A Novel Carbonization of Naphthalene and Other Aromatic Compounds in a Molten Mixture of $AlCl_3$–NaCl–KCl[1)]

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The use of molten salt as the solvent made it possible to carry out the carbonization process throughout in the liquid state. The process proceeded at a lower temperature than conventional ones, resulting in higher yields. The carbon was deposited from the reaction mixture as powder or flakes; it was similar to "raw coke" in its composition. Thus, 12.8 g of naphthalene was treated in a mixed melt (mp 95 °C) of $AlCl_3$, NaCl, and KCl (60:26:14 mol%) at 300 °C for 10 h, yielding 11.3 g of carbon. Anthracene, phenanthrene, substituted naphthalene, and biphenyl also gave carbon in yields 69—99% of the theoretical yields, while N-containing heterocycles hardly reacted at all. The X-ray parameters of the carbons, the d_{002} spacing and the crystal thickness, L_c, varied with the kind of compound used and with other factors; after heat-treatment at 2800 °C, these values were 3.37—3.52 and 20—700 Å respectively. As the mode of reaction, an acid-catalyzed ionic mechanism was proposed, and the role of hydrogen-disproportionation was discussed.

Carbonization in a homogeneous liquid system is interesting in many aspects. It would seem to favor, at least, theoretical studies facilitating the introduction of powerful analytical methods into the carbon chemistry. The coking of pitch is a typical process involving liquid carbonization, but in this case the whole system can not avoid solidifying as the reaction proceeds, since the reaction solvent is the reactant itself. Therefore, an inert solvent which is not incorporated into the resulting carbon is desirable for the carbonization in question.

Lewis and Singer[2)] presented *m*-quinquephenyl as an inert solvent for carbonization, but according to Evans and Marsh[3)] this compound polymerized and pyrolysed and did react with the reactant during carbonization. This seems to indicate that an organic material ultimately can not be an inert carbonization solvent.

On the other hand, some Lewis acids are known to be effective catalysts for the polycondensation of aromatic compounds.[4–6)] One of the present authors previously studied the effect of the aluminium chloride catalyst on the carbonization of coal-tar pitches.[7)] The catalyst acted to lower the carbonization temperature and to give graphitizable carbon. Recently Mochida and his coworkers[8)] reported similar effects of this catalyst on the carbonization of aromatic compounds.

On the basis of these facts, we attempted carbonization in an inorganic melt containing aluminium chloride as the reaction solvent. Among many reports on the use of inorganic melts for organic reactions, only a few[9)] have mentioned the formation of carbonaceous matter as an undesired by-product, and none have mentioned the use of a melt specially planned for the purpose of carbonization.

As the melt, a mixture of 60 mol% of anhydrous aluminium chloride and 40 mol% of alkali metal chlorides was used. The reasons for this choice were its relatively low melting point, its strong acidity, its low cost, and the ease of handling. According to Kikkawa *et al.*,[10)] this molten system is believed to be in an equilibrium state, as is shown in Scheme 1, and to exhibit the catalytic action of aluminium chloride only when its content is over 50 mol% because of the very large equilibrium constant. In this melt, therefore, about 20 mol% of aluminium chloride can be expected to be present as active Lewis acid.

$$0.6\,AlCl_3 + 0.4\,MCl \rightleftharpoons 0.4\,AlCl_4^- + 0.4\,M^+ + 0.2\,AlCl_3 \quad (1)$$

M: K and Na

As the raw material, naphthalene was mostly used, among other carbocyclic and heterocyclic aromatic compounds.

In consequence, carbonization was successfully carried out throughout in the liquid state; a remarkable lowering of the carbonization temperature as well as a high carbon yield also resulted. Here we wish to describe this quite new method of carbonization.

Experimental

Materials. *Phenanthrene*: Prepared from a raw product of technical grade (90% pure) by purifying[11)] it to a purity of 99% or more; mp 99 °C (ethanol).

Tetrabenzo[a,c,h,j]*phenazine*(*PZ*): Prepared according to Pschorr;[12)] mp 480 °C(nitrobenzene).

Other Aromatic Compounds and Inorganic Salts: Commercially available reagents of an extra pure and guaranteed grade were used without further purification.

Standard Procedure. A 100-cm³ three-necked flask was fitted with a stirrer, a thermometer, and an air condenser with a calcium chloride tube on the top. In the flask a mixture of 0.6 mol of anhydrous aluminium chloride, 0.26 mol of sodium chloride, and 0.14 mol of potassium chloride was placed, after which the mixture was heated to melt (mp 95 °C). With vigorous stirring 0.01 mol of a raw material was then added at once. The temperature was raised to 300 °C for 2 h at a constant rate, and held there (±5 °C) for an additional 10 h. After some cooling, but before solidification, the mass was poured into a mixture of 500 g of crushed ice and 50 cm³ of 1 mol dm⁻³-hydrochloric acid. The resulting black precipitate was filtered with suction, washed thoroughly with 0.1 mol dm⁻³-hydrochloric acid and distilled water successively, and dried on calcium chloride in a vacuum. The crude product thus obtained was refluxed with 100 cm³ of benzene for 1 h and filtered while still hot to separate it into benzene-soluble (BS) and benzene-insoluble (BI) portions. The BI was dried in air and then on phosphorus pentaoxide in a vacuum. Hereafter, the BI shall be called "carbon" for reasons to be

Table 1. Yields and elemental analyses of products

No. of runs	Raw material	Yield of products		Elemental analysis of BI					
		BS (%)[a]	BI(%)[b]	C (%)	H (%)	N (%)	Ash (%)	Total (%)	Atom. ratio H/C
1	Anthracene	6	96	87.93	3.64	—	3.40	94.97	0.50
2	Phenanthrene	22	71	86.51	3.48	—	0.51	90.50	0.48
3	Naphthalene	10	92	83.33	3.27	—	0.66	87.26	0.47
4	Biphenyl	19	69	84.86	3.71	—	1.36	89.93	0.52
5[c]	1-Bromonaphthalene	trace	98	82.96	2.76	—	0.27	85.99	0.40
6[g]	1-Naphthol	7	92	83.82	3.22	—	0.47	87.51	0.46
7[d]	1-Nitronaphthalene	trace	99	70.20	2.02	4.35	0.50	77.07	0.35
8	1-Methylnaphthalene	7	91	82.96	3.51	—	0.44	86.91	0.51
9	PZ[e]	46[f]	59	77.08	2.69	3.23	3.84	86.84	0.42
10[i]	Quinoline	0	0	—	—	—	—	—	—
11	*trans*-Stilbene	11	89	84.32	3.34	—	0.54	88.20	0.48
12[j]	Benzene	trace	0	—	—	—	—	—	—
13[h]	Naphthalene	6.3	94.1	85.92	3.28	—	0.61	89.81	0.45

a) Calcd for the amount of the raw meterial used, based on the assumption that BS is the unchanged raw material. b) Calcd for the theoretical amount of carbon in the raw material used, based on the assumption that BI consists of pure carbon. c) The evolution of HBr was obserbed at 150 °C. d) The evolution of a brown gas was observed at 120 °C. e) Tetrabenzo(*a,c,h,j*)phenazine. f) Extracts by nitrobenzene (not by benzene), almost pure PZ. g) The evolution of HCl was observed soon after the mixing. h) A run specially designed to obtain precise quantitative data with a scale 10 times the others. i) No reaction. j) Almost no reaction.

described later.

All the runs were carried out by this procedure unless otherwise stated.

Estimation of the Reactivity of the Raw Materials. During the reaction, a series of specimens of the reaction mixture were taken out at regular intervals and poured into 0.1 mol dm^{-3}-hydrochloric acid; the mode of the resulting precipitate was observed. The first substance to be yielded was a floating brown precipitate, which consisted of tar or pitch; then a sinking black precipitate was yielded, with an increase in the reaction time. The time necessary for the first appearance of such a heavy precipitate was regarded as a measure of the reactivity of the raw materials.

Evaluation of Graphitizability of the Carbon. The carbons obtained were heated at 2800 °C in an argon stream for 15 min. The X-ray parameters for the carbons before and after the heat-treatment were calculated from the 002-diffraction profiles.

Results and Discussion

Properties of the Carbon Obtained. Outline: Most of the BI's formed black powder or flakes, and most were insoluble in usual organic solvents. Even upon hot-quinoline extraction they lost only a small percentage of their weight. At red-heat they were infusible, and they only slowly disappeared after prolonged heating. As is shown in Fig. 1 as an example, the X-ray diffraction profile of every BI exhibited a rather broad peak near the diffraction angle (2θ) of 25°, indicating that every BI has a layer structure similar to those of known carbon materials. The results of the elemental analysis of the BI's, given in Table 1, show that the values of the atomic hydrogen-to-carbon ratio (H/C) fall mostly within a range of 0.4—0.5.[13] These values correspond with those of carbonaceous mesophase isolated from various carbon materials made by simple heating in the temperature range of 390—490 °C.[14] Raw coke[15a] and so-called carboid coke[15b] have been reported to have similar H/C values, 0.49 and 0.41 respectively. All these facts support the idea of calling the BI's "carbon material" or "carbon" in a broader sense.

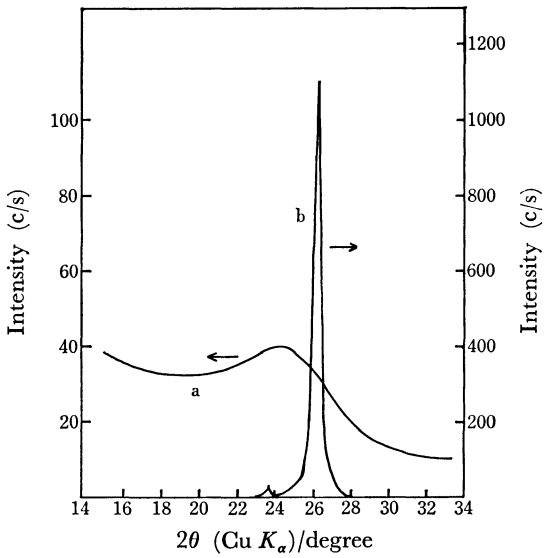


Fig. 1. 002-Diffraction profiles of a BI from naphthalene a) before and b) after heat-treatment at 2800°C.

The total value of the elemental analysis of each BI is short of 100%. The deficiency can be partly ascribed to the water and oxygen content. For example, the BI from anthracene (Run 1 in Table 1) lost 5.5% of its weight when heated in a glass tube over a small flame, yielding water drops on the cold wall of the tube. Regarding the oxygen content, no direct evidence has yet been obtained. However, as will be described below, some facts suggest that the

Table 2. X-Ray parameters of BI's before and after heating at 2800 °C

No. of runs	Raw Material	Parameters (Å)[b]				Graphitizability
		Before heating		After heating		
		d_{002}	L_c	d_{002}	L_c	
1	Anthracene	3.50	15	3.42	150	medium
2	Phenanthrene	3.70	20	3.37	700	high
3	Naphthalene	3.56	10	3.37	700	high
4	Biphenyl	3.68	10	3.45	60	low
5	1-Bromonaphthalene	3.74	15	3.40	200	medium
6	1-Naphthol	3.45	20	3.40	200	medium
7	1-Nitronaphthalene	3.72	10	3.52	20	low
8	1-Methylnaphthalene	3.56	15	3.40	200	medium
9	PZ	3.62	10	3.36[a] 3.44	—	low
11	*trans*-Stilbene	3.56	15	3.46	70	low

a) A composite profile. b) Throughout this paper 1 Å=0.1 nm.

BI's have a tendency to take in oxygen in some way.

Graphitizability: The results of the X-ray analysis, given in Table 2, show that the graphitizability of the carbons ranged widely. As factors influencing the graphitizability, besides the kind of raw material, the atmosphere during the reaction and the after-treatment proved important. An oxidative atmosphere showed a tendency to make the carbon nongraphitizable. About this problem a detailed investigation is now in progress.

Shape and Size: As Fig. 2 shows, the carbons were of various types as to their shape and size; that is, one type formed a fine powder, and another, rough films or plates. Some of the largest of the latter were 4—5 mm in diameter. The type seems to be determined mainly by the kind of raw material. The more reactive raw materials, such as bromonaphthalene and naphthol, gave large flakes, while the moderately reactive ones, such as naphthalene and anthracene, yielded fine particles. However, this is not always the case. A compound could often give different types of carbons when the reaction conditions are modified.

These results, considered together with those of the graphitizability, indicate the possibility of controlling the properties of the carbon by a proper combination of raw material and reaction conditions.

Mode of the Reaction. The standard melt is a colorless, clear liquid of a low viscosity in the temperature range of 95—400 °C, while it is immediately colored by the addition of a raw material. Only a few miligrams of every compound were enough for the coloration. The hue varied depending on the nature of the raw material; for example, it was deep blue with anthracene and dull orange with biphenyl. At the same time, the temperature of the reaction mixture rose by several degrees. No appreciable gas evolution was observed during all the period of reaction except in the cases described in the footnote in Table 1.

The temperature rise mentioned above indicates the dissolution of the raw material with a large heat of solution due to the strong solvation, and suggests, together with the coloration, the formation of some reactive intermediate.

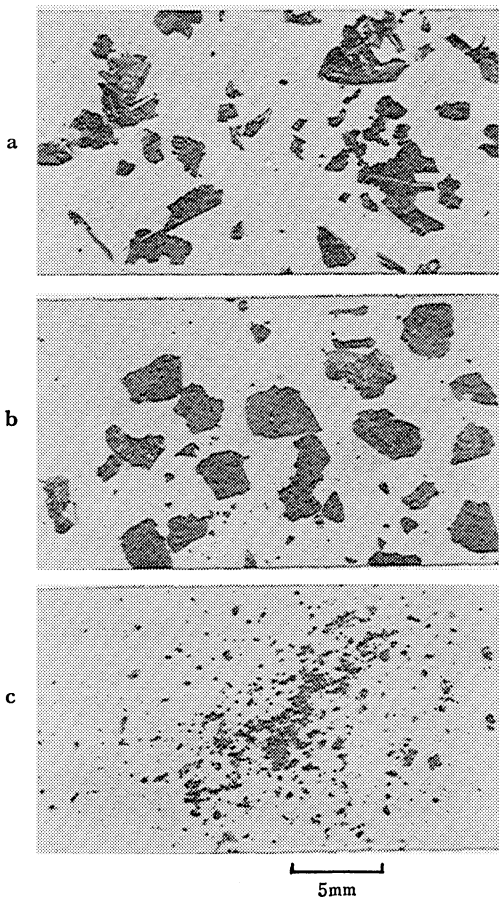


Fig. 2. Shape of BI's from a) 1-bromonaphthalene, b) 1-naphthol, and c) anthracene.

In the majority of cases, a reaction period of 4—8 h at 300 °C was almost enough for the first appearance of carbon in the reaction mixture. A longer reaction time increased the carbon yield.

In the case of naphthalene, during the first 1—2 h the reaction mixture was a homogeneous brown liquid, which yielded a tarry matter after the salts have been washed off; after 30 h, the mixture separated into

black precipitates and a clear, almost colorless medium. The BS from naphthalene, represented in Table 1, proved soluble in the melt at 100 °C, with a brown color.

From these facts, the reaction seems to proceed in solution, at least during the important stages.

Generally, in the precipitation polymerization of a linear polymer, the precipitating polymer does not grow further because the reactive chain end is deactivated by the entanglement of the chain. On the other hand, carbon is usually constructed from planar polymer, which is thought to be free from entanglement. The carbon here obtained is probably like this. Therefore, the fringe of the plate of carbon just produced should be still reactive for further polymerization, and the plate will continue to grow. Secondary aggregation among the plates may also be important for the growth to a visible size.

Regarding the mode of reaction, another possible one is as follows: the molten raw material is dispersed, not dissolved, in the melt as small oil drops, and inside of these oil drops the reaction proceeds under the catalytic action of aluminium chloride. In this case, the character of the reaction is essentially the same as that of the reactions mentioned above.[4-8] We can, however, find little support for this mode of reaction, but much counterevidence. For example, it can hardly explain why anthracene reacts far below its melting point, and yet more actively than naphthalene.

Reactivity of the Raw Materials. A rough evaluation of the reactivity of the raw materials was made from the estimation of the ease of carbonization. The carbon yields were also taken to consideration.

About this problem, an additional series of experiments were carried out with a shortened reaction time and at various reaction temperatures. The carbon (BI) yields of these runs, as is given in Table 3, clearly indicate the differences in reactivity among the compounds used.

From these results, the following sequences as to the reactivity may be drawn;

a) anthracene>naphthalene>phenanthrene>stilbene >biphenyl>PZ>benzene>quinoline

and b) 1-nitronaphthalene>1-bromonaphthalene>1-naphthol>1-methylnaphthalene>naphthalene.

The a) sequence indicates roughly that the larger conjugation system of the aromatic skeleton makes the compound more reactive. One of the reasons for the very small reactivities of PZ and quinoline is their general properties being inactive toward an electrophilic reagent. Another is probably the lack of a neutral molecule as the substrate for electrophilic attack. This lack can be caused by the almost complete formation of such a type of complex as $[-\overset{+}{N}=\cdots AlCl_3^-]$. The b) sequence is not likely to reflect simply the polar effect of substituents, but to show the reactivity of an individual compound in a complicated specific reaction involving the displacement and/or decomposition of the substituent itself. This view is based on the facts that nitronaphthalene decomposed soon after the mixing with the melt, evolving a brown gas; similarly, bromonaphthalene evolved hydrogen bromide. Moreover, bromonaphthalene gave carbon in a good yield at such a low temperature as 200 °C, as is shown in Table 3. These two compounds are generally less reactive toward the electrophilic reagent than naphthalene. These particular reactions present a tangential but interesting problem.

Table 3. Reaction temperatures and the yields of products[a]

No. of runs	Raw material	Reaction temp (°C)	Yield of products BS (%)[b]	BI (%)[b]
14	Naphthalene	350	8	92
15	Naphthalene	300	23	67
16	Phenanthrene	350	11	83
17	Phenanthrene	300	56	42
18	Quinoline	350	trace	3
19[c]	Quinoline	300	—	—
20	1-Bromonaphthalene	250	trace	100
21	1-Bromonaphthalene	200	8	92

a) All the runs were carried out in the same way as in the standard procedure, except that various reaction temperatures and a fixed reaction time of 2 h were employed and except that the raw material was added to the melt when the temperature of the melt became constant at the desired point b) Calcd, respectively, as stated in Table 1. c) No reaction.

Table 4. Compositions of melts and the yields of products[a]

No. of runs	Raw material	Composition of melt (mol)	Yield of products BS (%)[b]	BI (%)[b]
22[c]	Anthracene	$ZnCl_2$–NaCl–KCl (0.6 : 0.2 : 0.2)	—	—
1[d]	Anthracene	$AlCl_3$–NaCl–KCl (0.6 : 0.26 : 0.14)	6	96
23	Anthracene	$AlCl_3$–NaCl–KCl (0.49 : 0.35 : 0.16)	19	84
24	Anthracene	$AlCl_3$–NaCl–KCl (0.4 : 0.3 : 0.3)	25	76
25	Biphenyl	$AlCl_3$–NaCl–KCl (0.4 : 0.3 : 0.3)	91	2
26	Naphthalene	$AlCl_3$–NaCl–KCl (0.4 : 0.3 : 0.3)	80	16

a) All the runs were carried out in the same way as in the standard procedure, except for the use of melts of different compositions. b) Calcd, respectively, as stated in Table 1. c) The anthracene was recovered quantitatively. d) Transferred from Table 1 for the convenience of comparison.

Effect of the Acidity of Melt. Table 4 shows the effect of the acidity of various melts on the carbon yield. In the cases with [$AlCl_3$–NaCl–KCl] systems, the decreasing content of aluminium chloride resulted in a decrease in the yield of carbon. A melt containing 60 mol% of zinc chloride, known as a weaker Lewis acid than aluminium chloride, was quite inactive. These facts indicate the critical importance of the acidity of the melt.

It is also noteworthy that, although weaker, the

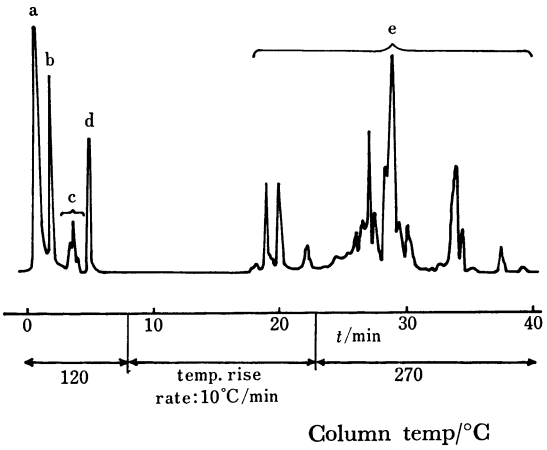


Fig. 3. Gas liquid partition chromatogram of a tar obtained from naphthalene by a reaction at 100 °C for 30 min. a: Solvent, b: *p*-dichlorobenzene as an internal standard, c: low boiler (Y: 1.02 mol%), d: naphthalene (Y: 2.78 mol%), e: high boiler (Y: 24.7 mol%).
Column: OV-17 5% on Chromosorb WAW DMCS 80—100 mesh, 3 mm×3 m; carrier gas: He, 60 cm³/min; detecter: TCD.

activity of the melt still remained when the content of aluminium chloride was lower than 50 mol%. This can be ascribed partly to the small amounts of aluminium chloride free in the equilibrium, and partly to the strong affinity of the compounds used to the Lewis acid. In the melt containing 40 mol% of aluminium chloride, anthracene, naphthalene, and biphenyl gave carbons, in yields decreasing in that order, in accordance with their decreasing basicity.

Products in the Earlier Stage of Reaction. Some runs with naphthalene were carried out with the standard procedure but at a fixed low temperature of 100 °C to yield the titled products. The tarry products were analyzed by TLC, GLPC, IR, UV, and NMR.

The results from GLPC, given in Fig. 3 as an example, show that the naphthalene reacted very fast, diminishing to a small percentage of the original amount during the first 30 min of the reaction. The products can be classified into three groups. The first (low-boiling, 1.02%) and the second (high-boiling, 24.7%) consists of substances with shorter and longer retention time than naphthalene respectively. The third (*ca.* 70%) consists of substances which did not give any peaks in the chromatogram because of their small volatility. The last two groups together form the greater part of the tar and can be accepted as consisting of polymerization products. The low-boiling group will be dicussed below.

The NMR spectrum of the tar, given in Fig. 4, shows that the tar contains aliphatic hydrogen atoms amounting to 50—60% for aromatic ones. This indicates that the polymerized naphthalene is partially hydrogenated. The IR spectrum of the tar supports this view. It shows a strong absorption band at 2920 cm^{-1} which can be assigned to the aliphatic C–H stretching vibration.

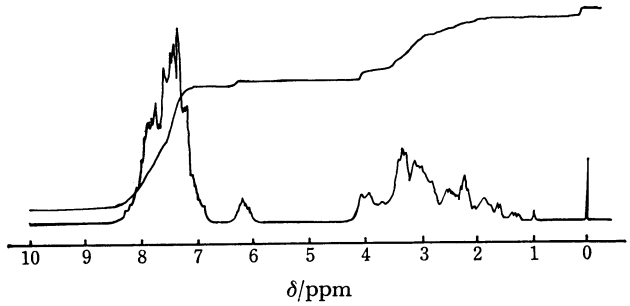


Fig. 4. ^{1}H-NMR Spectrum (60 MHz, in $CDCl_3$) of a tar obtained from naphthalene by a reaction for 30 min at 100 °C.

By TLC with the [silica gel–hexane] system, the tar was revealed to contain a number of substances which enamate a strong visible fluorescence when irradiated with ultraviolet rays. This indicates the formation of an aromatic condensed-ring structure with four or more rings. In fact, perylene was detected by a TLC-UV combined technique (R_f: 0.22, blue fluorescence; λ_{max}: 434 nm in ethanol).

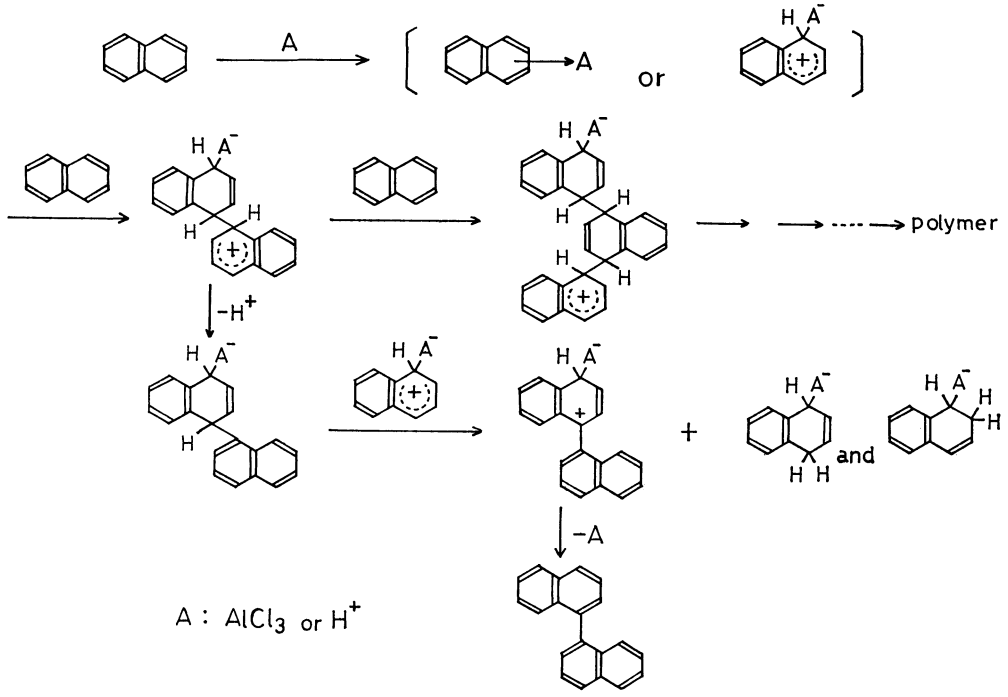
The formation of the low-boiler is noteworthy, though the amount was small. The GLPC analysis of the tar using a glass capillary column revealed that the low-boiler consists of 1,2,3,4-tetrahydronaphthalene, 1,2-dihydronaphthalene, and several other compounds.

Possible Reaction Mechanism and Pathway. Many of the facts mentioned above all indicate that the reaction proceeds through an ionic mechanism. No evidence has been obtained to support a radical mechanism, which is believed to control the carbonization by simple heating.

The first step in the polycondensation toward carbon must be a C–C bond formation between two aromatic nuclei. This reaction probably involves an electrophilic attack by a positively charged aromatic nucleus, which is produced from an aromatic molecule and Lewis acid or proton, on a remaining neutral aromatic molecule. Similar ideas have been presented[6] and supported[16] by several authors concerning the condensation of aromatic compounds in the presence of Lewis acid. In the present system the mechanism is thought to be essentially the same. The coloration of the melt seems consistent with this mechanism. This assumption regarding the coloration finds supports in Morita and Hirosawa's report[17] and in the studies[18–19] referred to therein.

In parallel with the C–C bond formation, hydrogen disproportionation must take place. The hydrogen atoms necessary for the formation of the hydronaphthalenes must be supplied from the condensation. This reaction is probably also catalyzed by acids, probably in a manner similar to that described by Wristers[20] in the hydrogenation of benzene in superacid systems. It is important to recognize that this hydrogen transfer occurs not only between monomers, but also between any organic species in the system, and that, therefore, it plays a certain role in all stages of the reaction.

From these facts, the reaction, for example, with naphthalene should proceed as is shown in Scheme 2.



Scheme 2.

The 1,1′-type of condensation product may be predominant at first, while it may rearrange to the 2,2′-type in a thermodynamically controlled reaction.[6]

The fluorescent substances mentioned above seem to be formed by the intra- and intermolecular condensation of the naphthalene polymers. This type of condensation will become more important in the middle and later stages of reaction, and the combination of all the types of reactions mentioned above should produce carbon at last.

The true character of the catalyst is not clear. Throughout this series of experiments the invasion of the reaction system by moisture could not be prevented, and as a result the evolution of hydrogen chloride occurred. Therefore, it is reasonable to postulate that the catalytic action of the melt is partly attributable to that of a superacid system of [hydrogen chloride–aluminium chloride].

Features of This Process. The present process is characterized as *a solution reaction* through *an ionic mechanism*, resulting in *a low carbonization temperature* and *a high carbon yield.*

When simply heated, most polycyclic aromatic compounds first begin to be carbonized near 500 °C;[21] therefore, the compounds boiling below that temperature can not be carbonized under an ordinary pressure. The addition of aluminium chloride lowers the carbonization temperature. For example, by the $AlCl_3$-addition process Mochida *et al.*[8] succeeded in obtaining "coke" from polycyclic aromatic compounds with 2—4 rings under an ordinary pressure at 300 and/or 380 °C. However, the carbon yield does not appear to be high.[22] In our experiment, by the $AlCl_3$-addition process with naphthalene under conditions (with 5 mol% of aluminium chloride at 300 °C for 10 h) similar to those employed by Mochida *et al.*, the yields of BI and quinoline-insoluble matter (QI) were 39 and 7% respectively for the theoretical yield of carbon, while by the present process these yields were determined to be 94 and 85% (Run 13). The observed high yield—in other words, the high reaction velocity— in the present process can be ascribed mostly to the highly ionic character of the solvent, including the strong acidity, although the details of how these properties influenced the reaction machanism are not clear. The molten salt system should, at least, be more favorable for the formation of the positively charged species, the assumed reaction intermediates, than the organic system in the $AlCl_3$-addition process. One of the reasons for the occurrence of nongraphitizable carbons in the present study may be the too fast reaction, which is believed often to prevent the growth of a layer structure.

In practice, being a solution reaction makes the inspection of a reaction easy. The low carbonization temperature made the use of an autoclave unnecessary for the carbonization of materials with low boiling points.

This process can be modified in use. When the reaction stops halfway, tar or pitch is generally obtained. For example, naphthalene gave a pitch suitable for making graphitizable carbon. Methylnaphthalenes proved to isomerize and disproportionate quickly through the migration of the methyl group in the earlier stage of reaction; as a result, tars with a fixed composition were obtained from the different isomers.[23] These may be of importance for the commercial use of this process.

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