

MODELING COAL LIQUEFACTION: DECOMPOSITION OF  
4-(1-NAPHTHYLMETHYL)BIBENZYL CATALYZED BY CARBON BLACK\*

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\*Reference in the paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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ABSTRACT

The early stages of coal liquefaction involve cleavage of methylene and ethylene bridges connecting aromatic rings. We modeled this process by the reaction of 4-(1-naphthylmethyl)bibenzyl (I) in the presence of a hydrogen donor (9,10-dihydrophenanthrene). The reactions were conducted over a range of temperatures (320-430°C) and reaction times (30-90 min). We found that the bond between the methylene group and the naphthalene ring and the methylene to methylene bond of the bibenzyl moiety are broken with equal probability. Addition of carbon black (BP 2000) as catalyst (2-10%) increases significantly the conversion of I. For instance, at 419°C and 1h, 18% of I is converted without catalyst and 42% is converted in the presence of 2% of BP 2000. The increase in conversion is due to additional breaking of the bond between the naphthyl and the methylene groups. This particular carbon black is, therefore, a very active and selective catalyst for the cleavage of the naphthyl-to-methylene bond.

INTRODUCTION

Cleavage of covalent bonds is the essential reaction occurring during coal liquefaction. Thermal cleavage requires temperatures so high, that other, mostly undesirable reactions take place resulting in little if any selectivity in the cleavage process. However, specific bonds can be cleaved catalytically, at temperatures where thermal reactions are not important.

Because of the complexity of coal structure, it is not possible to investigate and optimize conditions for cleaving specific bonds, or to sort out desired processes from side-reactions. In order to obtain meaningful data relevant to coal liquefaction and to be able to develop proper catalysts for the process, the study of model compounds containing the critical structural elements of coal in simpler structures is necessary. The study of appropriate model compounds allows determinations of kinetic parameters (rates, activation energies, selectivities) that can be applicable to the cleavage of specific bonds in coal.

To be relevant to coal liquefaction under heterogeneous catalysis, a study of model compounds should satisfy a number of requirements concerning the structure of the model compound, and the type of data to be gathered. Some of these criteria are:

1. The model compound should be liquid or solid under the reaction conditions to mimic the conditions prevalent during coal liquefaction.

This usually means that the model compound should have a molecular weight of at least 300. A macromolecular structure could be desirable in some cases.

2. The model compound should contain several types of potentially reactive chemical bonds under the reaction conditions. The presence of different reactive structures in the same molecule permits the study of competitive kinetics in the presence of intramolecular interactions. Many of the reactions taking place during coal liquefaction are influenced by other chemical structures present in the same molecule. Because competitive reactions certainly occur in coal processing, study of model compounds with only one type of bond that cleaves affords only limited information.
3. The products of reactions should be unambiguously identified and their rate of formation determined. Determination of rates (both absolute and relative) and of activation energies of different reactions is essential for the study of the mechanisms of reactions. Relative reaction rates and activation energies for cleavage of specific bonds is necessary information that cannot be obtained directly from the study of very complex systems such as coal. In the latter case only an overall conversion of a complex starting material to a complex product mixture can be determined. An attempt at calculating an activation energy for such a transformation gives a number with no physico-chemical meaning. In these cases the use of appropriate model compounds is highly desirable.

In the current study, we examined the cleavage of methylene and ethylene bonds linking aromatic fragments. These particular reactions are considered important for the chemistry of coal liquefaction (1). The model compound investigated, 4-(1-naphthylmethyl)biphenyl (I), contains a methylene and ethylene linkage in the same molecule. Thermal as well as catalytic cleavage of the bonds were studied. A novel catalyst was employed (carbon black, Cabot Corporation Black Pearls 2000) for the catalytic reactions. This material has been used as support for metal-based catalysts (2), but has never been reported to be a catalyst itself.

#### EXPERIMENTAL SECTION

Materials and Analytical Procedures. 9,10-Dihydrophenanthrene was obtained from Aldrich Chemical Co., Black Pearls 2000 carbon black was obtained from Cabot Corporation. Elemental analysis of the carbon black, performed by Huffmann Laboratories, Golden, CO, gave % C, 95.4; O, 1.4; S, 1.8; Ash, 1.3. Surface area (BET) quoted by Cabot is 1475 m<sup>2</sup>/g. 4-(1-naphthylmethyl)biphenyl (I) was prepared in the laboratory of Prof. Paul Dowd at the University of Pittsburgh. The compound was completely characterized by IR, UV, <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis and high and low resolution mass spectroscopy. The purity of the product was better than 99%. The above substances were used as received. Dichloromethane was stored over 4 Å molecular sieves.

Glass reaction tubes were made from Pyrex tubing, 5 x 7 mm (i.d. x o.d.). Sealed sample tubes were approximately 75 mm in length.

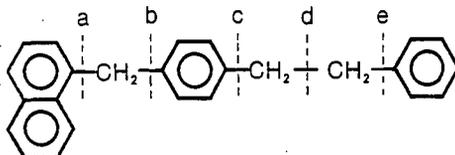
Gas chromatographic analyses were carried out on a Hewlett Packard Model 5730A gas chromatograph equipped with an SE-30 60 m column. Gas chromatography/mass spectra (GC/MS) were obtained on a Hewlett Packard GC/MS Model 5985 instrument operated using 70 eV electron impact voltage and equipped with a 30 m SE-52 column.

Identification of reaction products was accomplished by GC/MS analysis and, when possible, by GC comparison with authentic chemical samples. Reported products yields and overall conversion of I are based on GC measurements. The most volatile material, toluene, could not be determined accurately, but the quantity was always found to be close to that of naphthyl tolyl methane. The amount of toluene reported was set to equal the amount of naphthyl tolyl methane found.

**General Experimental Procedure.** The reaction components (9,10-dihydro-phenanthrene, ca. 100 mg; I, ca. 25 mg and carbon black, 0, 2, 5, 10 wt % based on I) were weighed into an open-ended glass reaction tube. The tubes were flame sealed, taking no precautions to exclude air. Warm water was used to melt the hydrogen donor and effect mixing of the reactants. The samples were placed upright in a temperature equilibrated Lundberg muffle furnace and heated at the indicated temperatures for the given times. The samples were then removed from the oven, cooled to room temperature and diluted with ca. 0.5 mL of dichloromethane. The samples were filtered through a plug of MgSO<sub>4</sub> and glass wool. An additional 0.5 mL of dichloromethane was used to wash the filter and, in catalytic reactions, the carbon black catalyst. An aliquot of the resulting solution was analyzed by gas chromatography.

#### RESULTS AND DISCUSSION

To facilitate the discussion of the results we identify in the structural formula of 4-(1-naphthylmethyl)biphenyl (I) different bonds that can be potentially cleaved, by the letters a through e, and identify in Table 1 the compounds that are formed after cleavage.



The conversion of I was studied under a variety of reaction conditions. The majority of the reactions were performed in the presence of 9,10-dihydro-phenanthrene (9,10-DHP) as hydrogen donor. Several experiments however, were performed in the absence of the hydrogen donor.

The overall conversion of I to products is given in Tables 2 and 3 for the reactions performed in the presence of 9,10-DHP under thermal and catalytic conditions at various temperatures and reaction times. As shown in Table 2, the thermal reaction is insignificant even at 400°C, (ca 3% conversion), and becomes important only at higher temperatures (18% at 419°C). Under the same reaction conditions, but with the addition of 5% Black Pearls 2000 (BP 2000) catalyst, the conversion at 400°C is ca 34%, and at 419°C it is increased to 63%. Using the data in Table 3 we have found that the cleavage of bond a follows reasonably well, first order reaction kinetics under both thermal and catalytic conditions.

Aside from increasing the overall rate of reaction of I, we found that this carbon black is an extremely selective catalyst for bond cleavage. Table 4 gives the product distribution obtained from I under thermal and catalytic conditions at 419°C. In the absence of the catalyst, bonds a and d are cleaved to almost the same extent, with nearly equimolar quantities of 4-methylbiphenyl (MeBz<sub>2</sub>) and naphthyl tolyl methane (NTM) being produced. Bond b (1-methyl-

naphthalene and bibenzyl products) is cleaved only to a very limited extent. In the presence of the catalyst, however, a remarkable selectivity toward cleavage of bond a is observed as seen in the increased amount of MeBz<sub>2</sub> formed. In fact, cleavage of bond a is practically the only reaction promoted by this catalyst. This activity and selectivity were observed for all temperatures and catalyst concentrations studied.

Reaction rate constants and activation energies for thermal and catalytic reactions are given in Tables 5 and 6. The values for these parameters illustrate the dramatic effect of the added catalyst on the reaction of I in the presence of 9,10-DHP. One of the most important results is the large difference in the activation energies calculated for the thermal and catalytic reactions for the cleavage of bond a; E<sub>a</sub> is -60 kcal/mole for the thermal reaction (Table 5) and 17-25 kcal/mole for the catalytic reactions (Table 6). The variation of the activation energy with the quantity of catalyst (Table 6) is an indication that diffusion may play a role in the catalytic process (3).

When I is allowed to react in the absence of the hydrogen donor, the selectivity of the thermal reaction changes and cleavage of bond d is favored. The catalytic reaction, in the absence of 9,10-DHP, still shows the same remarkable selectivity toward bond a cleavage (Table 7). In the absence of hydrogen donor, however, compounds heavier than I are formed in all experiments, indicating that I is acting as a hydrogen source by dehydrogenation and condensation reactions. Besides these heavier compounds we also observed the formation of some methylidihydrophenanthrene, formed perhaps by cyclization of MeBz<sub>2</sub>.

In order to put into perspective our findings regarding the high activity and exceptional selectivity of the BP 2000 catalyst in reactions with 4-(1-naphthylmethyl)bibenzyl, I, it is worth discussing the following points.

When the reactions of I, both with and without 9,10-DHP, are performed in the presence of a graphite carbon (Alfa) or of Illinois No. 6 coal, there is no increase in conversion of I above the thermal level nor is there any enhanced bond cleavage selectivity. Whether the behavior of BP 2000 is due to its physical structure or some other property is currently under investigation.

The BP 2000 catalyst appears to be specific for the cleavage of bonds between saturated carbons and polycyclic aromatic structures. This is illustrated by the reaction of diphenylmethane with BP 2000, both with and without 9,10-DHP. Even at 420°C, 1h, the methylene linkage in this compound remains intact.

Cleavage of bonds between methyl groups and polycyclic aromatic radicals in the presence of hydrogen donors has been explored extensively by McMillen, et al. (4). They have rationalized this reaction as a "solvent mediated hydrogenolysis", involving a H-transfer by a free radical mechanism. In this mechanism, a dihydroaromatic forms an ArH<sub>2</sub>· free radical in a rate-determining step. The ArH<sub>2</sub>· free radical then transfers a H-atom to the ipso position of the substituted polycyclic compound. The cyclohexadienyl-type free radical thus formed from the latter undergoes the aromatic carbon-methylene carbon bond scission. The above mechanism may be operating alongside other pathways, in the reaction of I in the presence of H-donors. Our findings for the reaction run in the presence of BP 2000, but in the absence of H-donor suggest however, that the radical-transfer sequence cannot be the prevailing mechanism for the cleavage of bond a in I under the catalytic conditions which we investigated.

Our work shows that it is possible to have high selectivity in breaking specific bonds under mild conditions if proper catalysts can be identified. Experiments are in progress toward the goal of understanding the mechanism of action of the BP 2000 catalyst. We are also investigating its use as a catalyst

for cleavage reactions in diquinolyl ethane and dehydroxylation reactions of some phenols.

#### CONCLUSIONS

Our study of the decomposition 4-(1-naphthylmethyl)bibenzyl as a model for reactivity of methylene and ethylene linkages during coal liquefaction showed that, in the presence of a hydrogen donor, the bond connecting 2 benzylic carbons and the bond between naphthyl and methylene units in naphthylphenyl methane, are broken with the same probability in a thermal reaction. We discovered that a high surface area carbon black (Cabot Corp., Black Pearls 2000) is a very active and selective catalyst for the cleavage of the naphthyl-methylene bond.

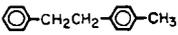
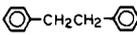
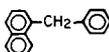
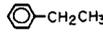
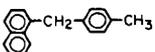
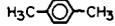
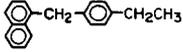
#### ACKNOWLEDGEMENTS

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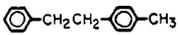
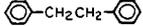
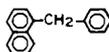
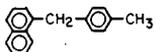
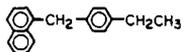
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**TABLE 1.**  
**IDENTIFICATION OF PRODUCTS RESULTING**  
**FROM BOND CLEAVAGE OF**  
**4-(1-NAPHTHYLMETHYL)BIBENZYL, I.**

<u>Bond Cleaved</u>	<u>Observed Products</u>	<u>Name</u>	<u>Symbol</u>
a		Naphthalene	N
		Tetralin <sup>1</sup>	Te
		4-Methylbibenzyl	MeBz <sub>2</sub>
		3-Methyl-9, 10-dihydrophenanthrene <sup>2</sup>	Me-9,10-DHP <sup>2</sup>
b		1-Methylnaphthalene	MeN
		Bibenzyl	Bz <sub>2</sub>
c		1-(Naphthyl)phenyl methane	NPM
		Ethyl benzene	EtB
d		1-(Naphthyl)-4-tolyl methane	NTM
		Toluene	To
		p-Xylene <sup>3</sup>	pX
e		1-(Naphthyl)-4-(ethyl phenyl) methane	NEPM
		Benzene	B

- 1 From hydrogenation of N  
2 From cyclization of MeBz<sub>2</sub>  
3 From further fragmentation of NTM

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**IDENTIFICATION OF PRODUCTS RESULTING**  
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<u>Bond Cleaved</u>	<u>Observed Products</u>	<u>Name</u>	<u>Symbol</u>
a		Naphthalene Tetralin <sup>1</sup>	N Te
		4-Methylbibenzyl	MeBz <sub>2</sub>
		3-Methyl-9, 10- dihydrophenanthrene <sup>2</sup>	Me-9,10-DHP <sup>2</sup>
b		1-Methylnaphthalene	MeN
		Bibenzyl	Bz <sub>2</sub>
c		1-(Naphthyl)phenyl methane	NPM
		Ethyl benzene	EtB
d		1-(Naphthyl)-4- tolyl methane	NTM
		Toluene	To
		p-Xylene <sup>3</sup>	pX
e		1-(Naphthyl)-4- (ethyl phenyl) methane	NEPM
		Benzene	B

- 1 From hydrogenation of N
- 2 From cyclization of MeBz<sub>2</sub>
- 3 From further fragmentation of NTM

Table 2. Influence of Temperature on Overall Conversion of I to Products at x% Carbon Black BP 2000 Catalyst.<sup>1</sup>

Temperature °C	Conversion at x% Catalyst			
	0	2	5	10
320	0	0.8	---	3.9
360	0	4.6	15	23
375	0	9.1	16.2	27.0
400	3.0	17.6	33.6	43.6
408	7.3	---	49.8	---
419	17.8	42.7	63.0	77.0
429	28.7	53.8	78.9	87.2

<sup>1</sup>Reaction conditions: 1h; wt ratio I:9,10-DPH 1:4; catalyst wt based on I.

Table 3. Influence of Reaction Time on Overall Conversion of I to Products at 421°C and x% Carbon Black BP 2000 Catalyst.<sup>1</sup>

Reaction Time Minutes	Conversion at x% Catalyst		
	0	5	10
30	7.1	39.1	58
60	17.8	63	77
90	24.5	67	86.6

<sup>1</sup>Reaction conditions: 1h; wt ratio I:9,10 DPH 1:4; catalyst wt based on I.

Table 4. Moles of Compounds<sup>1</sup> Formed/100 Moles I Consumed at x% Carbon Black BP 2000 Catalyst.<sup>2</sup>

Compound	Moles Compound Formed at x% Catalyst			
	0	2	5	10
To	52.1	10.1	4.9	2.5
pX	3.8	5.7	6.0	4.7
Te	14.1	21.3	24.8	25.8
N	22.4	64.4	68.4	64.6
MeN	3.6	4.3	4.3	3.9
Bz <sub>2</sub>	4.4	5.1	5.4	5.9
MeBz <sub>2</sub>	40.2	77.8	82.0	88.6
NTM	52.1	10.1	4.9	2.5

<sup>1</sup>Refer to Table 1 for compound identification.

<sup>2</sup>Reaction conditions: 419°C; 1h; wt. ratio I:9,10-DPH 1:4; catalyst wt based on I.

Table 5. Reaction Rate Constants (k) and Activation Energies (E<sub>a</sub>) for Thermal Reactions of Bonds a and d of I.<sup>1</sup>

Temperature °C	k <sub>a</sub> × 10 <sup>-4</sup> (min <sup>-1</sup> )	k <sub>d</sub> × 10 <sup>-4</sup> (min <sup>-1</sup> )
400	~ 2.4	~ 2.7
408	5.2	6.1
419	12.5	16.3
429	18.3	26.7
E <sub>a</sub> bond a (kcal/mol) ~ 60		E <sub>a</sub> bond d (kcal/mol) ~ 70

<sup>1</sup>Reaction conditions: 1h; wt. ratio I:9,10-DPH 1:4.

Table 6. Reaction Rate Constants (k) and Activation Energies (Ea) for Catalytic Reaction of Bond a of I at x% Carbon Black BP 2000 Catalyst.<sup>1</sup>

Temperature °C	k x 10 <sup>-4</sup> (min <sup>-1</sup> ) at x% Catalyst <sup>2</sup>		
	2	5	10
360	7.9	27.1	43.6
400	26.3	60.9	86.8
408	----	92.2	----
419	47.7	100.2	149.4
429	48.2	116.2	146.6
Ea at x% catalyst (kcal/mol)	~25	~19	~17

<sup>1</sup>Reaction conditions: 1h; wt. ratio I:9,10-DPH 1:4; catalyst wt based on I.

<sup>2</sup>Reported for catalytic contribution only. Thermal background has been subtracted.

Table 7. Moles of Compounds<sup>1</sup> Formed/100 MoI I Consumed in the Absence of 9,10-DPH Under Thermal and Catalytic Conditions.<sup>2</sup>

Compound	Moles Compound Formed at x% Catalyst <sup>3</sup>	
	0 (7.5)	5 (25.3)
To	70.6	35.4
pX	0	4.3
N	4.8	52.4
MeN	3.7	7.2
Bz <sub>2</sub>	3.4	5.2
MeBz <sub>2</sub>	19.3	49.6
NPM	17.4	8.5
NTM	70.6	35.4

<sup>1</sup>See Table 1 for compound identification.

<sup>2</sup>Reaction conditions: 408°C; 1h; catalyst wt based on I.

<sup>3</sup>Overall conversion of I at x% catalyst given in parentheses.