

THERMAL CRACKING OF COAL MODEL DIARYL ETHERS IN TETRALIN SOLUTION

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1. INTRODUCTION

Recently, the importance of aromatic ether structure(1,2) in coal molecule has been stressed, and so the thermal cracking of several aromatic ethers has been studied by several workers(3,4), in order to elucidate the coal liquefaction mechanism.

It is known that aliphatic ethers can be easily decomposed, but diaryl ethers such as diphenyl ether are quite stable at temperatures as high as 450°C.

Previously, we have reported that some diaryl ethers with polycyclic aromatic ring(5) were cracked relatively easily at 450°C.

In this paper, we wish to report the effect of ring structure of polycyclic aromatic ether as well as the effect of solvent on the thermolysis of diaryl ether, since aryl ether is one of key structures in coal liquefaction.

2. EXPERIMENTAL

Tetralin and other solvents were reagent grade and used after washing with sulfuric acid, alkali and water and subsequent distillation at 70°C under reduced pressure. Diaryl ethers were synthesized by refluxing a mixture of aryl bromide, phenolic compound, Cu_2O and γ -collidine for reaction time from 100 to 400 hr. According to repeated purification by SiO_2 - Al_2O_3 column and recrystallization, diaryl ethers employed were of purities above 99%.

Solvent and diaryl ether were added to 90 ml magnetic stirring(1000 rpm) autoclave. After pressurizing with hydrogen, the autoclave was heated to reaction temperature within 25 min and maintained at the reaction temperature during the reaction time. At the completion of an experiment, the autoclave was cooled by electric fan to room temperature. The reaction products were subjected to gas chromatographic analysis to determine the yield of products.

3. RESULT AND DISCUSSION

3.1 Thermolysis of dinaphthyl ethers

The conversion of 1,2'- and 2,2'-dinaphthyl ethers in tetralin at 430°C was plotted against the reaction time in Figure 1. Almost linear relations indicate

that the conversion of ethers is of first order with respect to substrate concentration and the first order rate constants are calculated to be 4.7×10^{-5} and $2.8 \times 10^{-5} \text{ sec}^{-1}$ for 1,2'- and 2,2'-dinaphthyl ethers, respectively. The yield of naphthols was plotted against the residence time as shown in Figure 2. The ratio of 1-naphthol to 2-naphthol from 1,2'-dinaphthyl ether was 1 to 4, indicating that 2-naphthoxy radical is favorably formed.

1-Naphthol and 2-naphthol were confirmed to be not so stable at 430°C and their first order rate constants of conversion in tetralin were measured to be 4×10^{-5} and $3.5 \times 10^{-5} \text{ sec}^{-1}$ at 430°C respectively.

On the basis of the above rate constants the cracking rate constant of dinaphthyl ethers to naphthols can be calculated to be 2.3×10^{-5} and $1.25 \times 10^{-5} \text{ sec}^{-1}$ for 1,2'- and 2,2'-dinaphthyl ethers.

3.2 Effect of chemical structure of aryl ether on the reaction rate of thermolysis

Nine kinds of diaryl ether with phenyl, diphenyl, naphthyl, phenanthryl and anthryl groups were treated in tetralin solution at 430°C for 5 hr, as shown in Table 1. Diphenyl ether was very stable, but phenanthryl or anthryl ethers have shown very high conversion values.

Generally, the conversion rate constant of diaryl ethers increased with increasing the number of polycyclic aromatic ring of aryl structure.

The rate of conversion of phenyl aryl ether increased as the following order with respect to aryl group: Phenyl < Diphenyl < 2-Naphthyl < 1-Naphthyl < Phenanthryl < Anthryl.

Apparent ratio of the cracking rate of aryl-oxygen bond of diaryl ether can be calculated on the basis of the rate of formation of phenolic compound from ether along with the rate of elimination of corresponding phenolic compound. Because of very complex reaction system these calculated values in Table 2 can not be evaluated with high accuracy, but it seems to show that the bond dissociation energy of phenyl-oxygen bond is the highest and that of aryl oxygen bond decreases with increasing the number of polycyclic ring.

In order to make clearer the effect of aromatic structure on the rate of cracking, several diaryl ethers were treated in 1-methylnaphthalene, a poor hydrogen donating solvent, at 450°C for 2 hr as shown in Table 3. In this case, the color of solution after reaction was dark brown, indicating that polymerization reaction took place. The order of reactivity of diaryl ethers evaluated by the conversion rate constant was almost the same as the order in tetralin, that is, the rate constant increased with increasing the number of polycyclic aromatic ring of diaryl ether. However, the difference in the relative value of k was larger in tetralin than in methylnaphthalene.

3.3 Solvent effect

Above results lead us to further experiments on solvent effect in cracking

reaction.

As shown in Table 4, the effect of hydrogen donor solvent on the pyrolysis of 2,2'-dinaphthyl ether was most remarkable. In a poor hydrogen donor such as 1-methylnaphthalene, the conversion of dinaphthyl ether was only 23%, but it was increased to 39% in tetralin and to 93% in 9,10-dihydroanthracene. As for n-hexadecane, this compound itself was cracked remarkably at 430°C and so could be a good hydrogen donor because of radical and olefin formations. Decalin also could be a hydrogen donor for hydrogenation of naphthalene nucleus.

The effect of dihydroanthracene was outstanding, and so the conversion rate constant in dihydroanthracene was five times as large as in tetralin. Dihydroanthracene itself was completely converted to other compounds by complex reactions involving dehydrogenation and disproportionation. The accelerating effect due to dihydroanthracene was so great that even diphenyl ether being the most stable diaryl ether was cracked to the conversion of 13.3% at 430°C in 5 hr. It was also observed that the conversion of 2,2'-dinaphthyl ether was proportionally increased with the concentration of dihydroanthracene in 1-methylnaphthalene.

The marked solvent effect by hydrogen donors on the conversion of polycyclic diaryl ethers can be attributed to the hydrogenation of aromatic rings by hydrogen transfer, because the hydrogen transfer reaction really occurs and the cracking of aliphatic ether proceeds very rapidly. A mixture of partially hydrogenated products from 2,2'-dinaphthyl ether by Pd-Pt catalyst was found to be cracked more rapidly than dinaphthyl ether.

Another interesting solvent effect was observed in the case of naphthol, that is, the rate constant of conversion of 2,2'-dinaphthyl ether was increased from 2.8×10^{-5} to $7.8 \times 10^{-5} \text{ sec}^{-1}$ by the addition of 26g of 1-naphthol.

It is known that hydrogen donor such as tetralin can partially hydrogenate aromatic nucleus(5) but not effective for the cracking of resulting aliphatic structure. Therefore, the main role of hydrogen donor solvent in coal liquefaction has been ascribed to the hydrogenation and stabilization of coal fragments being thermally produced.

If hydrogen donor only plays a role stabilizing coal fragments, it would not be so effective for the thermal cracking of coal and the successive oil formation reaction.

The remarkable effect of hydrogen donor on the cracking of polycyclic aromatic ethers would be a good explanation for the effective degradation of coal molecule in the presence of hydrogen donor solvent.

4. CONCLUSION

Nine kinds of diaryl ether were thermally cracked at 430°C in tetralin or 1-methylnaphthalene solutions and the following conclusions were obtained.

1. The rate of conversion of diaryl ether increased with increasing the number of polycyclic aromatic ring of the ether.
2. The cracking reaction of diaryl ether was of first order with respect to ether concentration.
3. In the case of phenyl polycyclic aryl ethers, phenol was preferably formed rather than the other polycyclic aromatic phenols as cracking products.
4. Hydrogen donor solvent and naphthol accelerated remarkably the cracking reaction of diaryl ethers.

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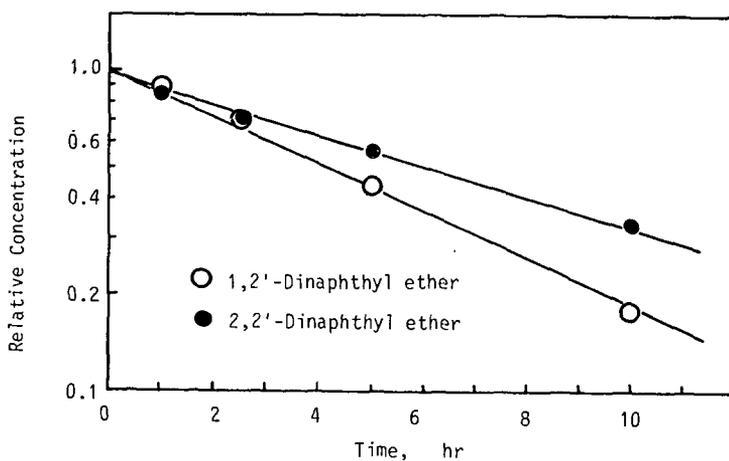


Figure 1. Thermal Cracking of Dinaphthyl Ethers in Tetralin at 430°C.
 (Ether 5.0g, Tetralin 30 ml, Initial P_{H_2} 50 kg/cm²)

TABLE 1 THERMAL CRACKING OF DIARYL ETHERS IN TETRALIN AT 430°C FOR 5 HR
 (Ether 5.0g, Tetralin 30 ml, Initial P_{H_2} 50 kg/cm²)

Ether	Conversion(%)	$k^*1, 10^{-6} \text{sec}^{-1}$	Relative Value of k	Products Yield(mole%)
Diphenyl ether	3.0	1.7	1.0	Phenol 0.84
4-Phenoxy diphenyl	7.6	4.4	2.6	Phenol 1.51 4-Phenylphenol 1.65
2-Phenoxy naphthalene	12.8	7.6	4.5	Phenol 4.64 2-Naphthol 1.16
1-Phenoxy naphthalene	38.0	26.6	15.7	Phenol 17.0 1-Naphthol 1.67
9-Phenoxy phenanthrene	53.0	42.0	24.9	Phenol 27.1 9-Phenanthrol 4.12
9-Phenoxy anthracene	(>99.9)	(>3840)	(>2260)	Phenol 72.8 Anthrone 0.53
2,2'-Dinaphthyl ether	39.2	27.6	16.3	2-Naphthol 12.8 1,2'-Dinaphthyl ether 4.7
1,2'-Dinaphthyl ether	57.0	46.9	27.8	2-Naphthol 19.5 1-Naphthol 4.6 2,2'-Dinaphthyl ether 2.2
2-Naphthyl-9-phenanthryl ether	66.1	60.1	35.5	2-Naphthol 19.1 9-Phenanthrol 4.4

*1; First order rate constant.

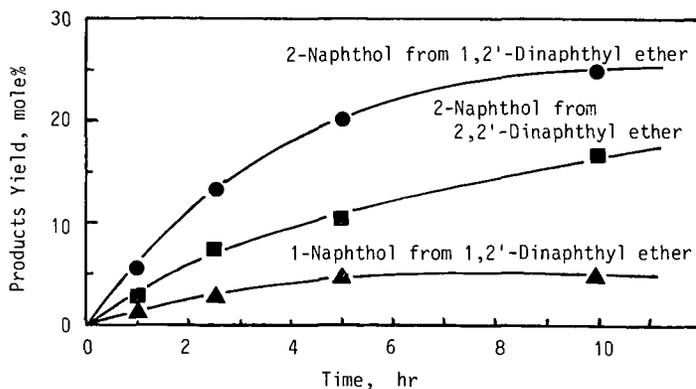


Figure 2. Reaction Products from Thermal Cracking of Dinaphthyl ether in Tetralin at 430°C.
 (Ether 5.0g, Tetralin 30 ml, Initial P_{H_2} 50 kg/cm²)

TABLE 2 THERMAL CRACKING RATE CONSTANT OF DIARYL ETHER

Diaryl Ether	Cleaved Aryl-Oxygen Bond	First Order Rate Constant $k, 10^{-6} \text{ sec}^{-1}$
Diphenyl ether	Phenyl-Oxygen	0.52
1-Phenoxy naphthalene	1-Naphthyl-Oxygen	13.0
	Phenyl-Oxygen	1.7
2-Phenoxy naphthalene	2-Naphthyl-Oxygen	3.1
	Phenyl-Oxygen	1.0
1,2'-Dinaphthyl ether	1-Naphthyl-Oxygen	22.6
	2-Naphthyl-Oxygen	5.6
2,2'-Dinaphthyl ether	2-Naphthyl-Oxygen	12.5

TABLE 3 THERMAL CRACKING OF DIARYL ETHERS IN 1-METHYLNAPHTHALENE AT 450°C FOR 2 HR
(Ether 5.0g, Solvent 30 ml, Initial P_{Ar} 50 kg/cm²)

Diaryl Ether	Conversion(%)	$k, 10^{-5} \text{ sec}^{-1}$	Relative Value of k
Diphenyl ether	8.3	1.2	1.0
2-Phenoxy naphthalene	22.2	3.5	2.9
1-Phenoxy naphthalene	68.2	15.9	13.3
9-Phenoxy phenanthrene	81.1	23.1	19.3
2,2'-Dinaphthyl ether	38.7	6.8	5.7
1,2'-Dinaphthyl ether	80.0	22.4	18.7

TABLE 4 EFFECT OF SOLVENT ON THE THERMAL CRACKING OF 2,2'-DINAPHTHYL ETHER
AT 430°C FOR 5 HR
(Ether 5.0g, Solvent 30 ml, Initial P_{H_2} 50 kg/cm²)

Solvent	Conversion of Ether(%)	$k, 10^{-6} \text{ sec}^{-1}$
1-Methylnaphthalene	23	14
n-Hexadecane	31	20
cis-Decalin	38	27
Tetralin	39	28
9,10-Dihydroanthracene	93	153