1478 © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 1478—1483 (1990) [Vol. 63, No. 5

Aromatic Skeletal Structures in Distillable Coal-Derived Liquids

Yoshikazu SUGIMOTO,* Yasuo MIKI, Masaaki OBA, and Shoko YAMADAYA
National Chemical Laboratory for Industry, Higashi 1-1, Tsukuba-shi, Ibaraki 305

(Received August 29, 1989)

Aromatic constitutents in Wandoan coal-derived distillate were analyzed by means of capillary gas chromatography/mass spectrometry (GC/MS) in order to clarify their aromatic skeletal structures. The major aromatic skeletons could be classified into several groups, the molecular weights of which were represented by $78+50n$, $118+50n$, $154+50n$, $166+50n$, $202+50n$, $242+50n$ ($n=0,1,2,\cdots$), and so on. The increase by 50 corresponded to an additional benzene ring fused to the original skeleton. Some new types of aromatic skeletons, such as dihydrophenalene and benzindan, were found to be present in significant amounts.

Coal-derived liquids are very complicated mixtures, but the elucidation of their chemical structures is necessary for their utilization as fuels, chemicals, and process solvents in coal liquefaction. Capillary GC and GC/MS have been used by many researchers to analyze aromatic compounds in coal-derived liquids.[1–7)]

The skeletal structures of hydroaromatic fractions from fossil fuels are constructed from benzene ring and naphthenic rings. Synder showed the structural range of petroleum hydrocarbons as a three-dimensional, continuous array.[8)] Similar diagrams have also been presented for coal-derived hydrocarbons.[9,10)] The hydroaromatic fractions in coal-derived liquids consist of alkylated homologues of several common aromatic skeletons, such as benzene, naphthalene and phenanthrene, and their hydrogenated derivatives. Therefore, it is very important to clarify the fundamental aromatic skeletons for a better understanding of their chemical structures. Although many aromatic skeletal structures are well known, there remain some aromatic skeletons which can be expected to be present in coal-derived liquids but which are as yet unconfirmed because of the lack of authentic standards.

In this work, the existence of some aromatic skeletal structures which are probable but which are as yet uncertain were investigated by means of capillary GC/MS analysis combined with separation by means of high-performance liquid chromatography (HPLC) and dehydrogenation treatment.

Experimental

Preparation of Coal-Derived Samples. Figure 1 shows the diagram for the preparation of coal-derived samples. The liquefaction of Wandoan coal was carried out at 450 °C for 1 h over α-Fe_2O_3(sulfided) under an initial pressure of 9.8 MPa H_2 and using toluene as the solvent. A nonpolar distillate (bp 180—430 °C) was obtained from the heptane-soluble product by distillation and separation on an alumina column; it was then divided into saturates (Fr. A), monoaromatics (Fr. B), diaromatics (Fr. C), and tri/tetra-aromatics (Fr. D).[3)] Furthermore, Fr. C and Fr. D were separated into seven aromatic subfractions (Fr. C-1, Fr. C-2, Fr. D-1, Fr. D-2, Fr. D-3, Fr. D-4, and Fr. D-5) by the use of a HPLC apparatus equipped with a semipreparative μBondapak-NH_2 column (19 mm×150 mm).

The nonpolar distillate was dehydrogenated over a Pt/Al_2O_3 catalyst at 325 °C[11)] to ascertain which peaks were hydrogenated derivatives. In addition, the nonpolar distillate was first hydrogenated and then dehydrogenated to clarify the existence of benzonaphthofuran skeletons. Upon this treatment, the quantities of benzonaphthofurans decreased markedly, while the other aromatic hydrocarbons did not decrease.

Preparation of Standard Samples. The methylation of aromatic compounds was performed at 350—400 °C over $Ni-W/SiO_2-Al_2O_3$ in an excess amount of 1,2,3,4-tetramethylbenzene,[12)] while the ethylation of aromatic compounds was done at 250—300 °C over $SiO_2-Al_2O_3$ with twice as many moles of ethanol.

The hydrocracking of naphthalene, phenanthrene, anthracene, chrysene, benz[*a*]anthracene, and benzo[*e*]pyrene was individually performed at 470 °C over a MoS_2 catalyst and under an initial pressure of 4 MPa H_2.

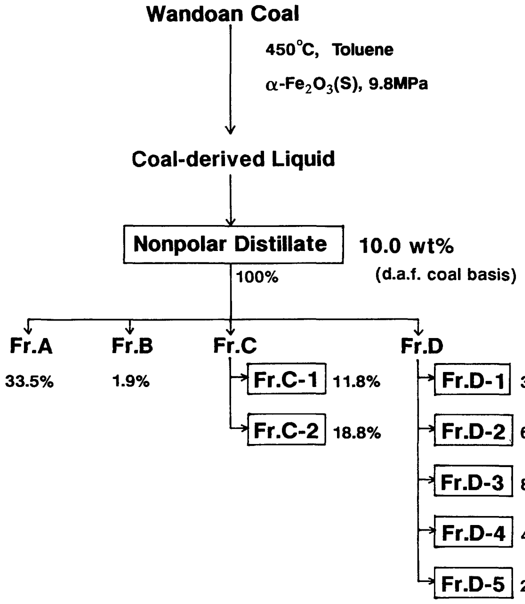

Fig. 1. Preparation of Wandoan coal-derived samples.

Analysis by Means of Capillary GC/MS and GC. The samples were analyzed by the use of a GC/MS apparatus (Hewlett-Packard 5890A g.c.+5970 MSD) equipped with a OV-1 fused silica capillary column (50 m×0.2 mm). The oven-temperature programme was; 50°C (25 min), 5°C min^{-1}, 100°C (5 min), 3°C min^{-1}, 150°C (3 min), 2.5°C min^{-1}, 260°C (hold). All the spectra were recorded in the electron-impact-ionization mode at 70 eV. The constituents of the seven aromatic subfractions were quantified by the use of a GC apparatus (Hewlett-Packard 5890A) with an FI-detector. The oven temperature was programmed from 50°C to 300°C at 2°C min^{-1} for GC analysis.

Results and Discussion

Analysis of Aromatic Subfractions. The seven aromatic subfractions were analyzed by means of capillary GC and GC/MS; the results are shown in Table 1 according to the molecular weight. Naphthalene, phenanthrene, acenaphthene, biphenyl, phenylnaphthalene, dibenzofuran, fluorene, benzofluorene, fluoranthene, pyrene, benzopyrene, and so on were easily confirmed to be present by comparing the mass spectra and the retention times with those of commercially available standard compounds. The aromatic skeletal structures present in coal-derived liquids could be classified into several groups, as diagrams previously proposed.[9,10] The most abundant group was composed of benzene, naphthalene, phenanthrene, chrysene, and so on, the molecular weights of which were represented by $78+50n(n=0, 1, 2, 3, \cdots)$. The increase by 50 corresponded to an additional benzene ring fused to the original skeleton. The existence of such skeletal groups as biphenyl/phenylnaphthalene/binaphthyl (MW $154+50n$), fluorene/benzofluorene (MW $166+50n$), and pyrene/benzopyrene (MW $202+50n$) were also established. Since indan, acenaphthene, and dibenzofuran were detected in coal-derived samples, benzindan, benzacenaphthene and benzonaphthofuran should also be present. However, those aromatic skeletons were not confirmed to be present because of the lack of authentic standards. In later papers, the existence of aromatic skeletons of MW 168, 204, 218, and 242, which correspond to benzindan, benzacenaphthene, benzonaphthofuran/dihydrocyclopentaphenanthrene, and dihydrocyclopentapyrene respectively,

Table 1. Major Compound Types of Each Aromatic Subfraction

Fr.	Major compound type	M.W.	Abundance (GC area/%)						
			n=0	1	2	3	4	5	Total
C-1	Benzenes	$(134+14n)$	4.7	3.5	1.3	0.4	1.6	0.2	12.3
	Indan/tetralins	$132+14n$	9.7	16.6	21.1	17.0	5.5	3.0	73.2
	Unknown	$158+14n$	1.0	3.6	3.2	2.3	1.1	0.6	12.3
C-2	Naphthalenes	$128+14n$	7.2	17.3	22.2	14.8	4.6	2.9	68.9
	Acenaphthenes	$154+14n$	0.8	7.2	8.4	6.5	2.0	0.1	24.9
D-1	Biphenyls	$154+14n$	0.7	4.9	14.5	21.1	11.6	3.1	68.4
	Acenaphthenes	$154+14n$	0.2	2.7	9.6				
	Naphthalenes	$128+14n$			2.0	11.1	7.1	0.2	20.4
	Unknown	$208+14n$	0.9	2.0	0.5				3.4
D-2	Biphenyls	$154+14n$	1.0	4.1	7.2	6.7	5.0	0.9	45.4
	Diphenylmethanes[a]	$(154+14n)$		1.2	4.0				
	Diphenylethanes[a]	$(154+14n)$			1.7				
	Dibenzofurans	$(154+14n)$		2.7	4.8	6.2			
	Fluorenes	$166+14n$	4.0	11.9	11.5	9.8	5.0	1.3	43.5
	Unknown	$206+14n$	0.4	2.1	1.6	1.2			5.2
D-3	Fluorenes	$166+14n$	0.9	1.6	1.6	0.7			4.8
	Phenanthrenes	$178+14n$	16.7	17.7	15.8	8.4	2.3	0.3	61.2
	Phenylnaphthalenes	$204+14n$	2.6	7.3	9.4	2.5			21.7
	Pyrenes	$202+14n$	1.8	2.6	2.3	0.6	0.9		8.1
D-4	Phenanthrenes	$178+14n$	1.1	0.8	0.2	0.4			2.5
	Phenylnaphthalenes	$204+14n$	3.0	7.7	6.7	1.5			18.9
	Fluoranthenes	$202+14n$	19.0	24.3	17.5	8.5	1.3		70.7
	Unknwn	$242+14n$	4.0	2.7					6.7
D-5	Unknowns	$208+14n$	0.9	1.4	0.8	0.4			3.5
	Bnzofluorenes	$202+14n$	1.0	4.9	6.0	2.6			14.5
	Chrysenes	$228+14n$	13.6	15.8	8.1	1.0			38.5
	Benzopyrenes	$252+14n$	6.4	5.3	1.0				12.6
	Binaphthyls	$254+14n$	4.6	6.4					11.0

a) These compounds were probably produced by the dimerization of toluene.

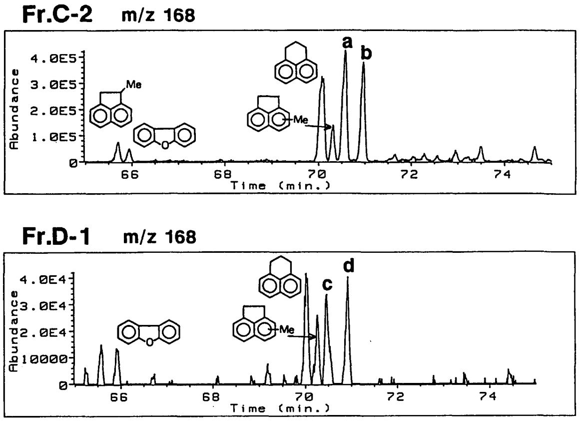

Fig. 2. Single-ion chromatograms of m/z 168 for Fr. C-2 and Fr. D-1.

will be investigated.

Skeletal Structures of MW 168. Figure 2 shows the single-ion chromatograms of m/z 168 for Fr. C-2 and Fr. D-1, in which benzindans are contained if they exist. The first four peaks in the chromatogram of Fr. C-2 were identified as 1-methylacenaphthene, dibenzofuran, dihydrophenalene, and methylacenaphthene. A standard sample of dihydrophenalene was prepared by the hydrogenation of perinaphthenone available commercially. Methylacenaphthenes have four isomers; the remaining two isomers were eluted at the same retention times as Peaks a(=c) and b(=d). Peak c was identified as one of the methylacenaphthenes because of the agreement of the mass spectra. However, the mass spectra of Peaks a, b and d were different from those of methylacenaphthenes, but were similar to that of dihydrophenalene. These three peaks (probably Peak b was the same compound as Peak d) were supposed to be benzindans.

The hydrocracking of naphthalene at 470°C over MoS_2 provided methylindans and indan in yields of 7.4% and 1.0% respectively. Therefore, phenanthrene and anthracene were hydrocracked under the similar conditions to convert them into methylbenzindans and benzindans. Figure 3 shows the gas chromatograms of the hydrocracking products and also the mass spectra of the three peaks, A, B, and C, of MW 168. Similar compounds were produced from the two feed samples, which showed that isomerization between hydrogenated phenanthrene and hydrogenated anthracene occurred under the present reaction conditions. Peak A was identified as dihydrophenalene by comparing it with a standard sample prepared from perinaphthenone. Peak C was produced in a greater yield from anthracene than from phenanthrene; it should be indentified as benz[f]indan. Peak B must be benz[e]indan. Five peaks, D—H, had molecular weights of 182; they were all supposed to be methylated homologues of dihydrophenalene and benzindans.

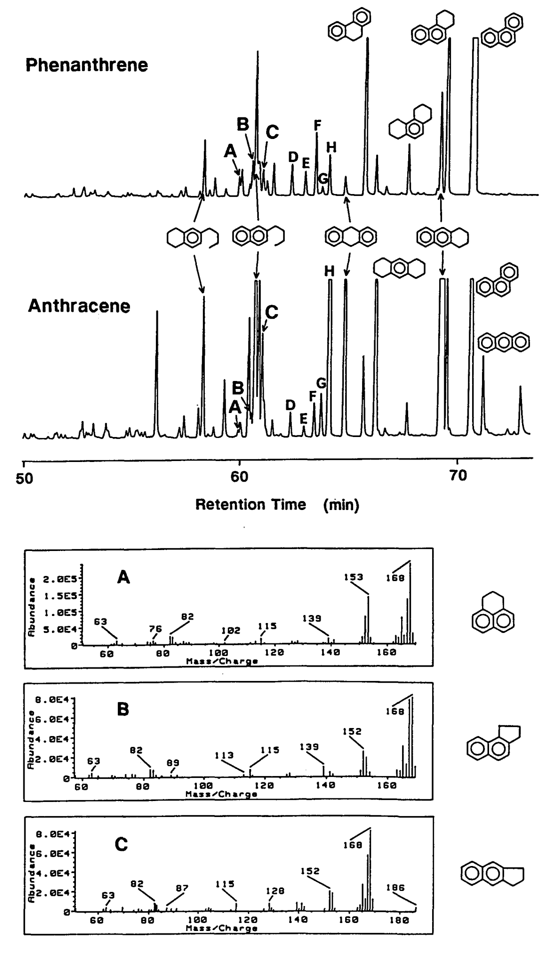

Fig. 3. Gas chromatograms of hydrocracking products from phenanthrene and anthracene, and mass spectra of peaks A, B, and C of MW 168.

By comparison with the retention times and the mass spectra of Peaks B and C, Peaks a and b(=d) in Figure 2 were indentified as benz[e]indan and benz[f]indan respectively. Dihydrophenalene and benzindans have first been reported to be present in coal-derived liquids in this paper.

Methyl-dihydrophenalene/benzindans were also expected to be present in coal-derived liquids. Figure 4 shows the single-ion chromatograms of m/z 182 for Fr. C-2 and Fr. D-1. The peaks donated by ○ and ◇ had the same retention times as the dimethylacenaphthenes and ethylacenaphthenes respectively thus prepared. Therefore, the peaks donated by ● were supposed to be methyl-dihydrophenalene/benzindans. The five peaks (●) eluted before 74 min corresponded to Peaks D—H in Figs. 3 and 4; they would have a methyl group on the naphthenic ring. There are many aromatic compounds which have naphthalene ring and molecular weights of $168+14n(n=0, 1, 2, \cdots)$; they have previously been considered to be alkylated homologues of acenaphthene. However, it has here been shown that alkylated homologues of dihydro-

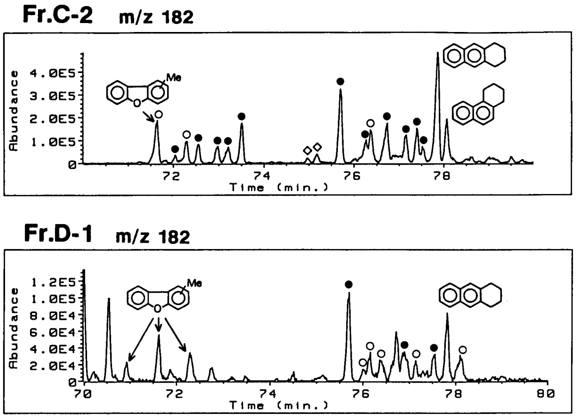

Fig. 4. Single-ion chromatograms of *m/z* 182 for Fr. C-2 and Fr. D-1.

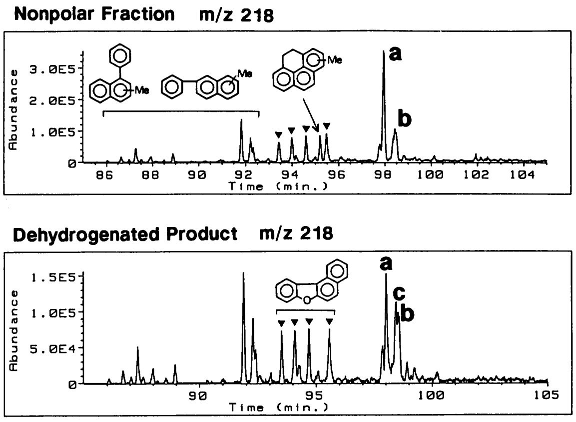

Fig. 6. Single-ion chromatograms of *m/z* 218 for nonpolar distillate and the dehydrogenated product.

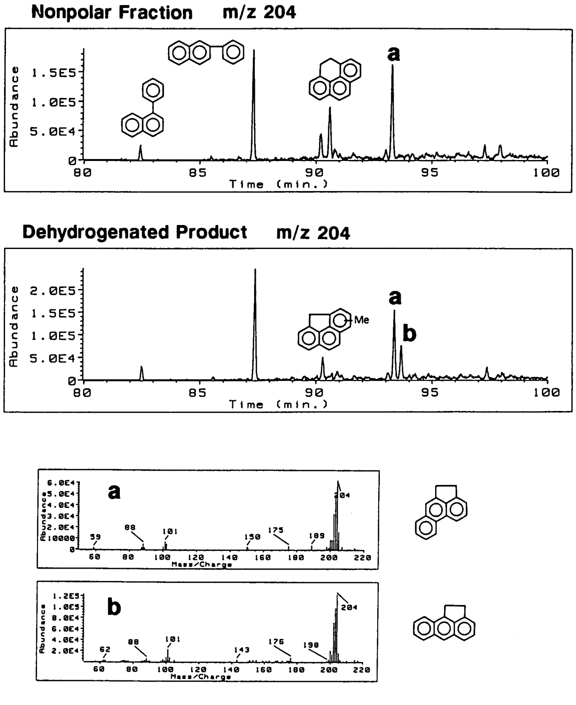

Fig. 5. Single-ion chromatograms of *m/z* 204 for nonpolar distillate and the dehydrogenated product, and mass spectra of peaks a and b.

phenalene and benzindans are more abundant than those of acenaphthene.

Skeletal Structures of MW 204. Figure 5 shows the single-ion chromatograms of *m/z* 204 for the nonpolar distillate obtained from Wandoan coal-drived liquid and the dehydrogenated product. Some peaks in the chromatograms were assigned to 1- and 2-phenylnaphthalenes, 1,2-dihydropyrene, and methyl-4*H*-cyclopenta[*def*]phenanthrenes by comparison with standard samples commercially available or prepared in this work. The remaining peaks, a and b, must be benzacenaphthenes. Peak b did not exist in the nonpolar distillate, but appeared in a significant amount after the dehydrogenation treatment. In a previous paper,11) it was shown that anthracene and 2-methylanthracene were scarcely present in coal-derived hydrocarbons, but they increased remarkably after dehydrogenation, while significant amounts of phenanthrene and methylphenanthrenes were present even before dehydrogenation. These results showed that anthracene rings were easily hydrogenated during coal liquefaction and existed as hydrogenated homologues in coal-derived liquids. Therefore, Peak b must have an anthracene ring. The mass spectral fragmentation patterns of Peaks a and b were similar to that of acenaphthene, the major ions of which were M^+, $(M-1)^+$, and $(M-2)^+$. It could be concluded that Peaks a and b in Fig. 5 were benz[*e*]acenaphthene and benz[*d*]acenaphthene respectively.

Skeletal Structures of MW 218. Figure 6 shows the single-ion chromatograms of *m/z* 218 for the nonpolar distillate and the dehydrogenated product. The possible structures of MW 218 were dihydrobenzophenalenes, dihydrocyclopentaphenanthrenes, benzonaphthofurans, and methylated homologues of phenylnaphthalenes, dihydropyrenes, and benzacenaphthenes. The methylation of 1- or 2-phenylnaphthalenes provided exactly the same product compositions, which implied that the migration of the phenyl group occurred easily under the present reaction conditions. The peaks eluted before 93 min were assigned to methylphenylnaphthalenes, while the small peaks eluted around 95 min and 98 min might be C_2-4*H*-cyclopenta[*def*]phenanthrenes and methylbenzacenaphthenes respectively. The peak disappearing upon the dehydrogenation treatment is probably methyldihydropyrene. The four peaks donated by ▼ may be assigned to benzonaphthofurans because of the marked decrease upon the hydrogenation-dehydrogenation treatment, but the number of the isomers are three. One of them must have another structure, but this problem could not be clarified. The three peaks, a, b

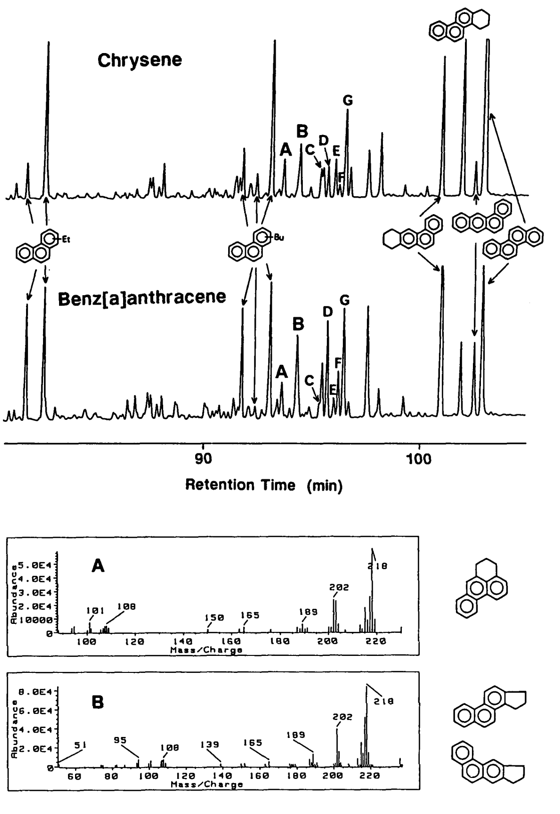

Fig. 7. Gas chromatograms of hydrocracking products from chrysene and benz[*a*]anthracene, and mass spectra of peaks A and B of MW 218.

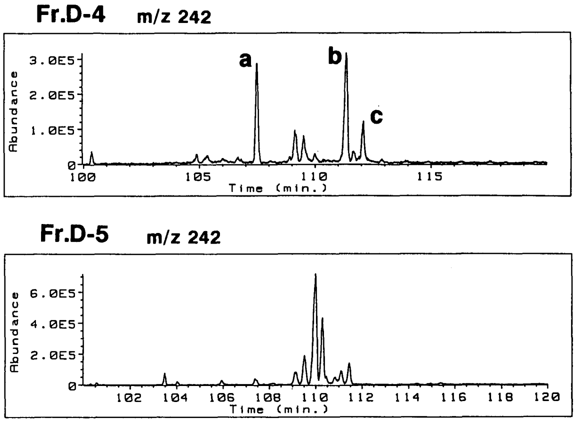

Fig. 8. Single-ion chromatograms of *m/z* 242 for Fr. D-4 and Fr. D-5.

and c, might be dihydrobenzophenalenes and dihydrocyclopentaphenanthrenes. Dihydrophenalene decreased substantially after the dehydrogenation treatment; Peak a also decreased, as is shown in Fig. 6, which might indicate that Peak a was dihydrobenzophenalene. Peak c, appearing after the dehydrogenation treatment, must have an anthracene skeleton as has been discussed above.

Chrysene and benz[*a*]anthracene were hydrocracked over a MoS_2 catalyst at 470 °C to convert them into dihydrobenzophenalenes and dihydrocyclopentaphenanthrenes. Figure 7 shows the gas chromatograms of the products and the mass spectra of Peaks A and B of MW 218. Peaks C—G of MW 232 would be methylated homologues of Peaks A and B. Since Peaks A and B were produced from chrysene, they should have a phenanthrene skeleton. The only significant difference in the mass spectra of Peaks A and B was the intensity of *m/z* 203. As is shown in Fig. 3, dihydrophenalene had a larger fragment ion at *m/z* 153 than did benzindans. Therefore, Peak A may be assigned to dihydrobenzo[*f*]phenalene, and Peak B, to dihydrocyclopenta[*a*]phenanthrene and/or dihydrocyclopenta[*b*]phenanthrene, as is shown in Fig. 7.

Peaks a and b in Fig. 6 correspond to Peak A(dihydrobenzo[*f*]phenalene) and Peak B(dihydrocyclopenta[*a*]phenanthrene and/or dihydrocyclopenta[*b*]phenanthrene) respectively. The mass spectrum of Peak c in Fig. 6 was quite similar to that of peak A; therefore, it may be assigned to dihydrobenzo[*e*]phenalene, which has an anthracene skeleton.

Skeletal Structures of MW 242. The existence of benzidan and dihydrocyclopentaphenanthrene indicates that dihydrocyclopentapyrene(MW 242) was also present. Figure 8 shows the single-ion chromatograms of *m/z* 242 for Fr. D-4 and Fr. D-5. The aromatic compounds of MW 242 in Fr. D-5 were assigned to methyl-chrysene/benz[*a*]anthracene/triphenylenes by comparison with standard samples. The retention times of Peaks a, b and c in Fr. D-4 were different from those of the methyl-chrysene/benz[*a*]anthracene/triphenylenes. In addition, the major constituents in Fr. D-4 should have a pyrene/fluoranthene skeleton because of the properties of the column used for HPLC separation. Therefore, Peaks a, b and c in Fr. D-4 might be pyrene/fluoranthene with one naphthenic ring, such as dihydrophenalene and benzindan.

The hydrocracking of benzo[*e*]pyrene was carried out at 470 °C over a MoS_2 catalyst; the gas chromatogram of the product is shown in Fig. 9. Peaks A and B had molecular weights of 242, while Peaks C, D and E had molecular weights of 256. Only two structures can be drawn for the compounds of MW 242, which were produced by the hydrocracking of benzo[*e*]pyrene. Peaks A and B might be 4,5-dihydro-3*H*-benzo[*c d*]pyrene and dihydrocyclopenta[*a*]pyrene respectively, because dihydrophenalene was eluted earlier than benzindans. Peaks b and c in Fr. D-4 correspond to Peaks A and B respectively in the hydrocracking product of benzo[*e*]pyrene. The mass spectrum of Peak a was not similar to those of Peaks b or c; its structure remains unknown, but it might be dihydrocyclopentafluoranthene.

In the present work, some new types of aromatic skeletons were found to be present in coal-derived

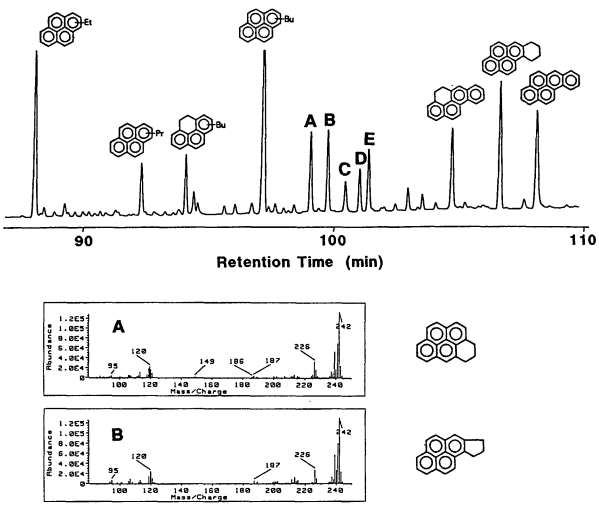

Fig. 9. Gas chromatogram of hydrocracking product from benzo[*e*]pyrene, and mass spectra of peaks A and B of MW 242.

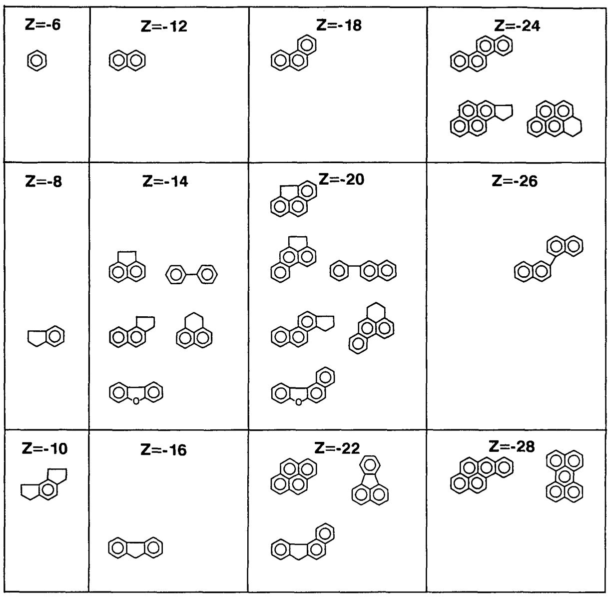

Fig. 10. Representative aromatic skeletons present in coal-derived distillate.

liquid. Some representative aromatic skeletons are summarized in Fig. 10. Benzene with two five-membered naphthenic rings was supposed to be present because aromatic compounds of MW 158+14*n* were present in significant amounts in Fr. C-1 and many of them did not decrease after dehydrogenation. Hydroaromatic compounds in coal-derived liquids are alkylated homologues of the aromatic skeletons and their partially hydrogenated derivatives.

Conclusion

By comparison with standard samples, some new types of aromatic skeletons, such as dihydrophenalene, benzindan, dihydrobenzophenalene, dihydrocyclopentaphenanthrene, and dihydrocyclopentapyrene were found to be present in coal-derived liquid. Major aromatic skeletons could be classified into several groups, the molecular weights of which were represented by 78+50*n*, 118+50*n*, 154+50*n*, 166+50*n*, 202+50*n*, 242+50*n* (*n*=0,1,2,···), and so on.

References

1) W. Bertsch, E. Anderson, and G. Holzer, *J. Chromatog.*, **126**, 213 (1976).

2) R. V. Schultz, J. W. Jorgenson, M. P. Maskarinec, M. Novotony, and L. J. Todd, *Fuel*, **58**, 783 (1979).

3) Y. Sugimoto, Y. Miki, S. Yamadaya, and M. Oba, *Nippon Kagaku Kaishi*, **1984**, 1954.

4) T. Katoh and K. Ouchi, *Fuel*, **64**, 1260 (1985).

5) R. B. Lucke, D. W. Later, C. W. Wright, E. K. Chess, and W. C. Weimer, *Anal. Chem.*, **57**, 633 (1985).

6) T. J. Wozniak and R. A. Hites, *Anal. Chem.*, **57**, 1320 (1985).

7) T. Katoh and K. Ouchi, *Fuel*, **66**, 58 (1987).

8) L. R. Synder, *Acc. Chem. Res.*, **3**, 290 (1970).

9) A. A. Herold, W. R. Ladner, and G. E. Snape, *Phil. Trans. R. Soc. Lon.*, **A300**, 3 (1981).

10) H. Uchino, S. Yokoyama, M. Satou, and Y. Sanada, *Fuel*, **64**, 842 (1985).

11) Y. Sugimoto, Y. Miki, M. Oba, and S. Yamadaya, *Bull. Chem. Soc. Jpn.*, **63**, 967 (1990).

12) Y. Miki and Y. Sugimoto, *Nippon Kagaku Kaishi*, **1983**, 697.