

CARBONIZATION OF AROMATIC COMPOUNDS IN MOLTEN SALT

Etsuro OTA

College of Technology, Gunma University, Kiryu, Gunma 376

Sugio OTANI

Faculty of Technology, Gunma University, Kiryu, Gunma 376

Aromatic compounds, such as naphthalene, anthracene, and biphenyl, were heated in mixed molten salt ( $\text{AlCl}_3:\text{KCl}:\text{NaCl}=3:1:1$  mole) for 10 hours at  $300^\circ\text{C}$ , giving carbon in good yields. The carbon was obtained mostly in the form of powder and partly film and plate, and its crystallite thickness after heating at  $2800^\circ\text{C}$  ranges from  $50\text{\AA}$  to  $700\text{\AA}$ .

The present studies concern with the carbonization reaction of aromatic compounds in molten salt and also with the graphitizability of the carbon thus obtained. This preparation method of carbon has not yet been reported.

General procedure: In a 100ml three-necked flask, fitted with a stirrer, thermometer, and air-condenser with a  $\text{CaCl}_2$ -tubing, a mixture of salts ( $\text{AlCl}_3$  0.6 mole,  $\text{KCl}$  0.2mole, and  $\text{NaCl}$  0.2mole) was heated to melt (ca.  $120^\circ\text{C}$ ). One gram of an aromatic compound was added with vigorous stirring. The temperature was raised to  $300^\circ\text{C}$  for 2 hours and maintained at this temperature ( $\pm 5^\circ\text{C}$ ) for another 10 hours. The hot reaction mixture was then poured into 500ml of cold 0.1N-HCl. The precipitates were filtered, washed thoroughly with 0.1N-HCl and distilled water successively, and dried on  $\text{CaCl}_2$  in vacuum. The crude product thus obtained was refluxed with 100ml of benzene for 1 hour, and filtered after cooling to separate the products into benzene-soluble (BS) and -insoluble ingredient (carbon). The "carbon" was dried in air and then on  $\text{P}_2\text{O}_5$  in vacuum.

Qualitative inspection on the rate of carbon formation: During all the reaction periods a series of the samples of the reaction mixture were taken out, and poured into 0.1N-HCl; the mode of the resulting precipitation was observed. The rate of the carbon formation was estimated qualitatively from the rate of increase of amount of heavy (apparent specific gravity  $> 1$ ), black precipitates.

Evaluation of graphitizability of the carbon obtained: The resulting carbons were heat-treated at  $2800^\circ\text{C}$  in an argon stream for 15 minutes. The carbon samples before and after the heat-treatment were subjected to X-ray diffraction analysis. The X-ray parameters were calculated from the (002) diffraction profiles.

Results and discussion: After the reaction all compounds examined except heterocyclic ones afforded a black matter, which is generally insoluble in common solvents and infusible at red-heat, and exhibits (002) diffraction line in the majority of cases; thus, it may be regarded as carbon. The yields were almost quantitative as shown in Table 1. The carbon was obtained mostly in the form of powder and partly film and plate of max. 4-6mm in diameter. The H/C atomic ratio

of the carbons ranged from 0.40 to 0.50. These values correspond to those of the mesophase isolated from the various carbonaceous materials obtained by the usual heating at a temperature range of 390-490°C<sup>1)</sup>. Concerning the rate of the carbon formation the following sequences were obtained: a) anthracene > naphthalene  $\approx$  phenanthrene > biphenyl  $\gg$  tetrabenzo(a,c,h,j)phenazine  $\gg$  quinoline and b)  $\alpha$ -nitronaphthalene  $\approx$   $\alpha$ -bromonaphthalene >  $\alpha$ -naphthol >  $\alpha$ -methylnaphthalene > naphthalene. The series a) and b) indicate the effect of the aromatic skeleton and the substituent group, respectively, on the rate. The graphitizability of the carbons thus obtained was varied widely on the nature of the raw materials as shown in Table 1.

Table 1. Yields of the products and X-ray parameters of the carbon before and after heating at 2800°C

No.	aromatic compound	amount of products(g)			X-ray parameters(Å)			
		crude	BS	carbon	before heating		after heating	
					d <sub>002</sub>	Lc	d <sub>002</sub>	Lc
1	anthracene	1.0	0.1	1.0	3.50	15	3.42	150
2	phenanthrene	0.8	0.2	0.5	3.70	20	3.37	700
3	naphthalene	1.0	0.2	0.8	3.56	10	3.37	700
4	biphenyl	0.9	0.2	0.7	3.68	10	3.45	60
5	$\alpha$ -bromonaphthalene	0.7	trace	0.7	3.74	15	3.40	200
6	$\alpha$ -naphthol	0.9	0.1	0.8	3.45	20	3.40	200
7	$\alpha$ -nitronaphthalene	0.7	trace	0.7	3.72	10	3.52	20
8	$\alpha$ -methylnaphthalene	1.0	0.1	0.8	3.56	15	3.40	200
9	tetrabenzophenazine	1.0	0.3*	0.6	3.62	10	3.36***	-
10	quinoline	trace**					3.44	-

\* The nitrobenzene-soluble ingredient, consisting of almost pure raw material

\*\* Almost no reaction \*\*\* Composite profile

The mixture of molten salts was originally almost colorless, whereas on addition of the first tiny amount of the raw material it immediately showed a color ranged from dark orange(biphenyl) to dull deep blue(anthracene). This seems to indicate the formation of the CT complex of the aromatic compound with AlCl<sub>3</sub>.

The features of the present process are that the reaction is carried out at such a low temperature as 300°C in a solution of very strong ionic strength. The lower reaction temperature make it unnecessary to use an autoclave in order to get carbon from many aromatic compounds of lower boiling point. Moreover, it is noteworthy that the reaction conditions and the results mentioned above suggest an ionic reaction mechanism for the process in contrast with the radical ones proposed for most of the conventional processes.

Reference: 1) Y.Sanada, T.Furuta, J.Kumai, and H.Kimura, J.Japan Petrol. Inst., 16, 902 (1973)

(Received January 6, 1975)