December, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (12), 3631—3634 (1978) 3631

The Hydrocracking of Alkyl-substituted Polynuclear Aromatic Hydrocarbons over $ZnCl_2/CuCl$ Molten Salt Catalyst[1)]

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(Received April 13, 1978)

The hydrocracking of alkyl derivatives of polynuclear aromatic hydrocarbons (naphthalene, anthracene, dihydroanthracene, phenanthrene, and dihydrophenanthrene) over $ZnCl_2/CuCl$ molten salt was examined at 400 °C for 3 h in a batch autoclave system. The kinds of alkyl groups, the positions of the alkyl groups, and the types of condensed rings were changed in order to clarify the decomposition process of the polynuclear aromatic hydrocarbons. On the basis of the detailed product distribution obtained by using GC-MS, the behavior of the alkyl group attached to the condensed ring under these reaction conditions was found to be different. Generally, in this investigation, the alkyl group was not completely dealkylated in the initial stage and remained in the products as monocyclic aromatics; the extent of dealkylation was found to be dependent upon the type of starting materials. In the hydrocracking of 9,10-dihydroanthracene, dehydrogenation occurred in preference to the opening of the central ring.

Hydrocracking is one of the important methods of obtaining liquid fuels from coal. In order to obtain the fundamental data with regard to the hydrocracking of coal, we have already employed the following model substances: 1) A pure substance:[2)] The properties of the starting material are known and the reaction process will be easily deduced. 2) A heavy anthracene oil:[3)] The NMR analyses can be applied, and the main components can be determined by using analytical methods (ex. GC-MS). 3) Solvent refined coal (SRC):[4)] This is considered to be representative of the structure of coal. The NMR analyses can be applied, but the constituents cannot be determined.

Previously,[2)] we used polynuclear aromatic hydrocarbons (anthracene, phenanthrene, pyrene, chrysene, and fluoranthene), which were supposed to be structural units of bituminous coal, as the model substances. The detailed product distributions and the differences of the catalytic activities among some molten salts were presented and discussed. The $ZnCl_2/CuCl$ molten salt was found to be one of the superior hydrocracking catalysts for polynuclear aromatic hydrocarbons.

In the study of structural units of coal, one of the major problems is to understand the behavior of the substituents which attach to the condensed aromatic rings in the hydrocracking reaction. From this standpoint, we will apply the findings reported in the previous paper[2)] to interprete the results obtained in the hydrocracking of alkyl-substituted polynuclear aromatic hydrocarbons, in order to clarify the effect of the alkyl substituents on the product distributions. The characteristic behavior of the alkyl groups on the starting material and the decomposition process will be described in this paper.

Experimental

General Procedure. A stainless steel vessel containing 8 g of feed (in the case of the unsubstituted aromatic hydrocarbon) and an equimolar amount of the catalyst ($ZnCl_2$: CuCl=60 mol %: 40 mol %) was placed in a stainless steel (SUS 32) autoclave with a capacity of 200 ml. In the hydrocracking of an alkyl-substituted or dihydro aromatic hydrocarbon, the quantity of feed used was equimolar with the unsubstituted derivative containing the same condensed ring. Hydrogen was introduced into the autoclave to achieve a pressure of 100 kg/cm^2; then the autoclave was heated up to the desired temperature. This took from 60 to 70 min. The reaction system was shaken in a horizontal direction (68 strokes/min) and maintained at 400 °C for 3 h. No attempts were made to maintain the hydrogen pressure at a constant level during the reaction. The identification and the determination of the products were carried out according to the methods described previously.[2)]

Materials. The naphthalene (Ia), 2,6-dimethylnaphthalene (Id), and fluorene (VII) were obtained from Wako Pure Chemical Industries, Ltd. The 1-methylnaphthalene (Ib), 2-methylnaphthalene (Ic), anthracene (IIa), and 9,10-dihydroanthracene (Va) were obtained from Nakarai Chemicals, Ltd. The phenanthrene (IIIa) and chrysene (IV) were obtained from the Tokyo Kasei Kogyo Co., Ltd. 9-Methylanthracene (IIb) and 9-propylanthracene (IIc) were prepared by the reaction of anthrone with methylmagnesium iodide and propylmagnesium bromide respectively.[5)] 2-Methylanthracene (IId) was prepared by the reduction of 2-methylanthraquinone with zinc dust in NaOH aqueous solution and toluene.[6)] 9,10-Dihydro-9-methylanthracene (Vb) was prepared from Va and methyl iodide by using BuLi.[7)] Similarly, 9,10-dihydro-9,10-dimethylanthracene (Vc) was synthesized by using Vb as the starting material. 9-Methylphenanthrene (IIIb) was prepared from 9-bromophenanthrene and methyl iodide in the presence of BuLi.[8)] 9-Bromophenanthrene was prepared by the addition of bromine to IIIa, followed by thermal elimination of hydrogen bromide. 9,10-Dihydro-9-methylphenanthrene (VI) was prepared by the reduction of IIIb by using Li in liquid NH_3 in the presence of iron(III) chloride.[8)] All the purities of these compounds, determined by GC, were more than 95%. The zinc chloride and copper(I) chloride were obtained from Nakarai Chemicals, Ltd. The mixture of $ZnCl_2$ and CuCl was dried before use at 400 °C for 1 h in nitrogen.

Classification of Products. In order to clarify the reactivity of the starting material over the molten salt, it is necessary to know the product distribution. The products were classified for convenience into seven groups as follows: **1**, C_1-C_4 gases; **2**, C_5-C_7 alkanes; **3**, cycloalkanes; **4**, monocyclic aromatics; **5**, indans, tetralins, and bicyclic aromatics; **6**, dihydrobenzindenes, tricyclic aromatics, and their hydrogenated compounds; **7**, coke.

Results and Discussion

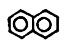
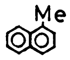
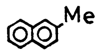
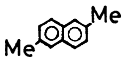
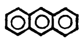
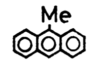
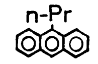
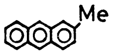
Table 1 shows the product distributions according to the classification described in the experimental section. The reaction conditions were decided by considering the extent of the progress of the hydrocracking, because a high conversion is required in order to discuss the reaction process of hydrocracking based on the product distribution.

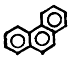
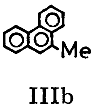
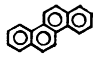
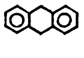
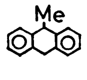
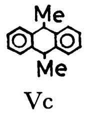
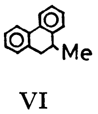
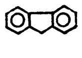
Influence of the Number of Rings in the Condensed Aromatic Hydrocarbon. Table 1 shows that the yield of cycloalkanes(**3**) increases with increasing number of rings, from the comparison of the results of naphthalene (Run 1), phenanthrene(Run 9), and chrysene(Run 11). Here, the yield of **3** in the hydrocracking of naphthalene is much lower than that in the hydrocracking of anthracene, phenanthrene, and chrysene. This finding strongly indicates that the cleavage of the C–C bonds of the central rings in highly hydrogenated polynuclear aromatic hydrocarbons containing more than three rings (ex. *unsym*-octahydroanthracene, *unsym*-octahydrophenanthrene, and so on) is one of the main decomposition pathways. Actually, the decomposition of *unsym*-octahydrophenanthrene to 1-cyclohexyl-2-phenylethane in the hydrocracking of phenanthrene and a similar cleavage in the hydrocracking of chrysene were found and reported in the previous paper.[2] This finding also demonstrates that the contribution of the pathway *via* decalin to the decomposition process of naphthalene is minor,[9] and that this type of catalyst is relatively inactive for the hydrogenation and hydrocracking of monocyclic aromatics. The latter seems to be desirable for obtaining a high yield of gasoline.[10]

Influence of Kinds of Alkyl Groups in the Hydrocracking of Anthracenes. Tables 2 and 3 describe the compositions of gases(**1**) and monocyclic aromatics(**4**) respectively. The behavior of the alkyl group can be deduced by using these results, because the difference in the composition of **1** or **4** between the alkyl polynuclear aromatic hydrocarbon and the corresponding unsubstituted compound is apparent. First we will discuss the results for anthracene derivatives and compare the reactivity of IIb with that of IIc. Two experiments(Runs 6 and 7) were carried out to investigate the difference of the composition of the products in accordance with the change in the alkyl group. The relative content of methane in Run 6 is higher than that in Run 5. Similarly the relative content of propane in Run 7 is quite a bit higher than that in Run 5. These findings show that the alkyl group is eliminated in the course of hydrocracking. In the case of methyl-substituted polynuclear aromatics, the ratio of benzene to toluene(R) is supposed to indicate the extent of demethylation, because the

Table 1. Distribution of hydrocracked products

Reaction conditions: $ZnCl_2$: CuCl=60: 40 (mol: mol); Feed/Catalyst=1.0 (mol/mol); initial hydrogen pressure, 100 kg/cm^2; reaction time, 3 h; reaction temperature, 400 °C.

		Run No.							
		1	2	3	4	5	6	7	8
									
	Feed	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId
Products (wt %)	**1**	45.7	33.4	39.3	40.7	38.1	42.3	25.7	28.8
	2	3.7	6.6	6.6	7.2	7.9	7.9	10.3	10.7
	3	1.5	2.0	1.8	1.6	10.8	7.6	8.5	10.3
	4	46.4	47.7	45.3	44.8	27.7	24.3	27.6	24.6
	5	2.2	9.8	6.4	5.5	8.9	10.5	15.2	15.2
	6	—	—	—	—	2.5	5.0	11.3	10.3
	7	0.5	0.5	0.6	0.2	4.1	2.4	1.4	0.1

		Run No.							
		9	10	11	12	13	14	15	16
									
	Feed	IIIa	IIIb	IV	Va	Vb	Vc	VI	VII
Products (wt %)	**1**	27.7	41.4	28.2	42.0	35.9	55.6	41.7	30.6
	2	7.2	7.7	10.7	7.2	8.5	7.8	6.7	4.2
	3	7.0	6.4	17.6	8.6	8.8	3.9	6.4	6.5
	4	33.2	34.0	25.2	29.5	24.5	28.0	30.1	25.0
	5	14.6	6.0	11.0	9.1	14.5	3.0	10.0	14.3[b]
	6	5.7	3.3	4.5[a]	2.4	7.2	1.3	5.0	17.5
	7	4.6	1.2	2.7	1.2	0.6	0.4	0.1	1.9

a) Containing tetracyclic compounds (1.1%). b) Containing biphenyls (10.5%).

Table 2. Relative distribution of gases (mol %)

	Run No.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Feed	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId	IIIa	IIIb	IV	Va	Vb	Vc	VI	VII
C1[a]	33.5	22.8	23.8	22.8	20.8	29.5	20.3	26.1	20.9	21.4	21.0	17.7	40.3	50.4	34.1	23.4
C2[b]	12.8	9.9	11.4	11.5	12.2	8.9	9.3	8.4	10.5	7.8	8.5	10.8	7.8	6.9	9.0	12.7
C3[c]	25.6	30.8	31.4	28.6	29.3	27.6	45.7	22.0	31.9	34.6	26.8	32.2	22.3	19.6	26.8	33.9
C4[d]	28.1	36.5	33.4	37.1	37.7	34.0	24.7	43.5	36.7	36.2	43.7	39.2	29.6	23.1	30.1	30.1

a) Methane. b) Ethane. c) Propane. d) Butanes and butenes.

Table 3. Relative distribution of monocyclic aromatics (mol %)

	Run No.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Feed	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId	IIIa	IIIb	IV	Va	Vb	Vc	VI	VII
A[a]	68.9	25.7	25.9	7.9	41.7	27.9	41.4	19.9	38.4	23.0	39.1	39.1	26.3	19.0	22.1	47.9
B[b]	16.5	34.4	35.8	33.7	26.9	27.8	28.8	31.8	23.4	31.0	26.3	24.4	27.1	25.1	29.2	26.8
C[c]	11.3	28.3	27.9	31.3	17.5	24.0	16.3	22.6	23.3	28.6	22.5	24.7	29.9	32.5	29.5	19.3
D[d]	1.9	9.0	8.5	20.0	7.7	13.7	8.7	13.7	8.2	11.2	7.3	7.0	10.8	17.5	13.9	4.8
E[e]	1.4	2.6	1.9	7.1	6.2	6.6	4.8	12.0	6.7	6.2	4.8	4.8	6.0	5.9	5.3	1.1
R[f]	4.18	0.75	0.72	0.23	1.55	1.00	1.44	0.63	1.64	0.74	1.49	1.60	0.97	0.76	0.76	1.79

a) Benzene. b) Toluene. c) Ethylbenzene and xylenes (C_2 alkylbenzenes). d) C_3 alkylbenzenes. e) Alkylbenzenes containing more than C_4. f) R=benzene/toluene (mol/mol).

value may increase with increasing demethylation according to the main reaction scheme, as shown later (*cf.* Fig. 1), and we used this ratio as a convenient measure of demethylation. The comparison of R in Run 6 with R in Run 5 shows that the methyl group of IIb is conserved in monocyclic aromatics in the course of hydrocracking. The ratio of the yield of unsubstituted tricyclic compounds to that of alkylated tricyclic compounds was 8.9 in the case of IIc and 2.3 in the case of IIb. In addition, the composition of monocyclic aromatics in Run 7 was very similar to that in Run 5. All of these findings indicate that the propyl group is dealkylated more easily than the methyl group. Similar phenomena were observed in the hydrocracking of alkylbenzenes in the presence of acidic catalysts.[11] These findings may be explained by considering that propylanthracene possesses the possibility of isomerization to isopropylanthracene and that the secondary alkyl group can be dealkylated in preference to the primary alkyl group.[11,12] The similarity between IIa and IIc in the composition of monocyclic aromatics would demonstrate that the propyl group of IIc is mainly dealkylated in the initial decomposition stage. On the other hand, the decomposition process of the marginal hydrogenated rings prior to dealkylation is also considered to be of importance in the case of IIb.

Influence of Positions of Alkyl Groups and Types of Condensed Rings. Since the presence of methyl group remarkably influenced the decomposition of the polynuclear aromatics, the methyl derivatives were used for the following experiments. The experiments of IIb and IId were carried out to clarify the effect of the position of methyl group attached to the anthracene skeleton on the composition of the decomposed products. The value of R in IId is lower than that in IIb; this finding suggests that the methyl group of IId is well conserved in monocyclic aromatics in comparison with that of IIb. This result is interpreted by the idea that the demethylation prior to the hydrocracking of the condensed ring has a minor contribution to the reaction process in the hydrocracking of IId, that is, the methyl group of IIb is eliminated more easily than that of IId. The experiments of IIb and IIIb were carried out to clarify the difference of the type of condensed rings. The ease of demethylation in the initial decomposition process differs in these two cases. The methyl group of IIIb is conserved in monocyclic aromatics much more frequently than that of IIb. It is noteworthy that the composition of monocyclic aromatics of IV is fairly similar to that of IIIa. The effect of the presence of the methyl group on the composition of monocyclic aromatics (Run 10) is observed more dramatically than that of the increase of the number of the aromatic rings(Run 11).

Hydrocracking of Naphthalenes. It is noteworthy that a remarkable difference in the R values was observed

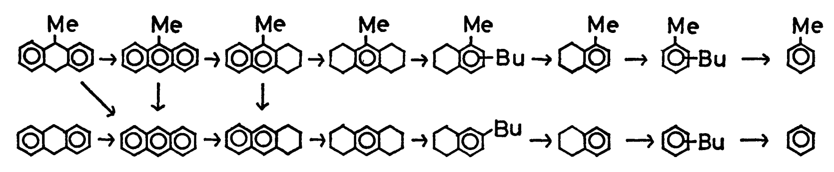


Fig. 1. Main reaction scheme of dihydroanthracene derivatives.

in the hydrocracking of naphthalene derivatives(Runs 1—3). This finding suggests that the unsubstituted ring is more easily hydrogenated than the methylated ring. This fact is the basis for asserting that the alkyl groups on the polynuclear aromatic hydrocarbons influence the composition of monocyclic aromatics in this hydrocracking. The effect of the position of the methyl group on the composition of monocyclic aromatics was hardly observed in the case of Ib and Ic(Runs 2 and 3). The experiment of Id (Run 4) seems to be most suitable for investigating the demethylation. If Id never undergoes the demethylation, the yield of benzene should become zero. The presence of a little quantity of benzene demonstrates the occurence of demethylation; however, the contribution of the demethylation in the initial stage to the composition of monocyclic aromatics seems rather insignificant.

Hydrocracking of Dihydro Tricyclic Aromatics. The hydrocracking of Va is of importance for clarifying the decomposition process of IIa.[13–15] If the central methylene bridge of Va is ruptured, the yield of monocyclic aromatics should increase remarkably compared with IIa. However, the product distributions of these two hydrocracking reactions are similar: Va seems to undergo dehydrogenation, followed by the decomposition process, in a way similar to IIa. The experiments of Vb and Vc were carried out in anticipation of the specific reaction caused by introducing the methyl group(s) to the central carbon atom(s) of 9,10-dihydroanthracene. The product distribution of Vb(Run 13) is successfully explained by considering that the dehydrogenation and demethylation occurred in the initial stage; that is, Vb was mainly decomposed *via* IIa or IIb. Vc is also considered to be decomposed in a manner similar to Vb, and so the opening of the central ring of this type of compound is considered to be small in this hydrocracking reaction. Fig. 1 shows the main decomposition scheme of 9,10-dihydroanthracene derivatives. The ease of dealkylation of the butyl group compared with the methyl group is considered to govern this decomposition process. If the C_{8a}–C_9 bond of VI is fairly well cleaved, the yield of biphenyl derivatives in the hydrocracking of VI should be higher than that in the hydrocracking of IIIb. However, no such increase of the yield of biphenyl derivatives could be observed, and so VI seems to undergo demethylation and dehydrogenation in the initial decomposition process. On the other hand, the pathway to the biphenyl derivatives becomes very important in the case of VII, because VII has no pathway of dehydrogenation to the stable aromatic compounds. In this case, the lowering of the reactivity was observed.

Conclusion

The hydrocracking of alkyl-substituted polynuclear aromatic hydrocarbons was carried out to clarify the decomposition scheme and the behavior of the alkyl group. The findings are outlined as follows: 1) The decomposition route *via* highly hydrogenated compounds becomes important with increasing numbers of rings of the polynuclear aromatics. 2) The alkyl group substituted on the polynuclear aromatic hydrocarbon is not completely dealkylated in the initial stage and remains in the products as monocyclic aromatics. The extent of dealkylation depends on the properties (that is, kinds and positions of alkyl groups, and types of condensed rings) of the starting materials. 3) In the hydrocracking of 9,10-dihydroanthracene, the dehydrogenation occurs in preference to the opening of the central ring; in the hydrocracking of the methylated 9,10-dihydroanthracenes and 9,10-dihydrophenanthrene, the dehydrogenation and demethylation take place in preference to the opening of the central ring; but in the hydrocracking of fluorene, the pathway to the biphenyls becomes important. These findings are expected to be useful for understanding the hydrocracked mechanism and the composition of the resulting products of coal.

References

1) Organic Reaction in Fused Salts. Part XIV, Part XIII: Y. Nakatsuji, T. Kubo, M. Nomura, and S. Kikkawa, *Bull. Chem. Soc. Jpn.*, **51**, 618 (1978); a part of this work was presented at the 38th National Meeting of the Chemical Society of Japan, Kanagawa, April 1978.

2) Y. Nakatsuji, T. Kubo, M. Nomura, and S. Kikkawa, *Bull. Chem. Soc. Jpn.*, **51**, 618 (1978).

3) Y. Nakatsuji, S. Fujioka, M. Nomura, and S. Kikkawa, *Bull. Chem. Soc. Jpn.*, **50**, 3406 (1977).

4) Unpublished data.

5) A. Sieglitz and R. Marx, *Chem. Ber.*, **56**, 1619 (1923).

6) E. L. Martin, *J. Am. Chem. Soc.*, **58**, 1438 (1936).

7) R. G. Harvey and H. Cho, *J. Am. Chem. Soc.*, **96**, 2434 (1974).

8) P. W. Rabideau and R. G. Harvey, *J. Org. Chem.*, **35**, 25 (1970).

9) S. Yamadaya, M. Oba, and Y. Miki, *Bull. Chem. Soc. Jpn.*, **50**, 79 (1977). They described the reaction process of the bicyclic compounds in detail on the basis of the hydrocracking of tetralin on supported Ni–W catalysts.

10) C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Costanza, and E. Gorin, *Ind. Eng. Chem., Process Des. Dev.*, **5**, 158 (1966).

11) R. Covini and H. Pines, *J. Catal.*, **4**, 454 (1965).

12) K. Itoh, R. Kurashige, S. Hamanaka, and M. Ogawa, *Kogyo Kagaku Zasshi*, **70**, 918 (1967).

13) J. M. L. Penninger and H. W. Slotboom, *Erdöl Kohle*, **26**, 445 (1972).

14) P. W. E. Blom, J. Dekker, L. Fourie, J. A. Kruger, and H. G. J. Potigieter, *J. S. Afr. Chem. Inst.*, **28**, 130 (1975).

15) S. Kikkawa, M. Nomura, and K. Murase, *Sekiyu Gakkaishi*, **19**, 863 (1976).