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Model Compound Studies of Coal Liquefaction with Zinc–Butyl Iodide under Mild Conditions

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A number of model compounds having representative coal structures were treated with zinc–butyl iodide under mild conditions. Gas chromatography and gas chromatography/mass spectrometry were used to identify the reaction products. Polynuclear aromatic compounds gave the butyl-substituted and butyl-addition products. In a reaction of anthracene, its aromatic backbone was cleaved. Alkoxynaphthalene and dibenzyl ether were butylated along with cleavage of ether linkage, while diphenyl ether gave only the butyl-substituted products without cleavage. Butylation and cleavage also took place in the reactions of diphenylmethane and bibenzyl. In the cases of substitution reaction, some butyl groups were rearranged to *s*-butyl. Because the formation of the most reaction products is interpreted by a similar mechanism to that of Friedel–Crafts alkylation and the formation of some butyl-addition products of polynuclear aromatic compounds is explained by assuming a radical reaction mechanism, it is suggested that both alkyl cation reaction and alkyl radical reaction occur competitively.

A new coal liquefaction concept has recently been developed: Depolymerization of coal by use of zinc metal and butyl iodide under atmospheric pressure at 130 °C.[1] This method can effectively convert coal to benzene-soluble products under mild conditions. For example, Kairan coal (carbon content, 87.2%) can be solubilized in benzene to the extent of 96.7% by this method. The effectiveness of the zinc–butyl iodide for depolymerization of coals has stimulated a further investigation into the mechanism of the conversion. An advantage of coal conversion study using model compounds is that both the starting materials and products are easily characterized by simple analytical techniques.

In the present study, some polynuclear aromatic compounds, aryl ethers, diphenylmethane, and bibenzyl have been treated with zinc–butyl iodide and the products were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry.

Experimental

The model compounds used in the present study were commercially available and used without further purification except anthracene which was recrystallized. The butylation reaction was carried out as follows: 11.9 mmol of a model compound, 8 g of zinc metal powder and 30 ml of butyl iodide were placed in a three-necked flask attached with a reflux condenser and a Teflon stirrer. While being agitated, the mixture was heated at 130 °C for 5 h under nitrogen stream in an oil bath. The reaction mixture was cooled to room temperature, and then extracted with benzene or pentane. After removing the solvent the products were analyzed by a Hitachi model 163 gas chromatograph (glass capillary column, 12 m×0.28 mm; SE-52) equipped with a YANACO model S-1000 integrator and by a JEOL model JMN-D3000 GC-MS (25 m×0.25 mm; SE-52).[2,3] Naphthalene and phenanthrene were used as internal standards.

Results and Discussion

The model compounds were selected on the basis of the structural information on coals. From time to time, various structures of coals have been suggested, depending upon the extent of knowledge available at the time; e.g., those suggested by Given,[4,5] Hill and Lyon,[6] Wiser,[7] and Heredy and Wender.[8] As coal has no uniform composition, the most widely

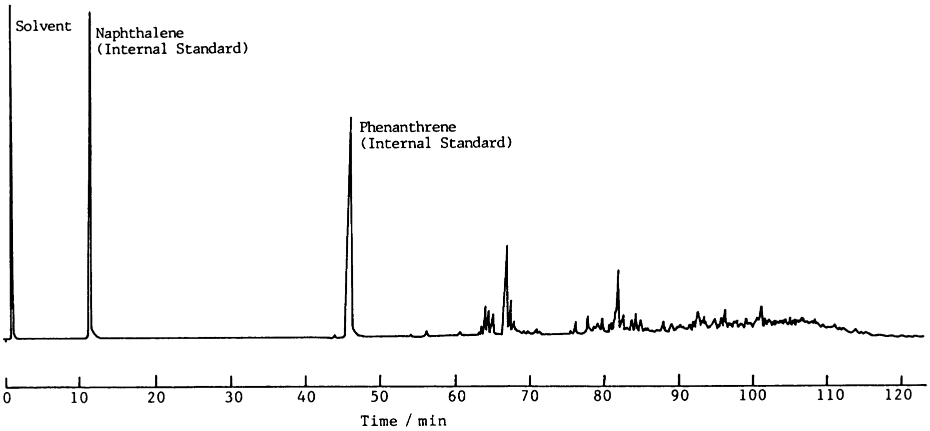

Fig. 1. Gas chromatogram of the products of phenanthrene.

Table 1. Results of the Butylation Reaction of Polynuclear Aromatic Compounds

	Reactant			
	1-Methylnaphthalene	Acenaphthene	Phenanthrene	Anthracene
Conversion/%	80	93	100	100
Product[a)]	Yield of fraction/area %			
BSD of Re	65.4	51.1	42.0	7.3
BAD of Re	15.8	20.4	20.5	43.7
BDAD of Re	1.8	Nil	Nil	0.2
BSD of pentylbenzene	—	—	—	2.6
BSD of dipentylbenzene	—	—	—	1.4
Hexabutylbenzene	—	—	—	3.3

a) BSD: mono and polybutyl-substituted derivatives; Re: reactant compound; BAD: butyl-addition derivatives; BDAD: butyl-diaddition derivatives.

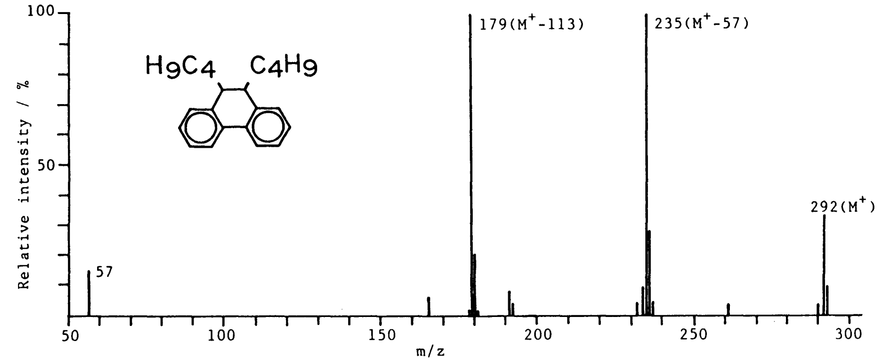

Fig. 2. Mass spectrum of the dibutyl-addition product of phenanthrene.

accepted structural view of bituminous coal contains statistical proportions of groups of fused aromatic and hydroaromatic ring clusters, composed of an average of two to six ring units connected with various aliphatic and ether bridges.

The model compounds selected as polynuclear aromatic compounds for this study are 1-methylnaphthalene, acenaphthene, phenanthrene, and anthracene. Every reaction product contained many components, showing over 200 peaks in each gas chromatogram. Figure 1 shows the gas chromatogram of the product of phenanthrene. Because of small area of each GC peak, the percentage of the components identified was meager: that of 1-methylnaphthalene, acenaphthene, phenanthrene, and anthracene were 83.0, 71.5, 62.5, and 58.5%, respectively. The reaction products and their yields are summarized in Table 1.

The reaction pattern observed with phenanthrene will be discussed first, because it is characteristic of other model compounds. Phenanthrene, when treated by this method, showed the quantitative conversion. The products consist of butyl-substituted derivatives (BSD) and butyl-addition derivatives (BAD)** of phenanthrene.

In our previous paper,[1)] we have reported that no evidence about the formation of butyl-addition products was found in the ^{13}C NMR spectra of the reaction products. However, in the present study, the products included not only the butyl-substituted components but also the butyl-addition components. Stobart and Zaworotko[9)] have shown that polynuclear aromatic compounds (naphthalene, anthracene, and phenanthrene) were hydrogenated, when treated with $AlCl_3$ in hexane and heptane at 20—70 °C. Therefore we considered initially that phenanthrene was hydrogenated, and subsequently butyl-substitution reaction occurred. However it was confirmed that phenanthrene was subjected to butyl-addition reaction. Figure 2 shows the mass spectrum of one of the products of phenanthrene whose molecular mass is 292. The mass spectrum showed the peaks at m/z M^+-57 and M^+-113 which are characteristics of dibutyl-addition compounds.[10)] 9,10-Dibutyl-9,10-dihydrophenanthrene[11)] was assigned to the product, but this product was not stereochemically followed up. Five isomers showing almost the same fragmentation were also observed. Accordingly, it is suggested that the products were formed from the butyl-addition. The use of ^{13}C NMR spectra failed to detect the formation of butyl-addition products, because the amount of these

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** Butyl-addition derivatives (BAD) of aromatic compound implies polybutylated derivatives of dihydroaromatic compound.

products was too little to be found. In addition, this butyl-addition products were included also in the reaction products of some other model compounds examined in this study.

1-Methylnaphthalene showed 79.5% conversion. The products were BSD and BAD of 1-methylnaphthalene. Moreover a small amount of the butyl-diaddition derivatives (BDAD)*** was also included.

Acenaphthene showed 93.1% conversion. The products were BSD and BAD of acenaphthene. Introducing of alkyl substituents to aromatic rings usually enhances[12] the reactivity of the aromatic compound for alkylation reaction and this is in accord with the fact that the conversion rate of acenaphthene was higher than that of 1-methylnaphthalene.

Anthracene also showed the quantitative conversion, giving BSD, BAD, and BDAD of anthracene. Differing from other three compounds, the products of anthracene included much more BAD than BSD. Furthermore the products included the components breaking the backbone of anthracene; BSD of dipentylbenzene and pentylbenzene, and hexabutylbenzene were 1.4, 2.6, and 3.3%, respectively. The first two compounds probably arose from butyl-addition to the 9 and 10 positions of anthracene, followed by cleavage, and it is suggested that hexabutylbenzene was formed from polybutylation of aromatic fragments which came out in aromatic ring destruction. The attack of the butyl groups at the 9 and 10 positions yields the structure of diphenylmethane type for anthracene and that of biphenyl type for phenanthrene. It is known that the linkage of diphenylmethane can be cleaved easily, but that of biphenyl cannot under various mild liquefaction conditions.[13,14] Therefore it is deduced that the aromatic rings of anthracene break, but those of phenanthrene do not.

As mentioned before, aliphatic linkages play an important role in linking aromatic and hydroaromatic ring clusters in coals. Other model compounds selected for this study include diphenylmethane and bibenzyl. The reaction products of these compounds contained over 100 components. The percentage of products identified in the runs of diphenylmethane and bibenzyl were 81.1 and 80.3%, respectively. Diphenylmethane showed 44.7% conversion. BSD of diphenylmethane was formed in 59.0% yield and the components which cleaves methylene linkage were also included. These were methylbiphenyl (6.2%), its monobutylated derivatives (5.2%), benzyltoluene (9.7%), and its monobutylated derivatives (1.0%). Bibenzyl showed 43.6% conversion, with BSD (69.1%) of bibenzyl, dibenzylated derivatives of bibenzyl (3.4%), their BSD (3.9%), pentylbenzene (2.8%), diphenylmethane (0.6%), and benzyltoluene (0.5%). The products other than BSD of bibenzyl are the compound with cleavage of ethylene linkage. No butyl-addition components were observed in both the reaction products.

Compounds containing aliphatic linkages gave the products with cleaved linkages, though their yields are low. Tuge and Tashiro[15] have reported that easiness of the cleavage of the methylene linkage of diphenylmethane increased with increasing the number of alkyl groups at benzene ring. Since both BSD of diphenylmethane and of bibenzyl in this study have only 1—2 butyl groups, the yields of linkage-cleaved products were low. Because coals themselves include many alkyl substituents on aromatic rings, one would expect that aliphatic linkages in coal structures can be cleaved by this method.

Another important feature of coal involves ether linkages, which are also believed to play an important role in the depolymerization of coal. The model compounds selected for this study include 2-methoxy-, 2-propoxynaphthalene, diphenyl ether, and dibenzyl ether. Every reaction product contained over 100 components. The percentage of the products identified in the reaction of 2-methoxy-, 2-propoxynaphthalene, diphenyl ether, and dibenzyl ether was 86.5, 81.6, 92.2, and 87.2%, respectively. When diphenyl ether was treated under this reaction system, 39.7% conversion was observed, and the products were only BSD (92.2%) of diphenyl ether. No ether linkage-cleaved components were found in the reaction products.

2-Methoxy- and 2-propoxynaphthalene showed 95.4 and 96.2% conversions, respectively. The reaction products of 2-methoxynaphthalene contained its BSD (29.5%) and BAD (23.4%), and similarly BSD (24.1%) and BAD (29.9%) of 2-propoxynaphthalene were found in its reaction products. The reactivity of the substrate did not differ with the alkyl chain length. In the reaction of 2-methoxynaphthalene, ether linkage-cleaved products, BAD (0.3%) of naphthalene, BSD (7.1%), and BAD (26.2%) of butoxynaphthalene were found. Similarly, in the reaction of 2-propoxynaphthalene, BAD (1.0%) of naphthalene, BSD (8.0%), and BAD (18.6%) of butoxynaphthalene were observed. The reaction products of alkoxynaphthalenes included the components which had been subjected to the cleavage of alkyl ether linkages and substituted by butyl groups. Furthermore, by means of a small amount of the components which cleaves the ether O-aromatic carbon linkage, BAD of naphthalene was observed in the reaction of alkoxynaphthalene.

Dibenzyl ether showed the quantitative conversion. All the reaction products were ether linkage-cleaved ones. Most of them were BSD (51.3%) of toluene, pentylbenzene, BSD (28.2%) of benzyltoluene, and its benzylated derivatives (6.3%). Other products were dibutylbenzene (0.5%), diphenylmethane (0.2%), and butyl benzyl ether (0.8%). The yield of the products,

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*** Butyl-diaddition derivatives (BDAD) of aromatic compound implies polybutylated derivatives of tetrahydroaromatic compound.

BSD of toluene and pentylbenzene, is shown together, because it is indistinguishable from fragmentation mass spectra whether they are toluene or pentylbenzene derivatives. It is known that alkyl ether linkage is easily cleaved, but aryl ether linkage hardly is.

As described above, it has been found in this reaction system that polynuclear aromatic compounds undergo the butyl-substitution and butyl-addition reactions, and aromatic compounds containing aliphatic linkages and some ether linkages cleave themselves. Therefore, the formation of most reaction products can be interpreted by assuming a similar mechanism to that of Friedel-Crafts reaction.[14,16] However, the formation of butyl-addition products cannot be interpreted. It has been already known that a radical reaction takes place in the early stage of this reaction.[17] The butyl-addition products can be explained by assuming a radical mechanism; butyl radical attacks the nucleus of aromatic compound, and the combination of the resulting radical with another butyl radical yields butyl-addition product.[18] In order to clarify whether this reaction mechanism is radical type or not, the fragmentation of the mass spectra of the products substituted by monobutyl group was analyzed, because butyl radical is not usually rearranged, but butyl cation is likely to be rearranged into *s*-butyl. The mass spectrum of the compound substituted by butyl group shows a peak at m/z M^+-43, whereas that of the compound substituted by *s*-butyl shows a peak at m/z M^+-29.[3] The results obtained on the seven compounds are shown in Table 2. In all the reaction products, a large amount of the components substituted by butyl was contained, but the components substituted by *s*-butyl were also contained. These results do not agree with the rule that rearrangement of the intermediate free radical does not occur.[19] Both of an observation of rearrangement of butyl to *s*-butyl and formation of BSD of polynuclear aromatic compounds can be interpreted by alkyl cation reaction mechanism,[1] whereas formation of BAD in the reaction of polynuclear aromatic compounds can be explained by assuming radical mechanism. Therefore it is suggested that both alkyl-cation and radical reaction occurred competitively in this reaction.

Table 2. Rearrangement of the Butyl Group of the Monobutyl-Substituted Model Compounds

Reactant	Yield of the fraction/area %	
	Butyl	*s*-Butyl
1-Methylnaphthalene	29.6	5.8
Acenaphthene	14.6	1.6
Phenanthrene	15.0	2.6
Anthracene	0.9	Nil
Diphenylmethane	34.0	14.5
Bibenzyl	42.6	15.6
Diphenyl ether	45.7	7.0

In view of the efficiency of this method on coal liquefaction it can be concluded that high benzene extractability of coal can be attained by introducing many butyl groups and the cleavage of the linkages in compounds, such as bibenzyl, diphenylmethane, dibenzyl ether, and alkoxynaphthalene. The reaction product of anthracene includes the components which cleave the aromatic backbone.

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