CARBONS PRODUCED FROM KNOWN ORGANIC COMPOUNDS
I—ANTHRACENE AND PHENANTHRENE

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(*Received* 27 *July* 1966)

Abstract—Carbons were prepared from anthracene, phenanthrene, and their mixtures by first charring in a bomb to 550°C, followed by coking in a flowing nitrogen stream at 900°C, and then heating in helium to 2500°C. The cokes and 2500°C carbons were characterized using X-ray diffraction, gas adsorption, density, and magnetic susceptibility measurements. All the cokes were found to be highly graphitizable when heated to 2500°C.

1. INTRODUCTION

It is well known that carbons produced by the low temperature charring of organic compounds exhibit wide variations in their graphitizability depending upon the structure of the organic compound.[1] This fact is of practical importance to the graphite manufacturers whose raw materials consist primarily of petroleum coke and coal tar pitch. Both these raw materials are derived from a complex mixture of organic compounds. The graphitizability of petroleum coke and coal tar pitch coke should then depend strongly on the nature and distribution of the organic compounds from which they are derived.

This paper is the first in a series which will describe studies on the graphitizability of carbons derived from known organic compounds and, in particular, binary mixtures of organic compounds. The binary mixture will generally consist of one organic compound which is highly graphitizable and a second organic compound which is poorly graphitizable. Of considerable interest will be the effect of the presence of the organic compound of poor graphitizability on the overall graphitizability of the mixture.

Kinney[1] and Kinney and co-workers[2] reported that the charring of anthracene yields a carbon of high graphitizability. This fact has been confirmed recently by workers from Union Carbide.[3] Anthracene is a compound of considerable practical interest, since it is in relative abundance in coal tar.[4,5] It will be one of the main compounds used in this study.

Kinney[1] reported that the charring of phenanthrene, a structural isomer of anthracene, yields a carbon of poor graphitizability. Kinney reasoned that phenanthrene, which has an angular shape, cannot condense into sheets of aromatic structure except by orientation of the molecules in a manner which does not correlate with the preferred chemical behavior of the molecule. He concluded that since the chemical behavior probably governs a sufficient number of the condensation reactions to strongly influence the structure of the char formed, a non-graphitizing carbon is formed. Phenanthrene is also a compound of considerable practical interest; it is found in even greater abundance in coal tar than is anthracene.[4] Phenanthrene was selected as the organic compound, which *supposedly* would lead to a non-graphitizable carbon in this initial study.

2. EXPERIMENTAL

A. Samples

The anthracene and phenanthrene were both obtained from the Gesellschaft fur Teerverwertung, West Germany. Both had purities of greater than 98 per cent, with the major impurity in each case being the other compound. The melt-

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ing points of the anthracene and phenanthrene were 217°C and 99.5°C, respectively.

B. Preparation of carbons

Samples of 150 g of anthracene, phenanthrene, and their mixtures (ratios of 3:1, 1:1, and 1:3) were held in a Pyrex liner and charred in a stainless steel bomb of *ca.* 1.3 l. capacity. The compounds were melted and thoroughly mixed in the liner prior to charring. The two compounds exhibit mutual solubility at all concentrations. Prior to charring, the bomb was thoroughly flushed with N_2 or He to displace air. The charring runs were started under one atmosphere of N_2 or He. The samples were heated at a fixed power input to the bomb up to 550°C over a 5 hr period and then held at 550°C for an additional 12 hr. During charring, the pressure in the bomb increased primarily because of the pressure of H_2 and low molecular weight hydrocarbons which were evolved.[6]

After cooling, the chars were removed from the liners and ground to −42 mesh in a hammer mill, except for half of the "1:1 sample" which was hand ground in an agate mortar. The 42×65 and 200×325 mesh fractions of each sample were then recombined and heated to 900°C in a tube furnace at a heating rate of 5°C/min in one atmosphere of flowing N_2. After soaking at 900°C for 2 hr, the samples were cooled and resieved. The 200×325 mesh fractions were used for X-ray diffraction studies; the 42×65 mesh fractions were used for surface area, density, and magnetic susceptibility studies.

A portion of the 42×65 and 200×325 mesh fractions were recombined and heated in an induction furnace under He to 2500±15°C during a 2.4 hr period. The samples were cooled immediately after reaching this temperature (4 hr from 2500°C to essentially room temperature). A specially constructed graphite sample holder permitted all the samples to be heated in the same furnace run and to be exposed to very similar temperature profiles. The 2500°C samples were resieved and studied.

C. Property measurements

1. *Crystallographic parameters*. X-ray diffraction data were obtained using a General Electric diffractometer XRD-5, emitting Ni filtered Cu radiation produced at 40 kv and 15 ma. Interlayer spacings and average crystallite heights (L_c) were determined from the (004) and (002) diffraction peaks, respectively. Sodium chloride was used as an internal standard, as previously described in detail.[7] Interlayer spacings of the 2500°C samples could be duplicated within ±0.0005A when reported at 15°C.

2. *Surface areas*. Surface areas were calculated, using the BET equation,[8] from adsorption isotherms of Kr at 77°K. One half hour was sufficient to reach equilibrium for each adsorption point. The surface areas, which were low, could be duplicated within 3 per cent.

3. *Densities*. Helium densities were determined using a constant pressure He displacement apparatus previously described.[9] These densities could be determined within ±0.005 g/cm³. Mercury densities were determined by Hg displacement under a pressure of 54 psia. This pressure was sufficient to force Hg into voids between the 42×65 mesh particles and yet not fill pores within the particles. Hence, the Hg density is equivalent to an apparent density of the particles. Mercury densities could be determined within ±0.01 g/cm³.

4. *Magnetic susceptibility*. Susceptibility measurements were made at five different field strengths above 7000 Oersteds, which is sufficiently high to attain saturation of the ferromagnetic components. The short specimen Gouy technique was used.[10] The susceptibility was plotted versus the reciprocal of the average field strength over the sample. The plots yielded straight lines. The intercept on the ordinate at infinite field was taken as the diamagnetic susceptibility of the carbon.[11] From the slope of the plot and the assumption that any ferromagnetic impurity present was metallic Fe, the amount of Fe in the sample was estimated.[11] Most of the data are from single determinations. Standard deviations are given when duplicate determinations were made.

3. RESULTS AND DISCUSSIONS

A. Crystallographic parameters

Average crystal heights of the 900°C cokes showed no significant difference, varying from only 16 to 18A for all the samples. Table 1 summarizes the results for the 2500°C carbons. As suggested by FRANKLIN,[12] interlayer spacing can be used as a measure of graphitizability—the lower the spacing the larger the amount of three-

TABLE 1. CRYSTALLOGRAPHIC PARAMETERS OF 2500°C CARBONS

Sample	Interlayer spacing (A)	L_c (A)
100A	3.3729	850
100P	3.3804	530
75A–25P	3.3696	1050
50A–50P	3.3700	1390
25A–75P	3.3746	1020

dimensional ordering present and the higher the graphitizability. Coke derived from anthracene (A) is clearly more graphitizable than coke derived from phenanthrene (P). This was expected from the studies by KINNEY.[1] However, quantitatively the interlayer spacing results presented here for phenanthrene differ significantly from those reported by Kinney. That is, Kinney reported the 2500°C carbon derived from phenanthrene to have an interlayer spacing of 3.44A, or to be completely turbostratic.[12,13] Our results indicate that phenanthrene coke indeed has a substantial degree of graphitizability. Recently, workers at Union Carbide[3] found phenanthrene· coke heated to 3000°C to have an interlayer spacing of 3.357A, again indicative of substantial graphitizability. Kinney reported phenanthrene coke heated to 3000°C to have an interlayer spacing of 3.42A (indicative of little graphitization occurring). The phenanthrene used in the studies reported by Kinney was obtained from the Eastman Kodak Co. and is said to be of "high purity".[14] It had an observed melting point of 99–100°C, in substantial agreement with the melting point given for high purity Phenanthrene.[15] The reason for the discrepancy between both our results and those of Union Carbide with those reported by Kinney is not clear. However, it is felt that it is valid to conclude that phenanthrene coke does have substantial graphitizability. Marked decreases in graphitizability can be produced by the presence of small amounts of cross-linking material. Marked increases in graphitizability can be produced by heating under ultra-high pressures[16] or by use of solid catalysts.[17] Ultra-high pressures were not used in this study. As discussed later, the cokes are thought to have contained some Fe but not enough to have a serious effect on graphitization.

Interlayer spacing results also indicate that cokes produced from mixtures of anthracene and phenanthrene are highly graphitizable. In fact, several of the mixtures appear to be more graphitizable than anthracene coke.

Crystallite height results, which are thought to be reproducible to *ca.* ± 10 per cent, are essentially consistent with above conclusions. The 2500°C carbon from phenanthrene coke has a smaller crystallite height than that from anthracene coke. The 2500°C carbons from anthracene-phenanthrene mixtures have larger crystallite heights than the 2500°C carbon from phenanthrene and probably larger crystallite heights than the 2500°C carbon from anthracene.

B. Surface areas

Results are presented in Table 2. Surface areas of the cokes are low, which indicates good crystallite alignment and negligible accessibility of the crystallite area to the adsorbate.[18] Good crystallite alignment in cokes is an important prerequisite to their being of substantial graphitizability.[9] Thus, these results are consistent with the results obtained from X-ray diffraction studies on the 2500°C carbons. Negligible changes in surface areas were produced upon heating the cokes to 2500°C.

TABLE 2. SURFACE AREAS OF COKES AND CARBONS

Sample	Areas m^2/g	
	Cokes	2500°C Carbons
100A	0.30	0.25
100P	0.28	0.28
75A–25P	0.37	0.29
50A–50P	0.39	0.42
25A–75P	0.53	0.39

C. Densities

Results are presented in Table 3. Helium and Hg densities of the cokes show little variation between samples. Mercury densities of the cokes are very similar to those reported for a wide range of petroleum cokes now being used commercially in the production of graphite.[19]

The He densities of the 2500°C carbons are high, approaching closely the true densities calculated from interlayer spacing data. For example, the true density of the 2500°C carbon from anthra-

TABLE 3. DENSITIES OF COKES AND CARBONS

Sample	He density, g/cm³		Hg density, g/cm³	
	Cokes	2500°C Carbons	Cokes	2500°C Carbons
100A	1.920	2.228	1.82	2.17
100P	1.950	2.219	1.80	*
75A–25P	1.942	2.251	1.80	2.04
50A–50P	1.923	2.230	1.78	2.00
25A–75P	1.918	2.217	1.79	2.03

*Insufficient sample.

cene is 2.256 g/cm³. Thus, the volume in this carbon which is closed to He represents only *ca.* 1 per cent of the total volume of the carbon. This figure is quite low[9,20] and indicates that the high degree of crystallite alignment in the cokes is carried over to the 2500°C carbons.[18] The He densities of several of the 2500°C carbons derived from anthracene–phenanthrene mixtures are still higher than that of the anthracene carbon. This is consistent with these samples having lower interlayer spacings than the anthracene carbon.

The Hg density of the anthracene carbon is high, closely approaching its He density. As a result, the open porosity of the carbon represents only *ca.* 2.5 per cent of the particle volume. The Hg densities of the carbons derived from anthracene–phenanthrene mixtures are significantly lower than the anthracene carbon density. The reason for this is not understood. It possibly may be caused by the presence of macropores, resulting from the imperfect packing of carbon regions derived alternately from anthracene and phenanthrene, if these compounds were not intimately mixed on a microscopic basis. The pores must be quite large, however, since the surface area of these carbons is low.

D. Magnetic susceptibility

Results are presented in Table 4. The diamagnetic susceptibility (χ) of the anthracene coke is greater than that of the phenanthrene coke. Based on the correlation presented by Akamatu and co-workers between $-\chi$ and crystallite diameter (L_a) for a randomly oriented unconsolidated particle sample,[21] this suggests that the anthracene coke has a slightly larger L_a. Akamatu and co-workers further show that the χ of carbons increases to a limiting value of *ca.* -6.5×10^{-6}/g

TABLE 4. MAGNETIC SUSCEPTIBILITY OF COKES AND CARBONS

Sample	$-\chi \times 10^6$/g	
	Cokes	2500°C Carbons
100A	1.00	6.28±0.07
100P	0.77±0.00	6.77±0.17
75A–25P	—	6.30
50A–50P	—	6.55
25A–75P	—	6.58

as L_a grows to *ca.* 130A. Further increases in L_a result in a negligible change in χ. The values of susceptibility of the 2500°C carbons are then as expected. Minor variations are not considered significant, but are attributed to slight deviations from perfectly random particle orientation.[21]

From χ measurements, it is estimated that the coke samples contained about 0.07 to 0.15 per cent metallic Fe. No ferromagnetic impurity could be detected in the 2500°C carbons. It was thought that the Fe contamination in the cokes resulted from their being ground in an iron hammer mill. Consequently, a sample of the coke produced from the 50A–50P mixture was hand ground in an agate mortar. This sample showed a negligible difference in graphitizability to the sample ground in the hammer mill. The interlayer spacing of its 2500°C carbon was 3.3702A.

4. CONCLUSION

Cokes derived from the low temperature charring of anthracene, phenanthrene, and their mixtures in a bomb, in the absence of oxygen, are all highly graphitizable. Some difference in the graphitizability of anthracene and phenanthrene cokes does exist, but it is minor when compared to the poor graphitizability of phenanthrene coke previously suggested.[1]

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