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The Hydrocracking of Polynuclear Aromatic Hydrocarbons over Molten Salt Catalysts[1)]

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The hydrocracking of phenanthrene, anthracene, pyrene, chrysene, and fluoranthene over molten salt catalysts at 400 °C in the batch autoclave systems was examined. The products were mainly identified by means of GC-MS, but the representative products were isolated by preparative GLC and characterized by using NMR, IR, UV, and mass spectrometry. Most of the isolated products are compounds not previously confirmed in detail, although their formation has been expected in the hydrocracking of the corresponding aromatic compounds. Probable reaction routes are offered based on the product distributions. The binary mixture of zinc chloride and copper(I) chloride is considered to act as a molten dual-functional catalyst.

The hydrocracking of the model compounds, which are supposed to be structural units of coal, has frequently been carried out in order to examine the function of catalysts and the reaction process. In the investigation reported by Qader,[2)] the hydrocracking of naphthalene, anthracene, and pyrene was found to proceed through a sequential occurence of hydrogenation, isomerization, and cracking reactions over silica-alumina-based dual-functional catalysts, which are extensively used in the industrial processing of petroleum feedstocks. Zielke *et al.*[3)] had shown molten zinc chloride to be a superior acidic catalyst for the hydrocracking of pyrene and coal extracts when used in high concentrations.

As a part of a study of organic reactions in molten salts,[4)] we examined the catalytic activity of molten salts in the hydrocracking of a heavy anthracene oil.[5)] In this experiment, a binary mixture of CuCl and $ZnCl_2$ was found to be more effective than $ZnCl_2$ alone in obtaining many lower-boiling fractions; both the analysis of the starting oil and the confirmation of the products were also carried out extensively. However, in this hydrocracking of the heavy anthracene oil, the behavior of the representative constituents of the starting oil, that is, anthracene, phenanthrene, chrysene, pyrene, and fluoranthene, could not be clarified in detail. Concerning the hydrocracking of anthracene, the efficient catalytic activity of the binary mixture of $ZnCl_2$ and CuCl was reported in a preliminary paper.[6)] In addition to the above results, this paper will describe the application of this catalyst to the hydrocracking of phenanthrene, chrysene, pyrene, and fluoranthene and their characteristic properties. The effects of two different-batch autoclave systems on their product distributions are also investigated. Moreover, the probable reaction routes for the respective reactions of phenanthrene, chrysene, and fluoranthene will be offered and discussed.

Experimental

Product Analysis. The GLC analyses were performed on a Shimadzu GC-3AH for the gaseous products and on a Shimadzu GC-4BPTF for the liquid and solid products. The GC-MS spectra were taken at 20 eV with a Hitachi RMU-6MG spectrometer connected with a Hitachi M 5201 gas chromatograph by using a 3 m×3 mm column of 5% Silicone OV-1 on Uniport KS. The main products were isolated on a Shimadzu GC-3BT using a 3 m×3 mm column of 10% Pluronic L 84 on Neopack IA (for products from phenanthrene) or a 3 m×3 mm column of 20% Silicone DC 550 on Celite 545 (for products from pyrene, chrysene, and fluoranthene). The NMR spectra were recorded on a Jeol JNM-PS-100 spectrometer, using tetramethylsilane as the internal standard. CCl_4 was used as the solvent for all the compounds. The UV spectra and the IR spectra were taken with a Hitachi 124 spectrometer and a Jasco IR-E spectrometer respectively.

Materials. The chrysene (G.R.), fluoranthene (E.P.), and phenanthrene (E.P.) were obtained from the Tokyo Kasei Kogyo Co., Ltd. The pyrene (G.R.) and anthracene (E.P.) were obtained from Nakarai Chemicals, Ltd., and Wako Pure Chemical Industries, Ltd., respectively. The anthracene and phenanthrene were recrystallized from ethanol. The fluoranthene (98% purity by GLC) contained a small amount of cyclopenta[*j,k*]phenanthrene. This impurity was not removed before use. The zinc iodide and the copper(I) bromide were obtained from the Mitsuwa Chemicals Co., Ltd., while the other metal halides used in this investigation were obtained from Nakarai Chemicals, Ltd. These salts were dried before use at 400 °C for 1 h in nitrogen.

General Procedure. All the experiments were carried out in the two different systems (A and B) as follows:

A) A stainless steel vessel containing 8 g of feed and an equimolar amount of the catalyst was placed in a stainless steel (SUS 32) autoclave with a capacity of 200 ml. The system was flashed and filled with hydrogen to 100 kg/cm^2; then the autoclave was heated up to the desired temperature. The time taken to reach the stage was from 60 to 70 min. The reaction system shaken in a horizontal direction (68 strokes/min) was maintained at 400 °C for the desired reaction period. No attempts were made to maintain the hydrogen pressure at a constant level during the reaction.

B) A stainless steel vessel containing 10 g of feed and an equimolar amount of the catalyst was placed in a stainless steel (SUS 32) autoclave with a capacity of 500 ml. Hydrogen was introduced into the autoclave to 100 kg/cm^2. The rate of the temperature rise was controlled to about 3 °C/min up to 400 °C, after which the temperature was held for the desired reaction period. The autoclave was shaken in a horizontal direction (70 strokes/min). No attempts were made to maintain the hydrogen pressure at a constant level during the reaction.

After the system (A or B) had been cooled to room temperature, gases were collected in a gas holder and analyzed by GLC (60—80 mesh Silica gel column). When the products were obtained in a solid state, they were dissolved in a proper solvent and analyzed by GLC (4.5 m×3 mm packed with 20% SE-30 on Uniport B 60—80 mesh, programmed from 30 to 270 °C, 5 °C/min, TCD, H_2 carrier). The products obtained in a liquid state were also analyzed by GLC in neat. The actual quantitative interpretation of a chromatogram is based on the peak area. The weight correction factors were determined by the measurement of the relative areas of authentic compounds. The values conveniently used in this study were as follows: retention time, 0—11 min, 0.9; 11—32 min, 1.0; 32—37 min, 1.1; 37—42 min, 1.2; 42—50 min, 1.3; 50 min-, 1.4 (Figs. 1—5). The mixture of coke and catalyst obtained after the extraction of the products was washed with hydrochloric acid in order to remove the catalyst. The coke obtained in this manner was dried and weighed.

Classification of Products. In order to characterize the activity of molten salt catalysts, the products were conveniently classified into 27 groups as follows: I, C_1—C_4 gases; II, C_5—C_7 alkanes; III, cycloalkanes; IV, monocyclic aromatics; V, indans and tetralins; VI, bicyclic aromatics; VII, dihydrophenanthrene; VIII, tetrahydrophenanthrene and its isomers; IX, octahydrophenanthrene and its isomers; X, phenanthrene; XI, higher-boiling compounds; XII, coke; XIII, benzindans, tricyclic aromatics, and their hydrogenated compounds; XIV, perhydropyrenes; XV, decahydropyrenes; XVI, tetrahydropyrene; XVII, hexahydropyrenes; XVIII, dihydropyrene; XIX, pyrene; XX, dodecahydrochrysene and its isomers; XXI, octahydrochrysene and its isomers; XXII, dihydrochrysene; XXIII, hexahydrochrysene and its isomers; XXIV, tetrahydrochrysene and its isomers; XXV, chrysene; XXVI, tetrahydrofluoranthene; XXVII, fluoranthene.

Results and Discussion

Identification of Products. The mass spectra of all the products in this study were obtained by means of GC-MS. The molecular weights of the products are given, and the chemical structures can be fairly deduced when specific cleavage patterns are found in the mass spectra. We previously published the results of the identification of the hydrocracked products of anthracene by considering their mass spectra in combination with the eluted order on the gas chromatogram estimated from their boiling points.[7] In that case, the isomerization of the skeleton of anthracene seemed not to occur. However, the isomerization between *sym*-octahydrophenanthrene and *sym*-octahydroanthracene was clearly found in this hydrocracking of anthracene over acidic molten salts,[6,8] so additional analytical methods were considered necessary for more detailed analyses. The main products were isolated by preparative GLC and analyzed by using NMR spectrometry. The NMR spectral data obtained for the isolated products were as follows: 6-butyltetralin, δ=0.92 (3H, t), 1.08—1.68 (4H, m), 1.78 (4H, m), 2.46 (2H, t), 2.66 (4H, m), and 6.6—7.0 (3H, m); 1,2,3,4,4a,9,10,10a-octahydrophenanthrene, 6.90 (4H, s); 1,2,3,4,5,6,7,8-octahydrophenanthrene, 1.75 (8H, m), 2.48 (4H, m), 2.65 (4H, m), and 6.60 (2H, s); 9,10-dihydrophenanthrene, 2.81 (4H, s), 7.02—7.33 (6H, m), and 7.48—7.72 (2H, m); 1,2,3,4-tetrahydrophenanthrene, 1.82 (4H, m), 2.88 (2H,m), 3.07 (2H, m), and 6.96—7.96 (6H, m); 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene, 6.5—7.0 (3H, m); 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene, 6.64 (2H, s); 4,5,9,10-tetrahydropyrene, 2.84 (8H, s) and 6.92 (6H, s); 1,2,3,3a,4,5-hexahydropyrene, 1.2—2.4 (6H, m), 2.6—3.4 (5H, m), and 6.8—7.7 (5H, m); 1,2,3,6,7,8-hexahydropyrene, 2.01 (4H, m), 3.0 (8H, t), and 6.92 (4H, s); 4,5-dihydropyrene, 3.24 (4H, s) and 7.16—7.68 (8H, m); 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene, 1.80 (4H, m), 2.72 (8H, m) and 6.76—7.80 (6H, m); 1,2,3,4,5,6-hexahydrochrysene, 1.84 (4H, m), 2.73 (8H, m), and 6.8—7.7 (6H, m); 8,9,10,11-tetrahydrobenz[*a*]anthracene, 1.80 (4H, m), 2.92 (4H, m), and 7.3—8.6 (8H, m); 1,2,3,4-tetrahydrochrysene, 1.96 (4H, m), 2.94 (2H, m), 3.16 (2H, m), and 7.2—8.8 (8H, m); 5,6-dihydrochrysene, 2.86 (2H, m), 3.20 (2H, m), and 6.8—8.1 (10H, m); 6-phenyltetralin, 1.82 (4H, m), 2.77 (4H, m), and 6.9—7.6 (8H, m); 5-phenyltetralin, 1.76 (4H, m), 2.56 (2H, m), 2.80 (2H, m), and 6.8—7.5 (8H, m). When the NMR spectrum of an isolated compound is complicated, the information about the molecular weight obtained from the mass-spectral measurements and the ratio of aromatic hydrogen to non-aromatic hydrogen from the NMR method often gave the correct structure (*e.g.*, the distinction between 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene and 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene). When the amount of a compound isolated was small, UV spectrometry was conventionally used for the structural confirmation. The type of aromatic hydrocarbon (that is, benzene, naphthalene, biphenyl, anthracene, phenanthrene, pyrene, fluoranthene, chrysene, and so on) is clarified based on the characteristic absorption bands. For example, the absorption wave numbers of phenanthrene, 4,5-dihydropyrene, 1,2,3,4-tetrahydrochrysene, and 8,9,10,11-tetrahydrobenz[*a*]anthracene differed to some degree, but their characteristic absorption bands were similar. This indicates that these compounds all have a phenanthrene skeleton. Of course, IR spectrometry played an important role

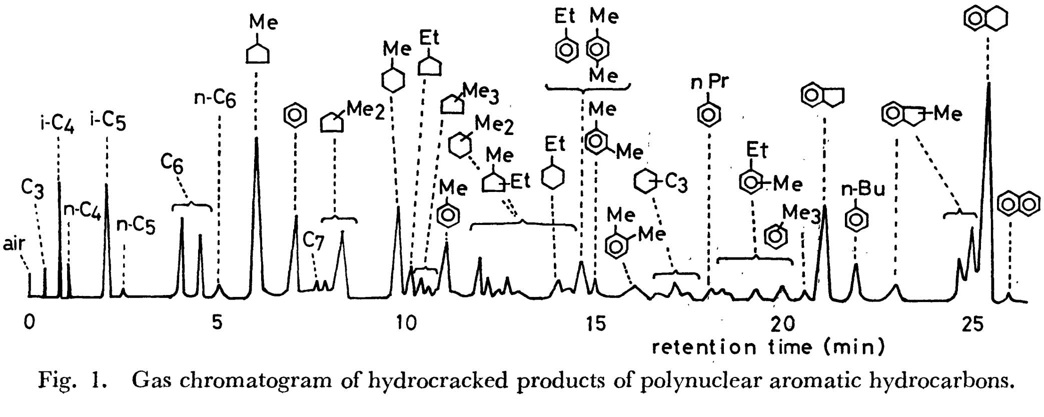

Fig. 1. Gas chromatogram of hydrocracked products of polynuclear aromatic hydrocarbons.

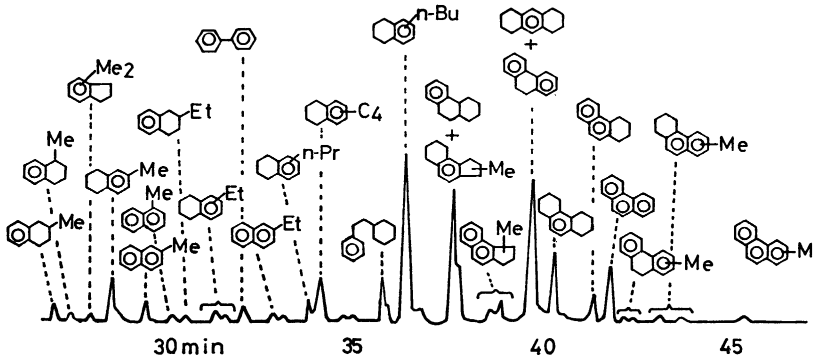

Fig. 2. Gas chromatogram of hydrocracked products of phenanthrene.

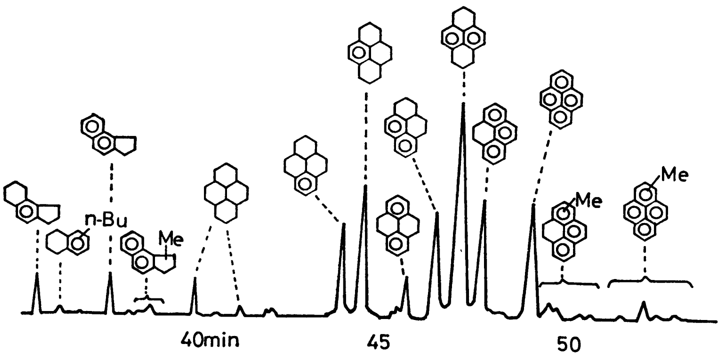

Fig. 3. Gas chromatogram of hydrocracked products of pyrene.

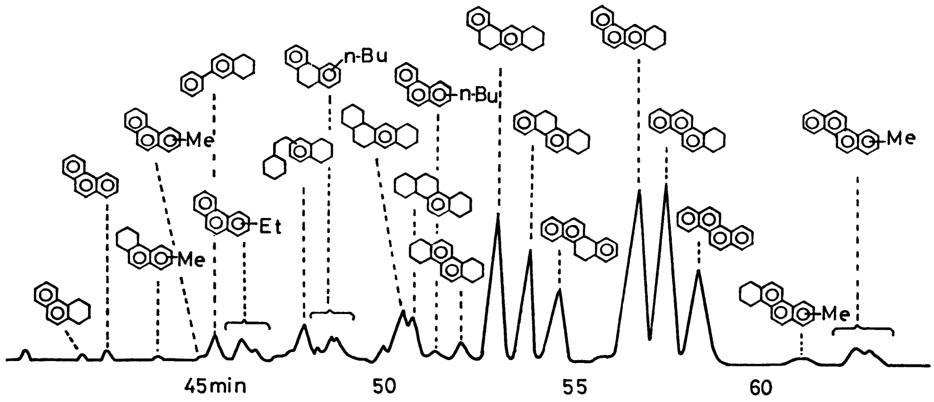

Fig. 4. Gas chromatogram of hydrocracked products of chrysene.

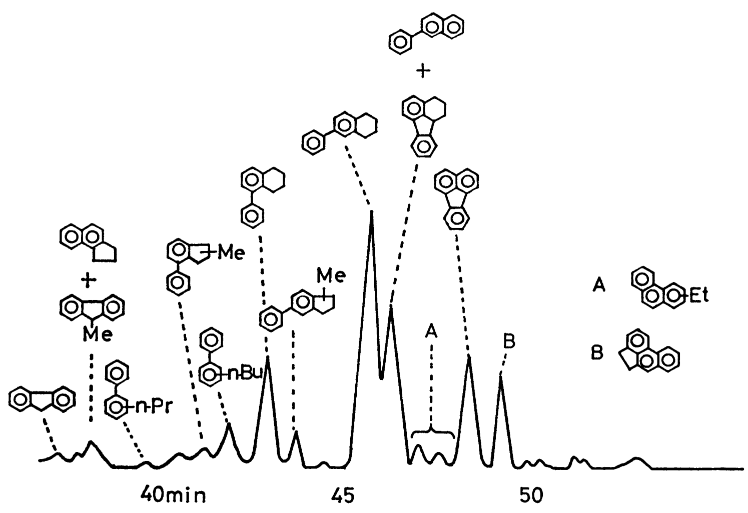

Fig. 5. Gas chromatogram of hydrocracked products of fluoranthene.

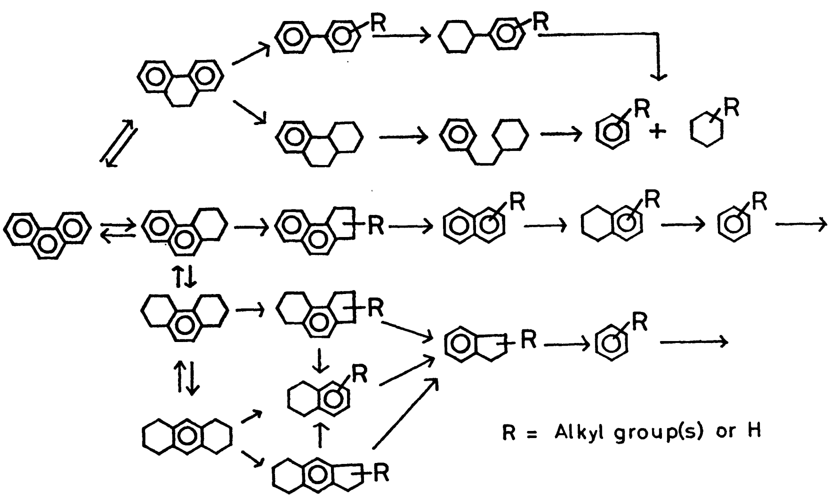

Fig. 6. Probable reaction process of phenanthrene.

in the analysis. The cleavage patterns of the mass spectra of the compounds identified by using these analytical methods could then be applied to other compounds. The GC charts of the hydrocracked products are shown in Figs. 1—5, where the structures characterized or assumed are listed. The structures of benzindan derivatives and their hydrogenated compounds are not certain because the distinction between 2,3-dihydro-1*H*-benz[*e*]indene and 2,3-dihydro-1*H*-benz[*f*]indene is not clear only by considering their mass spectra. Consequently, the structures for these compounds listed in these figures are chosen for convenience. By this exhaustive analysis, the probable reaction process can be estimated and the difference in catalytic activity among the molten salt catalysts can be clarified.

Hydrocracking of Phenanthrene. The most probable reaction process is shown in Fig. 6. The most important characteristic of the hydrocracking of phenanthrene is the isomerization between *sym*-octahydrophenanthrene and *sym*-octahydroanthracene. We also observed the isomerization in the hydrocracking of anthracene in the presence of a Lewis acid.6,8) A constant ratio of them in equilibrium was observed, so this isomerization is considered to be reversible. This finding is consistent with that observed over aluminum chloride by Schroeter.9) On the other hand, this isomerization was not observed in their hydrogenation in the presence of alkali metals.10) These findings suggest that the decomposition process of *sym*-octahydroanthracene must also be considered in the hydrocracking of phenanthrene over acidic catalysts.

The formation of 1-cyclohexyl-2-phenylethane was found in the products[$\delta=2.56$(2H,t,$J=8$ Hz)]. *unsym*-Octahydrophenanthrene is considered to be cleaved and hydrogenated to that compound, judging from the similarity of the structures of these two compounds. In the presence of aluminum chloride, secondary alkyl-

Table 1. Hydrocracking of phenanthrene

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction temperature, 400 °C; reaction system A: Catalyst/Feed=1.0 (mol/mol), Hydrogen/Feed=18.8 (mol/mol); B: Catalyst/Feed=1.0, Hydrogen/Feed=26.7.

		Run No.						
		1	2	3	4	5	6	7
Catalyst (mol: mol)		$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)	ZnI_2/KI (80:20)	$ZnCl_2/NiCl_2$ (90:10)	—	$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)
Reaction system		A	A	A	A	B	B	B
Reaction time (h)		3	3	3	3	1	1	1
Product (wt %)	I	0.4	27.7	0.2	11.2	2.0	1.6	3.2
	II	—	7.2	—	1.4	—	—	0.3
	III	—	7.0	0.1	7.5	—	—	2.2
	IV	0.1	33.2	—	10.5	—	0.3	3.3
	V	0.1	12.4	2.2	11.5	0.1	0.9	10.9
	VI	0.4	2.2	0.1	1.0	0.6	0.4	0.6
	VII	8.0	0.5	14.2	9.8	13.6	21.2	14.8
	VIII	3.5	1.4	13.7	6.9	5.7	9.5	7.5
	IX	—	1.1	5.2	4.8	3.5	7.0	22.6
	X	87.5	1.4	63.4	33.4	74.5	55.5	24.9
	XI	—	1.3	0.9	2.0	—	3.2	5.0
	XII	—	4.6	—	—	—	0.4	4.7

benzene was dealkylated in preference to primary alkylbenzene.[11] If this finding is extended to the case of *unsym*-octahydrophenanthrene, the preferable scisson of its C_{4a}–C_{4b} bond to produce 1-cyclohexyl-2-phenylethane may be reasonable. Although the above decomposition process has never been indicated in this connection, it is one of the most important decomposition routes in the hydrocracking of phenanthrene.

The product distributions are shown in Table 1. From the standpoint of the distribution of the gaseous products, especially the ratio of iso to normal isomers, the catalytic action of molten salts was discussed in a previous paper.[5] The constituents of the gaseous products in Run 2 were as follows: methane, 8.0 wt %; ethane, 7.5%; propane, 33.6%; isobutane, 38.0%; butane, 9.3%; butenes, 3.6%. Since the ratio of isobutane to butane is higher than that in the thermodynamic equilibrium, this hydrocracking is considered to proceed by means of a carbonium-ion mechanism.[12]

The catalytic activity of the binary mixture of zinc iodide and potassium iodide is superior to that of zinc chloride in the hydrogenation of phenanthrene (Runs 1 and 2). In this case, attention must be paid to the fact that the intrinsic cracking activity is lowered by the addition of potassium iodide because of the formation of the complex ions.[5,13] The conversion in the presence of the zinc chloride containing 10 mol % nickel(II) chloride is lower than that in the presence of zinc chloride containing 40 mol % copper(I) chloride, but the product distributions obtained over these two catalysts are similar (Runs 2 and 4). Therefore, the decomposition process of phenanthrene over $NiCl_2/ZnCl_2$ is considered to be intermediate between that over $ZnCl_2$ and that over $ZnCl_2$/CuCl. This finding suggests that zinc chloride has a good intrinsic cracking activity under these reaction conditions, but its hydrogenating activity is not so high. The addition of a good hydrogenating catalyst to zinc chloride will produce an excellent catalyst for the hydrocracking of polynuclear aromatic hydrocarbons. Consequently, these molten salt catalysts act as dual-functional catalysts, and appropriate molten mixtures of metal salts with the hydrogenating activity and metal salts with the cracking activity may be able to become effective catalysts.

A remarkable catalytic action of $ZnCl_2$/CuCl was observed in this investigation (Runs 1 and 2). The hydrogenating activity of zinc chloride is very low in this temperature range (Run 1). The intrinsic cracking activity of zinc chloride may not be able to operate because phenanthrene is little hydrogenated. The addition of copper(I) chloride to zinc chloride must contribute to the improvement of the hydrogenating activity of the catalyst. The difference in the yield of octahydrophenanthrene and its isomers (IX) between Run 6 and Run 7 indicates this improvement in the hydrogenating activity.

By comparing the results of Run 1 and Run 6, phenanthrene was found to be more hydrogenated in Run 6 than in Run 1. From this fact, it can be seen that the ratio of hydrogen to the feed must affect the product distributions. In addition, the material, the capacity, the stirring pattern, and the memory effect of the autoclave are also important factors in dominating these reactions. Therefore, even if the pressure, the temperature, and the ratio of hydrogen to the feed should be maintained at constant levels in the different systems, similar results may not be obtained.

Hydrocracking of Pyrene. Pyrene is liable to accept the hydrogenation (Runs 1 and 9), but is fairly stable to the catalytic cracking (Runs 2 and 10), com-

Table 2. Hydrocracking of pyrene

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction temperature, 400 °C; reaction system A: Catalyst/Feed=1.0 (mol/mol), Hydrogen/Feed=21.3; reaction system B: Catalyst/Feed=1.0, Hydrogen/Feed=30.5.

		Run No.						
		8	9	10	11	12	13	14
Catalyst (mol: mol)		—	$ZnCl_2$	$ZnCl_2$/CuCl (60:40)	ZnI_2/KI (80:20)	$ZnBr_2$/CuBr (60:40)	$ZnCl_2$	$ZnCl_2$/CuCl (60:40)
Reaction system		A	A	A	A	A	B	B
Reaction time (h)		3	3	3	3	3	3	3
Product (wt %)	I	—	0.7	13.7	—	22.8	6.4	11.3
	II	—	—	1.1	—	4.4	0.3	2.5
	III	—	—	1.9	—	9.7	2.9	6.3
	IV	—	—	3.0	—	5.1	2.0	3.8
	V	—	—	3.2	—	4.3	2.1	5.7
	VI	—	—	tr	—	tr	0.2	0.1
	XIII	0.5	0.4	3.6	1.6	5.6	2.1	3.2
	XIV	—	—	1.2	3.5	2.3	4.3	4.8
	XV	—	1.5	7.5	16.7	4.5	20.4	14.4
	XVI	1.0	3.0	2.6	3.5	1.5	4.3	3.5
	XVII	3.6	8.5	21.3	40.4	7.7	31.1	20.9
	XVIII	16.7	23.7	13.5	15.8	4.3	9.6	7.8
	XIX	78.2	62.2	19.7	18.5	4.6	8.5	6.0
	XI	—	—	3.9	—	2.2	4.8	8.2
	XII	—	—	3.8	—	21.0	1.0	1.5

pared with phenanthrene. If the decomposition of dihydropyrene to phenanthrene takes place, the hydrocracking may occur easily. In practice, however, dihydropyrene was converted further to highly hydrogenated pyrenes, and so the probable decomposition routes of pyrene could not be clarified in detail in this investigation. In the hydrocracking of pyrene, a binary mixture of zinc bromide and copper(I) bromide was used for the purpose of examining the effect of the difference of halide (Run 12). A high catalytic activity was found, but a fairly large amount of coke was also formed. This is probably the reason why the reaction conditions are not adequate for this catalyst. There is still much room for an examination of the reaction conditions. No remarkable difference in the product distributions of Runs 13 and 14 was observed because the large amount of hydrogen and the other factors mentioned above might serve to make uniform the characteristics of these two catalysts. This may be considered to be indirect evidence for the improvement of the hydrogenating activity by the addition of copper(I) chloride. The binary mixture of zinc iodide and potassium iodide displayed an excellent hydrogenating activity and a lack of the cracking activity (Run 11).

Hydrocracking of Chrysene. The results of the hydrocracking of chrysene are shown in Table 3. Chrysene is hydrogenated to hydrochrysenes, which then isomerize to hydrobenz[*a*]anthracenes (Fig. 7). For example, 1,2,3,4,5,6-hexahydrochrysene (containing a *sym*-octahydrophenanthrene skeleton) isomerizes to 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene (containing a *sym*-octahydroanthracene skeleton) in the presence of a Lewis acid. The formation of 8,9,10,11-tetrahydrobenz[*a*]anthracene is attributed to either the isomerization of 1,2,3,4-tetrahydrochrysene or the dehydrogenation of 5,6,8,9,10,11-hexahydrobenz[*a*]anthracene; it is not certain which occurred in practice. The main decomposition pathways of hydrochrysenes and their isomers are probably the formations of butylphenanthrene and the hydrogenated compounds. These phenanthrene-type compounds are hydrocracked in a manner similar to that described in the hydrocracking of phenanthrene. The decomposition route from dodecahydrochrysene and benz[*a*]anthracene to 5- and 6-(2-cyclohexylethyl)-tetralin respectively becomes fairly important in the B system (Run 18), because the extent of the hydrogenation is relatively high. Of course, the saturated six-member rings of tetra-, octa-, dodecahydrochrysenes, and hydrobenz[*a*]anthracenes isomerize to five-member rings. The probable reaction process of chrysene is shown in Fig. 7. A high catalytic activity of $ZnCl_2/CuCl$ was also observed in the hydrocracking of chrysene. Chrysene accepts hydrogenation relatively easily in comparison with phenanthrene (Runs 1 and 15).

Table 3. Hydrocracking of chrysene

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction temperature, 400 °C; reaction system A: Catalyst/Feed=1.0, Hydrogen/Feed=24.1; reaction system B: Catalyst/Feed=1.0, Hydrogen/Feed=34.4.

		Run No.			
		15	16	17	18
Catalyst		$ZnCl_2$	$ZnCl_2/CuCl$	$ZnCl_2$	$ZnCl_2/CuCl$
(mol: mol)			(60:40)		(60:40)
Reaction system		A	A	B	B
Reaction time (h)		3	3	3	3
Product (wt %)	I	2.3	28.2	6.7	7.0
	II	—	10.7	—	3.7
	III	—	17.6	1.3	19.5
	IV	—	25.2	0.6	8.3
	V	0.4	10.1	4.5	24.1
	VI	—	1.0	0.6	2.2
	XIII	3.6	3.4	12.0	24.3
	XX	—	—	5.1	4.0
	XXI	2.3	0.3	2.9	0.5
	XXII	8.6	—	7.5	0.2
	XXIII	7.3	0.3	14.8	2.2
	XXIV	11.3	0.4	26.0	2.0
	XXV	64.2	0.1	9.2	—
	XI	—	—	7.7	—
	XII	—	2.7	1.1	2.0

Hydrocracking of Fluoranthene. In order to examine the initial decomposition process of fluoranthene, 1 h was used as the reaction time. The results are shown in Table 4. The tetrahydrofluoranthene formed by the hydrogenation of fluoranthene is ruptured to 5-phenyl-

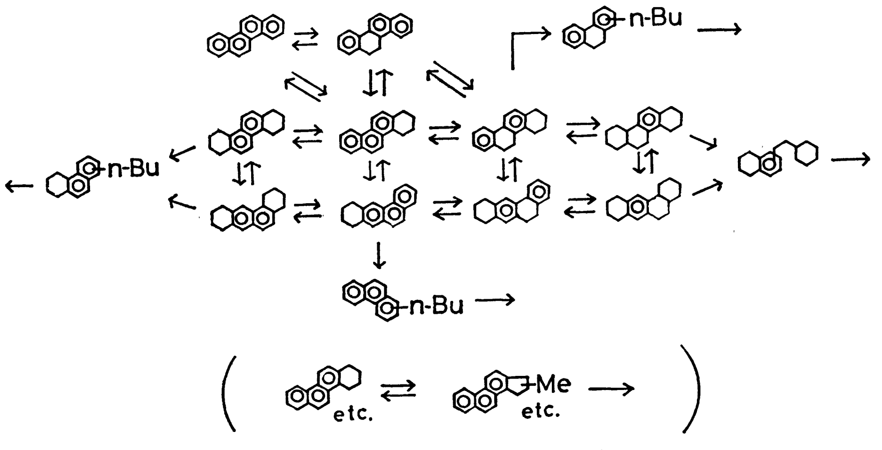

Fig. 7. Probable reaction process of chrysene.

Table 4. Hydrocracking of fluoranthene

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction temperature, 400 °C; reaction system A: Catalyst/Feed=1.0, Hydrogen/Feed=21.3; reaction system B: Catalyst/Feed=1.0, Hydrogen/Feed=30.5.

	Run No.	
	19	20
Catalyst (mol: mol)	$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)
Reaction system	A	A
Reaction time (h)	1	1
I	—	14.9
II	—	3.3
III	—	5.8
IV	—	10.4
V	—	7.9
VI	—	5.4
XIII	2.4	31.5
XXVI	15.6	4.2
XXVII	80.4	5.2
XI	1.6	6.1
XII	—	5.3

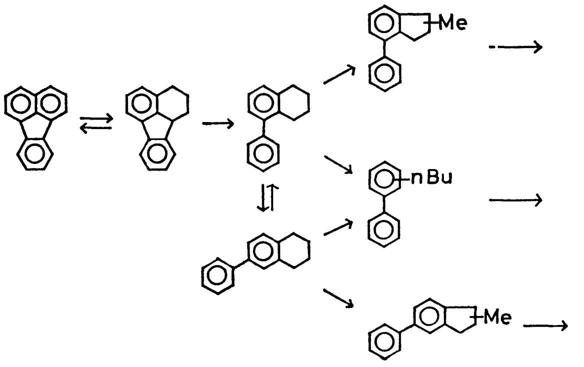

Fig. 8. Probable reaction process of fluoranthene.

tetralin in the presence of hydrogen, followed by isomerization to 6-phenyltetralin. Consequently, the amounts of biphenyl derivatives were fairly large. The great formation of biphenyls in the hydrocracking of a heavy anthracene oil[5] may be attributed to this decomposition pathway. The decomposition process of fluoranthene is shown in Fig. 8.[14]

Hydrocracking of Anthracene. The details of the hydrocracking of anthracene have been reported in a preliminary study.[6] Anthracene is more easily hydrogenated than phenanthrene. The product distribution of anthracene is similar to that of phenanthrene when the hydrocracking proceeds to some degree. This phenomenon is attributable to the fact that the marginal hydrogenated ring is ruptured in preference to the central ring in a dihydro derivative, for the cleavage of a saturated single C–C bond of dihydroanthracene or phenanthrene should result in a different type of compound. In addition, it is necessary to take into account the fact that the isomerization between *sym*-octahydroanthracene and *sym*-octahydrophenanthrene does away with the difference in their product distributions.

Concerning the reaction routes over these molten salt catalysts, the findings in this investigation may be outlined as follows: 1) the isomerization between *sym*-octahydrophenanthrene and *sym*-octahydroanthracene in the hydrocracking of phenanthrene and anthracene, and a similar isomerization in the hydrocracking of chrysene; 2) the decomposition of *unsym*-octahydrophenanthrene to 1-cyclohexyl-2-phenylethane in the hydrocracking of phenanthrene and a similar cleavage in the hydrocracking of chrysene; 3) a decomposition pathway leading to biphenyls in the hydrocracking of fluoranthene. On the other hand, $ZnCl_2/CuCl$ salt, which is considered to act as a dual-functional catalyst, displayed a more efficient catalytic activity for *cata*-condensed aromatic hydrocarbons (phenanthrene, anthracene, and chrysene) than for *peri*-condensed aromatic hydrocarbons (pyrene). Moreover, these results (listed in Figs. 1—5) were useful in the identification of the hydrocracked products of Yūbari coal.[16]

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