1.220E-06   1.004E-09   1.221E-06   1.773E-11   9.733E-09   1.769E-04
        8.960E-08   7.152E-05   7.729E-05


TIME =  2.000E+03                    INTERVAL =  5.409E+01
    CO          CO2         CO2H        CO2=       P5H         P4          P2H         P1          PO          CO2N
   CO2S         BC          BC2         CO-H        M

  CONCENTRATIONS
  6.700E-03  5.929E-08  6.606E-02  3.696E-02  6.459E-07  5.446E-12  6.986E-11  3.753E-07  1.000E+00  2.083E-09
  2.276E-02  9.108E-01  3.918E-02  3.842E-09  2.082E+00

NET RATES
 -6.576E-06  4.813E-11  1.566E-05 -1.541E-06 -1.797E-10  0.000E-01 -1.819E-12 -2.401E-10  4.184E-10 -6.795E-13
  9.086E-06 -1.006E-05  1.006E-05 -2.093E-12  1.663E-05
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Comparison and interpretation of the computed rates of solvent-mediated hydrogenolysis engendered by the various radicals under different conditions is, itself, a complex process, and output for the three different solvents and more than 12 different conditions thus far explored is not reproduced in this report. Use of the model and computer programs to explore the effect of different solvents, starting conditions, and mechanistic assumptions is still in progress. Summarized below are several important respects in which the liquefaction model in its current stage successfully mimics the liquefaction of real coals and also an important respect in which it does not.

Characteristics of Liquefaction in Aromatic and Hydroaromatic Solvents Successfully Reproduced

- When starting dihydroaromatic (ArH_2) concentration is low, the order of liquefaction effectiveness is
  pyrene > phenanthrene > anthracene
- Differences between the three solvents are greatest in the initial stages of the reaction when more highly reactive coal products are rapidly "dumping" hydrogens into the respective aromatic systems to be shuttled via ArH to the coal.
- The advantage of pyrene over phenanthrene decreases markedly when there is a substantial initial concentration of ArH_2.

Quantitative Predictions Borne Out by the Model

- P1 x P1 radical disproportionation (which produces the highly unstable 1,2-dihydropyrene) is only 5% efficient as compared with 90% for P1 x P4 and P4 x P4.
- When initial PyH_2 is zero, the principal generation of carriers PyH•(P1 and P4) is from coal fragments, and the carrier steady-state concentrations substantially exceed those that would have been dictated by equilibrium considerations if ArH• had been generated by molecule-induced homolysis (reactions 17 and 16 in Table 5).

- The extent to which ArH• steady-state concentrations can exceed those dictated by molecule-induced homolysis is far less for the anthracene system, where termination by disproportionation of A9 radicals is very efficient.

Factors Not Successfully Reproduced

- The benefit of initial nonzero ArH_2 concentration is actually predicted to be less for anthracene than for the pyrene system. This is in apparent contrast with the general observation[2] that, whereas anthracene is a markedly poorer shuttler than pyrene, high dihydro content makes virtually any aromatic solvent a reasonable liquefaction solvent.

The incomplete correspondence of predicted with observed relative liquefaction effectiveness notwithstanding, the present hypothesis concerning the solvent-mediated hydrogenolysis in coal liquefaction does a substantially better job explaining experimental observations than any previous theory of coal liquefaction. We have not discussed here several secondary mechanistic assumptions that have been made for all conditions explored with the model thus far. We are in the process of examining these assumptions by making the appropriate variations in the model. The results of these variations will be presented and discussed in the next quarterly report.

REFERENCES

1. (a) D. S. Ross, G. P. Hum, D. F. McMillen, and W. C. Ogier, "Exploratory Study of Coal Conversion Chemistry," Quarterly Reports Nos. 4 and 6, Contrct No. DE-AC22-81PC40785, SRI Project 3304, SRI International, Menlo Park, California (June and September 1982).

   (b) D. F. McMillen, W. C. Ogier, and R. H. Fleming, "Mechanisms of Hydrogen Transfer and Scission of Strongly Bonded Coal Structures in Donor-Solvent Systems," submitted to Fuel.

   (c) D. F. McMillen, W. C. Ogier, S. J. Chang, R. H. Fleming, and R. Malhotra, "Mechanisms of Hydrogen Transfer and Associated Bond Cleavage Reactions: A Rationalization of the Effectiveness of Pyrene in Coal Liquefaction Solvents," Proceedings of 1983 International Conference on Coal Science, Pittsburgh, PA, 15-19 August 1983, p. 199.

2. G. O. Davies, F. J. Derbyshire, and R. J. Price, J. Inst. Fuel, 50, 121 (1977).

3. C. W. Curtis, J. A. Guin, and K. C. Kwon, "Coal Solvolysis in a Series of Model Systems," to be submitted to Fuel.

4. F. P. Burke and R. A. Winschel, "Process and Product Oil Characterization in Two-Stage Coal Liquefaction," presented at Eighth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, CA, 11-13 May 1983.

5. M. Orchin, C. Columbic, J. E. Anderson, and H. H. Storch, U.S. Bureau of Mines Bull. No. 505 (1951).

6. (a) B. C. Bockrath and R. P. Noceti, Am. Chem. Soc., Fuel Division Preprints, 26, 94 (1981). See also, L. F. Schanne and M. W. Haenel, in Proceedings of the International Conference on Coal Science, Dusseldorf, Germany, 7-9 September 1981 (Verlag Gluckauf GmbH, Essen, Germany, 1981), p. 416.

   (b) B. C. Bockrath, E. Bittner, and J. McGraw, "Relative Rate Constants of Hydrogen Transfer to Benzyl Radical," J. Am. Chem. Soc. (in press).

7. J. Franz and D. Camaioni, presented at the American Chemical Society National Meeting, Seattle, WN, 14-18 March 1983.

8. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic Press, New York, 1970).

9. H.-H. King and L. M. Stock, Fuel, 61, 257 (1982).

10. (a) S. E. Stein, "A Fundamental Chemical Kinetics Approach to Coal Conversion," *Advances in Chemistry Series 192* (American Chemical Society, Washington, DC, 1982) p. 97.

    (b) D. F. McMillen, W. C. Ogier, and D. M. Golden, "The Stability of Cyclohexadienyl Radicals in Polycyclic Aromatic Systems," in preparation.

    (c) D. F. McMillen and D. M. Golden, "Hydrocarbon Bond Dissociation Energies," Ann. Rev. Phys. Chem., 33, 497 (1982).

11. I. Mochida, A. Takanabe, and K. Takeshita, Fuel 58, 17 (1979).

12. C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice-Hall, Englewood Cliffs, NJ, 1971. The actual computer code used was based upon one written by G. Z. Whitten.

SUBTASK B.1: DEVELOPMENT AND EVALUATION OF CO/H_2O/CATALYST SYSTEMS

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Introduction

This work is a study of the OH^--promoted CO/H_2O coal conversion system. One objective is to determine the pressure, temperature, reaction time and initial pH bounds for favorable conversion. We therefore extended our study of the conversion behavior of an Illinois No. 6 coal at 400°C and 20 min to different reaction times, initial pH's, and temperatures. Although the study is at present incomplete, some of the work has progressed far enough to merit discussion.

In previous reports, we demonstrated that the conversion of an Illinois No. 6 coal (PSOC-1098) to toluene-soluble (TS) material (400°C/20 min) correlated with the degree of CO disappearance.[1,2]

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

An intermediate in the water-gas-shift reaction WGSR, not the H_2 derived from it, is principally responsible for the conversion in this system. The degree of WGSR, and ultimately the conversion of coal to soluble product, is controlled by the initial pH of the solution. At pH's above 12, the WGSR is strongly promoted and the rate of coal conversion is high. At pH's below 12, both the rate of CO and coal conversion are low.

This quarter, we report on the results of the conversion of the Illinois No. 6 coal at various initial pH's and reaction times. The results reveal that significant conversion of coal to soluble products can be achieved even under neutral conditions, providing that the reaction time is extended to allow significant CO conversion. Moreover, the amount of TS material produced in any given run follows the CO disappearance, irrespective of the initial pH or the reaction time (0-180 min). Thus the amount of CO that enters the reaction pathway, not the rate at which it enters, controls the conversion of coal to soluble material in this system.

Experimental Details

The elemental analysis of the Illinois No. 6 coal (PSOC-1098) is given in Table 7.

Table 7

ELEMENTAL ANALYSIS OF DRY, MINERAL-MATTER-FREE
PSOC-1098 ILLINOIS NO. 6 COAL

Element (%)	Weight (%)
Carbon	82.98
Hydrogen	5.69
Nitrogen	1.51
Organic sulfur	1.91
Oxygen (difference)	7.91
Mineral matter[a]	19.32

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[a] Calculated according to MM = 1.13 Ash + 0.47S_p, where S_p is pyritic sulfur.

The coal was ground and sieved under dry N_2. The -60 to 200 mesh fraction was then dried in a vacuum oven at 105°C overnight.

All reactions were performed in a 300 mL Magne-Drive-stirred Hastelloy C autoclave. The autoclave was loaded with 5 g of dry coal and 30 g of H_2O that was previously adjusted to the desired pH with solid KOH. The system was sealed, purged with N_2, purged twice with CO, and then charged with 500 psig CO.

The coal was converted by heating the autoclave to the appropriate temperatures for the appropriate time. Maximum pressures attained generally ranged from 3500 to 5000 psig. The heat-up and cool-down times for the system were generally 1 h, depending upon the desired reaction temperature.

Quantitative analyses of the product gases CO, CO_2, and H_2 were made by gas chromatography. The percent CO conversion was based on the measured disappearance of CO at the end of the reaction.

The aqueous phase was pipetted from the autoclave, and suspended material was filtered if necessary. The nonvolatile coal products were quantitatively removed from the autoclave with tetrahydrofuran (THF) and transferred to a round-bottom flask. The THF was removed by rotary evaporation, 400 ml of toluene was added, and the mixture was refluxed for 2 h in a Dean-Stark trap.

Azeotropic distillation removed any water. After cooling, the mixture was filtered to separate the TS material from the toluene-insoluble (TI) material. The toluene was removed from the filtrate by rotary evaporation. Both the TS and TI fractions were dried overnight at 80°C under vacuum and weighed.

Results and Discussion

The results of the conversion of the Illinois No. 6 coal at various times, temperatures, and initial pH's are presented in Table 8. Most of the runs were conducted at 400°C, but a few runs were conducted at temperatures above and below 400°C. The results of the conversions at 400°C are discussed in some detail below.

We will be concerned primarily with the interrelationship between the rate of production of TS material, the rate of CO disappearance, and the initial pH of the aqueous solution. Before proceeding, it is important to note that the reaction times refer to the times during which the autoclave was maintained at 400°C. For example, a run at

Table 8

CONVERSION OF PSOC-1098 ILLINOIS NO. 6 COAL IN CO/H_2O

Run No.	Initial pH	Reaction Time (min)[a]	Temp. (°C)	% TS[b]	% CO Conversion[c]	Mass Balance (%)[d]	Initial Pressure of CO (psig)[e]	Final Pressure (psig)[e]	Reaction Pressure (psig)[f]
HC-6	13.3	20	400	53	85	82	500	820	5000
HC-36	7.0	20	400	27	23	82	500	580	4300
HC-52	7.0	20	400	29	24	83	500	560	4300
HC-140	7.0	30	400	34	37	91	500	580	3650
HC-142	7.0	0	400	20	14	92	490	520	3700
HC-146	9.5	30	400	34	40	88	510	580	3900
HC-148	9.5	20	400	29	22	87	490	530	3650
HC-150	9.5	0	400	20	16	90	500	520	3750
HC-162	12.5	0	400	23	19	94	510	610	3750
HC-166	12.5	20	400	38	70	88	520	790	4100
HC-168	12.5	70	400	49	88	82	520	830	4250
HC-170	7.0	70	400	43	54	86	500	640	4100
HC-172	7.0	180	400	40	67	80	480	630	3900
HC-174	13.3	180	400	29	24	83	500	560	4300
HC-178	13.3	0	400	27	23	82	500	580	4300
HC-152	13.0	105	330	33	81	93	510	760	3250
HC-160	13.1	15	430	45	90	84	510	810	4500
HC-164	12.5	0	475	46	83	80	510	785	4900

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[a] Time that autoclave was held at indicated temperature.
[b] Weight % dmmf starting coal.
[c] As determined from CO disappearance.
[d] Weight % of dry starting coal accounted for in nonvolatile products.
[e] Cold pressure (25°C).
[f] Maximum pressure attained during reaction.

400°C/0 min indicates that the autoclave was heated to 400°C and immediately allowed to cool. The heat-up and cool-down times for the system were about 50 min. Thus, the system has been allowed to react, and the "true" reaction time is not 0 min.

CO and WGSR

Figure 1 is a plot of time versus the percent CO disappearance at various initial pH's at 400°C in the pressure of Illinois No. 6 coal Three aspects of the figure that deserve consideration are as follows: (1) CO reacts much more rapidly at high initial pH's, (2) significant levels of CO react even under neutral conditions, and (3) the rate of CO disappearance at pH's of 7.0 and 9.5 are virtually identical.

Because the WGSR is base-catalyzed, the rapid conversion of CO to CO_2 at high pH's is expected. The equilibrium constant, K_p, for the WGSR at 400°C is 15.3. Hence, 98% of the CO should be converted to CO_2 if the system is at equilibrium. At an initial pH of 13.3, equilibrium is quickly approached and virtually achieved at 20 min reaction time.

Surprisingly, for the less basic and neutral systems, significant levels of CO are converted at reaction times on the orders of tens of minute. However, even after 180 min, the system initially at pH 7 had gone to only about 60% CO conversion. For the runs with initial pH values of 12.5 and 7.0, such estimates show a rate difference of only a factor of 4 for an apparent hydroxide concentration difference of 5.5 orders of magnitude. Clearly, the system is not operating in a simple stoichiometric manner, and we conclude the following: (1) added base does promote CO conversion, (2) however, a good deal of the added hydroxide is irreversibly consumed by the coal, and (3) significant participation in the WGSR by the reactor walls and mineral matter in the coal is probable.

The suggested irreversible scavenging of hydroxide by the coal is consistent with the finding that the pH 7 and 9.5 results are virtually identical. Only at high pH's does a significant quantity of OH^- survive to catalyze the reaction. This result is consistent with the earlier

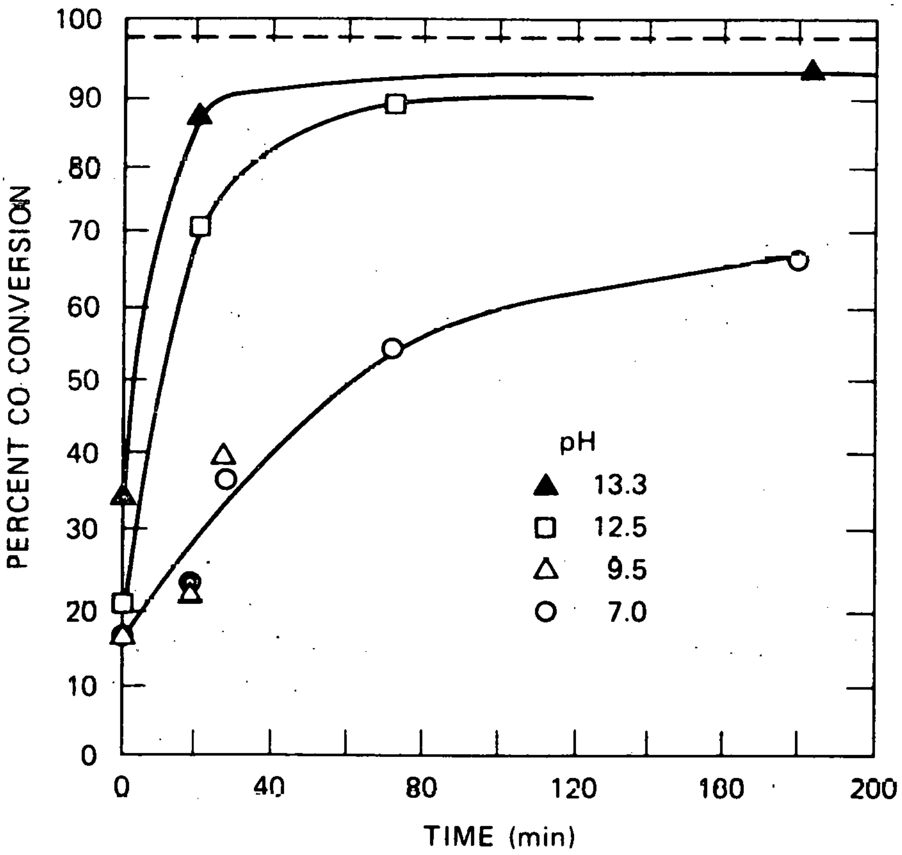

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FIGURE 1 TIME VERSUS PERCENT CO CONVERSION AT 400°C AND VARIOUS INITIAL pH'S FOR AN ILLINOIS No. 6 COAL (PSOC-1098) results of Ross et al. on the beneficiated Illinois No. 6 coal.[3] In addition, we have found that when the coal is heated in N_2/H_2O at 400°C for 20 min at an initial pH of 13, the pH at the end of the reaction drops to 8. Thus the coal scavenges hydroxide in some manner.

Finally, the role of base in this system is even more complicated. Calculations show that for our system most of the hydroxide ion should be scavenged by the first quantities of CO_2 that are produced. The results of these calculations are presented and discussed in an appendix to the report.

Coal Conversion

Figure 2 is a plot of time versus the amount of TS material produced from the coal. The results suggest, but do not confirm, that the ultimate conversion of the coal is a function of the initial pH. Approximately 50 wt% of TS material is produced within 20 min at an initial pH of 13.3. The amount of TS material then gradually increases to 60 wt% at a reaction of 180 min. Note in Figure 1 that virtually all the CO is depleted within 20 min. One might expect repolymerization reactions to dominate after the CO is depleted because CO is the active reducing species in this system. In this regard, the product H_2 may play a role in the prevention of such reactions. The solvolytic power of the supercritical water may play an important role here as well.

Finally, Figure 3 is a plot of the percent CO conversion (as measured by its disappearance) against the amount of TS material produced for all runs at 400°C. There exists a good single general correlation between the percent CO converted and the amount of TS material produced from the coal, regardless of the initial pH or the reaction time. Thus, the amount of CO that is allowed to enter the reaction pathway, not the rate at which it enters, appears to control the conversion to TS material in this system.

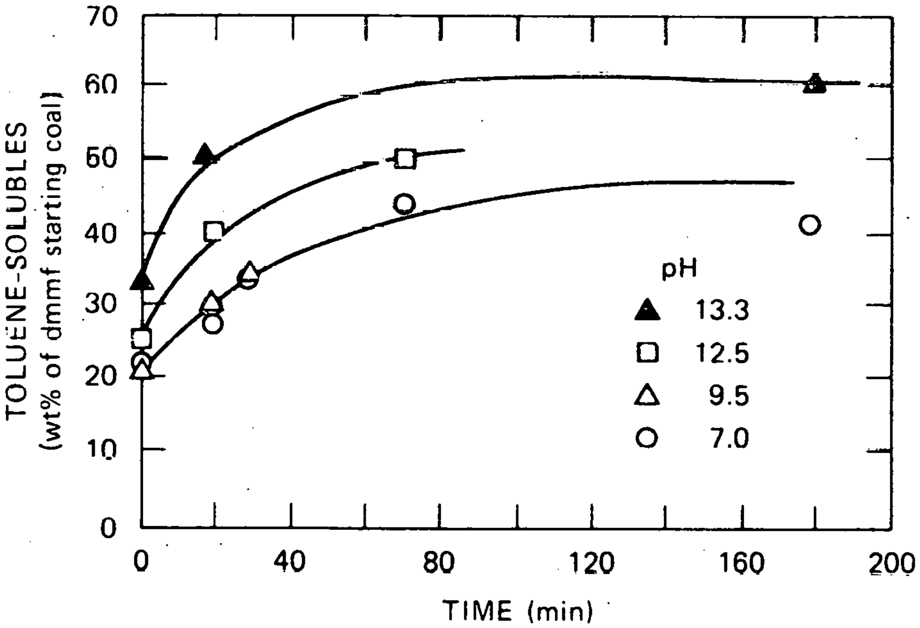

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FIGURE 2 TIME VERSUS CONVERSION TO TOLUENE-SOLUBLES AT 400°C AND VARIOUS INITIAL pH'S FOR AN ILLINOIS No. 6 COAL (PSOC-1098)

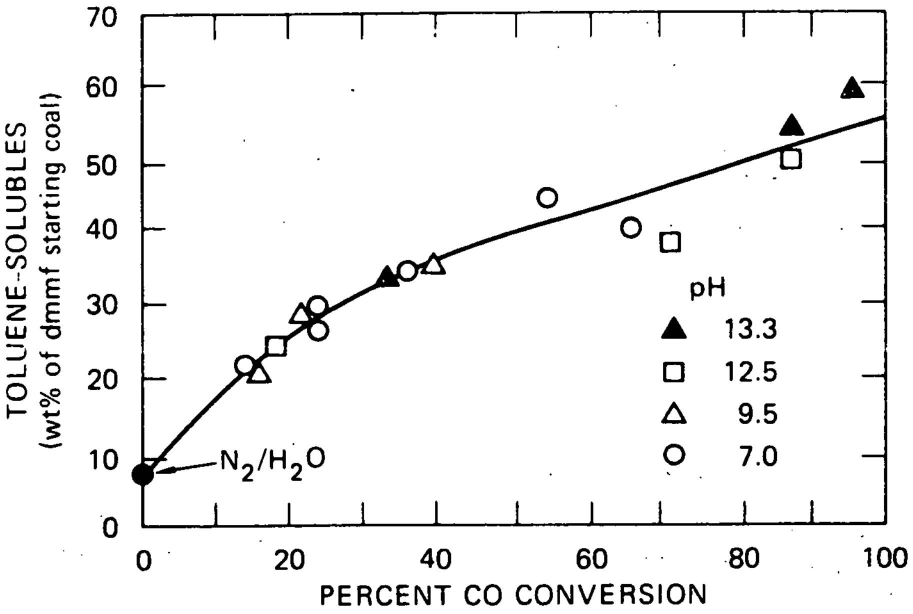

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FIGURE 3 PERCENT CO CONVERSION VERSUS CONVERSION TO TOLUENE-SOLUBLES AT 400°C AND VARIOUS TIMES AND INITIAL pH'S FOR AN ILLINOIS No. 6 COAL (PSOC-1098)

Interpretation

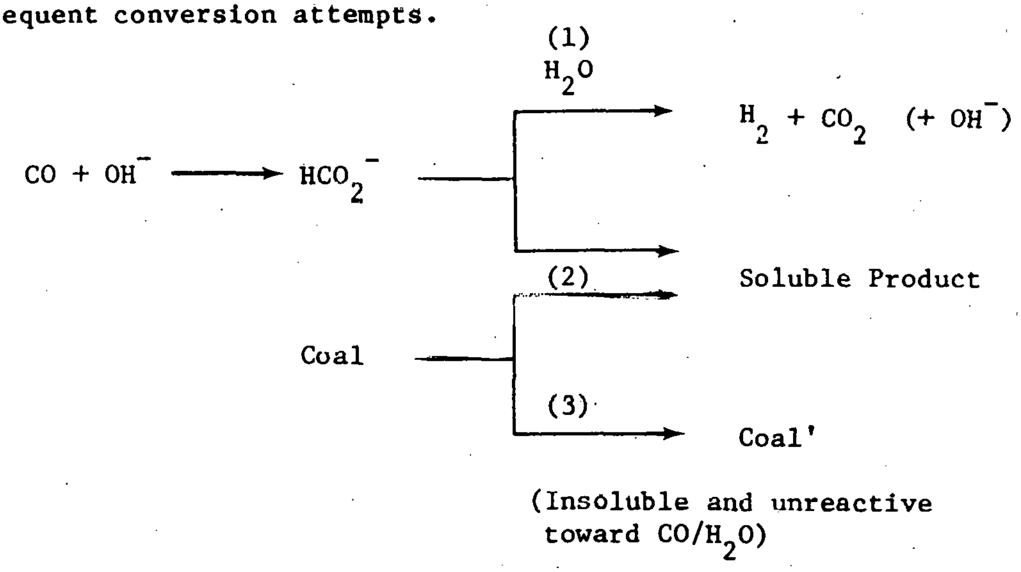
A scheme for this behavior in this system can be suggested. It must take into consideration the following facts:

(1) The conversions of both CO and coal are promoted by the addition of hydroxide to the system.

(2) The conversions take place in parallel, with the observed coal tracking the CO conversion over a wide range of initial pH values and reaction times.

(3) From earlier work on this task, the substitution of D_2O for H_2O results in a higher coal conversion for a given CO conversion.[2] Most significantly, the ultimate (i.e., exhaustive) conversion of coal was increased by going to the deuterio medium.

The following scheme serves as a working model for the conversions and is consistent with the observations. This scheme is somewhat different from conventional explanations for conversion and is based on the simple view that when coal is heated, it is converted to both soluble and insoluble products. This elementary position becomes a bit more complex with the added requirements that (1) the degree of soluble product formation is a function of the effectiveness of the reducing system, and (2) the insoluble portion (char) is not convertible in subsequent conversion attempts.



Routes 2 and 3 represent the branching paths for coal liquids or char and are competitive with one another. The rate of route 2 is a function of the effectiveness of the conversion system, so that the faster the conversion is, the more ultimate conversion takes place.

The similar branching in the reducing system itself, routes 2 and 1, is a necessary consequence of the parallel in CO and coal conversion and further explains the inverse isotope effect. Route 1 experiences a normal isotope effect, that is, a decline in rate in substitution of deuterium for protium, and therefore the relative rate of 2 increases. We note that the production of H_2 and CO_2 are "wasteful" in the sense that the intermediate formate is the active reducing species* and is withdrawn from the system in the production of the two gases.

As regards the specific effects of hydroxide concentrations in the conversions, we can suppose as a working hypothesis that the rate at which coal goes to coal' is independent of the initial hydroxide concentration. Then the relative rates through routes 2 and 3 would be governed by the initial hydroxide concentration. As the basicity of the initial solution decreases, the rate through route 2 decreases relative to that through route 3. Under this circumstance, one might expect more coal to follow route 3 than 2, thus resulting in lower conversion to soluble products.

However, the picture is not all that clear. Recall that in Figure 3 the amount of TS material produced from the coal always follows the CO disappearance, regardless of the initial pH or the reaction time. For example consider that at an initial pH 7 and a reaction of 180 min, about 70% of the CO is converted, which results in 40 wt% TS product. Now consider that at an initial pH of 12.5 and 20 min, about 70% of the CO is converted, which also results in 40 wt% TS product. Thus, the

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*We have no evidence that formate is the specific reducing species. It has been demonstrated, however, that aqueous sodium formate converts coal.[4-7]

rate at which CO enters the reaction pathway has no ultimate effect on the amount of coal converted to soluble product; the amount of TS product is only a function of the amount of CO that enters the reaction pathway. This result therefore suggests that routes 2 and 3 are not simply related as presented in the scheme, and the nature of their competition must be questioned.

To establish the integrity of the scheme, it is necessary to test the relationship between proposed routes 2 and 3. This work has begun, and in the first run we treated the Illinois No. 6 coal first in N_2/H_2O at pH 7 (400°C/20 min) and then in CO/H_2O at pH 13 (400°C/20 min). Based on the amount of CO that was converted (83%), we predict the coal to be converted to 50% TS product (from Figure 3). However, the toluene solubility of the product was 36%. Thus, the pretreatment in N_2/H_2O lowered the conversion by about 30%.

Although it is clear that the conversion was lowered by the pretreatment in N_2/H_2O, the coal nevertheless remained substantially reactive toward CO/H_2O. This result may help to explain why a change in the rate of CO conversion does not have a substantial effect on the amount of TS material produced from the coal. More experiments of this nature may provide a more complete picture, including runs in N_2/H_2O at pH 13.

This result also requires that a substantial number of structural groups that are reactive toward CO/H_2O survive the thermal pretreatment. The types of structures in bituminous coal that are both reactive toward CO/H_2O and lead to soluble, lower molecular weight products are not at present known. Our laboratory is searching for model structures that satisfy both requirements.

Work in Progress

We are at present conducting mass and atom balances on the starting coal and products of conversion. Of particular concern is the oxygen loss we reported last quarter.[6] Thus, we are examining the oxygen functionalities that are lost or retained during the conversion process. Sulfur forms are also being examined. This work has not proceeded far enough to merit discussion.

REFERENCES

1. D. S. Ross, D. F. McMillen, W. C. Ogier, S. J. Chang, G. P. Hum, R. Mansani, and T. K. Green, "Exploratory Study of Coal Conversion Chemistry," Quarterly Report No. 7, Contract No. DE-AC22-81PC40785, SRI International, Menlo Park, California (March 1983).
2. D. S. Ross, D. F. McMillen, W. C. Ogier, S. J. Chang, G. P. Hum, R. Mansani, and T. K. Green, "Exploratory Study of Coal Conversion Chemistry," Quarterly Report No. 8, Contract No DE-AC22-81PC407845, SRI International, Menlo Park, California (June 1983).
3. D. S. Ross, D. F. McMillen, W. C. Ogier, and Q. Nguyen, "Exploratory Study of Coal Conversion Chemistry," Final Report, Contract No. DE-AC22-79-ET14855, SRI International, Menlo Park, California (August 1981).
4. F. Fischer and H. Schrader, Brennstoff Chem. 2, 161 (1921); C.A. 15, 3193 (1921).
5. E. Gorin in "Chemistry of Coal Utilization, Second Supplementary Volume," M. A. Elliott, ed. (John Wiley and Sons, New York, 1981), pp. 1894-1896.
6. D. S. Ross, D. F. McMillen, W. C. Ogier, S. J. Chang, G. P. Hum, R. Mansani, and T. K, Green, "Exploratory Study of Coal Conversion Chemistry," Quarterly Report No. 9, Contract No. DE-AC22-81PC40785, SRI International, Menlo Park, California (September 1983).
7. D. S. Ross, T. K. Green, and R. Mansani, Proceedings of the 1983 International Conference on Coal Science, Pittsburgh, PA, August 1983.

Appendix

THE ROLE OF HYDROXIDE ION IN CO/H_2O CONVERSION SYSTEMS

In our conversion, we used catalytic quantities of potassium hydroxide (1-3 mmoles) to bring about the ultimate transfer of hydrogen to the coal using initially 78 atm of CO (hot, 500 mmole). The reaction sequence we have used for sometime is

$$OH^- + CO \rightleftharpoons HCO_2^- \qquad (1)$$

$$HCO_2^- + H_2O \rightleftharpoons OH^- + CO_2 + H_2 \qquad (2)$$

$$HCO_2^- + \text{Coal} \rightleftharpoons \text{Reduced Coal} + OH^- \qquad (3)$$

The reduction of coal therefore parallels the water-gas-shift reaction and a key part of the series is the maintenance of a steady-state level of hydroxide to in turn maintain the chain.

It is, of course, recognized that carbon dioxide is generated. Thus, before we can use this scheme as an explanation, we have to appreciate that carbon dioxide could scavenge the hydroxide via

$$OH^- + CO_2 \rightleftharpoons HCO_3^- \qquad (4)$$

and the reaction might be a self-limiting system. The calculated value for K_4 at 400°C is 6.33 atm^{-1}, with the position of the equilibrium being fully variable according to the partial pressure of carbon dioxide. Some pressures and fractions of hydroxide conversions are presented below for a solution initially 0.1 M in hydroxide and at 400°C.

PCO_2 (atm)	OH^- Converted (%)
0.02	10
0.16	50
1.4	90
3.0	95
16.0	99
158.0	99.9

Because in our conversions we accumulate CO_2 to yield pressures near 80 atm, the hydroxide available quickly falls to very low levels. And if we consider that the rate reaction is proportional to hydroxide, then the rate falls similarly. For example, 16 atm of carbon dioxide represents about 20% conversion of the CO and therefore about 20% reaction. At that pressure, the hydroxide concentration, and therefore the reaction rate, is down to 1% of its original value. In other words, after only one fifth of the reaction has taken place, its rate is 1/100th of its initial value. We must therefore ask how the reaction proceeds. At present we have no satisfying explanation, but these results suggest that the reaction does not require hydroxide for the reaction of CO. This suggests that other chemistry may be operating, and we plan investigations along these lines.

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