THERMAL TREATMENT OF COAL-RELATED AROMATIC ETHERS IN TETRALIN SOLUTION

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INTRODUCTION

The important elementary reactions of coal liquefaction are the decomposition of coal structure, the stabilization of fragments by the solvent and the dissolution of coal units into the solution.

These reactions proceed smoothly in the presence of hydrogen donating aromatic solvent (1-4) at temperatures from 400°C to 450°C, resulting in the formation of so called solvent refined coal with carbon content of 86-88% on maf basis independent of coalification grade of feed coal.

While, oxygen containing structures of coal must be playing important parts in the course of coal liquefaction. It will be key points that what kinds of oxygen containing structure are decomposed and what kinds of structure are formed in the course of reaction. It has been proposed (5,6) and recently stressed (7-11) that the units of coal structure are linked by ether linkage.

We have studied the thermal decomposition of diaryl ether in detail, since the cleavage of ether linkage must be one of the most responsible reactions for coal liquefaction among the various types of decomposition reaction and we found that the C-O bond of polynucleus aromatic ethers is cleaved considerably at coal liquefaction temperature.

EXPERIMENTAL

Tetralin and 1-methylnaphthalene were reagent grade and 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 reagent grade, and some of them were used after recrystallization. Phenyl naphthyl ether and phenyl 9-phenanthryl ether were synthesized by refluxing a mixture of aryl bromide, phenol, Cu_2O and γ-collidine (12).

Samples were added to 300 ml or 90 ml magnetic stirring (500 rpm) autoclaves. After pressurizing with 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 electric fan to room temperature and the autoclave gases were vented through gas meter and analyzed by gas chromatography. Liquid portions of the samples were subjected to gas chromatographic analysis to determine the composition of products.

RESULTS AND DISCUSSION

Thermal treatment of various aromatic compounds

In order to study the reaction of coal structure, various aromatic compounds were chosen as the coal model and treated at 450°C. The conversion of the reaction along with the detected products were shown in Table 1.

Recently, the thermal decomposition of diaryl alkanes such as dibenzyl and 1,3-diphenylpropane has been studied by Sato and coworkers (13), Collins and coworkers (14). These compounds were confirmed to be decomposed to alkylbenzenes gradualy as a function of carbon chain length.

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

The apparent activation energy for the thermal decomposition of phenyl benzyl ether was calculated to be about 50 kcal/mole from the data obtained at 320-350°C.

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

Phenolic compounds were confirmed to be very stable against thermal treatment. Diphenyl methanol and benzophenone were stable against decomposition but hydrogenated to form diphenylmethane quantitatively. Phenyl benzyl ketone was found to be partially hydrogenated or decarbonylated to form diphenyl alkanes.

Naphthoquinone was completely eliminated and hydrogenated to naphthol and dihydroxynaphthalene as reported by Brower (15).

Carboxylic acid and carboxylate were completely decarboxylated to the parent hydrocarbons. According to Brower, carboxylic acid is quite stable in glass apparatus, but decomposed completely in a stainless steel autoclave.

The thermal decomposition of aromatic ethers

According to the results of Table 1, the bond scission of oxygen containing polynucleus aromatic structure of coal at liquefaction temperature of 450°C seems to occur mainly at methylene or ether structures. Therefore, it will be very important to study the characteristics of these structures in the thermolysis.

It has been often proposed that the units of coal structure are linked by ether linkages. Recently, Ruberto and his coworkers (7,8), Ignasiak and Gawlak (9) concluded that a significant portion of the oxygen in coal occurs in ether functional groups.

Thermal decomposition of seven diaryl ethers at various reaction conditions and the composition of reaction products are shown in Table 2.

The decompositions of phenyl benzyl ether and dibenzyl ether proceeded very rapidly at 400°C, and these results corresponded well to the low bond dissociation energy of $PhCH_2$-O.

Phenyl benzyl ether was mostly converted to toluene and phenol, but partly isomerized to benzyl phenol.

Dibenzyl ether was entirely converted to toluene and benzaldehyde. The formation of products can be explained by the following reaction scheme. $PhCH_2OCH_2Ph \longrightarrow PhCH_2O\cdot + \cdot CH_2Ph \longrightarrow PhCHO + PhCH_3$

$PhCHO \longrightarrow PhH + CO \qquad PhCHO + 2H_2 \longrightarrow PhCH_3$

The high yield of toluene over 100% was confirmed to be due to the hydrogenation of benzaldehyde by tetralin. As shown in Figure 1, the yield of toluene increases with increasing reaction time, on the other hand, benzaldehyde decreases gradually after reaching a maximum value, giving toluene as the hydrogenated product and benzene and carbon monoxide as the decomposition products.

Although diphenyl ether and dibenzofuran were very stable for thermolysis at 450°C for 120 min., the rate of decomposition increased with increasing the number of benzene nucleus, that is, phenyl naphthyl ether was converted to the value of 25% and phenyl phenanthryl ether 46% at the same reaction conditions.

These results strongly suggest that in coal structure the covalent bond of benzyl ethers composed of aliphatic carbon and oxygen will be entirely ruptured at temperatures lower than 400°C, and the covalent bond composed of aromatic carbon and oxygen will be considerably decomposed at 450°C, since the unit structure of bituminous coal is considered to be composed of polynucleus of several benzene rings.

The effect of phenolic compounds on the decomposition of diaryl ethers

It has been known that phenolic compounds (16,17) in the presence of hydrogen-donating solvent have a remarkable effect on the dissolution of coal. Therefore, it is important to clarify the fundamental structure of coal being decomposed effectively by the addition of phenol.

The thermal decomposition of dibenzyl was not affected by the addition of phenol or p-cresol. In contrast, the decomposition of 2,2'-dinaphthyl ether increases remarkably in the presence of phenolic compounds as shown in Table 3, and the effect seems to increase with increasing the electron donating property of substituent on the benzene nucleus.

The effect of hydroquinone and p-methoxyphenol is remarkable, but this seems beyond argument at present because considerable parts of them can not be recovered after reaction, suggesting that very complex side reactions are taking place.

Furthermore, we studied the effect of phenolic compounds on the thermolysis of phenyl benzyl ether at 320°C, because even reactive phenols such as p-methoxy phenol are quite stable at this temperature.

As shown in Table 4, all phenols tested were confirmed to accelerate the conversion of phenyl benzyl ether. In this thermolysis, benzyl phenyl ether was decomposed to toluene and phenol (ca. 60%) and also isomerized to benzyl phenol (ca. 40%).

Accelerating effect due to phenols on the rupture of ether linkages

Phenols are weak acids and polar solvent, and so often observed to enhance the thermal decomposition of covalent bond, but we could not observe any accelerating effect due to phenol on the decomposition of dibenzyl.

Therefore, phenols must be participating directly in the course of scission of ether linkage.

Phenolic compounds may 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 alkoxy radicals.

Previously we have shown that phenolic compounds have a remarkable positive effect (4) on the coal liquefaction in the presence of tetralin, depending strongly on the character of coal as well as on the concentrations of phenols. The effect of phenols on the decomposition of diaryl ethers will give a good explanation for the previous results, because aliphatic ether structures of some young coals will be decomposed rapidly at relatively low temperatures and so the rate of coal dissolution will not be affected by the addition of phenols, on the other hand, the polycondensed aromatic ether structures will be decomposed effectively by the addition of phenols in the course of coal liquefaction.

The effect of mineral matters on the decomposition ethers

Recently, the effect of mineral matters of coal on the coal liquefaction has attracted much attention. It was shown that small amounts of FeS or pyrite are responsible for the hydrogenative liquefaction of coal. Therefore, it is interesting to elucidate the effect of mineral matters of coal on the decomposition rate and products of aromatic ethers, and so three diaryl ethers were thermally treated in the presence of coal ash obtained by low temperature combustion of Illinois No.6 coal.

It was found that the addition of coal ash remarkably accelerates the rate of decomposition of dibenzyl ether and also drastically changes the distribution of reaction products, that is, benzyl tetralin becomes the main reaction product instead of a mixture of toluene and benzaldehyde, as shown in Table 5.

This result is quite surprizing, but can be ascribed to the acidic components of coal ash, since Bell and coworkers (18) reported that benzyl ether acts as an alkylating reagent in the presence of Lewis acid such as $ZnCl_2$.

In the cases of phenyl benzyl ether and phenyl 9-phenanthryl ether, the effect of ash components was not so remarkable.

CONCLUSIONS

Diaryl ether must be one of the important structures responsible for the liquefaction of coal among various oxygen-containing organic structures of coal.

The rate of decomposition of polynucleus aromatic ethers increases with increasing the number of nucleus of aryl structure and are enhanced by the addition of phenolic compounds.

The rate of decomposition and the distribution of products of some diaryl ethers can be affected in the presence of coal ash.

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TABLE 1 THERMAL TREATMENT OF COAL-RELATED AROMATIC COMPOUNDS IN THE PRESENCE OF TETRALIN
(Tetralin 220 mmole, 1-Methylnaphthalene 140 mmole, Model compounds 10 mmole)

Model compounds	Reaction conditions		Coversion(%)	Products (mole% to reacted model compounds)
	Temp. (°C)	Time (min)	Model compounds	
Diphenylmethane	450	30	1.7	Benzene 100, Toluene 95
Dibenzyl	450	30	31.1	Toluene 200
Dibenzyl	450	60	54.1	Toluene 194
Diphenyl ether	450	30	0	———
Dibenzofuran	450	30	3.3	———
Phenyl benzyl ether	400	30	100	see Table 2
Dibenzyl ether	400	30	65	see Table 2
2,2'-Dinaphthyl ether	450	120	23.3	see Table 2
Phenyl 1-naphthyl ether	450	120	25	see Table 2
Phenyl 9-phenanthryl ether	450	120	45.5	see Table 2
Benzyl benzoate	450	30	100	Benzene 53, Toluene 98
Benzophenone	450	30	29.4	Diphenylmethane 100
Benzyl phenyl ketone	450	30	25.3	Dibenzyl 37, Diphenylmethane 37, Benzene 5, Toluene 7
1-Naphthol	450	30	1.4	———
2-Naphthol	450	30	1.4	———
Diphenylmethanol	450	30	79	Diphenylmethane 96
1,4-Naphthoquinone	450	30	100	1-Naphthol 74, Naphthalene
2-Naphthoic acid	450	30	100	Naphthalene
Diphenyl amine	450	30	8.2	Benzene 60, Aniline(trace)
Diphenyl sulfide	450	30	10.7	Benzene 183

TABLE 2 THERMAL DECOMPOSITION OF DIARYL ETHERS IN TETRALIN

Diaryl ether	Temp (°C)	Time (min)	Conversion (%)	Products (mole% of reacted ether)
Diphenyl ether	450	30	0	———
	450	120	2	———
Dibenzofuran	450	30	3.3	———
Phenyl 1-naphthyl ether	450	120	25	PhOH 66
2,2'-Dinaphthyl ether	450	60	12.5	2-Naphthol 84
	450	120	23.3	2-Naphthol 63
Phenyl 9-phenanthryl ether	450	120	45.5	PhOH 50, Phenanthrene 15
Phenyl benzyl ether	320	30	31.4	$PhCH_3$ 55, PhOH 50, Benzylphenol 40
	400	30	100	$PhCH_3$ 61, PhOH 66, Benzylphenol 27
Dibenzyl ether	400	30	65	$PhCH_3$ 106, PhCHO 73, PhH 12

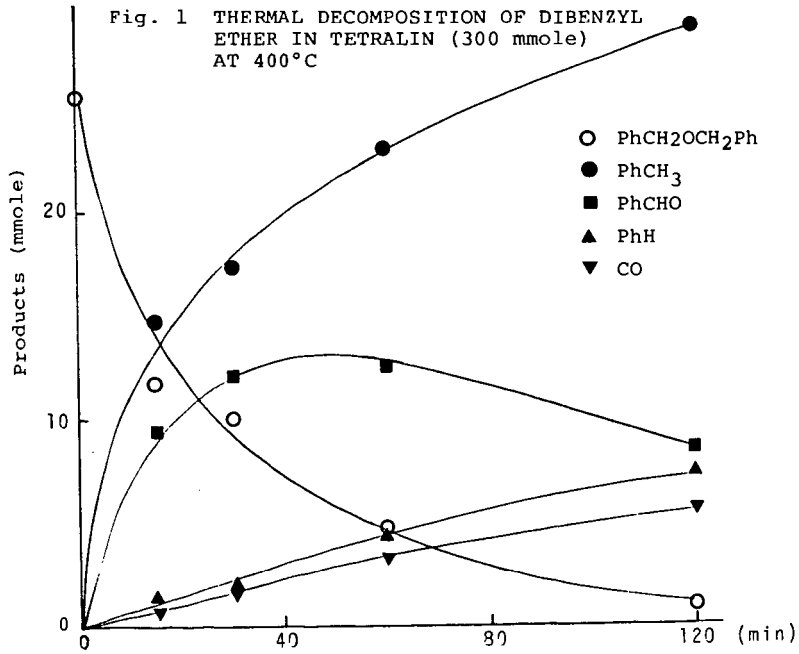

Fig. 1 THERMAL DECOMPOSITION OF DIBENZYL ETHER IN TETRALIN (300 mmole) AT 400°C

TABLE 3 EFFECT OF PHENOLS ON THE THERMAL DECOMPOSITION 2,2'-DINAPHTHYL ETHER AT 450°C FOR 60 MIN
(2,2'-Dinaphthyl ether 11 mmole, Tetralin 225 mmole, Additive 150 mmole)

Additive	Conversion (%) Dinaphthyl ether	Phenol
1-Methylnaphthalene	12.6	—
Phenol	17.1	1.5
p-Cresol	21.0	0
2,4,6-Tremethylphenol	26.0	3.5
1-Naphthol	33.7	22.1
p-Phenylphenol	34.1	0
p-Methoxyphenol	49.5	100
Hydroquinone	63.5	57.7

TABLE 4 EFFECT OF PHENOLS ON THE THERMAL DECOMPOSITION OF PHENYL BENZYL ETHER AT 320°C FOR 30 MIN
(Phenyl benzyl ether 27 mmole, Tetralin 220 mmole, Additive 140 mmole)

Additive	Beznyl phenyl ether	Phenols
1-Methylnaphthalene	31.4	—
p-Cresol	40.2	0
p-Methoxyphenol	44.1	1.1
1-Naphthol	43.0	0

TABLE 5 EFFECT OF COAL ASH ON THE THERMAL DECOMPOSITION OF DIARYL ETHERS
(Ethers 4 mmole, Tetralin 40 mmole)

Ethers	Added Ash(g)	Temp (°C)	Time (min)	Coversion (%)	Products (mole% of reacted ether)
Dibenzyl ether	——	400	30	65	$PhCH_3$ 110, PhCHO 77, PhH 13 Benzyltetralin 2.2
	0.015	400	30	100	$PhCH_3$ 6, PhH trace, Benzyltetralin 152
Phenyl benzyl ether	——	400	30	100	$PhCH_3$ 61, PhOH 66, $PhCH_2Ph$ 6, Benzylphenol 27, Benzyltetralin 2
	0.015	400	30	100	$PhCH_3$ 38, PhOH 58, $PhCH_2Ph$ 3, Benzylphenol 39, Benzyltetralin 13
Phenyl 9-phenanthryl ether	——	450	120	46	PhOH 50, Phenanthrene 17
	0.05	450	120	55	PhOH 45, Phenanthrene 16