~~275~~ 275
5-6-82

(2)

Dr. 490

DOE/PC/40785-2
(DE82011703)

MASTER

FOSSIL ENERGY

EXPLORATORY STUDY OF COAL CONVERSION CHEMISTRY

Quarterly Report No. 2 for the Period August 19—November 18, 1981

January 29, 1982
Date Published

Work Performed Under Contract No. AC22-81PC40785

SRI International
Menlo Park, California

U. S. DEPARTMENT OF ENERGY

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts, (ERA); Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR);* and publication, NTIS-PR-360 available from (NTIS) at the above address.

DOE/PC/40785-2
(DE82011703)
Distribution Category UC-90d

EXPLORATORY STUDY OF COAL CONVERSION CHEMISTRY

Quarterly Report No. 2

Covering the Period August 19, 1981 to November 18, 1981

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Date Published--January 29, 1982
Under Contract No. DE-AC22-81PC40785

ABSTRACT

This report describes work accomplished under two tasks: Task A, mechanisms of donor-solvent coal liquefaction, and Task B, CO/H_2O conversion systems.

Under Task A, we describe additional evidence relating to the question of the mechanism of the iron oxide catalyzed cleavage of hydroxydiphenylmethanes. <u>o</u>-Hydroxydiphenylmethane is relatively more sensitive to catalysis by Fe_3O_4, a possible one electron oxidant, and triphenylmethane is relatively more sensitive to catalyzed cleavage by SiO_2/Al_2O_3, a strong Bronsted acid catalyst. This provides further evidence that in the former case the reactions of radical cations are important in the cleavage mechanism. Tests with Cr_2O_3 show it to be ineffective under our reaction conditions as a catalyst for hydroxydiphenylmethane cleavage. We have also used the decomposition of diphenylether in tetralin, which we have previously shown to occur by a radical displacement reaction, as an indicator of steady state radical concentration in tetralin. The results of these experiments indicate that radical concentrations in tetralin are not significantly increased by spiking the tetralin with 1,2-dihydronaphthalene. This in turn suggests that rapid disproportionation of 1,2-dihydronaphthalene to tetralin and naphthalene takes place by way of a concerted reaction, in addition to a slower radical disproportionation process that may provide the steady state radical concentration supported by the equilibrium concentration of 1,2-dihydronaphthalene.

Under Task B1, we have found a correlation between initial pH and CO pressure on the conversion of PSOC-26 coal to toluene soluble products. A pH dependence was also observed for PSOC-233 coal, similar to results with PSOC-26. Under Task B2, we have studied anisole as a model oxygen containing structure in coal. The products from its conversion with D_2O, and the degrees of deuterium substitution in the various products were determined.

CONTENTS

Tables

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 mechanisms in donor solvent liquefaction. Task B is a study of the conversion of coal and model compounds in the CO/H_2O system.

Both efforts 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.

TASK A: MECHANISMS OF DONOR-SOLVENT COAL LIQUEFACTION

Donald F. McMillen and Walter C. Ogier

Introduction

The objectives that our work has focused on this quarter are the development of an understanding of the iron-oxide-catalyzed cleavage of coal structures, and characterization of the radical initiation processes responsible for the cleavage of diphenyl ether structures under coal liquefaction conditions.

Towards the first objective, we are attempting to further define the role of iron oxide in catalyses of pyrolyses of single-methylene bridged aromatic coal-model structures in tetralin. This quarter we compared the activity of two catalysts with several model compounds in an attempt to distinguish between the candidate mechanisms for catalyzed degradation of these coal structures.

Towards the second objective, we are attempting to study the radical initiation effect using a diphenyl ether, a model structure whose principal cleavage mechanism had previously been determined in this work to involve a radical displacement process, as a monitor of absolute concentration of radicals in tetralin. This quarter we examined a reaction postulated by Stein[1] to account for a substantial concentration of radicals in tetralin; that is, we have assessed this postulated source of radicals in light of our previously obtained and our additional new evidence concerning radical displacement reactions with aromatic ethers.

Results and Discussion

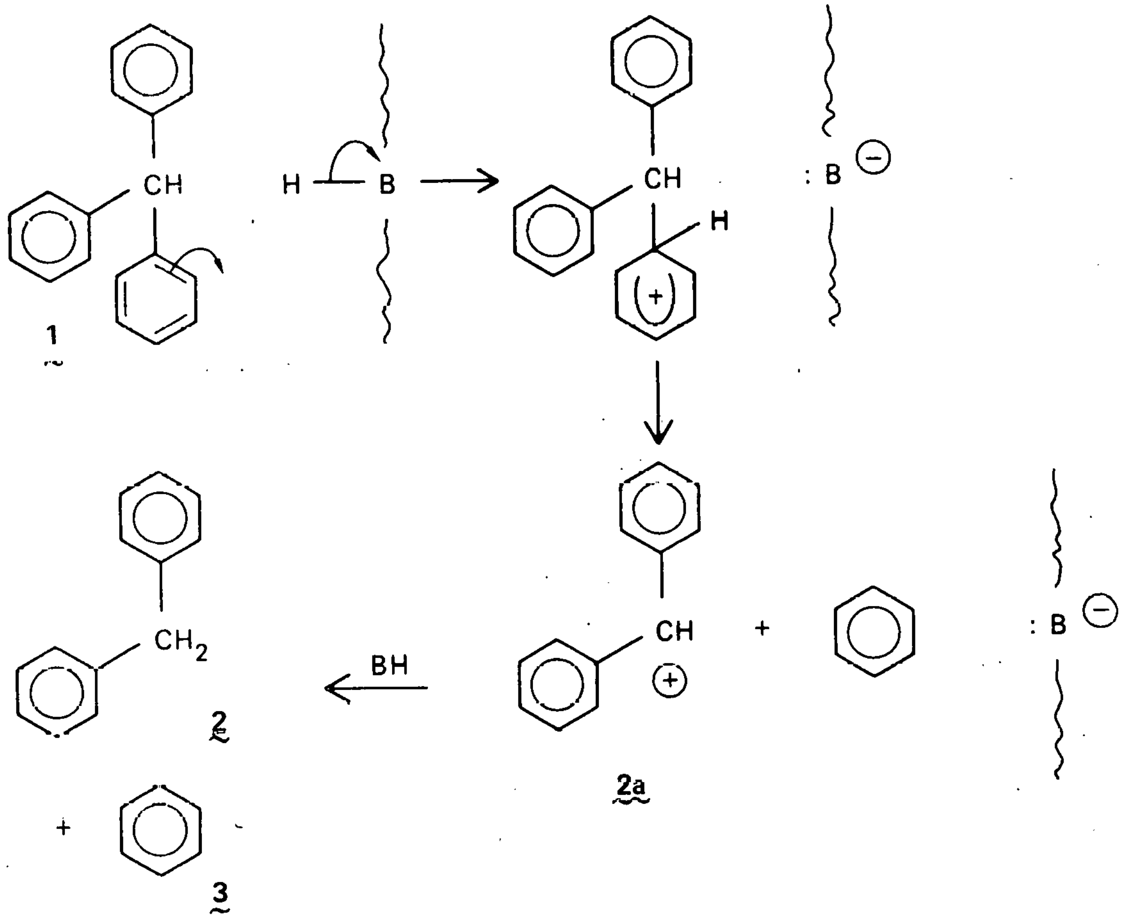
Iron Oxide Catalysis of the Cleavage of Methylene Linkages

Iron oxides catalyze the cracking of hydrocarbons under a variety of experimental conditions. They have been employed for many years as coal liquefaction catalysts as well.[2] Previous research in this laboratory[3] has been indicated that iron oxides catalyze the cleavage of the aryl-benzyl bond in diphenyl methanes and diphenyl ethers in tetralin at 400°C, and that this catalysis is much more marked when one (or more) of the phenyl rings is hydroxylated. In spite of the long history of the use of iron oxides as low cost catalysts in coal conversion processes, and in spite of recent studies of ZnO/Fe_2O_3 phenol de-alkylation catalysts,[4] the mechanism(s) by which the iron oxide(s) functions does not appear to have been established. Similarly, results previously reported under this contract[3a] have resulted in an ambiguous distinction between the two principal candidate mechanisms.

The products of the iron-oxide-catalyzed cleavage of hydroxydiphenylmethane (benzyl phenol) are those expected from acid-cracking types of processes, yet iron oxides are not generally thought to possess strongly acidic surface character.[5] Results reported in the literature since our previous report suggest other situations as well where cracking and coal liquefaction catalysis by certain mixed oxides catalysts do not correlate with acid strength or total surface acidity.[6] These results thus support the possibility that processes distinct from Bronsted acid catalysis are responsible for the observed activity of iron oxides. We have previously advanced[3a] the hypothesis that radical cations generated by contact with one-electron oxidants may occur as intermediates not only in reaction of the hydroxylated coal-models we have studied, but also in catalyzed pathways leading to liquefaction products from real coals.

Our first goal upon resuming work in this task was to further characterize the surface area and pore size distribution of catalysts we had used so that we could make rough normalizations of activity based on surface area. This was done first by scanning electron microscopic (SEM) examination of the catalysts and will be followed by BET surface area measurements. The results of the SEM examination will be discussed where pertinent.

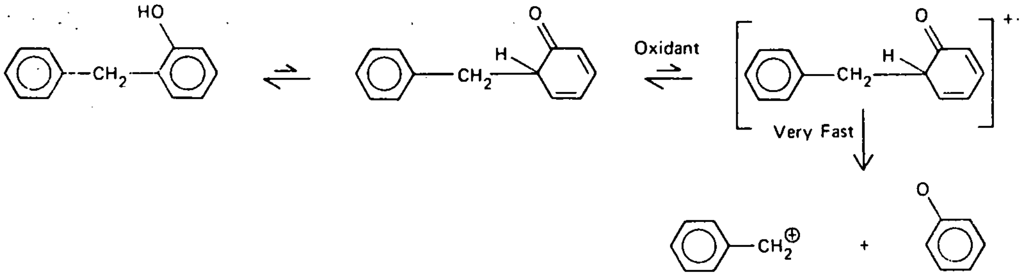
The second goal was to perform experiments comparing the catalytic activity of several catalysts for cracking of two coal models: the hydroxylated diphenylmethanes whose degradation mechanism we suspect involves radical cation formation; and unhydroxylated diphenylmethane and triphenylmethane whose cracking is presumed to involve the generally invoked[5] Bronsted acid attack.



Scheme 1

Presumably, tetralin would be the proton/hydride ion source. The enhanced resonance stability of structure 2a should promote protic acid-cracking in this molecule.

Diphenylmethanes, as activated aromatics, should certainly be susceptible to this kind of reverse Friedel-Crafts process. However, thermochemical considerations that we have discussed before[3a] suggest that radical cation formation from the keto forms of hydroxydiphenylmethanes should sufficiently weaken the central bond so that homolytic thermal cleavage should take place (at 400°C) in a microsecond or less.



Scheme 2

While the phenylmethane strengths in di- and tri-phenylmethanes are roughly halved (from 89 to 46 kcal/mole) upon formation of the radical cation,[7] the strength of hydroxyphenyl-methylene bonds is reduced from 89 to < 25 kcal/mole in ortho- and para-hydroxy diphenylmethanes by an isomerization to the keto form followed by one-electron oxidation. At 400°C a 25-kcal/mole bond will thermally cleave in less than 1 μ second. Thus perhaps any substantial loss of electron density from an adsorbed keto-form could lead rapidly and irreversibly to cleavage.

That such a mechanism is important seemed to be supported by the fact that iron oxides (materials not considered to be strong Bronsted acids, but which might be expected to be effective one-electron oxidants) exhibit one of the highest specific activity of the catalysts we have tested for cracking of hydroxydiphenylmethanes.

Thus hydroxydiphenylmethane (HODPM), as a benzyl phenol, should be very susceptible to Bronsted acid attack. Under some circumstances, it may also be reacting via another pathway, formation of a radical cation. We wish to determine which pathway accounts for the iron-oxide-catalyzed cracking of HODPM: Bronsted acid attack or radical cation formation.

We first observed the susceptibility of HODPM to catalysis by Fe_3O_4 and to catalysis by Al_2O_3/SiO_2 (a good Bronsted acid catalyst). Then we observed the susceptibility of triphenylmethane (TPM) (which can cleave by Bronsted acid attack, but cannot cleave by an oxidized keto-form) to catalysis by Fe_3O_4 and to catalysis by Al_2O_3/SiO_2. Finally, we compared the results to determine which of the two substrates, HODPM (which reacts via two pathways) or TPM (which reacts via one pathway), benefited more by going from Fe_3O_4 to Al_2O_3/SiO_2.

For this comparison we chose to examine the pyrolysis behavior of these two models in tetralin. For the two catalysts we used a typical acid-cracking catalyst (Alfa 45:53% Al_2O_3:SiO_2) and Fisher Fe_3O_4 practical grade. Visible light and SEM examination reveals that the Fe_3O_4 consists of dense particles of average diameter ~ 0.2 µm (external surface area ~ 6 m^2/gram). The silica-alumina was crushed, sieved, and a 325/400 mesh fraction (average diameter ~ 40 µ) was used. SEM examination reveals that these particles are microcrystalline agglomerates with a bi-modal pore size distribution, probably with a total surface area in excess of 100 m^2/gram. Previously reported results (including those on diphenylmethane (DPM)) and new results pertinent to this comparison are shown in Table 1. With the aid of the matrix below, these results can be considered in the following manner.

	Al_2O_3/SiO_2	Fe_3O_4
o-HODPM	$4.6 \times 10^{-4}\ s^{-1}$	$4.5 \times 10^{-5}\ s^{-1}$
TPM	$1.1 \times 10^{-4}\ s^{-1}$	$1.1 \times 10^{-4}\ s^{-1}$
DPM	--	$1.1 \times 10^{-6}\ s^{-1}$

First, with the Bronsted acid Al_2O_3 /SiO_2, o-HODPM is modestly more reactive (4x) than TPM. This is not surprising because HODPM is a highly activated substrate for proton attack. With Fe_3O_4, a much weaker Bronsted acid catalyst, the reactivity of o-HODPM drops by a factor of 10, but the reactivity of TPM, the substrate susceptible only to Bronsted acid attack, drops by a factor of 100. This suggests that with Fe_3O_4 there is an alternative cracking mechanism (i.e., a radical cation process) accessible to HODPM, but not to TPM. Thus Al_2O_3/SiO_2 is more effective with TPM while Fe_3O_4 is more effective with o-HODPM, and this supports the radical cation cracking mechanism that we suggested for HODPM. These results, however, do not conclusively prove such a mechanism. There are two alternatives consistent with cracking via Bronsted acid attack: The smaller rate decrease of HODPM between Al_2O_3/SiO_2 and Fe_3O_4 could reflect a reactivity-selectivity relationship, because o-HODPM/Al_2O_3-SiO_2 is slightly more reactive than

Table 1

COMPARISON OF CATALYTIC SUSCEPTIBILITIES OF *ortho*-HYDRODIPHENYLMETHANE (*o*-HODPM) AND DIPHENYLMETHANE (DPM)

Run	Model	Wt%	Catalyst	Wt%	Time (hr)	C/C_o	k_1 (sec^{-1})
216	*o*-HODPM	4.1[c]	--	--	3/0	.97	3.3×10^{-6}
243	*o*-HODPM	4.1[c]	Al_2O_3/SiO_2	5.0	0.5	~ .44	$\sim 4.6 \times 10^{-4}$
244	*o*-HODPM	4.1[c]	Fe_3O_4	1.0	0.5	~ .92	$\sim 4.5 \times 10^{-5}$
1801	TPM	7.3[d]	--	--	22.6	$\geqslant$ .9994	$\leqslant 8 \times 10^{-9}$
1806	TPM	6.3[c]	Al_2O_3/SiO_2	1.0	2.8	~ .32	$\sim 1.1 \times 10^{-4}$
1807	TPM	6.3[c]	Fe_3O_4	5.0	2.8	~ .988	$\sim 1.1 \times 10^{-6}$[e]
1804	TPM	7.3[d]	Al_2O_3/SiO_2	1.0	22.8	$\leqslant$ .016	$\geqslant 8 \times 10^{-5}$
1805	TPM	7.3[d]	Fe_3O_4	5.0	22.8	~ .91	1.1×10^{-6}[e]
902[b]	DPM	4.8	--	--	18.5	$\geqslant$ .998	$\leqslant 2 \times 10^{-8}$
903[b]	DPM	5.0[d]	Fe_3O_4	5.0	22.5	~ .92	$\sim 1.1 \times 10^{-6}$

---

[a] All reactions were carried out in purified (> 99%) tetralin, 300 µl total solution, at 400°C, after evacuation of ampoule. Products were analyzed by GC and GC/MS (243, 244).

[b] Previously reported data.

[c] Equimolar.

[d] Equimolar.

[e] Comparison of these results suggests that defined first-order rate constants are suitable for the comparisons made for different times of reaction.

TPM/SiO_2-Al_2O_3, or better binding to the catalyst with the hydroxylated substrate and greater importance of this better binding for the weaker Bronsted acid catalyst. It is curious that diphenylmethane should be as reactive as triphenylmethane on Fe_3O_4. Both one-electron oxidation and a reverse Friedel-Crafts reaction should be enhanced by the resonance of a further ring in the reactant.[7] Perhaps steric effects are to blame, or it may also be caused by rate limitation in a binding-to-the surface step.

We plan to complete the matrix on page 6 with a reaction of diphenylmethane on Al_2O_3/SiO_2. We also plan to assess the order of these reactions more carefully. This will provide some information about the number of catalytic sites, from which we will be able to learn if the rate is limited by saturation of catalytic sites in one catalyst and not the other. This will permit us to also examine the behavior of the solvent (tetralin) on these catalysts; some differences in solvent degradation are discernible but are not readily amenable to kinetic comparisons.

The recent study by Yamaguchi et al.[5] indicated coal liquefaction catalyst effectiveness for mixed transition metal oxides does not correlate with surface acidity. Their results also suggest that the electronic character of amphoteric oxides may be critical in determining effectiveness of catalysts for cracking not only model coal structures but also for real coals.

We conducted an experiment to examine the effect of a chromium oxide that might have acid-base properties similar to those of Fe_2O_3 (an effective catalyst with HODPMs). However, fine powder Cr_2O_3 (Sargent-Welch) (similar in appearance to Fe_2O_3), was an ineffective catalyst. The results in Table 2 for o-HODPM degradation suggest that the previously reported ineffectiveness of $Na_2Cr_2O_7$ was not casued by just poor distribution (large particle size) or an improper combination of oxidation states. Chromium does have a wide range of oxidation states available; both Cr(IV) and Cr(II) are known.[8] Thus, as an amphoteric oxide Cr_2O_3 might have been an excellent catalyst for reactions of hydroxydiphenylmethanes.

Table 2

CATALYSTS ACTIVITY OF CHROMIUM OXIDES IN HYDROXYDIPHENYLMETHANE CLEAVAGE

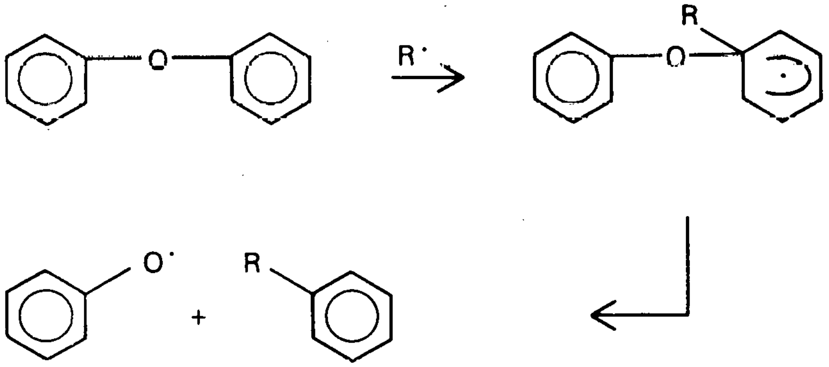
Run	Model	Wt%	Catalyst	Wt%	Time (hr)	Mass Balance (%)	C/C_o	k_1 (sec^{-1})
220[b]	*o*-HODPM	4.1	--	--	21.7	98	.77	3.28×10^{-6}
219[b]	*o*-HODPM	4.1	$Na_2Cr_2O_7$	0.5	22.2	94	.79	3.03×10^{-6}
245	*o*-HODPM	4.1	Cr_2O_3	5.0	18.0	--	.75	4.4×10^{-6}

---

[a] See Table 1 for experimental details.
[b] Previously reported data.

Identification of the Initiation Steps for Free Radical Processes in Hydrogen Donor Solvents

The second principal focus of our work this quarter has been to improve our understanding of the radical sources (initiators) in tetralin systems. This is important because of 1) the likelihood that radical-chain reactions are partly responsible for coal liquefaction, and 2) our conclusion, based largely on evidence obtained earlier in this project and described in previous reports, that radical displacement reactions of the type



Scheme 3

can account for the moderate lability of diphenyl ether linkages in tetralin solutions. This lability was initially surprising because diphenyl ether is one of the principal ingredients of high temperature heat transfer fluids. Table 3 lists some of our previously reported data that prompted the conclusion that diphenyl ether decomposition in tetralin at 400°C is largely a radical displacement reaction. Also listed are the results of some current experiments which were performed to ascertain the nature of the initiation reaction which is ultimately responsible for the tetralyl radicals that displace phenoxy radical from diphenyl ether.

The particular observations which support a radical displacement mechanism for diphenyl ether change are: 1) diphenyl ether never yields benzene as a product but phenyltetralins instead, 2) bibenzyl and o-HODPM are effective promoters of diphenyl ether linkages scission, 3) diphenyl ether is considerably more stable as a neat liquid than as a

Table 3[a]

RATES OF DIPHENYL ETHER CLEAVAGE IN TETRALIN

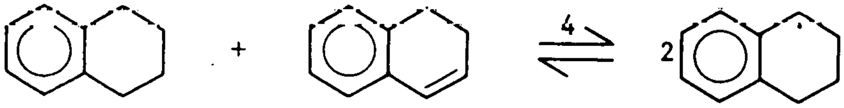
Run	Model	Wt%	Additive	Wt%	Time (hr)	C/C_o	k_1 (sec^{-1})	Products
1101[b]	$\phi O\phi$	5.0	--	--	18.5	.99	$\sim 1.1 \times 10^{-7}$	Phenol, phenyltetralins
1106[b]	$\phi O\phi$	5.0	Bibenzyl	5	18.3	.98	$\sim 3.2 \times 10^{-7}$	Phenol, phenyltetralins
1105[b]	$\phi O\phi$	neat	--	--	18[c]	> .9985	$< 2 \times 10^{-8}$	None
1103[b]	$\phi O\phi$	5.0	--	--	24[c]	.96	$\sim 4.7 \times 10^{-7}$	Phenol, phenyltetralins
1201	p-$\phi O\phi OH$	4.7	--	--	21.3	.88	1.60×10^{-6}	Phenol(2)
1204	p-$\phi O\phi OH$	4.7	Bibenzyl	5	18.3	.84	2.7×10^{-6}	Phenol, o-$\phi O\phi OH$, high MWs
1110	$\phi O\phi$	5.0	--	--	1.3	.9985	3.4×10^{-7}	Phenol, phenyltetralins
1111	$\phi O\phi$	5.0	1,2-Dihydronaphthalene	10	1.3	.9985	3.4×10^{-7}	Phenol, phenyltetralins
1107	$\phi O\phi$	5.0	1,2-Dihydronaphthalene	--	20.0	.989	1.4×10^{-7}	Phenol, phenyltetralins
1108	$\phi O\phi$	5.0	1,2-Dihydronaphthalene	5	20.0	.984	2.1×10^{-7}	Phenol, phenyltetralins
1109	$\phi O\phi$	5.0	1,2-Dihydronaphthalene	10	20.0	.982	2.3×10^{-7}	Phenol, phenyltetralins
1112	$\phi O\phi$	5.0	1,2-Dihydronaphthalene	--	88.8	.959	1.3×10^{-7}	Phenol, phenyltetralins
1113	$\phi O\phi$	5.0	1,2-Dihydronaphthalene	10	88.8	.958	1.3×10^{-7}	Phenol, phenyltetralins
1205	p-$\phi O\phi OH$	33.3	--	--	18.3	.48	1.1×10^{-5}	Phenol, high MW mat'l (3.3%)
224	o-$\phi CH_2\phi OH$	33.3	--	--	18.5	.79	3.55×10^{-6}	Phenol, toluene, trace high MW mat'l < 0.4%)

---

[a] All experiments at 400 ± 0.5°C, 300 μl solutions in evacuated fused silica ampoules, except as noted.
[b] Previously reported data.
[c] 420°C.

tetralin solution, and 4) concentrated p-phenoxyphenol results in much more polymerized-typed product, with a tetralyl group attached to the ring bearing the hydroxy groups, than does concentrated HODPM. These products are not likely results from secondary reactions because phenol is usually inert in reactions of this type.

Apparently a high concentration of alkyl radicals can promote scission of aryl ether bonds. We were intrigued that diphenyl ether might thus serve as a titrant for the number and/or character of radicals in a given system. In particular, Stein[1] and Stock et al.[9] have separately proposed that hydroaromatics can become disproportionate via radical-forming processes, and thereby raise the concentration of radicals in a system and act as radical initiators. Virk et al.[10] have proposed that in many cases these disproportionations involve Woodward-Hoffman "group transfers" of H_2 elements, as defined by orbital symmetry "allowedness." Stein has presented[1] thermochemical estimates that suggest an impurity of 0.01% 1,2-dihydronaphthalene in tetralin at 400°C will produce a 10^{-7} M steady-state concentration of radicals by the disproportionation



Scheme 4

Our experiments using 5% bibenzyl as a radical initiator should result in a steady-state radical concentration (primarily α-tetralyl radicals) of approximately

$$\left(\frac{8.4 \times 101^{-6}\ s^{-1} \cdot 0.25\ ml^{-1}}{10^{9.5}\ lm^{-1}\ s^{-1}\ (0.01)} \right)^{1/2} = 3 \times 10^{-7} M$$

that is obtained from the expression

$$\text{concentration} \cong \left(\frac{k_{\text{initiation}} \cdot \text{conc.}_{\text{initiator}}}{k_{\text{termination}}} \right)^{1/2},$$

where the only effective termination is radical disproprotionation (Reaction 4) at ~ 0.01 of the recombination rate expected for large resonance stabilized radicals. A radical concentration of 3×10^{-7} M is enough to promote radical displacement reaction in diphenyl ether at a rate that results in a defined first order rate constant of 3.2×10^{-7} sec^{-1}. The data in Table 2, shows that no significant enhancement of radical displacements of diphenyl ether in tetralin was observed when as much as 10 wt.% 1,2-dihydronaphthalene (> 99% pure) was added. Based on Stein's estimated equilibrium constant $K_4 = k_4/k_{-4}$ for the reaction in Scheme 4, we expect at least first to see a steady-state radical concentration increased by a factor of $(1000)^{1/2}$, i.e., to ~ 3×10^{-6} M. This is two orders of magnitude greater than the steady state concentration of radicals estimated for the bibenzyl-promoted systems. However, the observed rate of diphenyl ether disappearance was less than that with added bibenzyl.

It was necessary to have some knowledge of the kinetics of the overall disproportionation to tetralin and naphthalene to determine how long the initial high concentration (0.5 M) of 1,2-dihydronaphthalene remained. We conducted experiments with and without "spiking" at 1 1/4, 18, and 88 3/4 hours.

Even at 1 1/4 hours, > 90% disproportionation of 1,2-dihydronaphthalene to tetralin and naphthalene had occurred. The high concentration of dihydronaphthalene did not persist for even the 1 1/2 hr. reaction period. The data in Table 3 show no significant difference between the unspiked and spiked cases, even at the shortest time examined. Rapid disproportionation via a radical process, resulting in a larger "burst" of radicals, would have been evident from an increased extent of radical attack on diphenyl ether. Moreover, this would have been progressively more discernable at shorter reaction times. Therefore, we tentatively conclude that the disproportionation of 1,2-dihydronaphthalene does not involve radical formation but instead occurs via a concerted mechanism similar to those proposed by Virk et al.[10] Stock et al.[9] have cast doubt upon some of the importance of concerted mechanisms in disproportionations of dihydroaromatics, but from the results of this work discussed above, 1,2-dihydronaphthalene would seem to be a case where concerted mechanisms are important.

Note that the pseudo-first-order rate constant for the disappearances of diphenyl ether decreases at longer reaction times. At such low extents of conversion, this cannot be due to a drop in diphenyl ether concentration: even at 88 3/4 hours of reaction, only 4% reaction has occurred. The declining first-order rate constants is probably caused by impurities other than 1,2-dihydronaphthalene in tetralin: probably trace oxidation products that build up in stored solvents, e.g., α-tetralol, and hydroperoxytetralin. These materials rapidly disappear from solutions upon heating to 400°C, and account for < 1% of tetralin initially. These oxidized impurities are probably also responsible, via active alkoxy and hydroxy radicals, for the rapid rate of tetralin isomerizationn to methylindane recently reported by Cronauer and coworkers.[11] This would be consistent with the observation of Franz and coworkers[12] that traces of oxygen markedly increase the rate of tetralin isomerizations. Using reagent grade tetralin undoubtedly increases these oxidized impurities, more so than using tetralin distilled from lithium aluminum hydride. We will test the effect of using reductively purified solvent. Also, we are continuing experiments to determine the effects that radicals in solution have upon polynucleararomatic ethers, which should be more reactive than those upon their mononuclear counterparts.

In addition, this quarter we have begun to synthesize p-hydroxynaphthyl phenyl ether to determine whether thermochemically based extrapolations of our results with monocyclic hydroxy diaryl ethers accurately predict the behavior of polynuclear aromatic ether systems.

The ultimate objective is to provide an improved background from which the liquefaction mechanisms of real coals can be inferred.

REFERENCES

1. S. E. Stein, "A Fundamental Chemical Kinetics Approach to Coal Conversion," Adv. in Chem. Series 192, p. 97.

2. E. E. Donath in Chemistry of Coal Utilization, H. H. Lowry, Ed. (John Wiley and Sons, New York, 1963), p. 1050.

3. (a) D. S. Ross, D. McMillen, W. Ogier, and Q. Nguyen, "Exploratory Study of Coal Liquefaction Chemistry," Final Report Sept. 20, 1979 to March 19, 1981, Contract No. DE-AC22-79-ET14855.

   (b) D. F. McMillen, W. C. Ogier, and D. S. Ross, "Coal Structure Cleavage Mechanisms: Scission of Methylene and Ether Linkages to Hydroxylated Rings," J. Org. Chem., 46, 3322 (1981).

   (c) D. F. McMillen, W. C. Ogier, and D. S. Ross, "Rapid Cleavage of Carbon-Carbon and Carbon-Oxygen Bonds in Coal Structures," Proceedings of the International Conference on Coal Science, Dusseldorf, Germany, Sept. 9-11, 1981, p. 104.

4. (a) T. Kotanigawa, K. Shimokawa, T. Yoshida, and M. Yamamoto, J. Phys. Chem., 83, 3020 (1979).

   (b) T. Kotanigawa, Bull Chem. Soc. Japan, 47, 950 (1974).

   (c) K. Arata, K. Yabe, and I. Toyoshima, J. Catalysis, 44, 385 (1976).

5. K. Tanabe, Solid Acids and Bases (Academic Press, New York, 1970).

6. T. Yamaguchi, M. Yamaguchi, and K. Tanabe, "Catalytic Activities of Complex Metal Oxides for Hydrocracking of Coal," Proceedings of the International Conference on Coal Science, Dusseldorf, Germany, Sept. 7-9, 1981, p. 362.

7. (a) S. W. Benson, Thermochemical Kinetics, 2nd Ed. (John Wiley and Sons, New York, 1976).

   (b) A. J. Colussi, F. Zabel, and S. W. Benson, Int. J. Chem. Kinetics, 9, 161 (1977).

   (c) H. M. Rosenstock, K. Draxl, B. W. Stein, and J. T. Herron, J. Phys. Chem. Ref. Data 6, Supplement No. 1 (1977).

   (d) M. J. Rossi, S. E. Buttrill, and D. S. Ross, "The Chemistry of Radical Cations," unpublished work (1981).

8. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (John Wiley and Sons, New York, 1962).

9. H. King and L. M. Stock, Fuel, <u>59</u>, 447 (1980).

10. P. S. Virk, Fuel <u>58</u>, 149 (1980).

11. R. J. McNeil, D. C. Cronauer, and D. C. Young, "The Importance of Hydrogen Transfer in Solvent Isomerization," Proceedings of the International Conference Coal Science, Sept. 7-9, 1981, p. 410.

TASK B1: OH^--PROMOTED CO/H_2O CONVERSION SYSTEM

David S. Ross and Richard Bunnell

Introduction

The object of this work is to determine the effectiveness of the OH^--promoted CO/H_2O conversion of various coals and to develop an understanding of the chemistry. This research continues the work done under DOE contract DE-AC22-79-ET14855. The previous work dealt with the pH dependence of Illinois No. 6 (PSOC-26) coal with respect to conversion to benzene soluble products. With increasing pH, PSOC-26 coal was found to increase from ~ 10% to ~ 50% under certain conditions.

This work is meant to continue the work on PSOC-26 coal as well as to extend the study to other coals. We will look at how temperature, pressure, and duration of reaction affect conversion.

Experimental Procedures

All reactions were carried out 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. 10 g of the desired coal (PSOC-26 or PSOC-233) was then 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 has been ground and sieved under N_2 and the 60 to 100 mesh fraction dried in a vacuum oven at 120°C overnight. Elemental analysis of these coals appears in Table 4.

Once the reactor is loaded with coal and solution, 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 temperature. The heat-up and cool-down times for the system are

Table 4

ULTIMATE ANALYSIS OF DRY ASH-FREE STARTING COALS[a]

Ultimate Analysis	PSOC-26	PSOC-233
% Carbon	78.78	77.36
% Hydrogen	5.15	5.48
% Nitrogen	1.72	1.91
% Sulfur	2.12	0.56
% Chlorine	--	0.02
% Oxygen (Diff)	12.23	14.67
% Ash	2.0	9.09

---

[a] Analytical data from Penn State coal data base.

both about 1 hr.

Qualitative analysis of the gases formed is done by GC analysis. Gases identified are H_2, CO_2, N_2, CH_4, and CO.

The condensed products are removed from the autoclave as either a aqueous or coal fraction. First the water is pipetted out of the reactor. The water is filtered if suspended material is present in it. The pH of the water is then 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 (T.S.) and toluene-insoluble (T.I.) fractions.

The T.I. fraction is dried overnight in a vacuum oven at 120°C. A rotary evaporator strips the solvent from the T.S. product. After the solvent is removed the T.S. fraction is dried on the rotary evaporator for about 1 hr at 95°C.

Results and Discussion

pH and Pressure Dependence of PSOC-26 Conversion

A number of experiments were performed observing pH values from 6.7 to 12.9. In these experiments the % T.S. fraction was determined. The initial CO pressure was also varied from 505 and 620 psig. The results of these experiments appear in Table 5.

The results support the findings of Ross and Nguyen[1] that there is a correlation between pH and the amount of T.S. product formed. There is a discrepancy, however, in the degree of conversion to T.S. product. Ross and Nguyen reported 48% T.S. product, while under similar conditions our results never exceeded about 35% T.S.

The results also indicate that the amount of T.S. product formed

Table 5

PSOC-26

INFLUENCE OF INITIAL pH AND INITIAL PRESSURE ON COAL CONVERSION IN CO-H_2O SYSTEM AT 400°C FOR 20 MIN

Run No.	pH	Initial CO Pressure	% Recovery[a]	%TS[b]	H/C TS	H/C TI
Starting coal	--	--	--	< 1	--	0.74
101	12.8	608	75.9	34.6	1.01	0.58
102	12.6	505	81.3	25.5	1.04	0.52
105	12.9	610	85.1	33.3	1.00	0.48
107	12.8	508	80.2	26.2	1.04	0.49
108	6.7	505	80.6	10.9	1.05	0.55
109	12.9	620	81.9	33.6	1.01	0.53

---

[a] % Recovery based on initial and final masses.

[b] % T.S. based on ash-free starting mass of coal.

partly depends on initial CO pressure. At initial pressures ranging from 505 to 508 psig of CO and pH ranging from 12.6 to 12.8 the average T.S. product was 25.9% (± 0.4), while at CO pressures ranging from 608 to 620 psig and pH ranging from 12.8 to 12.9 the average conversion to T.S. product was 33.8% (± 0.8).

pH Dependance of PSOC-233 Conversion

Three experiments were performed on this coal at different pH values while holding other variables constant. The results appear in Table 6.

The results indicate that the amount of T.S. product formed depends on pH: just as in PSOC-26, T.S. product increases with increased pH. Unlike the PSOC-26, there does not appear to be a well-defined cut- off for T.S. products of pH = 12.6. It will require further experiments to determine if there is a sharp cutoff at some other pH or if PSOC-233 has a more gradual pH profile.

Future Work

The correlation between coal conversion and the water gas shift reaction needs to be looked at for both systems. While at this time qualitative data concerning the product gas mixture has been obtained, quantitative interpretation of these results has not yet been completed.

Experiments designed to optimize conditions for conversion will be performed. Both temperature and pressure profiles versus conversion should be obtained. These experiments will be extended to other coals to establish the general nature of pH dependance on coal conversion.

Table 6

PSOC-233

INFLUENCE OF INITIAL pH ON COAL CONVERSION IN $CO-H_2O$ SYSTEM AT 400°C FOR 20 MIN

Run No.	pH	Initial CO Pressure	% Recovery[a]	% TS[b]	H/C	
					TS	TI
Starting coal	--	--	--	< 1	--	--
110	6.30	530	76.7	14.4	1.20	0.58
111	12.70	530	73.3	26.8	1.12	0.49
114	13.99	535	78.8	36.1	--	0.52

---

[a] % Recovery based on initial and final masses.
[b] %T.S. based on ash-free starting mass of coal.

REFERENCES

1. "Exploratory Study of Coal Conversion Chemistry," Final Report DOE/ET/14855-19 DOE Contract DE-AC22-79-ET14855 (August 12, 1981).

TASK B2: LABEL STUDIES IN THE CO/D_2O SYSTEM

David S. Ross and Georgina P. Hum

Introduction

The objective of this task is to develop a better understanding of the CO/H_2O system in coal liquefaction chemistry. We are therefore studying the reactions of model compounds under coal conversion conditions to elucidate the reaction mechanisms that occur during liquefaction. By using D_2O instead of H_2O, we label the products from conversion at the sites where bond cleavage has taken place on the coal model.

It has been proposed[1] that ether bonds are one of the major linkages in coal structures. An important consideration is therefore what kind of oxygen linkages in coal break, and what are the products from conversion. We are currently studying anisole as a model oxygen-containing structure in coal. The products from its conversion and the degrees of deuterium substitution in the various products have been determined, and are described below.

Experimental

Reactions were conducted in a 300-ml, stainless steel, Magne-Drive-stirred autoclave unit at 400°C for 20 min. The autoclave was charged with 10-g of substrate and 20-g D_2O. When pH 13 was desired 200-mg KOH was added to the reaction solution. After checking for leaks with 1000 psi of N_2, we flushed the autoclave two times with either CO or N_2, and finally charged the autoclave to 500 psi. One hour was generally the heat-up time required to reach 400°C, and another hour was required to cool the reactor to room temperature. Reaction gases were sampled and analyzed by gc. The condensed phases were removed by pipet. Ethyl ether was used to collect any organic traces in the autoclave. The D_2O and organic phases were isolated using a separatory funnel. The organic phase was collected, and the ethyl ether removed by a rotary evaporator. Conversions were monitored by gc. Per cent deuterium exchange was determined by GC/MS.

Results

Control Experiments with Toluene.

To establish the degree of deuterium incorporation in compounds expected products of the conversion runs, some control runs were performed with toluene. The data are presented in Table 7: no significant quantity of deuterium has been introduced. Any exchange in the benzene, toluene, or similar products anticipated in the anisole work, must therefore be the result of the conversion chemistry.

Anisole Conversion.

Experiments were performed in D_2O with anisole at three conditions: N_2/pH 7.0, CO/pH 7.0, and CO/pH 13.0. For the three series, the products were as shown in Table 8.

Under the experimental conditions, 20-40% of the anisole was converted, with the mass balance in the order of 84%. Benzene and phenol were consistently the major products. Toluene, benzyl alcohol and benzaldehyde were found in smaller quantities; the relative yields apparently depend upon the conditions. Thus in the absence of CO toluene is favored, while with CO present benzaldehyde and benzyl alcohol were formed at the expense of the toluene. Similar products were reported by Collins et al. in the study of the pyrolysis of phenyl ethyl ether in tetralin.[2]

The deuterium labeling in the recovered anisole and the products is shown in Table 9. The recovered anisole was found not to exchange to a significant degree. Only small quantities of labeled benzene were recovered in the N_2 runs, with increases in the deuterium content occurring with the presence of CO. The most prominently labeled product compound is phenol. We expect, however, that phenol under the conditions used here would readily exchange; and we plan to confirm this expectation.

Table 7

DEUTERIUM LABELLING RESULTS WITH TOLUENE

Conditions[a]	Product	d_o-	d_1-	d_2-
$CO/D_2O/pH = 13$	Toluene	96.7	3.0	0.3
$N_2/D_2O/pH = 13$	"	100	--	--

---

[a] 400°C for 20 min.

Table 8

DISTRIBUTION OF PRODUCTS FROM THE REACTION OF ANISOLE IN D_2O AT 400°C FOR 20 MIN

Conditions (gas/pH)	Anisole Recovered[a] (%)	Products[b] (%)				
		Benzene	Toluene	Phenol	Benzaldehyde	Benzyl Alcohol
N_2/7.0	72	51	20	24	3	2
CO/7.0	60	42	8	32	10	8
CO/13.0[c]	71	41	10	29	12	8
	78	41	11	26	13	9

---

[a] Fraction of starting anisole.

[b] The products are presented here as their respective fractions of the product mixture. The mass balances in these runs were 84-91.5%. No cresols were observed.

[c] Two separate runs.

Table 9

DEUTERIUM INCORPORATION IN THE PRODUCTS FROM THE REACTIONS OF ANISOLE IN D_2O AT 400°C FOR 20 MIN

Conditions (gas/pH)	Product	Deuterium in Products %					
		d_0	d_1	d_2	d_3	d_4	d_5
N_2/7.0	Anisole	96	4	tr	--	--	--
CO/7.0	"	84	13	2	--	--	--
CO/13.0	"	90	9	1	--	--	--
		90	9	1	--	--	--
N_2/7.0	Benzene	87	11	2	--	--	--
CO/7.0	"	58	32	6	3	1	--
CO/13.0	"	69	25	4	2	--	--
		70	24	3	2	--	--
N_2/7.0	Toluene	72	23	4	1	--	--
CO/7.0	"	41	31	19	7	--	--
CO/13.0	"	81	11	5	2	--	--
	"	81	11	5	2	1	--
N_2/7.0	Phenol	--	1	16	80	2	--
CO/7.0	"	--	2	15	57	23	2
CO/13.0	"	--	5	28	54	10	2
	"	--	1	11	71	15	2
N_2/7.0	Benzaldehyde	93	7	--	--	--	--
CO/7.0	"	70	30	--	--	--	--
CO/13.0	"	60	40	--	--	--	--
	"	67	33	--	--	--	--
N_2/7.0	Benzyl alcohol	--	--	--	--	--	--
CO/7.0	"	29	40	24	6	1	--
CO/13.0	"	30	40	23	6	1	--
	"	23	44	25	6	1	--

The toluene, benzaldehyde and benzyl alcohol seem linked in some common chemistry. It is likely that the deuterium substituted in these products is attached to the noncyclic carbon, rather than to a ring carbon.

Discussion

It is apparent that the formation of benzene and phenol are independent of the presence of CO, and that the formation of toluene, while decreased in the CO runs, is significant here as well in the N_2 runs. Thus the chemistry operative here is not important in the CO/H_2O conversion of coal. However, the results are of interest and will be discussed with reference to runs we have performed with anisole in tetralin.[3]

The major differences in results for the aqueous and tetralin conversions of anisole are presented in Table 10.

Table 10

CONVERSIONS OF ANISOLE IN AQUEOUS AND TETRALIN SYSTEMS AT 400°C

Feature	Aqueous	Tetralin[b]
Rate constant	3.9×10^{-4} sec^{-1}[a]	4.7×10^{-6} sec^{-1}
Major products	Phenol, benzene, toluene[c] 0.25 0.54 0.21	Phenol, toluene 0.86 0.14
Other[d]	No cresols in product	Traces of cresols, and no benzene

---

[a] Estimated from the degree of anisole conversion. No formal kinetic study has been performed.

[b] See reference 3.

[c] The toluene as described in the text was a major product in the runs in the absence of CO.

[d] It is estimated that 0.1% of benzene and cresols in the product mixtures could be detected.

The presence of water as the reaction medium increases the rate of reaction by a strikingly two orders of magnitude. Thus while the half-life of anisole in tetralin at 400°C is about 41 hr, it is about 30 min in the aqueous system. And while phenol is the major product in tetralin, with no benzene seen at all, phenol is formed in water but in quantities about half those of the product benzene.

A preliminary evaluation of these data suggest that the supercritical water medium serves well to allow deoxygenation of the aryl methyl ether, and at a reasonably rapid rate. Our initial reasons for performing the work included the anticipated conformation of an ionic reaction path for the conversion of anisole, with hydride transfer being the expected reduction step.

$$OH^- + CO \longrightarrow HCO_2^-$$

$$HCO_2^- + \text{coal} \longrightarrow \text{coal}H^- + CO_2$$

However, as stated above, because the conversion of anisole takes place in the absence of CO, it is not significant in the anisole case.

It is thus necessary to explain for water as a medium

- The rapid rate of anisole disappearance;
- The formation of benzene, with the major fraction of the benzene not substituted with deuterium;
- The formation of phenol;
- The formation of toluene, benzyl alcohol and benzaldehyde.

At this time we have no firm understanding of all of the chemistry involved. However, we suggest that the substantial rate increase over what was observed in tetralin is because in tetralin no chain process can take place. The tetralin caps all reactive radicals with a hydrogen atom and for anisole therefore (tetralin = TH)

$$Ph{-}O{-}CH_3 \longrightarrow Ph{-}O\bullet + \bullet CH_3$$

and

$$Ph{-}O\bullet + T{-}H \longrightarrow Ph{-}OH + T\bullet$$

$$CH_3\cdot + T\text{-}H \longrightarrow CH_4 + T\cdot$$

The tetryl radicals (T·) are not very reactive, and the net reaction observed is therefore

$$Ph\text{-}O\text{-}CH_3 + 2T\text{-}H \longrightarrow PhOH + CH_4 + 2T\cdot$$

In water, however, the hydrogen atom transfers create the very reactive OH as an intermediate, and rapid chain reactions can be initiated. We suggest, therefore, that the phenol and benzene are formed in the following chain sequences.

Benzene

$$PhOCH_3 \longrightarrow PhO\cdot + CH_3\cdot \qquad (1) \quad \text{initiation}$$

$$CH_3\cdot + PhOCH_3 \longrightarrow CH_4 + PhOCH_2\cdot \qquad (2)$$

$$PhOCH_2\cdot \longrightarrow PH\cdot + H_2CO \qquad (3) \quad \text{propagation}$$

$$PH\cdot + PhOCH_3 \longrightarrow Ph\text{-}H + PhOCH_2\cdot \qquad (4)$$

Phenol

$$PhOCH_3 \longrightarrow PhO\cdot + CH_3\cdot \qquad (5) \quad \text{initiation}$$

$$CH_3\cdot + H_2O \longrightarrow \cdot OH + CH_4 \qquad (6)$$

$$\cdot OH + PhOCH_3 \longrightarrow \cdot\, OH + CH_3O\cdot \qquad (7) \quad \text{propagation}$$

$$CH_3O\cdot + H_2O \longrightarrow \cdot OH + CH_3OH \qquad (8)$$

These reactions account for most of the benzene formed. The small quantity of labeled benzene could result from

$$Ph\cdot + D_2O \longrightarrow Ph\text{-}D + \cdot OD \qquad (9)$$

which should be somewhat slower than the reaction of the phenyl radical with the starting anisole.

One difficulty with this explanation is reaction (8), which while rapid enough in the direction written at 400°C, is most certainly reversible. Thus the steady-state concentration of OD in the system should be very small. It is difficult to do more than speculate on the quantitative nature of these reactions at this time, however, and we expect to present a more complete and somewhat quantitative view of the chemistry in future reports.

In this same vein, we presently have no explanation for the formation of toluene with substantial deuterium label, and its decline with the addition of CO. A reaction such as

$$CH_3 + Ph \longrightarrow Ph\text{-}CH_3 \qquad (10)$$

would not only be too slow, but even if faster than expected, would yield only unlabeled toluene. Thus more experimental work must be performed for a more complete understanding.

Future Work

We are continuing our effort to elucidate the reaction mechanisms of anisole in the CO/D_2O system. By studying the intermediate products, i.e., phenol and benzyl alcohol, we can develop a better understanding of the reaction mechanisms involved. We are also extending our study to other oxygen-containing coal models, i.e., diphenyl ether and 1-methoxynaphthalene.

References

1. L. A. Heredy and P. Fugassi, Adv. Chem. Ser., No. 55, 448 (1968).

2. C. J. Collins, V. F. Reaen, B. M. Benjamin, D. H. Maupin, and W. H. Roark, J. Am. Chem. Soc., 1979, 101, 5009.

3. a) D. S. Ross, D. McMillen, W. Ogier, Q. Nguyen, "Exploratory Study of Coal Conversion Chemistry," Final Report, DOE/ET/14855, Dist. Cat. UC-90-d SRI International, covering the period, Sept. 20, 1979 to March 19, 1981.

   b) D. F. McMillen, W. C. Ogier, and D. S. Ross, J. Org. Chem. 46, 3322 (1981).

☆ U.S. GOVERNMENT PRINTING OFFICE: 1981-740-145/2986