Thermal Decomposition of Coal-related Aromatic Compounds in Hydrogen-donating Solvent

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In order to elucidate the reaction mechanism of coal dissolution in the hydrogen-donating solvent, twenty aromatic compounds related to coal were treated at 450 °C in the presence of tetralin. Diphenylmethane and bibenzyl slowly decomposed giving alkylbenzenes almost quantitatively. Diphenylmethanol and benzophenone were hydrogenated to diphenylmethane, and benzyl phenyl ketone to a mixture of diphenylmethane and bibenzyl. Diphenyl ether and dibenzofuran are very stable, di-2-naphthyl ether decomposing slowly and benzyl phenyl ether or dibenzyl ether very rapidly. The conversion of aromatic compounds by thermolysis can be correlated as a function of bond dissociation energy. The bond rupture of coal-related polynuclear aromatic compounds at 450 °C was concluded to occur mainly at methylene or ether structures. Addition of phenolic compounds or quinoline is very effective for the decomposition of di-2-naphthyl ether. The effect of phenolic compounds and quinoline on the thermal decomposition of aromatic ether was discussed on the basis of stabilization of transition state due to solvation.

Thermal treatment of coal at 400—450 °C in hydrogen-donating solvent results in successful dissolution of coal and high yield of solvent refined coal[1] (SRC) containing small amounts of sulfur compounds and mineral matters. This is a most promising coal liquefaction process because of very simple and non-catalyzed reaction.

However, the fundamental chemistry of coal liquefaction has received little attention, a very limited number of compounds[2,3] being subjected to thermal treatment. Recently, the thermolysis[4-6] of a number of diarylalkanes and phenolic compounds was studied to elucidate the reaction mechanism.

The most important and interesting reaction in coal liquefaction[7,8] should be the deoxyganation and subsequent dissolution reaction of coal, which starts at 400 °C and almost finishes at 450 °C, resulting in the formation of the solvent refined coal with carbon contents of 86—88% on maf basis independent of coalification grade of the feed coal. Oxygen containing structures should play an important part in the coal liquefaction reaction. It is essential to know what kinds of oxygen containing structure are decomposed and what kind of structure is formed at coal liquefaction temperatures.

We wish to report in this work on the thermal decomposition of diaryl ethers along with other types of coal model structure, and also on the additive effect of phenols and quinoline for the scission of ether linkage. We found that a diaryl ether with polynuclear aromatic is decomposed at coal liquefaction temperature, and that phenols[9] accelerate the liquefaction of coal strongly depending on the character of coal. The effect of additives would be most important for finding out good solvent character for coal liquefaction.

Experimental

Tetralin and 1-methylnaphthalene of reagent grade were used after washing with sulfuric acid, alkali, and water and the subsequent distillation at 70 °C under reduced pressure. Various additives and model compounds were of grade. Some of them were used after recrystallization.

Samples were put into a 300 ml magnetic stirring (500 rpm) autoclave. After being pressurized with 15 kg/cm^2 of hydrogen, the autoclave was heated to the reaction temperature within 45 min and maintained at the temperature for the desired reaction time.

At the completion of a run, the autoclave was cooled by an electric fan to room temperature and the autoclave gases were vented through a gas meter and analyzed by gas chromatography. Liquid portions of the samples were subjected to gas chromatographic analysis in order to determine the composition of solvent.

Results and Discussion

Thermal Treatment of Tetralin and 1-Methylnaphthalene. In order to investigate the stability of solvent, thermal treatment of tetralin and 1-methylnaphthalene was carried out at 450 °C for 30 min. Their conversion was 3.0 and 1.5%, respectively, indicating that they are very stable under the reaction conditions.

The consumed tetralin was explained to be converted into naphthalene (23%), decalin (40%) and alkylbenzenes (30%), although thermal decomposition of tetralin has been reported by many workers[6,10,11] to yield dihydronaphthalene, decalin, methylindane and ethylbenzene. Only 44% of consumed 1-methylnaphthalene was recovered as naphthalene, indicating considerable formation of polymerized products according to GLC analysis.

Thermal Treatment of Various Aromatic Compounds. In order to study the reaction of coal structure, twenty aromatic compounds were chosen as the coal model and treated at 450 °C. Conversion of the reaction and the detected products are given in Table 1.

Polynuclear aromatic was found to be partially hydrogenated by tetralin. Heredy and coworkers[12] demonstrated that –CHR–, $-CH_2-$, and $-CH_2-CH_2-$ bridges connect aryl groups in coal. However, diphenylmethane and bibenzyl were thermally decomposed slowly giving benzene and toluene almost quantitatively.

Recently, the thermal decomposition of diarylalkanes such as bibenzyl and 1,3-diphenylpropane has been studied by Sato and coworkers[6] and Collins and coworkers.[4,5] These compounds were confirmed to decompose into alkylbenzenes very slowly as a function of carbon chain length at 400 °C.

Table 1. Reaction products from the thermal treatment of aromatic compounds related to coal in the presence of tetralin

Charge (mmol)				Reaction conditions		Conversion (%)		Product (mol % to reacte model compound)
Model compound		Tetralin	1-Methylnaphthalene	Temp (°C)	Time (min)	Model compound	Tetralin	
Naphthalene	78.1	226	—	450	60	2.8	7.2	—
1-Methylnaphthalene	141.0	217	—	450	30	3.3	8.3	—
Phenanthrene	16.9	301	—	450	60	0.8	9.1	9,10-Dihydrophenanthrene 70
Diphenylmethane	6.1	220	141	450	30	1.7	8.0	Benzene 100, Toluene 95
Bibenzyl	16.6	217	140	450	30	31.1	11.2	Toluene 207
Bibenzyl	27.5	300	—	450	60	54.1	21.4	Toluene 194
Diphenyl ether	5.9	220	141	450	30	0	8.0	—
Benzyl phenyl ether	5.4	287	80	400	30	100	12.7	Toluene 71, Phenol 66, Benzyl phenol 17
Dibenzyl ether	5.1	220	141	400	30	65	9	Toluene 100, PhCHO, PhH, $PhCH_2OH$
Di-2-naphthyl ether	11.2	228	141	450	60	12.6	11.9	2-Naphthol 84
Dibenzofuran	6.1	218	141	450	30	3.3	12	—
Benzyl benzoate	4.7	219	141	450	30	100	13.1	Benzene 53, Toluene 98
Benzophenone	5.7	224	141	450	30	29.4	11.2	Diphenylmethane 100
Benzyl phenyl ketone	16.2	435	—	450	30	25.3	9.1	Bibenzyl 37, Diphenylmethane 37, Benzene 5, Toluene 7
1-Naphthol	7.1	223	141	450	30	1.4	10.7	—
2-Naphthol	6.9	214	141	450	30	1.4	11.2	—
Diphenylmethanol	5.7	218	141	450	30	79	10.2	Diphenylmethane 96
1,4-Naphthoquinone	6.4	218	141	450	30	100	16.2	1-Naphthol 74, Naphthalene
2-Naphthoic acid	5.5	218	141	450	30	100	9.3	Naphthalene
Diphenylamine	6.1	218	141	450	30	8.2	12.4	Benzene 60, Aniline(trace)
Diphenyl sulfide	5.6	222	141	450	30	10.7	10.8	Benzene 183

When the molar ratio of tetralin to a mixture of 1-methylnaphthalene and tetralin were increased from zero to 1.0, the conversion of bibenzyl increased from 14 to 30%. This can be attributed to the capability of hydrogen donation of solvent, since the conversion reaches almost a constant value at the equimolar mixture of tetralin and 1-methylnaphthalene.

Although diphenyl ether and dibenzofuran were very stable at 450 °C, di-2-naphthyl ether decomposed slowly and benzyl ethers completely.

The apparent activation energy for the thermal decomposition of benzyl phenyl ether was calculated to be about 50 kcal/mol from the data obtained at 320—350 °C, since the first order rate constants were 1.39×10^{-4} at 320 °C, 5.19×10^{-4} at 340 °C and 9.52×10^{-4} s^{-1} at 350 °C, respectively.

These results indicate that highly aromatic ether linkages will be broken to a great extent at coal liquefaction temperatures resulting in a main source of phenolic groups of the dissolved coal.

Naphthols were confirmed to be very stable against thermal treatment. Diphenylmethanol and benzophenone were stable against decomposition but hydrogenated to form diphenylmethane quantitatively. Benzyl phenyl ketone was found to be paritally hydrogenated or decarbonylated to form diphenylalkanes. 1,4-Naphthoquinone was completely eliminated and hydrogenated to naphthol and dihydroxynaphthalene as reported by Brower.[13]

Carboxylic acid and carboxylate were completely decarboxylated to the parent hydrocarbons. Carboxylic acid is quite stable in a glass apparatus, but decomposes completely in a stainless steel autoclave.[13]

Generally, the conversion of aromatic compounds by thermal treatment can be correlated as a function of bond dissociation energy of the weakest structure of the substrate as shown in Table 2 and Fig. 1. A few exceptions observed in the cases of benzophenone, benzyl benzoate and naphthoic acid can be ascribed to hydrogenation or the wall effect.

Effect of Phenolic Compounds on the Thermal Decomposition of Aromatic Ethers. According to the results given in Table 1, the bond scission of oxygen containing polynuclear aromatic structure of coal at coal liquefaction

Table 2. Bond dissociation energies of ten aromatic compounds

Structure of bond	Bond dissociation energy (kcal/mol)	Remark
$PhCH_2$–Ch_2Ph	64.5	Ref. 14, 15
$PhCH_2$–Ph	78.4	Ref. 15
PhO–Ph	86.0	Ref. 14, 15
PhO–CH_2Ph	50	Ref. 16
PhCOO–CH_2Ph	66.4	Ref. 14
PhCO–Ph	87.5	Ref. 16
Naph–CH_3	100	Ref. 14
Ph_2CH–OH	78	Ref. 14
Ph–Ph	118.1	Ref. 16
$PhCH_2CO$–CH_2Ph	65.4	Ref. 14

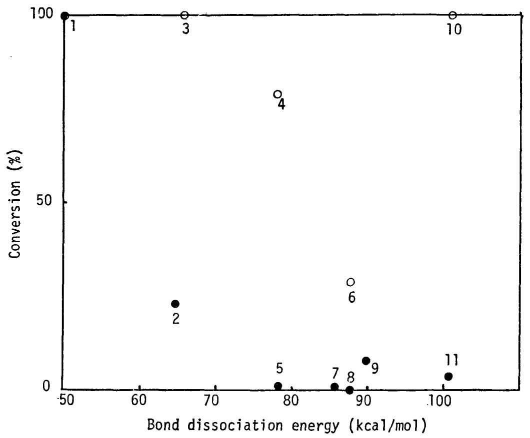

Fig. 1. Relation between the bond dissociation energy and the conversion of aromatic compounds.
1: Benzyl phenyl ether, 2: bibenyl, 3: benyl benzoate, 4: diphenylmethanol, 5: diphenylmethane, 6: benzophenone 7: diphenyl ether, 8: naphthol, 9: diphenylamine, 10: 2-naphthoic acid, 11: 1-methylnaphthalene.

temperature 400—450 °C seems to occur mainly at methylene or ether structures. Thus, a study of the characteristics of these structures in the thermolysis is important.

It has been proposed that the units of coal structure are linked by ether linkages.[17,18] Recently, Ruberto and his coworkers[19] concluded that a significant portion of the oxygen in solid subbituminous coal occurs in saturated ether functional groups α- or β- to the aromatic moieties or as furan systems. Ignasiak and Gawlak[20] concluded from the increase in hydroxyl functions in the protonated coal concentrate that for each 4.6 ruptured covalent bond two were ether linkages.

As shown in Table 1 the decomposition of di-2-naphthyl ether proceeds slowly. We have chosen this ether and studied in detail the effect of various phenols on the decomposition of the aromatic ether since phenols remarkably enhance coal dissolution among the several types of oxygenated compounds.[9]

The thermal decomposition of bibenzyl is not affected by the addition of phenol or *p*-cresol (Table 3). In contrast, the decomposition of di-2-naphthyl ether increases remarkably in the presence of phenolic compounds (Table 4). The effect seems to increase with increase in the electron donating property of substituent on the benzene nucleus.

The effect of hydroquinone and *p*-methoxyphenol is remarkable. However, no decisive argument can be made since they can not be recovered sufficiently, indicating that very complicated side reactions take place.

Although 1-naphthol is quite stable against thermal decomposition (Table 1), its recovery after the thermolysis of dinaphthyl ether is not successful. This is in line with our previous findings[9] that about half the amount of naphthol can be recovered after the dissolution of coal in contrast to the very high recovery of phenol and *p*-cresol. This indicates that a naphthyloxyl radical is decomposed into alkylbenzene or alkylnaphthalene after reacting with some other free radicals.

Phenolic compounds might enhance the rate of decomposition of aromatic ether by solvating transition state of the scission of ether linkage and by hydrogen transfer to the formed alkoxyl radicals.

Effect of Quinoline. Quinoline shows no effect on the decomposition of bibenzyl, but considerably increases the conversion of dinaphthyl ether as in the cases of phenols (Tables 3 and 4).

The yield of 2-naphthol from dinaphthyl ether was

TABLE 3. EFFECT OF PHENOL AND QUINOLINE ON THE THERMAL DECOMPOSITION OF BIBENZYL AT 450 °C FOR 60 min

Charge (mmol)				Conversion (%)		
Phenol		Bibenzyl	Tetralin	Bibenzyl	Tetralin	Phenol
1-Methylnaphthalene	70.2	16.7	225.7	35.5	12.3	5.7
Phenol	107.1	16.5	226.2	33.1	12.2	1.5
Quinoline	76.8	16.6	226.1	35.6	10.9	18.6

TABLE 4. EFFECT OF PHENOLS AND QUINOLINE ON THE THERMAL DECOMPOSITION OF DI-2-NAPHTHYL ETHER AT 450 °C FOR 60 min

Charge (mmol)				Conversion (%)		Yield (mol % to reacted ether)
Phenols or quinoline		Di-2-naphthyl ether	Tetralin	Dinaphthyl ether	Phenol or quinoline	2-Naphthol
1-Methylnaphthalene	141	11.2	228.4	11.5	5.0	67.4
Phenol	210	11.1	230.0	17.1	1.5	57.2
p-Cresol				21.0		
p-Methoxyphenyl[a]	135.3	14.5	225.5	49.5	100	61.3
p-Phenylphenol	117.6	11.1	225.7	34.1	0	54.2
2,4,6-Trimethylphenol	147.0	11.3	226.1	26.0	3.5	30.0
1-Naphthol	138.7	11.2	225.7	33.7	22.1	—
Hydroquinone[b]	182	11.2	225.8	63.4	57.7	24.0
Quinoline	154	11.2	226.5	23.6	22.1	7.0

a) *p*-Methoxyphenol was converted into phenol, hydroquinoline, and benzene. b) Hydroquinone was mostly converted into phenol and benzene.

lowered in the presence of quinoline, suggesting that a considerable amount of naphthyloxyl radical was reacted with quinoline as a result of close interaction between the ether and quinoline during the course of thermal decomposition reaction.

Accelerating Effect Due to Additives on the Rupture of Ether Linkage. Phenols are weak acids and polar solvent, and often enhance the thermal decomposition of covalent bond. However, we could observe no accelerating effect due to phenol on the decomposition of bibenzyl. Pyridine bases accelerate the depolymerization of coal.[10,21] Thus, phenols and quinoline should participate directly in the scission of ether linkage.

Huyser and Van Scoy[22] observed that the thermal decomposition of di-*t*-butyl peroxide is remarkably accelerated in acetic acid or *t*-butyl alcohol. They ascribed this effect to the solvation of *t*-butoxyl radical by the solvents.

Mahoney and Da Rooge[23] found that the hydrogen abstraction from phenols by phenoxyl radicals proceeds very rapidly in spite of very low enthalpy change. Howard and Furimsky[24] suggested that the hydrogen atom transfer between peroxyl radical and phenol involves the formation of a hydrogen bonded free radical reactant complex.

A phenoxyl radical from the thermal decomposition of aromatic ether can be stabilized by solvation or hydrogen bonding with phenolic compounds, giving rise to the subsequent hydrogen transfer reaction from phenols or hydrogen donor solvents.

Stabilization of the transition state of bond dissociation or the formed alkoxyl radical might be the best explanation for the rate enhancement, since quinoline also remarkably accelerates the decomposition of dinaphthyl ether. Alkoxyl radical would be electron donor and phenols or quinoline electron acceptors.

In view of bond dissociation energy, phenolic compounds having electron supplying substituent such as naphthol and *p*-methoxyphenol can be easily converted into phenoxyl radicals by reacting with the phenoxyl radicals resulting from the thermal decomposition of ether structure, and will result in further decomposition reaction including deoxygenation reaction.

Easiness of bond rupture of an ether depends strongly on its chemical structure. Diphenyl ether and dibenzofuran are quite stable against thermal treatment at 450 °C, while dibenzyl ether and benzyl phenyl ether can be completely decomposed at 400 °C.

Almost all $-CH_2-O-$ linkages in coal structure would be ruptured at temperatures below 400 °C and diaryl ether with polynuclear aromatic moderately at coal liquefaction temperatre. Some coals containing aliphatic ether structure would be decomposed remarkable at lower temperatures and their decomposition would not be affected by the addition of phenols or pyridine bases. Some coals containing polynuclear aromatic diaryl ethers would be decomposed effectively by the addition of phenolic compounds or pyridine bases.

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