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Carbonization of Aromatic Hydrocarbons. II. Carbonization of Modified Pyrene in the Presence of Aluminum Chloride

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The carbonization of four hydrogenated and two methylated pyrene derivatives in the presence of aluminum chloride was investigated to elucidate the effects of the slight structural perturbation on the carbonization properties of pyrene. Hexahydropyrene was found to give coke having a needle-like structure *via* similar carbonization steps as naphthalene followed. In contrast, dihydropyrene formed coke of a mosaic structure for the most part. Although 1-methylpyrene produced coke with a needle-like structure, in part, reductively methylated pyrene was converted to a mosaic structure as was pyrene. In the case of needle-coke formation, the carbonization process of hydrogenated and methylated pyrene followed the steps of appearance, growth and coalescence of anisotropic spheres where the reaction started at a lower temperature and proceeded more moderately compared with the case of pyrene. It is thus indicated that a partially lowered aromaticity of pyrene may favor its carbonization into needle coke.

Two kinds of anisotropic graphitizable coke were reported in the carbonization of aromatic hydrocarbons in a previous paper.[1] The first type had a needle-like appearance, which was observed on the coke formed from naphthalene, anthracene, chrysene, *etc.* The second one obtained from pyrene and perylene showed a mosaic structure without any regularity in the arrangement of the anisotropic compounds. The size of orientated domains was found to depend on the rate of carbonization which could be modified by the carbonization conditions such as the holding temperature, time and quantity of the catalyst in the process. The carbonization reactivities should also be controlled by a modification of the aromaticity of the aromatic hydrocarbons. In fact, the carbonization properties of quinoline insoluble of pitches were improved by reductive alkylation and hydrogenation.[2,3]

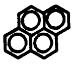
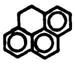
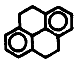
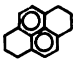
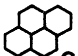
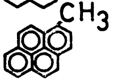
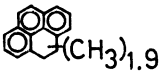
In the present study, the carbonization of four hydrogenated and two methylated pyrene derivatives was investigated to learn the effect of slight structural changes on the condensation reactivity of the starting material, as well as, on the structures of the resulting coke. By following the carbonization process through microscopic observation, analysis of the evolved gases, and the solubility index, which may indicate the degree of carbonization, the mechanism of needle-like coke formation is discussed.

Experimental

Materials. The materials used in the present study are listed in Table 1. Commercially available materials (from the Wako Co. and the Tokyo Kasei Co.) were carbonized without further purification except for the perhydropyrene and the reductively methylated pyrene (RA-pyrene). Perhydropyrene was synthesized from pyrene by Birch reduction with lithium ethylenediamine.[4] Reductive methylation of pyrene was carried out according to the method reported by Sternberg *et al.*[5] NMR spectra indicated that RA-pyrene had 1.9 methyl groups on the average.

Procedure. Carbonization was carried out in the presence of aluminum chloride ($AlCl_3$/aromatics=0.1 mole ratio). The carbonization was carried out in flowing nitrogen. The rate of the temperature increase and the holding time at a fixed temperature were 150 °C/hr and 2 hr, respectively.

Table 1. Aromatic samples

	Structure
Naphthalene	
Pyrene	
Dihydropyrene	
Tetrahydropyrene	
Hexahydropyrene	
Perhydropyrene	
1-Methylpyrene	
RA-pyrene	

Experimental details in this study have been described in a previous paper.[1]

Analysis of Gases Evolved during Carbonization. Hydrogen and methane evolved during carbonization under a programmed temperature increase (150 °C/hr up to 560 °C) were analyzed by means of a gas chromatograph with a molecular sieve column, the evolved gas being sampled every 15 min.

Results

Carbonization of Hydrogenated Pyrene Derivatives. Dihydropyrene: Microscopic photographs of coke obtained from dihydropyrene at several holding temperatures are shown in Fig. 1. Slightly warped spheres several microns in diameter were observed in the coke maintained at 380 °C (Fig. 1a). Within a narrow range beyond this temperature, the coke was completely converted into an anisotropic carbon with a disordered mosaic structure such as that observed in the coke from pyrene (Fig. 1b). Before small anisotropic spheres could grow into large oriented domains, the whole coke sample became anisotropic. It should be noted,

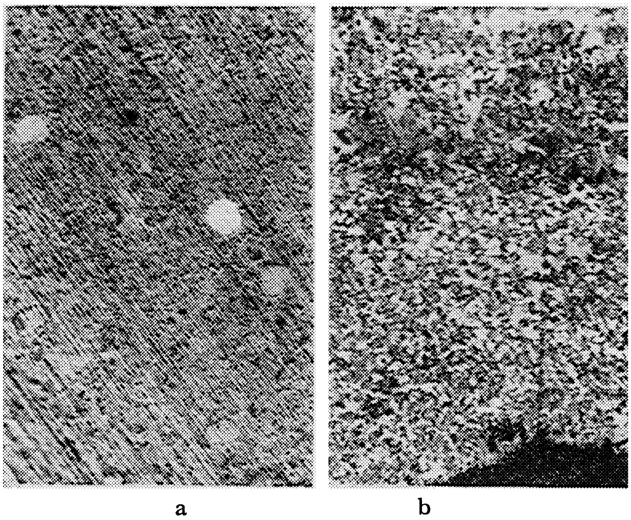


Fig. 1. Microphotographs of carbon obtained from dihydropyrene (under crossed nicols, ×200).
a; carbonization at 380 °C, b; carbonization at 500 °C.

however, that the temperature at which the anisotropy occurred was lower by 20—30 °C than that in the pyrene carbonization.[1]

Tetrahydropyrene: The coke from tetrahydropyrene remained isotropic up to 380 °C, and then the coke became completely anisotropic at 400 °C, at which temperature the mixed appearance of the oriented and mosaic domains was observed (Fig. 2a). This result may indicate that the hydrogenation of pyrene into tetrahydropyrene produced the structure of a partial-flow pattern, and lowered the temperature for the appearance of anisotropy.

Hexahydropyrene: Hexahydropyrene gave such a sticky carbon below 360 °C that it was impossible to grind it for microscopic observation. As shown in Fig. 2b, the structure of the anisotropic flow pattern was observed for coke maintained at 520°, as well as 380 °C. This flow pattern was quite similar to that of the coke from naphthalene.

Perhydropyrene: In marked contrast, the coke from perhydropyrene remained entirely isotropic up to 500 °C. A photomicrograph of it is shown in Fig. 2c. The yield of carbon was only 5—10%. Because the carbon yield of hexahydropyrene, for example, was 58% at 500 °C, it should be noted that the yield of perhydropyrene was extraordinarily low in comparison with the three other hydropyrenes. Aluminum chloride may not work as a catalyst for the carbonization of non-aromatic hydrocarbons.

TABLE 2. CRYSTALLOGRAPHIC PARAMETERS OF TYPES OF COKE
soaking temp. and time; 2500 °C—0.5 hr
pretreatment; 2 hr at 380 °C and 0.5 hr at 1250 °C

Samples	C_0(002) (Å)	L_c(002) (Å)	Feature of coke
Naphthalene	6.737	690	needle
Pyrene	6.744	450	mosaic
Dihydropyrene	6.734	540	mosaic
Tetrahydropyrene	6.747	370	needle and mosaic
Hexahydropyrene	6.734	510	needle

C_0(002); lattice constant (CuK_α). L_c(002); crystal size.

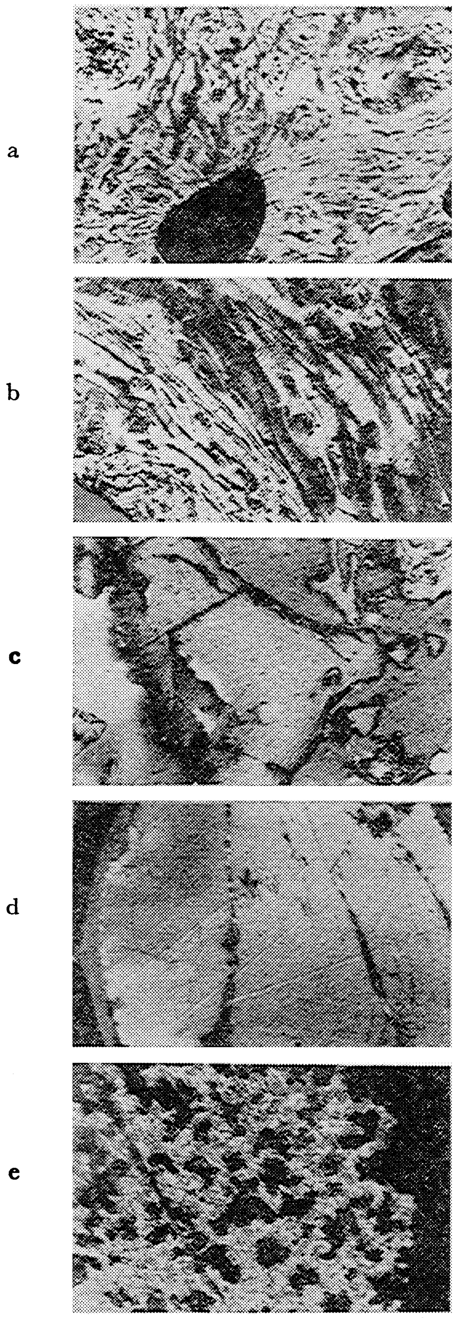


Fig. 2. Microphotographs of carbon obtained from modified pyrenes (under crossed nicols, ×200).
a; tetrahydropyrene at 560 °C, b; hexahydropyrene at 520 °C, c; perhydropyrene at 500 °C, d; 1-methylpyrene at 560 °C, e; RA-pyrene at 560 °C.

X-Ray Analysis of Coke from Hydrogenated Pyrenes.
Table 2 shows the crystallographic parameters of coke obtained from pyrene derivatives at 2500 °C. All carbons showed considerable crystal growth indicating the formation of graphite except for the coke from perhydropyrene. No significant difference in the parameters obtained by X-ray analysis was observable among these types of coke in spite of the different structural features revealed with an optical microscope, as indicated in Table 2.

Carbonization of Methylated Pyrene Derivatives.

1-Methylpyrene: Photomicrographs of the coke obtained from 1-methylpyrene are shown in Fig. 2d. Anisotropic spheres were observed in the coke maintained at 300 °C, and the coke was converted completely anisotropic having large oriented domains by further heat-treatment. Methylation of pyrene provided the flow pattern structure, and lowered the temperature necessary for the appearance of anisotropic structures.

RA-pyrene: As shown in Fig. 2e, a fine mosaic structure was observed for the coke maintained at 560 °C. It should be noted that reductive methylation of pyrene did not produce the same flow pattern structure as that of 1-methylpyrene, although both derivatives had methyl groups.

The Reactivity of Aromatic Hydrocarbons to Carbonization. The yields of benzene insoluble (BI %) in the cokes obtained from four kinds of aromatic hydrocarbons are plotted against the carbonization temperature in Fig. 3, because the value of BI% is considered to be one of the criteria for the degree of carbonization. The BI% of the coke from naphthalene increased from 37% at 250 °C to 90% at 300 °C. In contrast, that of the coke from pyrene increased rather rapidly from 25% at 400 °C to 85% at 410 °C. The profiles of the BI% increase in the carbonization of hexahydropyrene and tetrahydropyrene were located in the intermediate between pyrene and naphthalene, as shown in Fig. 3. Furthermore, it is interesting to note that the order of increasing size of the needle-like domains determined by microscopic observation (naphthalene>hexahydropyrene>tetrahydropyrene>pyrene) coincides with the decreasing carbonization temperature necessary for the coke to be insoluble in quinoline.

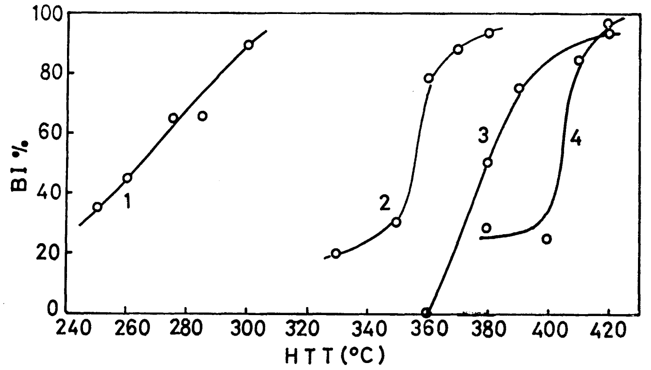


Fig. 3. BI content of carbon from modified pyrenes 1; naphthalene, 2; hexahydropyrene, 3; tetrahydropyrene, 4; pyrene.

Hydrogen and methane evolved during the carbonization of dihydropyrene, hexahydropyrene, 1-methylpyrene, and RA-pyrene are shown in Figs. 4 and 5, where the temperature was programmed to rise at the rate of 150 °C/hr up to 560 °C. Analysis of the evolved gases indicated that the modified pyrenes of two pairs (dihydropyrene and hexahydropyrene, and 1-methylpyrene and RA-pyrene) followed different carbonization processes, giving the coke of a needle-like or a mosaic structure, respectively (see Figs. 1 and 2). There are some precautions necessary in the analysis of the present observation of the gases evolved during carbonization. First, the evolution of gases during the heat treatment was ascribed to the elimination reaction, as well as the carbonization reaction, however these two reactions are rather difficult to distinguish clearly. Second, heating conditions for the analysis of the gases and the microscopic observation or BI% analysis were not the same as those described in the experimental section. Thus, a direct comparison of these results is not possible. In general, longer holding times may cause advanced carbonization. Thus, carbonization reactivities of these compounds should be discussed taking into account these conditions.

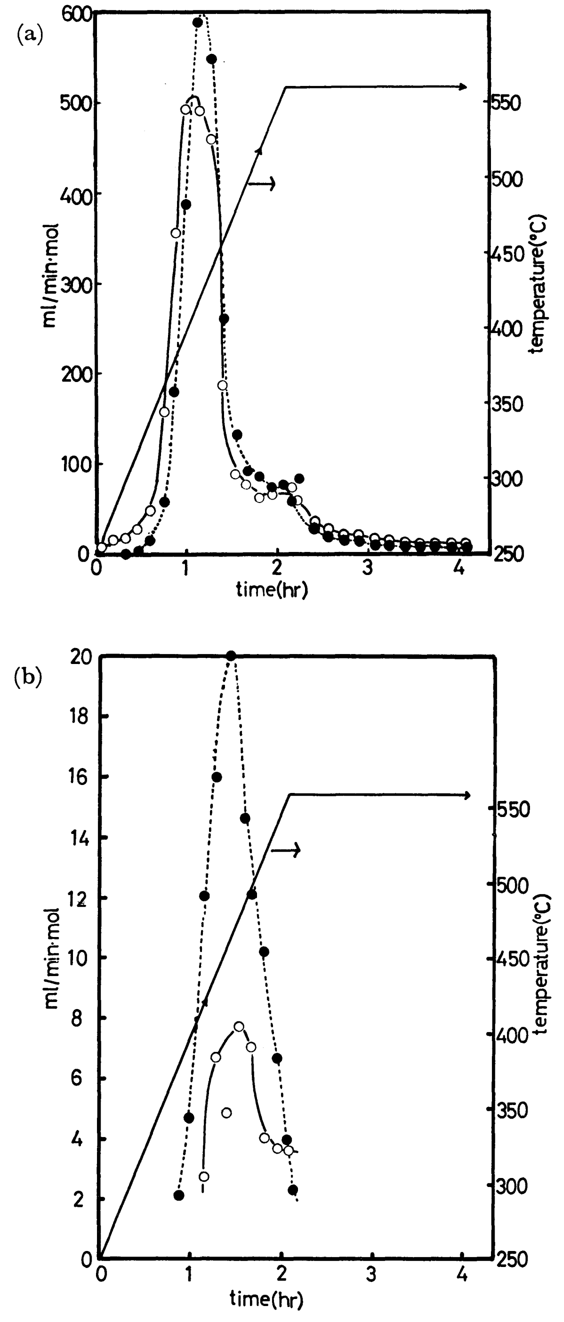


Fig. 4. Evolved gases during the carbonization of dihydropyrene and hexahydropyrene
(a); H_2, (b); CH_4,
—○—; dihydropyrene, ---●---, hexahydropyrene.

Three significant differences were noticed in the carbonizations of dihydropyrene and hexahydropyrene.

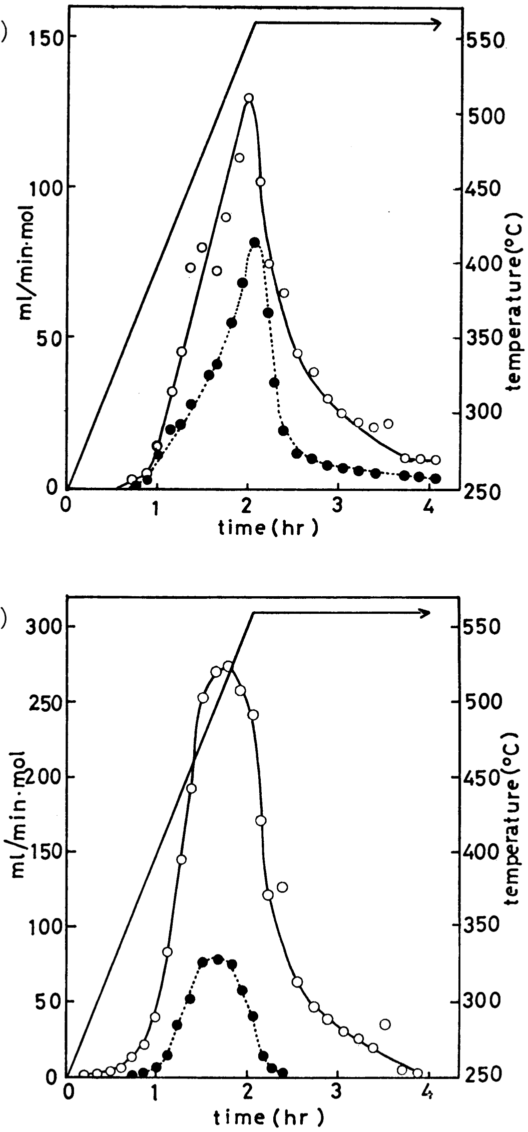


Fig. 5. Evolved gases during the carbonization of 1-methylpyrene and RA-pyrene.
(a); H_2, (b); CH_4,
—○—; RA-pyrene, ---●---; 1-methylpyrene.

First, dehydrogenation of dihydropyrene started at a temperature lower by 50 °C than that for hexahydropyrene perhaps indicating a faster reproduction of pyrene from dihydropyrene, although the total features were quite similar. Second, the amount of evolved methane was much less in the carbonization of dihydropyrene than in that of hexahydropyrene. Such a difference was also observed in the carbonization of pyrene and naphthalene, which resulted in mosaic and needle-like coke structures, respectively. Third, dehydrogenation and demethylation occurred almost simultaneously at 300 °C in the case of hexahydropyrene, indicating that "dehydrogenation" which may convert hexahydropyrene back to pyrene did not take place before carbonization. On the other hand, "dedehydrogenation" of dihyd ropyrene occurred 150 °C below that of demethylation, bringing about a reproduction of pyrene before carbonization.

Methyl groups of RA-pyrene started to evolve at *ca.* 250 °C which was lower by 100 °C and much more methane was evolved compared with 1-methylpyrene, as shown in Fig. 5, although the peaks of the evolution were located at closer temperatures. Methane started to evolve earlier than hydrogen in the case of RA-pyrene. In contrast, both gases started at the same temperature in 1-methylpyrene. Such results may indicate that "demethylation" of RA-pyrene started before the carbonization reaction occurred, converting RA-pyrene to pyrene.

Discussion

The results of X-ray analysis shown in Table 2 show that all carbonization processes of the five kinds of aromatic hydrocarbons may proceed *via* molten phases at the early stage of carbonization and that all of the cokes calcined at 2500 °C show considerable crystal growth, indicating the formation of graphite. However, it is revealed that the types of coke have two different anisotropic structures when examined with an optical microscope, namely, a mosaic structure with small domains and a flow pattern structure with large oriented domains. This fact again indicates that carbonization through the molten phase is not sufficient for the formation of a flow pattern structure, as discussed in a previous study.[1)]

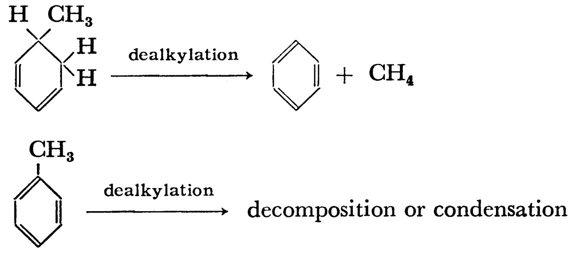
An improvement in the carbonization properties of pyrene into the needle-like coke is clearly achieved by partial hydrogenation and alkylation, as is shown in Figs. 1 and 2. Such an improvement may come from the modified reactivity of the pyrene by a slight structural change. Lowered aromaticity seems to favor the carbonization of pyrene into needle coke. It has been pointed in a previous paper[1)] that the steps of appearance, coalescence, and growth of anisotropic spheres may be essential for the formation of the needle cokes as Taylor and Brooks have indicated,[6)] and that the starting material should have the appropriate condensation reactivity for the carbonization process to follow these steps because the increase of the molecular weight and of the viscosity of the carbonizing material occurs at the same time during carbonization where molecular arrangement should be completed before solidification.

A change in the reactivity of pyrene by this modification is shown in Figs. 3, 4, and 5. In every case, hydrogenation lowers the temperature at which carbonization begins as indicated by the BI% increase in Fig. 3. If the temperature and the rate of carbonization are decreased enough by hydrogenation or alkylation, the carbon obtained shows a needle-like structure similar to that produced by hexahydropyrene. In such cases, modifying groups introduced should stay on the pyrene nuclei long enough until carbonization has progressed to some extent.

The structures of hexahydropyrene and tetrahydropyrene can be compared to naphthalene and diphenyl, respectively. In a previous paper,[1)] the latter two compounds have been found to have quite different reactivities. The different reactivities of the former two compounds due to their structures may bring about the different features of the coke structures.

In contrast, if the introduced groups are eliminated at an early stage of the heat treatment, modification cannot longer be expected to produce a needle-like coke structure which does not occur in the case of pyrene. Dihydropyrene and RA-pyrene are such cases, although warped anisotropic spheres were observed on the coke from dihydropyrene. Dehydrogenation may take place before the anisotropic spheres grow into the flow-pattern structure.

A marked elimination of methyl groups from RA-pyrene should be noted. In reductive alkylation, the introduction of a methyl group should accompany the reduction of the aromatic double bond. Dealkylation of the alkyl-naphthene to form a double bond occurs more easily at elevated temperatures than for the alkyl-aromatic compound, so that the different features of carbonization may be observed as in the cases of 1-methylpyrene and RA-pyrene.



A modification of the carbonization properties of quinoline-insolubles in coal-tar and petroleum pitches has been reported for reductive alkylation and hydrogenation in previous papers,[2,3,7] where both methods could convert some parts of the QI soluble in the solvent (benzene or chloroform). However, hydrogenation produced fusibility at the same time resulting in anisotropic needle coke, whereas reductive alkylation did not. The same situation was observed for the model compounds of pitches in the present study. These results can be explained in terms of elimination reactivity of the groups introduced during the carbonization. The present study indicates that the alkylation may be expected to be effective for a modification of the carbonization properties, and its application to pitches is now in progress.

Reference

1) I. Mochida, K. Kudo, N. Fukuda, K. Takeshita, and R. Takahashi, *Carbon*, **13**, 135 (1975).

2) I. Mochida, K. Kudo, K. Takeshita, R. Takahashi, Y. Suetsugu, and J. Furumi, *Fuel*, **53**, 253 (1974).

3) I. Mochida, Y. Tomari, K. Maeda, and K. Takeshita, *ibid.*, **54**, 265 (1975).

4) L. Reggel, R. Raymond, S. Friedman, R. A. Freidel, and I. Wender, *ibid.*, **37**, 126 (1958).

5) H. W. Sternberg, C. L. Delle, Donne, P. Patages, E. C. Moroni, and R. E. Markby, *ibid.*, **50**, 452 (1971).

6) J. D. Brooks and G. H. Taylor, "Chemistry and Physics of Carbon," Vol. 4, ed. by P. L. Walker, Jr., Edward Arnold, New York (1968), p. 243.

7) I. Mochida, K. Maeda, and K. Takeshita, *Fuel.*, **55**, 70 (1976)