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DOE/PC/40785-5
(DE83002456)

FOSSIL ENERGY

EXPLORATORY STUDY OF COAL CONVERSION CHEMISTRY

Quarterly Report No. 5, May 19—August 18, 1982

By
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Donald F. McMillen
Walter C. Ogier
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October 1982

Work Performed Under Contract No. AC22-81PC40785

SRI International
Menlo Park, California

U. S. DEPARTMENT OF ENERGY

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Distribution Category UC-90d

EXPLORATORY STUDY OF COAL CONVERSION CHEMISTRY

Quarterly Report No. 5
For the Period May 19, 1982, to August 18, 1982

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Prepared for:
U.S. Department of Energy
Division of Energy Technology
Under Contract No. DE-AC22-81PC40785

ABSTRACT

In Task A, "Mechanisms of Donor-Solvent Liquefaction," work has begun on Subtask A.3 "Improved Correlation Between Donor-Solvent Structure and Coal Conversion Effectiveness." Initial runs of coal liquefaction products through the automatically switched, multicolumn, solvent-extraction/high-pressure liquid chromatography systems have been performed. This separation was followed by field ionization mass spectrometric analysis of the volatile portions of each of the separated fractions. The separation scheme is described, and results of one of the initial separations are summarized. The FIMS spectrum of one of the fractions (lower molecular weight nitrogen heterocycles) is presented and the types of information available from this less-than-ideal case (i.e., broad HPLC fraction) are discussed in the context of the objective of this subtask.

In Subtask B.1, we studied the effect of initial pH on the degree of conversion of Kentucky No. 9 (PSOC-213) coal to toluene-solubles in the CO/H_2O system [previously we studied Illinois No. 6 (PSOC-26) and Colorado Wadge (PSOC-233) coals]. We find that the toluene-soluble products increased with increasing pH. At initial CO pressures ranging from 475 to 525 psig, the toluene-soluble and -insoluble fractions increased with increasing conversion.

In Subtask B.2, we studied the thermolysis of bibenzyl in D_2O at 400°C. The major products were toluene and stilbene. Minor products were benzene, ethylbenzene, styrene, diphenylmethane, and phenanthrene. The recovered bibenzyl and products contained significant quantities of deuterium. From the degree of deuterium incorporation, a statistical determination for a simple series of consecutive exchange reactions was derived. The reaction scheme involves an initial slow homolysis of the starting bibenzyl to yield benzyl radical, which, in turn, reacts with D_2O to form OD. OD then rapidly reacts with bibenzyl to yield bibenzyl

radical, and the formed bibenzyl radical abstracts deuterium from the medium to form products. The chemistry suggested here demonstrates that water can act as an H-donor because it readily transfers hydrogen to organic free radicals. We further suggest that water, can generate hydrogen atoms if CO is present.

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INTRODUCTION

SRI International is conducting a program on the chemistry of the conversion of coal to liquid fuels. The study is divided into two tasks: Task A deals with the general subject mechanisms of donor solvent liquefaction. Task A is divided into three subtasks: A.1, "Mechanism of Iron Oxide and Sulfide Catalysis of C-C Bond Cleavage in $PhCH_2PhOH$", A.2 "The Rate and Mechanism of Thermal Degradation of Methylene-Bridged Polymers," and A.3, "Improved Correlation Between Donor-Solvent Structural Parameters and Coal Conversion Effectiveness." Work during the last three quarters has concentrated on Subtask A.2, but has also provided a baseline of understanding not previously available for undertaking Subtask A.3, which we began this quarter.

Task B is a study of the conversion of coal and model compounds in the CO/H_2O system. Task B is divided into two subtasks: B.1, in which we are studying how various parameters affect coal conversion, and B.2, in which we are studying the reactions of various model compounds in D_2O.

Tasks A and B both involve the use of different coals (extending from lignites to bituminous coals) and appropriate model compounds. Our overall objective is to develop a better understanding of the operative chemistry in donor-solvent and CO/H_2O coal conversion processes.

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

Donald F. McMillen, Walter C. Ogier, and Ronald H. Fleming

Introduction

In the previous three quarters, studies of central bond cleavage in the structures ArOAr, $ArCH_2Ar$, ArOAr(OH), and $ArCH_2Ar(OH)$ have provided considerable information about the rates and mechanisms by which certain bonds, which are too strong to undergo homolysis, can be cleaved on time scales of possible importance for coal liquefaction. These cleavages occur in donor solvents, without added H_2 pressure. They sometimes involve cleavage initiated by hydrogen-atom transfer and sometimes involve hydrogen transfer only after cleavage. This quarter, we began subtask A.3, in which we hope to extend the insight gained with model coal structures to the chemistry of fragmentation of real coal structures. More specifically, subtask A.3 is based on the premise that a significantly improved, quantitative understanding of model coal structure cleavage mechanisms, particularly as influenced by the presence of the most common polar functionality, phenolic OH, can be combined with functional-group-based chromatographic separation of liquefaction products and mass spectrometric and IR analysis of the separated fractions to obtain an improved understanding of why some solvents work better than others under certain conditions.

This quarter we have focused on the high pressure liquid chromatography (HPLC) system. That is, we first selected a separation scheme for our HPLC system, which we had previously timed with automatically operated column switching valves. Then we began preliminary runs of the liquefaction products through that system. The separated fractions were analyzed by field ionization mass spectroscopy (FIMS). Below, we describe the results of these preliminary runs and the configuration of the current HPLC system.

Also this quarter, we have summarized the results presented in the last quarterly report in a manuscript for publication. These results provide evidence for a previously undocumented hydrogen-transfer reaction involving species common in donor-solvent media and have withstood the test of further scrutiny.

The objective of subtask A.3 is to select an HPLC scheme that meets two requirements. First, the HPLC system should adequately separate the liquefaction products on the basis of functionality so that subsequent FIMS analysis of the separated fractions will indicate what functional groups (i.e., polar "centers") in the coal structure are preferentially "operated upon" by the more effective solvent. Second, the system should accomplish this goal with as few HPLC fractions as possible; this will enable us to survey enough coals and solvents to ultimately choose among the various solvent structural parameters that may affect coal liquefaction. To maximize the differences in effectiveness of different solvents, we will use two dramatically different solvents and a bituminous coal of high-softening temperature and very low fluidity. That is, we will use solvents that are expected to be greatly different in conversion effectiveness and a type of coal that is known[1] to be particularly sensitive to donor-solvent effectiveness.

HPLC Separation Scheme

After considering several alternative chromatographic schemes described by various groups for coal liquid separations/analysis, we decided to begin with the separation scheme described by Boduszyinski.[2] This procedure combines a packed-column, solubility-based separation with subsequent chromatographic separation of the

---

[1] I. Mochida, A. Takanabe, and K. Takeshita, Fuel, (1979) 58, 17.

[2] M. M. Boduszynski, R. J. Hurtubise, and H. F. Silver, Anal. Chem. (1982), 54, 372.

Table 1

EXTRACTION AND CHROMATOGRAPHY SOLVENT SEQUENCE
AND DERIVED LIQUEFACTION PRODUCT FRACTIONS
(Molecular weights based on FIMS analysis of
separated fractions for conversion in tetralin at 400°C)[a]

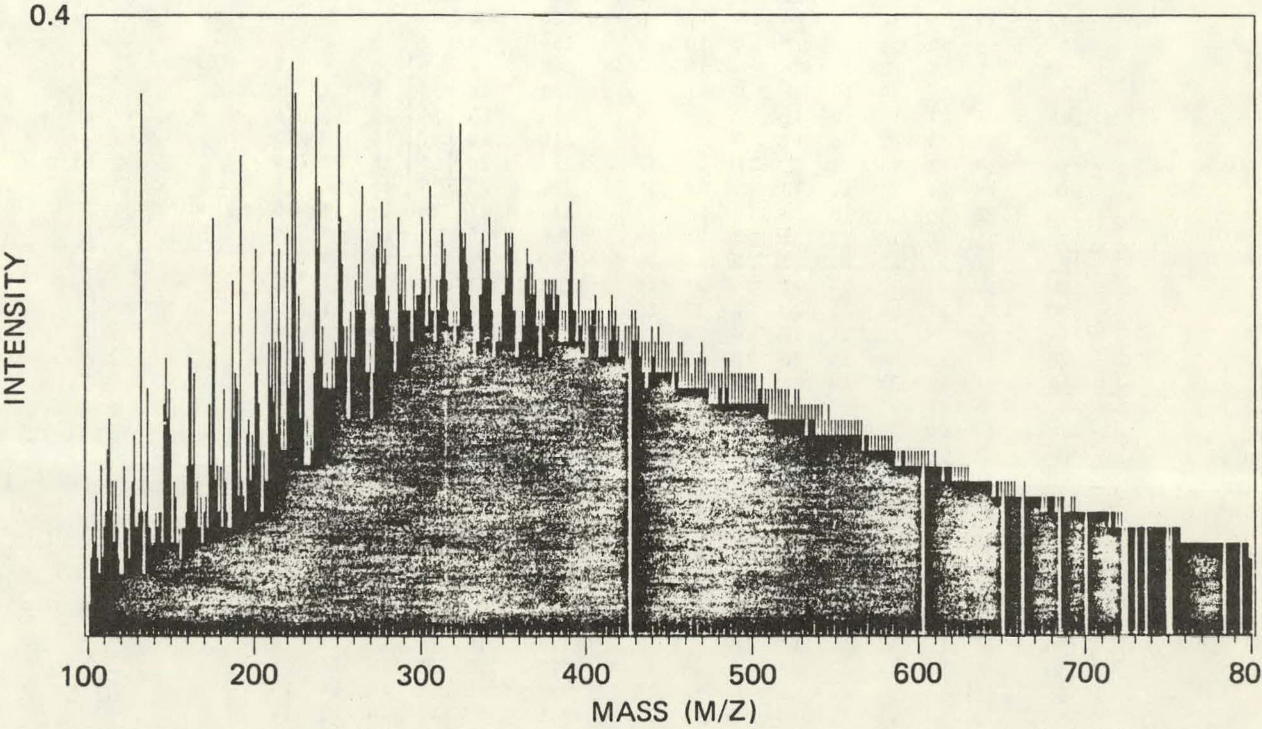
Fraction Number	Extraction Solvent	Chromatographic Solvents	Predominant Functional Groups or Eluted Materials[b]	Weight (mg)	$\overline{MW}_n$	$\overline{MW}_w$	Maximum Inlet Temp. (°C)	% Volatile at Maximum Temp.
1	n-Hexane (oils)	N-hexane	Light hydrocarbons	13.2	291.3	336.3	268	96
2		Toluene	Hydrocarbons	4.2	418.0	478.6	339	90
3		Chloroform	N-heterocycles	1.2	412.1	483.2	339	75
4		Backflush $CHCL_3$:MeOH 4:1(v:v)	Hydroxyl aromatics	5.8	376.5	443.1	339	70
5	Toluene (asphaltenes)	Toluene	N-Heterocycles	1.0	455.4	495.2	339	61
6		$CHCl_3$	N-Heterocycles	1.8	385.0	446.4	388	55
7		Backflush $CHCl_3$:MeOH 4:1(v:v)	Hydroxyl aromatics	9.0	413.9	468.1	388	55
8	Chloroform (preasphaltenes)	Chloroform	N-Heterocycles	1.9	420.9	469.4	388	42
9		Backflush $ChCl_3$:MeOH 4:1(v:v)	Hydroxyl aromatics	13.1	400.1	453.9	388	43
10	Pyridine (preasphaltenes)	No alumina chromatography	Polyfunctional compounds	63.4	299.6	367.9	388	--[c]
			Total	115.2				

---

[a] Tetralin was used as a solvent; the coal was PSOC-1116 (from Sunnyside, Utah); the solvent:coal ratio was 2:1; the reaction time was 30 min (heat-up time was ~ 1 min).

[b] From Reference 2, based on model compound chromatography and IR analyses of separated SRC fractions.

[c] Not available.



JA-3304-14

FIGURE 1 FIELD IONIZATION MASS SPECTRUM OF EXTRACTION/CHROMATOGRAPHY FRACTION 3, Lower Molecular Weight Nitrogen Heterocycles.

Table 2

NORMALIZED INTENSITIES FOR FIELD IONIZATION MASS SPECTRUM OF FRACTION NO. 3, MASSES 90 to 817

```
A24303 SUM  704 PKS W MIN  100 CNTS  02 SEP-82  09:08:28  SUM I: 0.2119E+06
G.HUM, EXP#1, FRACTION#3 1-9                                   N AV MW: 412.1
ACQUIRED 9- 1-82 15:35:10  CHAN.#S  0-4095; 10 MS/CHAN       WT AV MW: 483.2
MAG. RET. TIME: 9999 MS,  8 SCANS/SPECTRUM.          -93 TO 339 DEG. C  SF = 1
NORMALIZED INTENSITIES                                                  PG. 1
```

	0	1	2	3	4	5	6	7		0	1	2	3	4
Mass			AR		U3		U2		Mass	U1		RH		ROH
90	0	0	0	0	0	0	0	0	98	0	0	0	2	5
104	6	9	5	4	11	5	7	8	112	12	14	8	10	6
118	7	5	4	4	11	7	7	5	126	9	10	13	7	7
132	35	8	4	8	16	7	7	6	140	6	8	7	8	8
146	15	18	14	16	13	6	10	9	154	6	7	5	7	7
160	11	18	18	11	17	8	10	7	168	9	6	8	9	7
174	11	27	19	10	11	8	11	7	182	16	10	8	7	7
188	14	17	16	9	31	10	9	8	196	13	14	10	13	11
202	17	15	12	8	12	10	10	19	210	16	27	15	19	13
216	19	12	14	12	26	16	17	37	224	24	35	18	22	14
230	18	11	14	11	13	12	17	36	238	25	29	18	20	16
244	17	16	16	18	16	19	18	33	252	27	24	20	18	20
258	21	18	18	23	21	24	21	29	266	22	21	17	17	19
272	17	22	25	26	23	28	24	25	280	21	22	20	19	20
286	19	27	22	24	21	24	21	21	294	21	19	23	21	22
300	22	27	24	23	20	22	29	21	308	21	19	23	21	23
314	24	25	23	21	20	20	21	19	322	21	20	33	26	25
328	24	23	22	21	20	18	20	19	336	22	22	26	23	25
342	27	23	21	18	19	19	20	19	350	22	22	26	23	26
356	26	21	21	18	19	19	21	20	364	23	25	24	22	24
370	23	20	21	18	21	20	23	22	378	23	22	23	21	23
384	22	19	21	19	21	19	23	28	392	25	21	21	19	23
398	21	19	21	18	21	20	21	21	406	22	19	21	18	21
412	20	18	21	19	22	20	21	19	420	20	18	19	18	20
426	20	0	21	19	21	19	20	18	434	19	17	19	16	19
440	20	18	19	17	20	17	19	17	448	19	17	19	17	18
454	18	17	19	16	19	16	18	16	462	18	16	17	16	18
468	18	16	19	16	18	16	17	15	476	17	15	17	15	17
482	17	15	18	16	18	15	17	15	490	17	15	17	15	17
496	17	15	17	15	17	15	17	15	504	16	16	17	15	16
510	16	14	16	14	17	14	16	14	518	16	14	16	14	16
524	15	14	16	14	16	14	15	14	532	15	13	15	14	15
538	15	13	15	13	15	13	14	13	546	15	13	14	13	14
552	14	13	14	13	14	13	14	13	560	14	13	14	13	14
566	14	12	13	13	13	12	13	12	574	13	12	13	12	13
580	13	12	13	12	13	12	12	11	588	12	11	12	12	12
594	12	11	12	11	12	11	12	11	602	12	0	12	11	12
608	11	11	12	11	11	11	11	10	616	11	11	11	11	11
622	11	10	11	10	11	10	11	10	630	11	10	10	10	10
636	10	10	10	10	10	10	10	10	644	10	9	9	10	10
650	10	0	10	9	10	9	10	9	658	10	9	9	9	9
664	10	9	9	9	9	9	9	9	672	9	9	9	8	9
678	9	9	9	9	9	9	8	9	686	9	9	8	8	8
692	9	8	9	8	8	8	8	8	700	8	0	8	8	8
706	8	8	8	8	8	8	8	8	714	8	7	8	8	8
720	8	7	8	0	7	0	7	7	728	7	7	7	0	7
734	7	7	7	0	7	7	7	7	742	7	7	7	7	7
748	7	7	0	7	0	7	7	7	756	7	7	6	6	6
762	6	6	6	6	6	6	6	6	770	6	6	6	6	6
776	6	6	6	6	6	6	6	6	784	0	6	6	6	6
790	6	6	6	6	6	0	6	6	798	6	5	5	5	5
804	5	5	5	6	0	0	0	0	812	0	0	0	0	0

various solubility classes on alumina columns. The initial solubility separation will provide classes that can be compared with the traditionally reported, hexane, toluene, and pyridine solubles. Then the chromatographic separation will divide the classes primarily according to functional groups, which will allow us to determine the functional groups that are most important in the coal structure fragmentation.

Briefly, the method consists of loading the tetrahydrofuran (THF)-soluble portion of the coal liquefaction products, typically 400 to 800 mg, as a thin layer onto grated Teflon (20/40 mesh) by pouring 8-10 mL of the THF solution onto 16 g of Teflon in a round-bottom flask. The bulk of the THF is removed by flushing the flask with N_2 and removing the remainder on a rotary evaporator at 100°C and ~ 0.2 torr. The coal-coated Teflon is then loaded into a chromatographic column (10 mm ID x 25 cm). This column is then flushed with n-hexane, toluene, and pyridine in succession (~ 3 column volumes each solvent). After each flushing in which the effluent is directed onto the basic alumina column, (Aldrich Co., 10 mm ID x 25 cm), the coal-Teflon column is isolated by automatically operated values and the alumina column is developed with a series of solvents. Table 1 shows the results of the experiments to date, including the series of solvents used, the resulting fractions, and the average molecular weights as determined by FIMS.

FIMS of Extraction/Chromatography Fractions

Figure 1 shows the FIMS spectrum of fraction 3 (lower molecular weight N-heterocycles according to Reference 2) from the series shown in Table 1. The appearance of peaks at every mass indicates (as expected) that even this degree of chromatographic separation does not result in FIMS spectra that give a complete chemical breakdown upon cursory examination. However, even a FIMS spectrum as "black" as Figure 1 can yield certain kinds of detailed information. For example, let us examine a portion of the data in Table 2, which were taken from the spectrum in Figure 1. Table 2 is a printout of the normalized intensities for all masses (molecular ions) from 90 to 817, arranged so that it is easy to identify the homologous series. The intensities at various masses are listed in 13 columns so that directly below the intensity at some mass M, one finds the intensity of mass M + 14 in the next row, M + 2(14) in the row after that, and so forth. This makes it possible to readily pick out a series M + $(CH_2)_n$. The intensities are normalized to a total intensity of 10,000.

For example, the intensities of the series at the circled odd masses 169, 183, 197, 211, 225, and 239, with intensities of 6, 10, 14, 27, 35, and 29, respectively, suggests the presence not only of carbazole at m/e 169, but also of substantially more (5 to 10X) of the alkylated carbazoles [carbazole + $(CH_2)_2$, n = 1 to 5] than of the parent compound. This observation is one that cannot be readly made on the basis of either low-energy electron-impact mass spectrometry or HPLC because of fragmentation of the alkyl aromatics (even with low-electron energy) and because of the multiplicity of isomeric peaks in the liquid chromatogram.

We hope that the ability to distinguish nitrogen-containing from nitrogen-free compounds (odd versus even masses) and to pick out homologous series [e.g., $M(CH_2)_n$, $M(OH) + (CH_2)_n$, $M(OH)_2(CH_2)_n$, etc.], together with the summarized functional group information provided by IR analysis of the various fractions, will allow us to achieve the objective of deriving an improved understanding of the functional groups or structures with which the more effective donor solvents preferentially operate.

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

David S Ross and Georgina P. Hum

Background

The principal research goal under Subtask B.1 is to develop an understanding of the CO/H_2O system in coal liquefaction chemistry by studying the conversion of various coals. Previous work[1] dealt with the pH dependence of Illinois No. 6 (PSOC-26) coal with respect to conversion to benzene-soluble products. The products of the conversion were very similar to those obtained in tetralin under the same reaction conditions. We also studied the effect of pH on coal conversion using water-soluble metal salts. High oxidation state oxyanions of metals such as Cr, Mo, and Mn in the 3000-ppm range affected conversion at initial pH values of 6 to 12.6.

We are continuing the work described above by extending the study to other coals. We have previously reported[2] the effect of initial pH on a second, high-volatile, bituminous coal, Colorado Wadge (PSOC-233). The toluene-soluble product increased with increasing pH. This quarter, we conducted experiments to determine the effect of initial pH on the conversion of a third coal, Kentucky No. 9 (PSOC-213).

---

[1] D. S. Ross, D. F. McMillen, W. Ogier, and Q. Nguyen, "Exploratory Study of Coal Conversion Chemistry," SRI Project 8992, DOE Contract No. DE-AC22-79-ET14855, Final Report (August 1981).

[2] D. S. Ross and R. Bunnell, "Exploratory Study of Coal Conversion Chemistry," SRI Project 3304, DOE Contract No. DE-AC22-PC140785, Quarterly Report No. 3 (March 1982).

Experimental Procedures

All reactions were performed in a 300-mL, Magne-Drive-stirred, Hastelloy-C autoclave. The autoclave was loaded with 36 g of deionized water, which was brought to the desired pH by addition of KOH. Then 10 g of the desired coal (PSOC-26, PSOC-213, or PSOC-233) was added. PSOC-26 is a beneficiated coal that has been ground and sieved under N_2 to -60 mesh and dried at 120°C overnight in a vacuum oven. PSOC-233 and PSOC-213 had been ground and sieved under N_2 and the 60- to 100-mesh fraction dried in a vacuum oven at 120°C overnight. Results of the elemental analysis of these coals are shown in Table 3.

Once the reactor is loaded with coal and water, the system is purged once with 1000 psig of N_2, then twice with 1000 psig of CO, and finally the autoclave is charged with the desired pressure of CO. The coal is converted by heating the autoclave to 400°C (± 5°C) for 20 min (± 1 min). Pressures in excess of 5000 psig are typically attained at these temperatures and are recorded for each run as discussed below. The heat-up and cool-down times for the system are both about 1 hr.

A Carle gas analyzer is used for quantitative analysis of the product gases, which include H_2, CO_2, N_2, CH_4, and CO.

The condensed products are removed from the autoclave as either an aqueous or a coal fraction. First, the water is removed from the reactor with a pipette, and the water is filtered if suspended material is present. The pH of the water is measured.

Solid material is removed from the autoclave with a spatula and is transferred to a flask. The reactor walls are rinsed with toluene to collect any remaining oil or tar; this solution is combined with the solid material. Refluxing the coal fraction in a Dean-Stark trap for 2 hr removes any remaining water through azeotropic distillation. A medium-porosity glass filter is then used to separate the products into toluene-soluble (TS) and toluene-insoluble (TI) fractions.

The TI fraction is dried overnight in a vacuum oven at 120°C. A rotary evaporator strips the solvent from the TS product. After the

Table 3

ANALYSIS OF STARTING COALS[a]

(Percent)

Element	PSOC 26	PSOC 233	PSOC 213
% C	81.44	78.28	80.61
% H	5.92	5.42	5.65
% N	1.19	1.94	1.78
% S (org)	--	0.47	2.10
% O (diff)	11.45	13.88	9.68
% Mineral matter	2.45[b]	10.32	11.47

---

[a] The data are from the Penn State coal data base and are presented on a DMMF basis.

[b] Mineral matter removed by Penn State through a flotation process. Value here is the ash content.

solvent is removed, the TS fraction is dried on the rotary evaporator for about 1 hr at 95°C.

Results and Discussion

We performed experiments with a Kentucky No. 9 coal, PSOC-213, at different initial pH values in the CO/H_2O system at 400°C for 20 min. The data, summarized in Table 4, show that the toluene-soluble product increases with increasing pH. At initial CO pressures ranging from 475 to 525 psig and initial pH values of 9.0 to 11.7, the conversion to toluene-soluble products ranged from 16.1 to 16.7%. However, at initial pH values of 12.6 to 13.6, the conversion increased from 22.7 to 24.5%.

Figure 2 shows the results for the three coals we have studied to date, Illinois No. 6 (PSOC-26), Colorado Wadge (PSOC-233), and Kentucky No. 9 (PSOC-213). The degree of conversion to toluene-soluble products versus the initial pH of the water at 25°C is plotted in the bottom half of the figure. With the Illinois coal (PSOC-26), a sharp change in conversion is observed at pH 12. The other two coals also display similar behavior. However, with the Colorado coal (PSOC-233), the increase in conversion is spread over a much broader pH range than the Illinois coal. The Kentucky coal (PSOC-213) only shows a small increase, but the trend is the same as the other two coals.

On the top half of Figure 2, the composite H/C values of the TS and TI fractions are plotted against pH. We find that the H/C ratio increases with increasing pH for all three coals. Therefore, there is a net increase in hydrogen incorporation in the products with increasing conversion.

During the next research period we plan to conduct similar conversions using D_2O in place of H_2O. We expect the positions of the deuterium in the product materials will provide significant insight into the conversion process. The model compound work described next in Subtask B.2 has been performed as a preclude to the D_2O-conversion effort.

Table 4

INFLUENCE OF INITIAL pH ON THE CONVERSION OF PSOC-213, KENTUCKY No. 9 COAL IN THE CO/H_2O SYSTEM AT 400°C FOR 20 MIN

Run No.	Initial pH[a]	Initial CO (psig)[a]	Reaction Pressure (psig)[b]	Final Pressure (psig)[a]	Mass Balance % Balance[c]	% TS[d]	H/C (molar) TS	H/C (molar) TI
Untreated Coal	--	--	--	--	--	2.3	--	--
71	9.0	525	5085	660	72.4	16.3	0.95	0.47
72	10.0	525	5155	680	67.6	16.7	0.98	0.46
74	11.7	475	4730	610	71.2	16.1	0.98	0.46
91	12.6	475	4745	610	71.8	22.7	0.90	0.49
70	13.6	510	4915	695	74.0	24.5	0.99	0.50

---

[a] Measured at 25°C.
[b] The observed pressure at reaction temperature, 400°C.
[c] Mass balance based on the TS and TI products only, does not include any volatile products.
[d] Percent is based on a dry ash-free basis.

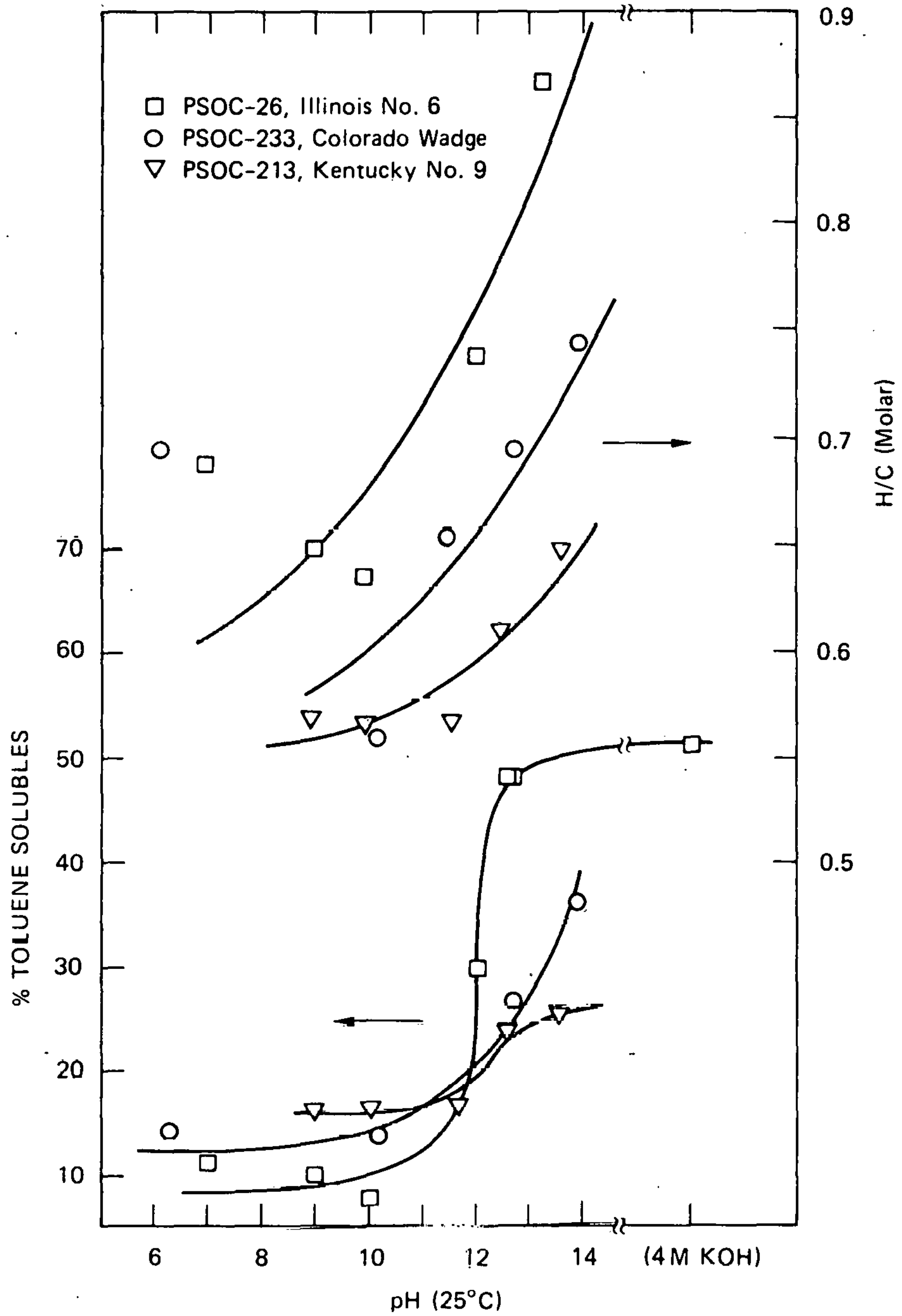


FIGURE 2 CONVERSION OF PSOC-213, PSOC-233, AND PSOC-26 COAL TO TOLUENE-SOLUBLE FRACTIONS VERSUS INITIAL pH

The H/C values are composites of the toluene-soluble and -insoluble fractions.

Subtask B.2: LABEL STUDIES IN THE CO/H_2O SYSTEM

David S. Ross and Georgina P. Hum

The study of the thermolysis of bibenzyl in D_2O at 400°C is complete. The results are summarized in a paper, attached as an appendix, to be submitted for publication to <u>Fuel</u>.

Appendix

THE THERMOLYSIS OF BIBENZYL IN D_2O

THE THERMOLYSIS OF BIBENZYL IN D_2O

David S. Ross and Georgina P. Hum
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SUMMARY

The thermolysis of bibenzyl has been studied at 400°C in D_2O. The D_2O is above its critical temperature, and the bibenzyl is fully in the vapor state, so that homogeneous conditions prevail. Control runs with toluene show neglible d-incorporation, while recovered bibenzyl is heavily exchanged. The recovered toluene and unreacted bibenzyl from the thermolysis are heavily exchanged. We conclude that the exchange is due to the operative chemistry, which includes rapid reaction of the benzyl and bibenzyl radicals present in the system with D_2O. This reaction is endothermic by about 32 kcal/mole; however it is nonetheless much more rapid than any other reaction in the system, including disproportionation of the bibenzyl radical. Water can thus serve as an H-donor in coal conversion. The resulting OD(H) apparently does not add to the aromatic systems, but rather only H-abstracts. This surprising result must be confirmed, but the presence of OH in the system offers the possibility of new conversion chemistry.

INTRODUCTION

For many years the study of the thermal decomposition of bibenzyl ($PhCH_2-CH_2Ph$) has been a major aspect of the broad study of coal liquefaction chemistry. The general philosophy and approach to the understanding of coal conversion has been the presumption that the reactions leading to liquefaction during the heating of coal at temperatures between 400°-500°C are primarily the thermal homolyses of bonds in the coal structure weak enough to break within several minutes. In turn, because most common organic structures contain C-C and C-O bonds too strong for scission at reasonable rates under these conditions,[1] it has been necessary to consider structures with features particularly favoring rapid scission. Thus structures such as bibenzyl and phenyl benzyl ether have been considered significant in coal structure.[2]

However, we are aware of no firm evidence supporting the presence of these structures in coal in significant amounts. We have suggested that ionic reactions, in contrast to free radical chemistry, could be at least in part responsible for conversion.[1] Nonetheless, the issue remains an open one, and the chemistry of bibenzyl under conversion conditions continues to be of interest. Recently, detailed analyses of the thermal chemistry of liquid bibenzyl in the absence of added H-donors have been presented.[3,4] Because we have found that bituminous coals can be converted in CO/H_2O systems to upgraded products similar to those obtained in tetralin conversions,[5] it was of interest to consider the chemistry of bibenzyl in that system. The studies reported here were conducted at 400°C, using D_2O in place of H_2O. The discussion below deals with the operative kinetics and mechanism in the absence of CO. Our work with CO will be reported later.

BACKGROUND

The work of Poutsma[3] demonstrated that the conversion of neat bibenzyl in the liquid phase is a reasonably complicated process, with the initially formed benzyl radical abstracting hydrogen from bibenzyl to give the corresponding radical.

$$PhCH_2CH_2Ph \longrightarrow 2Ph\dot{C}H_2 \tag{1}$$

$$Ph\dot{C}H_2 + PhCH_2CH_2Ph \longrightarrow PhCH_3 + PhCH_2\dot{C}HPh \tag{2}$$

That radical, in turn, undergoes several reactions leading to a series of products, including stilbene and triphenyl propane.

Miller and Stein[4] presented a detailed kinetic picture of the pyrolysis of bibenzyl in the liquid phase consistent with the report by

Poutsma, in which the bibenzyl radical is a major intermediate in the process. The net major reaction of the radical is a bimolecular reaction, resulting in disproportionation of the starting bibenzyl

$$2\ \mathrm{PhCH_2\dot{C}HPh} \longrightarrow \mathrm{PhCH{=}CHPh} + \mathrm{PH\dot{C}H_2CH_2Ph} \qquad (3)$$

with a considerably slower unimolecular reaction also taking place

$$\mathrm{PhCH_2\dot{C}HPh} \longrightarrow \mathrm{H\cdot} + \mathrm{PhCH{=}CHPh} \qquad (4)$$

They also delineated several minor reactions, including rearrangements and radical couplings, for which the rate constants are provided.

Finally, Vernon has recently studied bibenzyl thermolysis in the presence of hydrogen.[6] In this case, a hydrogen atom chain process results in the net hydrogenolysis of a Ph-C bond in the starting hydrocarbon.

EXPERIMENTAL PROCEDURES

Experiments were performed in 3-in. 316 stainless steel tubes (1/4 in. OD x 0.5 mm ID), sealed with Parker caps. The reactor, 2.1 ml in volume, contained 300 mg of D_2O and about 100 mmole of organic substrate in each run. At 400°C the system was homogeneous, with both components fully in the vapor state. D_2O here was above its critical temperature, and the quantities of bibenzyl in each run were below those required for the presence of any liquid phase.[4] Thus, the concentration of D_2O at 400°C was 8.3 M and bibenzyl 2.5×10^{-3} M.

The reactor tubes were heated by plunging them into a molten salt bath at 400°C for the desired time, and then they were quenched in water. Heat-up time from room temperature to within 10°C of the reaction temperature was 30 sec and the cool-down time was 15 sec. After the reaction, the tubes were frozen in dry ice before they were opened. The contents were collected with a pipette, using ethyl ether.

All conversions were determined quantitatively by GC. Levels of deuterium exchange were determined by gas chromatography/mass spectrometry (GC/MS).

RESULTS

The experimental work included the initial performance of control runs with toluene and benzene in D_2O. The exchange data are presented in Table 1.

Table 1 Benzene, toluene, bibenzyl in D_2O at 400°C for 1200 min[a]

	% Deuterium				
Compound[b]	d_0	d_1	d_2	d_3	d_4
Benzene	98	1	--	--	--
Toluene	94	6	--	--	--
Bibenzyl	27	41	25	7	1
	17	35	31	14	3

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[a] The runs were conducted in capped, stainless steel tubes, 2.1 mL in volume, containing 300 mg of D_2O and about 100 mmole of organic substrate.

[b] Benzene and toluene were recovered quantitatively. The bibenzyl was recovered after partial conversion, as noted in Table 2.

Benzene in these 1200-min runs is recovered virtually unlabeled. This result demonstrates the absence of catalytic action by the reactor surfaces, which might be expected to promote exchange under these rather severe conditions. This favorable finding extends to the toluene case, where less than 10% of the recovered material is exchanged. While we have no evidence on the position of the deuterium substitution, it seems that the benzylic position is the most likely spot for substitution.

Because bibenzyl is similar structurally to toluene, we expect little exchange in that case as well. The substantial exchange for bibenzyl, therefore, is of particular interest. The product distributions and label data for two bibenzyl runs are presented in Tables 2 and 3 respectively. Because we were interested in establishing whether silica provided any catalytic effect, we performed one run (run 95, Table 2) with ground silica present. There was no apparent effect, and the two bibenzyl runs are considered as duplicates. For comparison, we performed a run with tetralin under the same conditions (run 96, Table 2). The exchange results for bibenzyl from Table 1 are repeated in Table 3.

In addition to the labeled bibenzyl, both the benzene and toluene recovered in the D_2O runs contain substantial quantities of deuterium, in clear contrast to the control runs, with benzene and toluene shown in Table 1. The major products are toluene and stilbene, the major products from the thermolysis of neat bibenzyl.[3,4]

DISCUSSION

It is clear that the chemistry taking place is similar to that reported for bibenzyl itself.[3,4] Reactions (1) through (4) are thus important in this system. However, the level of deuterium incorporation in the recovered bibenzyl suggests that there is a significant and rapid interaction with the medium. The fact that multiple exchange occurs is consistent with a rapid exchange with D_2O, followed by the chemistry that yields the stilbene.

Table 2 Product Distribution for Bibenzyl Thermolysis in D_2O at 400°C for 1200 min

Run	Initial Bibenzyl (Mmol)	Mass Balance (%)	Recovered Bibenzyl	Percent of starting bibenzyl (molar)						
				Benzene	Ethylbenzene	Toluene[a]	Diphenylmethane	Stilbene	Phenanthrene	1,1-Diphenylethane
94	93.3	82	17.5	3.0	1.2	27.8	6.6	22.6	3.8	—[b]
95[c]	86.7	84	20.1	2.1	1.2	26.8	7.6	22.1	4.1	—[b]
96[d]	114.7	95	49.3	—[b]	—[b]	40.6	2.5	—[b]	—[b]	2.7

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[a] The values here reflect the fraction of bibenzyl proceeding to two toluenes.
[b] Not detected; estimated < 0.1%.
[c] Contained about ~ 0.02 g of crushed Pyrex glass (-200 mesh).
[d] Run in tetralin.

Table 3 Label data for bibenzyl thermolysis in D_2O at 400°C and 1200 min

Product	%Deuterium in Product[a]				
	d_0	d_1	d_2	d_3	d_4
Bibenzyl	27	41	25	7	1
	17	35	31	14	3
Toluene	49	38	12	2	--
	35	40	19	5	1
Stilbene	67	28	4	1	--
	39	41	15	4	1
Phenanthrene	75	19	5	--	--
	51	35	12	3	--
Benzene	83	17	--	--	--
	76	20	4	--	--

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[a] Analysis carried out by mass spectrometry. For those products not present in this table insufficient quantities were present for analysis.

We have assumed that the positions of substitution are at the benzylic positions, although we have currently no definite supporting data. The expected patterns of statistical exchange for both bibenzyl and toluene are shown in Figure 1, with the curves derived from the application of a simple series of consecutive exchange reactions. (We have assumed no kinetic isotope effect.) The abscissa is in terms of "tenth lives," a convenient dimensionless term for use in kinetic considerations. The abscissa values represent 10% decrements in the d_0 isomer in terms of the first-order rate constant for exchange.[*] The experimental results for the 1200-min runs are shown in the figure and are positioned by "sliding" the values along the abscissa for the best fit.

The 1200-min reaction period corresponds in the bibenzyl case to about 14 tenth lives. For toluene, the fit falls at about 7 tenth lives. The factor of two difference is expected, because bibenzyl contains twice the number of carbons bearing exchangeable hydrogens.

Because the data are for runs conducted for 1200 min, we can establish that under our conditions

$$k_{ex} = 2.14 \times 10^{-5}\ s^{-1}$$

This value can be compared with k_1, the known homolytic rate constant for reaction (1)[4]

$$k_1 = 8.01 \times 10^{-6}\ s^{-1}$$

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[*] If we consider the exchange to be a psuedo-first-order process with a rate constant k_{ex}, then for a 10% reduction in the reactant in period t_0,

$$-k_{ex}t_0 = \ln 0.9 = -0.11.$$

For n decrements of 10% in period t,

$$n = \frac{k_{ex}t}{0.11}$$

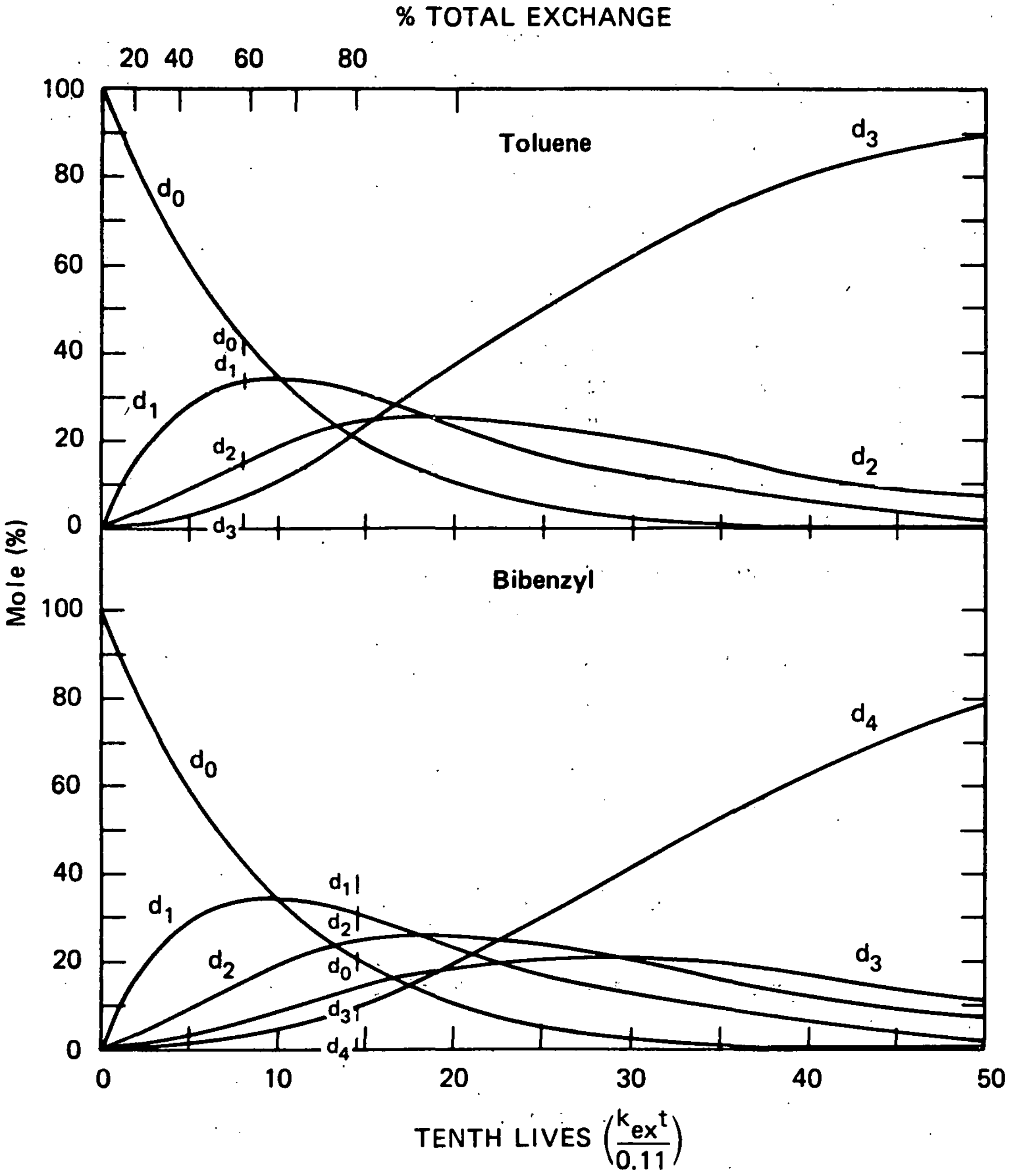

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FIGURE 1 LABEL DATA FOR TOLUENE AND BIBENZYL AT 400°C FOR 1200 min IN D_2O

The curves are thos anticipated for reversible exchange under under the condition $D_2O \gg PhCH_2CH_2Ph$, and presuming no kinetic isotope effect. The vertical bars represent the experimental label data, "slid" along the abscissa to the best-fit positions.

The two constants agree to within a factor of three. The chemistry resulting in the exchange must therefore be rapid relative to stilbene formation, reaction (3). The reactions under consideration here and a measure of their importance under competitive conditions are listed in Table 4. (The characteristic time, τ, is the reciprical of the first-order, or psuedo-first-order rate constants governing the respective reactions).

From Table 4, the reaction sequence begins with the initial, slow homolysis of the starting bibenzyl, yielding benzyl radicals. Then BB and D_2O compete in reaction with benzyl, with the D_2O reaction favored by at least a factor of ten. The OD formed rapidly reacts with bibenzyl, yielding the bibenzyl radical.

In the thermolysis of neat bibenzyl, the formation of BB• was followed by the very rapid disproportionation, reaction (3). That chemistry does occur here, but it is preceded by the even more rapid reaction with D_2O

$$PhCH_2\dot{C}HPh + D_2O \longrightarrow \cdot OD + PhCH_2CHDPh \qquad (5)$$

This reaction is about 32 kcal/mole endothermic, but at 400°C the reaction rate is sufficient to make it a highly significant reaction in the system. However, note that the competition among the rates of all the reactions in the sequence are dependent on the relative concentrations of the starting D_2O and bibenzyl. In our current work, the BB_0/D_2O ratio is about 3×10^{-4}; with greater relative quantities of bibenzyl, the degree of deuterium incorporation would be decreased.

We have shown that in one sense water can act in this system as tetralin does, in that it readily transfers hydrogen to organic free radicals. Indeed, the benzyl radicals considered here are relatively unreactive, and yet the degree of reaction with water is substantial.

Table 4 Reactions Significant in the Thermolysis of Bibenzyl in D_2O at 400°C

Reaction	Tau (τ)[a]
$\mathrm{PhCH_2CH_2Ph \longrightarrow 2Ph\dot{C}H_2}$ (BB)	2200 min
$\mathrm{Ph\dot{C}H_2 + BB \longrightarrow PhCH_3 + BB\bullet}$	12 s
$\mathrm{Ph\dot{C}H_2 + D_2O \longrightarrow PhCH_2D + \bullet OD}$	< 1 s
$\mathrm{\bullet OD + BB \longrightarrow HOD + BB\bullet}$	10^{-8} s
$\mathrm{D_2O + BB\bullet \longrightarrow \bullet OD + BB_{d_1}}$	< 1 s
$\mathrm{2BB\bullet \longrightarrow BB}$ + stilbene	> 1 s
$\mathrm{BB\bullet \longrightarrow H\bullet}$ + stilbene	3 s

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[a] The characteristic time for a reaction is that time required for the starting concentration of the reactant to be reduced to 1/e of its initial value. This period corresponds to about a 67% reaction. For the second-order reactions, τ was calculated on the basis of pseudo-first-order rate constants for 8.3 M D_2O or 2.5×10^{-3} M bibenzyl. The second-order rate constants of Miller and Stein[4] were used for all reactions except those involving D_2O or OD. For abstractions of benzylic hydrogen by OD, we used the data of Hendry and Kenley[7] for OH + toluene. The rate constant for the reaction of D_2O with benzyl and bibenzyl radicals was assumed to be that for H_2O, which in turn, was estimated to be $\log k(M^{-1}\ s^{-1}) = 9.8 - (33/\theta)$ from the thermochemistry and kinetics of the toluene/OH reaction.

However, in contrast to tetralin, the water does not reduce the organic substrate, because the reactive OH (OD) intermediate rapidly creates another radical.

The presence of CO in the system can bring about reduction of organic species through the generation of hydrogen atoms via the known reaction between CO and OH[8]

$$CO + \cdot OH \longrightarrow CO_2 + H\cdot \qquad (6)$$

This reaction is very rapid at 400°C ($k = 2 \times 10^8\ M^{-1}\ s^{-1}$) and could play a role in the CO/water coal conversions we have performed. This chemistry will be discussed in a future manuscript.

ACKNOWLEDGMENT

We acknowledge the generous support of the U.S. Department of Energy on Contract No. DE-AC22-81PC40785.

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☆ U.S. GOVERNMENT PRINTING OFFICE: 1982-646-069/320