

## The Effects of Aromatic Compounds on the Hydrogen-Transfer Reaction to Coal Model Compounds

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**Synopsis.** A hydrogen-transfer reaction from a hydrogen molecule to benzophenone in 1-methylnaphthalene without a donor was accelerated in the presence of anthracene. Phenanthrene and pyrene were detrimental to the reaction. Dibenzyl ether conversion was also accelerated by the addition of anthracene, pyrene, and fluorene. Conversions of coal model compounds in 1-methylnaphthalene under a hydrogen atmosphere correlated well with conversions in tetralin under a nitrogen atmosphere.

In coal liquefaction the solvent plays a vital role as both a hydrogen donor and a reaction medium to dissolve reactants and products.<sup>1)</sup> The selection of the solvent is an important factor for effective coal liquefaction. Hydroaromatic compounds, such as tetralin, are known to be donors.<sup>2)</sup> We have already reported that aromatic compounds, such as anthracene and fluorene, are effective hydrogen shuttlers in hydrogen-transfer reactions from a donor, tetralin, to coal model compounds.<sup>3)</sup> Such hydrogen-shuttling reactions contribute to an increase in the net amounts of transferred hydrogen from donors to coal.<sup>4)</sup> Furthermore, it is well-accepted that the reactive coal fragments not only abstract hydrogen from the donor solvent, but also react with dissolved hydrogen molecules to yield liquefaction products.<sup>5)</sup> For example, in the pyrolysis of bibenzyl without a catalyst, significant amounts of benzene and ethylbenzene have been produced, indicating a mechanism involving the direct participation of hydrogen molecules in free-radical reactions.<sup>6)</sup> Ouchi and Makabe reported that naphthalene as a model of solvent did not convert under a hydrogen atmosphere without a

catalyst.<sup>7)</sup> However, recycle solvents include many compounds, and the role of solvent on the reaction of coal with hydrogen molecules has not been clearly understood.

Though it is appropriate to use coal model compounds, in many cases the effectiveness of various hydrogen-donor solvents were investigated. In this study, in order to understand the function and importance of coal liquefaction solvents, the reactions of coal model compounds were performed in the presence of aromatic compounds with hydrogen molecules without a donor and a catalyst.

### Experimental

Reagent grade benzophenone and dibenzyl ether were used. All of the reactions were carried out in magnet-driven stainless-steel autoclave according to a method described previously.<sup>3)</sup> The liquid products after reactions were washed from the autoclave with acetone and analyzed by gas chromatography (GC).

### Results and Discussion

Six aromatic compounds were used in the reaction of benzophenone as a coal model. 1-Methylnaphthalene was used as a diluent since the hydrogen-shuttling ability of 1-methylnaphthalene is very low, as already reported.<sup>3)</sup> When no aromatic compound was added, the conversions of benzophenone were 43 to 45% (Table 1). These values were larger than 9.3%, in which initial hydrogen pressure was 2.0 MPa and reaction time was 0.5 h.<sup>9)</sup> No benzhydrol was observed in the products. The highest conversion was obtained

Table 1. The Effects of Aromatic Compounds on the Hydrogen Transfer Reaction<sup>a)</sup> to Benzophenone (BZP)

Run No.	Aromatic compound	Conv. of BZP	Yield of DPM <sup>b)</sup>
		mol%	mol%
1	1-Methylnaphthalene	42.9, 45.0	32.9, 35.4
2	Anthracene	52.4	43.1
3	Phenanthrene	23.8	21.9
4	Pyrene	29.9, 26.4	24.4, 22.6
5	Fluorene	44.7	38.3
6	Diphenylmethane	45.9	31.0
7	Triphenylmethane	43.2	32.9
8	Dihydroanthracene	52.2	52.2
9	Dihydroanthracene <sup>c)</sup>	31.3	23.6
10	Dihydrophenanthrene	38.8	38.8
11	Dihydrophenanthrene <sup>c)</sup>	9.8	9.8

a) Aromatic compound (1.00 g), 1-methylnaphthalene (10.00 g) and benzophenone (1.00 g) were used. Reaction temperature 430 °C; initial hydrogen pressure 3 MPa; reaction time 1 h. b) DPM=Diphenylmethane. c) Under a nitrogen atmosphere.

by adding anthracene (Run 2). It was confirmed that, in the absence of benzophenone, 47% of the anthracene was hydrogenated to dihydroanthracene (DHA; 44%) and tetrahydroanthracene (3%) in 1-methylnaphthalene under a hydrogen atmosphere at 430 °C. DHA was a good donor for benzophenone (Runs 8 and 9). Certainly, no DHA was observed in the reaction of benzophenone with 1-methylnaphthalene and anthracene. This shows that hydrogen transfer from DHA to benzophenone came to completion if DHA was produced. It was considered that a positive effect of anthracene on the hydrogen-transfer reaction was given by its high ability to accept hydrogen. Lower conversions of 20 to 30% than without additive were obtained when phenanthrene or pyrene was used as an aromatic compound (Runs 3 and 4). The facts indicated that pyrene and phenanthrene had negative effects on the conversion of benzophenone. When pyrene alone was reacted under a hydrogen atmosphere, 2% of the pyrene was hydrogenated to give dihydropyrene. In the same reaction, 1% of the phenanthrene was hydrogenated. They have lower abilities to accept hydrogen than does anthracene. However, the presence of 2% dihydrophenanthrene after the reaction of benzophenone in 1-methylnaphthalene and phenanthrene was observed. The presence of dihydrophenanthrene after the reaction and low benzophenone conversion indicated that phenanthrene was hydrogenated in preference to benzophenone and that hydrogen transfer from dihydrophenanthrene to benzophenone was slow. Conversions with additives of fluorene, diphenylmethane and triphenylmethane were the same without additives (Runs 5–7). Their abilities to accept hydrogen may be very low in consideration of their structures.

Dibenzyl ether easily decomposed at 375 °C. About 15% of the dibenzyl ether converted to toluene and benzaldehyde in 1-methylnaphthalene alone (Run 12). No benzyl alcohol was observed in the products. An intramolecular reaction of dibenzyl ether does not give toluene and benzaldehyde through free radicals. On the other hand, two free radicals result from an intermolecular reaction. It is considered that highly reactive radicals would participate in the reaction with hydrogen molecules directly. Simmons and Klein reported that a free-radical chain reaction occurred in

preference to an intramolecular type reaction. They evaluated it at 400 °C. However, the exact intermolecular/intramolecular reaction ratio under our reaction conditions has not been estimated. Phenanthrene, diphenylmethane, and triphenylmethane were not effective additives (Runs 14, 17, and 18). These results indicate that the hydrogen-transferring ability of such aromatic compounds is fairly small. On the other hand, the conversion increased to 40% upon the addition of anthracene (Run 17). The high hydrogen-accepting ability of anthracene must contribute to the high conversion. Fluorene and pyrene were also effective additives for the conversion of dibenzyl ether (Runs 15 and 16).

Figure 1 shows the relationship between the conversion of coal model compounds in 1-methylnaphthalene under a hydrogen atmosphere and conversion in tetralin under a nitrogen atmosphere. The hydrogen shuttling ability and the hydrogen-transfer ability from hydrogen molecules are considered to be different. However, the correlation factor between them was as

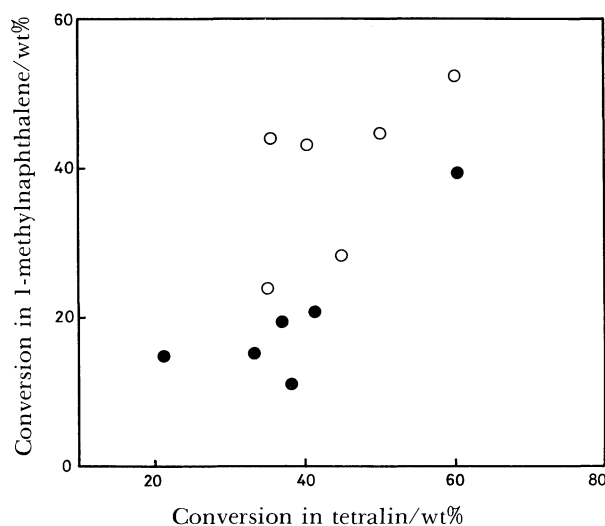


Fig. 1. The relationship between conversion of benzophenone (○), dibenzyl ether (●) in 1-methylnaphthalene under a hydrogen atmosphere and conversion in tetralin under a nitrogen atmosphere.

Table 2. The Effects of Aromatic Compounds on the Hydrogen-Transfer Reaction<sup>a)</sup> to Dibenzyl Ether (DBE)

Run No.	Aromatic compound	Conv. of DBE	Yield of TOL <sup>b)</sup>	Yield of BZA <sup>b)</sup>
		mol%	mol%/2	mol%/2
12	1-Methylnaphthalene	14.6, 15.0	8.9, 9.5	5.7, 5.5
13	Anthracene	39.2	12.7	7.8
14	Phenanthrene	15.2	8.2	4.9
15	Pyrene	19.7	8.9	5.6
16	Fluorene	20.7	11.6	9.1
17	Diphenylmethane	13.8	8.6	3.8
18	Triphenylmethane	12.9	6.9	4.0

a) Aromatic compound (1.00 g), 1-methylnaphthalene (10.00 g) and dibenzyl ether (1.00 g) were used. Reaction temperature 375 °C; initial hydrogen pressure 3 MPa; reaction time 1 h. b) TOL=Toluene. BZA=Benzaldehyde.

high as 0.68. This indicates that the role of aromatic compounds in the hydrogen-transfer reaction with a donor solvent is similar to that with hydrogen molecules.

It is suggested from our results that anthracene has both the highest hydrogen-shuttling ability<sup>3)</sup> and the highest ability to transfer hydrogen molecule. Coal liquefaction with an aromatic compound under an argon atmosphere has been reported.<sup>11)</sup> In the report coal conversions based on quinoline-insoluble matter with anthracene were 31—34%. The conversions were lower than 48.1% with 1-methylnaphthalene. This indicated that anthracene might play an important role in coal conversion when anthracene is mixed with other compounds as the solvent.

Though the participation of hydrogen molecules in coal liquefaction is fairly complex, we believe that our methods to evaluate the abilities of hydrogen shuttling from a solvent<sup>3)</sup> and the transference of hydrogen molecules are appropriate for evaluating solvent abilities.

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