

# CARBON-CARBON BOND FISSION DURING HEAT TREATMENT OF COAL IN THE PRESENCE OF POLYCYCLIC AROMATIC COMPOUNDS

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## INTRODUCTION

Coal liquefaction is believed to be one of the most important processes among coal utilization technologies in near future, which can convert solid coal to liquid fuel. In Japan, two coal liquefaction processes, brown coal liquefaction process (so called, NBCL process) and bituminous coal liquefaction process (NEDOL process), have been developed under financial support provided by NEDO. Many studies were conducted concerning the effects of the reaction temperature, residence time, the structures of recycle solvents, properties of iron catalysts, etc on the yield of liquid products.

Coal liquefaction had been thought to proceed via thermal cleavage of relatively weak bonds followed by stabilization of the resulting radicals by hydrogen donatable solvents, these mechanisms being described in the paper published in early 80's. In 1987, Malhotra *et al.* proposed another mechanism including radical hydrogen transfer (RHT) instead of thermal cleavage, with which they explained the experimental results of coal liquefaction and coprocessing of coal with heavy oil.<sup>1)</sup> On the other hand, Franz *et al.*<sup>2)</sup> and Savage *et al.*<sup>3)</sup> proposed reverse radical disproportionation (RRD). The radical formed from RHT or RRD reaction, released alkyl radicals via  $\beta$ -cleavage, which will be stabilized by hydrogen donatable solvents. In this paper, we have investigated methyl groups generated from C-C bond fission of coal during heating in the presence of polycyclic aromatic compounds.

## EXPERIMENTAL

### Reagents and Coal Samples.

In the present study, about forty kinds of coal samples with carbon contents ranging from 67 % to 91 % (wt%, daf) were employed, which were provided by Nippon Steel Chemical Ltd., Center of Coal Utilization, Japan (CCUJ), the Iron and Steel Institute of Japan (ISIJ), and Nippon Brown Coal Liquefaction Co. Ltd. (NBCL). These coals were ground under 100 mesh and dried at 40 °C for a night before use. 9-Methyl-, 9-ethyl-, and 9-methoxyanthracenes were prepared by the method reported previously. The other reagents employed in this study were commercially available and purified by conventional recrystallization or distillation prior to use.

### Reaction of Coal Samples with Aromatic Compounds.

Details of reaction of coal samples with polycyclic aromatic compounds were described elsewhere.<sup>4)</sup> Typical procedure was as follows: A mixture of 100 mg of a sample coal and 100 mg of anthracene was put in a pyrex tube ( $\phi$  6 mm x 100 mm long), then the tube being sealed. The resulting tube was put into an electric furnace preheated at 420 °C and kept for 5 min. After the reaction was quenched by removing the tube from the furnace, the products were recovered by washing the inside of the tube with methylene chloride and submitted to GC and GC-MS analyses.

### MO Calculations.

All MO calculations were carried out on an Apple Macintosh computer by using a semiempirical molecular orbital calculation program, CAChe (Computer Aided Chemistry) MOPAC.94, which was purchased from CAChe Scientific Inc. The values of heat of formation for the polycyclic aromatic hydrocarbons were determined by solving the Schrödinger equations using the AM1 semiempirical Hamiltonians.

### Solid State NMR Spectroscopy.

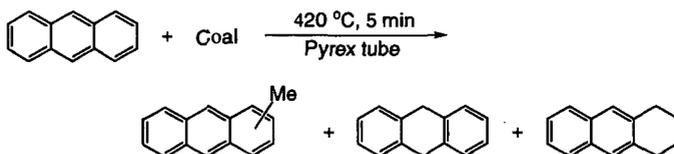
SPE/MAS <sup>13</sup>C NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer under the following conditions; resonance frequency for <sup>13</sup>C 75.5 MHz; pulse width 45°; proton decoupling frequency 83 kHz (90° pulse width=3.0ms); scan number 1000; pulse delay 100 s; and MAS

frequency 10.5 kHz. Curve fitting was conducted on an Apple Macintosh computer with a data processing software, MacFID (TechMag Inc., Ver. 5.4). The classification of carbon types was as follows: carbonyl and carboxyl (the deconvoluted peak centered at 187 and 178 ppm), aromatic carbons attached to oxygen (167 and 153 ppm), aromatic carbons attached to carbon or hydrogen (140, 126 and 113 ppm), methoxy (56 ppm), methylene (40 and 31 ppm),  $\alpha$ -methyl to aromatic ring and branched methyl (20 ppm) and terminal methyl in side chains (13 ppm).

## RESULTS AND DISCUSSION

### The Reaction of Coal Samples with Aromatic Compounds.

More than forty kinds of coal samples ranging from brown to semi-anthracite were employed in this study. The reaction of the coal samples (100 mg) with anthracene (100 mg) was conducted at 420 °C for 5 min in a pyrex tube. The main products containing anthracene skeleton were 9,10-dihydroanthracene (DHA), 1,2,3,4-tetrahydroanthracene (THA), and methylanthracene isomers (MA, mainly consisted of 9-methyl isomer along with minor amount of 1- and 2-methyl ones).



Although dimethylanthracenes and methyl-dihydroanthracenes were also detected, their yields were very small. In almost all runs, the recovery of anthracene derivatives was more than 90 mol%, which seems to be a reliable value for the following discussion. The results are summarized in Figure 1. DHA and THA were produced *via* hydrogen abstraction by anthracene from hydrogen donatable parts in the coal samples, while the formation of MA suggests that anthracene could capture the methyl radicals produced by C-C bond fission. Yields of DHA and THA became the highest from the reaction of the coal with *ca.* 86% of carbon (Figure 1a), while yield of MA showed different tendency, *i.e.*, the lower the coal rank was, the higher the MA yield was (Figure 1b). With elongation of reaction duration from 5 min to 30 min, MA yield increased monotonously.

We also conducted the reaction of the coal samples with pyrene and acridine, radical acceptability of which is known to be different from that of anthracene. Therefore, we would like to investigate correlation between radical acceptability and methylarene yields. The results are shown in Figure 2. In the every coals employed, yield of methylarenes obeyed the following sequence; pyrene < anthracene < acridine. We evaluated radical acceptability of these arenes according to the following equation using MO calculation program package (MOPAC 94):

$$\Delta\Delta H_f = \Delta H_f(\text{ArHMe}\cdot) - \Delta H_f(\text{ArH}) - \Delta H_f(\text{Me}\cdot)$$

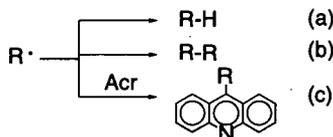
where  $\Delta H_f$  means standard heat of formation. The values of  $\Delta\Delta H_f$  for pyrene, anthracene, and acridine were calculated to be +1.1, -4.8, and -28.6 kcal/mol, respectively. This indicates that using the arenes with higher radical acceptability, methyl radical migrates to the arenes more easily.

It is known that various kinds of carbon or methyl group are present in coal. The methyl migration reaction observed in this study should be caused by a certain type of methyl group. In order to get an information concerning the source of the methyl groups migrated, we measured solid state  $^{13}\text{C}$  NMR spectra for the sample coals, the resulting spectra being divided into twelve curves and the carbon distribution was estimated as shown in experimental section. Figure 3 shows the plots of MA yield (wt%, from the reaction at 420 °C for 5 min) against concentration of methyl groups (methoxy,  $\alpha$ -methyl, terminal methyl and their total) in the coals (mol%) estimated from the  $^{13}\text{C}$  NMR spectra. The concentration of methoxy, terminal methyl and total methyl groups seemed to correlate weakly. Since the errors in the NMR measurements and estimation of carbon types were not so small, we could not determine what the origin of methyl groups migrated is. Only what we can say is larger amount of methyl gave higher yields of methylanthracenes in the reaction of coal with anthracene.

### Migration of Methyl Groups from Methyl-Containing Compounds to Polycyclic Aromatics.

To discuss about the mechanism of methyl groups-migration reaction, we conducted the reaction of model compounds. We selected 9-methyl-, 9-ethyl-, and 9-methoxyanthracenes (abbreviated as 9-MA, 9-EA, and 9-MeOA, respectively). This reaction requires a hydrogen donatable solvent and a radical accepting compound, for which 9,10-dihydroanthracene (DHA) and acridine (Acr) were employed, respectively. The reaction was conducted at 420 °C for 5 min in a pyrex tube, the results being summarized in Table 1. The order of reactivity (judging from the conversion) of the anthracenes obeyed the following sequence; 9-MA  $\approx$  9-EA < 9-MeOA. The reaction of 9-MA afforded methylacridines (M-Acr), dimethylanthracenes (DMA), and methane in 18, 2.4, and 1.1 % yield, respectively, as the major methyl group-containing products. In the case of 9-EA, main products were ethylacridines (E-Acr, 15 %), diethylacridines (DE-Acr, 2.7 %), and ethane (3.9 %) along with small amount of methylacridines (2.2 %). In the reaction of 9-MeOA, the main products were M-Acr (44 %), methane (36 %), and anthrone (42 %).

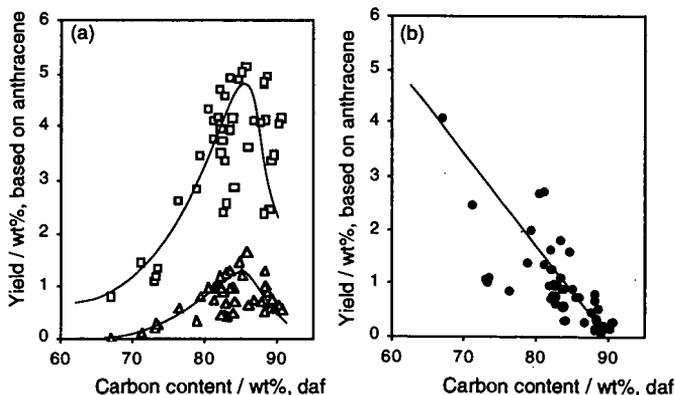
Formation of light hydrocarbon gases and alkylacridines indicate that alkyl radicals participate this reaction and there are three possibilities for the fate of the radicals formed (Scheme 1), i.e., a) hydrogen abstraction to form alkanes, b) dimerization to alkanes, and c) capture with aromatics to form alkylarenes.



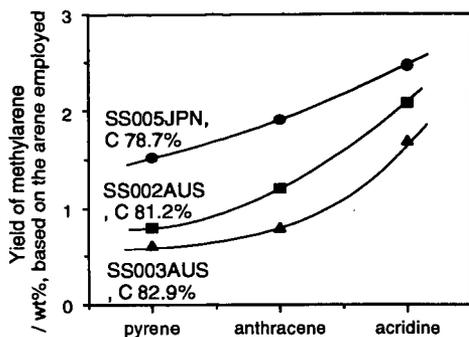
Contribution of these pathways a,b,c seemed to be varied depending on the functionality of methyl groups. Now, we are investigating the factors affecting the products distribution.

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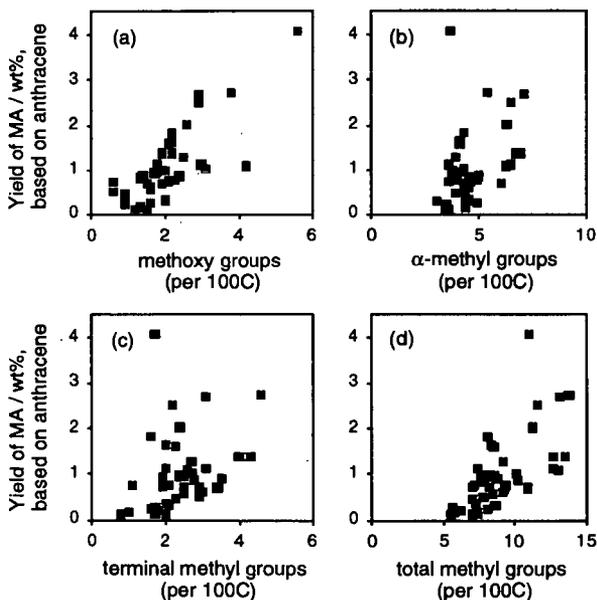
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**Figure 1** Plots of the yield of DHA ( $\square$ ), (a), THA ( $\triangle$ ), (a) and MA ( $\bullet$ ), (b) from the reaction of coal with anthracene at 420 °C for 5 min against carbon content of the coals



**Figure 2.** Yield of methylarenes from the reaction of coal with polycyclic aromatics (at 420 °C, for 5 min, in a pyrex tube)



**Figure 3.** Plots of the yields of methylanthracene (MA) against concentration of each type of methyl group in the coal samples

**Table 1.** The reaction of methyl group-containing anthracene with acridine in the presence of DHA<sup>a)</sup>

Substrate	Conv. of Subst. (mol%)	Yield (mol%)			Yield of gas (mol%)			
		DMA	M-Acr	E-Acr	DE-Acr	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
9-MA	28	2.4	18	-	-	0.41	1.1	-
9-EA	28	-	2.2	15	2.6	0.37	-	3.9
9-MeOA	87	5.3	44	-	-	0.35	36	0.6

a) A mixture of substrate (0.25 mmol), Acr (0.25 mmol), and DHA (0.0625 mmol) was heated at 420 °C for 5 min in a pyrex tube.