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Evaluation of the Hydrogen Shuttling Ability of Coal Liquefaction Solvents

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Synopsis. The hydrogen-shuttling ability of coal liquefaction solvents were evaluated using benzophenone and dibenzyl ether as hydrogen acceptors. Hydrogen-transfer reactions from tetralin to acceptors were accelerated by shuttlers and the ranking of the shuttling ability was determined to be as follows:

anthracene > fluorene > pyrene≅triphenylmethane > phenanthrene > 1-methylnaphthalene

It is generally well-accepted that the hydrogen-donation of solvents plays an important role in the noncatalytic dissolution of coal.[1] Therefore, many researchers have attempted to evaluate the hydrogen donor ability of coal liquefaction solvents.[2] Hydroaromatic compounds, such as tetralin, are known as donors. On the other hand, polynuclear fused aromatics, such as pyrene, have been identified as being effective solvent components in spite of their low donor abilities. For example, when mixtures of pyrene and tetralin were used in the presence of hydrogen, coal conversions almost as high as that in pure tetralin were achieved at 30% tetralin.[3] Pyrene is not a donor; however, the ability of condensed aromatics to assist in liquefaction by physical solvation has been well recognized,[4] and an important role of pyrene as the hydrogen shuttler is suggested. In order to fully understand the function and importance of liquefaction solvents, an evaluation of the hydrogen-shuttling ability must be undertaken. We have developed a method by which the relative hydrogen-shuttling ability of liquefaction solvents can be evaluated using two different types of model hydrogen acceptors.

Experimental

Benzophenone and dibenzyl ether were used as hydrogen acceptors. An acceptor (1 g), tetralin (10 g) and a solvent (1 g) were placed in a magnet-driven autoclave and pressurized to 3 MPa with nitrogen. When benzophenone was used as an acceptor, the autoclave was heated to 430 °C and maintained at this temperature for 1 hour. The yields of diphenylmethane and benzhydrol were determined by gas chromatography (GC). Dibenzyl ether was unstable and decomposed completely at 430 °C. Therefore, the reaction was carried out at 375 °C for 1 h when dibenzyl ether was used as an acceptor. The yields of toluene, benzaldehyde and benzyl alcohol were determined by GC. Benzene was scarcely produced.

Results and Discussion

It has already been reported that benzophenone accepted hydrogen from tetralin as follows:[5]

$$2\mathrm{Ph_2CO} \xrightarrow{\text{donor}} 2\mathrm{Ph_2CHOH} \longrightarrow \mathrm{Ph_2CO} + \mathrm{Ph_2CH_2} + \mathrm{H_2O}. \qquad (1)$$

Table 1. The Effect of Hydrogen Shuttlers on the Hydrogen Transfer Reaction[a] from Tetralin to Benzophenone (BZP)

Shuttler	Conv. of BZP/mol%	Yield of DPM[b]/mol%	Yield of BZH[b]/mol%
None	36.3	32.9	2.0
None	37.5	33.5	2.0
1-Methyl-naphthalene	35.5	32.9	2.6
Anthracene	59.8	56.4	≈0
Phenanthrene	35.1	27.5	2.1
Pyrene	44.6	36.0	5.5
Fluorene	49.2	39.2	8.6
Triphenylmethane	40.2	33.1	5.0

a) Shuttler (1 g), tetralin (10 g) and benzophenone (1 g) were used. Reaction temperature 430 °C; initial nitrogen pressure 3MPa; reaction time 1 h. b) DPM= Diphenylmethane, BZH=benzhydrol.

In this work 36—38% of the benzophenone was hydrogenated by tetralin at 430 °C for 1 h (Table 1). Diphenylmethane is thermally stable, whereas benzhydrol is considered to be an unstable intermediate. When the mixture of benzhydrol and 1-methylnaphthalene was heated at 270 °C in a nitrogen atmosphere for 1 h, over 50% of the benzhydrol disproportionated to diphenylmethane and benzophenone. Actually, in the reaction of tetralin with benzophenone, the yield of benzhydrol was only 2%. Polyaromatic nondonor solvents such as 1-methylnaphthalene, anthracene, phenanthrene, pyrene, and fluorene were used to rank their shuttling ability. Triphenylmethane was also used because we had already confirmed that it accelerated the decomposition of bibenzyl in spite of a nondonor.[6] The ranking according to the degree of the reduction of benzophenone is as follows:

Anthracene > fluorene > pyrene > triphenylmethane > 1-methylnaphthalene≅phenanthrene.

We must pay attention to the fact that the two benzhydrol molecules disproportionate and produce one benzophenone molecule. Therefore, the total yield of products must be considered as the summation of the yield of diphenylmethane and one half of the yield of benzhydrol. The total yield of the products was 1.3 to 6.6% lower than the conversion of benzophenone. This indicates the presence of undetermined compounds. The high shuttling ability of anthracene is closely related to the fact that anthracene can be readily hydrogenated to dihydroanthracene. When anthracene was reacted with tetralin at 430 °C for 1 h,

Table 2. The Effect of Hydrogen Shuttlers on the Hydrogen Transfer Reaction[a)] from Tetralin to Dibenzyl Ether (DBE)

Shuttler	Conv. of DBE /mol%	Yield of TOL[b)] /mol%/2	Yield of BZA[b)] /mol%/2	Yield of BYA[b)] /mol%/2
None	21.4	8.7	7.5	3.5
None	21.8	7.2	5.8	5.1
1-Methylnaphthalene	21.3	8.8	6.9	5.6
Anthracene	60.4	21.6	22.4	7.1
Phenanthrene	33.4	14.5	12.0	5.9
Pyrene	36.9	8.5	8.7	3.5
Fluorene	41.4	17.4	15.8	8.2
Triphenylmethane	38.3	9.3	12.8	4.8

a) Shuttler (1 g), tetralin (10 g) and dibenzyl ether (1 g) were used. Reaction temperature 375 °C; initial nitrogen pressure 3MPa; reaction time 1 h. b) TOL= Toluene, BZA=benzaldehyde, BYA=benzyl alcohol.

26% of the anthracene was hydrogenated to dihydroanthracene. Dihydroanthracene is a hydrogen donor which was confirmed in a reaction with benzophenone. When dihydroanthracene (1 g) was heated with benzophenone (1 g) in 1-methylnaphthalene (10 g), 31.3% of the benzophenone was reduced. In blank tests (Table 1), 36—38% of the benzophenone was reduced by tetralin; however, the injection weight of tetralin was 10 times that of dihydroanthracene. The same mechanism, including the dihydroaromatic compound, may be applied to pyrene.

The high conversions noted for fluorene and triphenylmethane can possibly account for the high reactivity of their benzylic hydrogen.[7)]

It is well-known that intermolecular (2) and intramolecular (3) reactions are involved in the dibenzyl ether thermolysis.[8)]

$$PhCH_2OCH_2Ph \longrightarrow PhCH_2\cdot + \cdot OCH_2Ph \xrightarrow{\text{donor}} PhCH_3 + HOCH_2Ph \qquad (2)$$

$$PhCH_2OCH_2Ph \longrightarrow PhCH_3 + OHCPh. \qquad (3)$$

That two free radicals resulting from the fission of a C-O bond possess a higher dehydrogenation ability than benzophenone. Table 2 shows the effect of the hydrogen shuttler on the hydrogenation reaction of dibenzyl ether in tetralin. The yield of benzaldehyde is higher and the yield of toluene is lower than that expected from Reactions 2 and 3. This may be due to further reactions of benzyl alcohol and the benzyl radical to benzaldehyde and undetermined compounds.[9)] The ranking for the dibenzyl ether conversion is

anthracene > fluorene > triphenylmethane > pyrene > phenanthrene > 1-methylnaphthalene.

This is almost similar to that of Table 1, except for triphenylmethane and phenanthrene. It is considered that triphenylmethane readily donates hydrogen and that the resulting triphenylmethyl radical initiates the bond fission of dibenzyl ether as a molecule-induced homolysis.[7)] This indicates the possibility of an overestimation of the triphenylmethane shuttling ability if the ability is estimated only from the ranking for the dibenzyl ether conversion. Although the mixture of phenanthrene and tetralin was heated at 430 °C for 1 h, dihydrophenanthrene was scarcely produced. Furthermore, only 9.8% of the benzophenone was reduced when dihydrophenanthrene (1 g) was heated with benzophenone (1 g) in 1-methylnaphthalene (10 g). This indicates that the hydrogen-shuttling mechanism through dihydrophenanthrene is minor. Another mechanism, in which phenanthrene donates hydrogen to a free radical and the resulting phenanthryl radical abstracts hydrogen from tetralin, is possible.

From these results, using different types of hydrogen acceptors, the hydrogen-shuttling ability of the liquefaction solvent could be evaluated as follows:

anthracene > fluorene > pyrene ≅ triphenylmethane > phenanthrene > 1-methylnaphthalene.

It appears that the presence of the hydrogen shuttler constitutes a necessary and important component of coal conversion. A more effective solvent for coal liquefaction can be prepared by determining the capabilities of various solvents.

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