Carbonization of Anthracene and Graphitization of Anthracene Carbons

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To study the processes by which graphitizable chars and carbons are produced, anthracene chars were prepared in several different ways, calcined at temperatures up to 1000° C., and finally graphitized at about 2500° C. Calculated x-ray diffraction parameters of the carbons and graphite were used for comparing the structural changes induced by the varying conditions employed.

Anthracene chars prepared at about 500° C. have interlayer spacings of 3.44 A. and well defined (002) peaks as shown by high ratios of I_v/I_p. However, biphenyl chars prepared in the same way have much higher interlayer spacings and lower I_v/I_p ratios. Because anthracene chars are highly graphitizable and biphenyl chars are not, formation of a well-ordered initial char is essential for the production of an easily graphitized carbon.

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High temperatures, high rates of charring, and/or removal of tars before further carbonization favor formation of graphitizable chars from anthracene

AMORPHOUS carbons vary greatly in the ease with which they are graphitized by heat treatment, but the fundamental reason for this, as well as the chemical processes by which a wide variety of carbons are produced from organic raw materials, are incompletely understood. Anthracene produces a graphitizable carbon when pyrolyzed at 500° C. under its own vapor pressure (11). Therefore, it is an ideal substance for studying the processes by which graphitizable carbons, such as petroleum coke and coal tar pitch coke, are produced and graphitized. Phenanthrene, isomeric with anthracene, yields a nongraphitizing char under the same conditions. Biphenyl char is even more resistant to graphitization, and for comparison, some data on this char have been included.

Franklin (5) has classified all carbons, other than crystalline diamond and graphite, into two main classes—graphitic and nongraphitic carbons. Graphitic carbons are considered to be composed of crystallites containing both layer planes showing three dimensional ordering (d spacing of 3.35 A.) and those having only two dimensional ordering

(d spacing of 3.44 A. or greater). The relative proportions of these two structures determine the graphitic character of the carbon. Nongraphitic carbons are considered to be composed of the randomly oriented type of layer structure and carbon of variously disoriented structures that is gaslike in its effect on x-ray diffraction. Nongraphitic carbons, therefore, are considered to have a minimum d spacing of 3.44 A. but may have values much higher.

Nongraphitic carbons are further subdivided into graphitizable and nongraphitizable varieties. depending on whether or not the d spacing falls below 3.44 A. when the carbon is heated in the range of 1700° to 3000° C. On this basis, carbons which produce spacings of less than 3.44 A. when heated to graphitizing temperatures are believed to contain an amount of graphitizable carbon proportionate to the resultant spacing (5).

In the present work, the chemical aspects of the processes by which anthracene is converted to char were investigated by separating the tar molecules formed during the charring and attempting to identify them on the assumption that they were intermediates in the process. Samples were prepared by heating anthracene in a closed steel bomb under the pressure developed by the vaporization of anthracene and the hydrogen

formed in the charring process. The tar produced was then extracted with benzene.

Physical differences in the chars induced by different charring temperatures, rates of heating, soak time, and removal of tars before further heat treatment were also investigated. For this purpose, interlayer spacings and crystallite heights were calculated from x-ray diffraction data. Calcinings at higher temperatures, up to 1000° C., were carried out under the same conditions of heating rate and soak time. Graphitizations were made in the range of 2400° to 2650° C. in an induction furnace.

Equipment and Procedures

Anthracene was charred in a small steel bomb containing a glass liner which held 5 grams of sample. The free space in the loaded bomb was about 5 ml. A gas-tight closure was made with a silver gasket backed with copper. Heating was effected by an automatically controlled electric furnace. Heating rates of 3°, 5°, and 10° C. per minute were maintained over the range of 25° to 600° C. by means of a temperature controller which received its sensing current from an iron-constantan thermocouple inserted in a well

drilled in the head of the bomb. Temperatures were obtained by an automatic recorder which was activated by a second iron-constantan thermocouple inserted in a second well. Heating rates were maintained with an accuracy of ±0.5° C.

The temperature controller was able to maintain the bomb temperature within ±2° C., but it was not possible to preset soak temperatures. Consequently, this was done manually, and in some cases the desired temperature was over- or undershot a few degrees. In these cases the controller maintained this temperature for the soak period. In one run a heating rate of 45° C. per minute was attained by placing the cold bomb in the furnace preheated to 700° C. This raised the bomb to 552° C., and the run was completed at this temperature.

Char samples were taken from the product within the liner only and were ground to −60 mesh (U. S. sieve series); 0.5-gram portions were placed in porcelain boats and calcined in a stream of helium in a 96% silica glass tube heated in an electric furnace. The heating rates and the soak temperatures were controlled as before by two iron-Constantan thermocouples inserted over the boat. The helium was purified by passing it over copper oxide at 350° C. and then Anhydrone at room temperature. The helium flow rate was 85 ml. (STP) per minute. The samples received the same heating rates as those used during their formation. Soak times at the final temperature were for 1 hour in each case.

The heat-treated carbons were graphitized in an Ajax-Northrup No. 308 induction furnace. The samples were placed in small, covered graphite crucibles, inserted in a graphite tube closed at the lower end. The latter was packed in Norblack in a fused quartz tube which was closed with a water-cooled head. The system was evacuated to about 25 microns of mercury. When the samples were heated to about 2500° C., the pressure rose to about 1000 microns, but on cooling it returned to the original pressure. To permit the gas to be evolved slowly, the temperature was raised to about 900° C. and held there for about 15 minutes. The temperature was then raised to about 2500° C. in about 15 minutes and held for 30 minutes. Difficulty was experienced in anticipating the

power setting required to obtain the temperature desired, and, therefore, graphitizing temperatures varied within ±50° C. Temperatures were measured with a Leeds & Northrup 8622-C optical pyrometer by sighting on the upper tier of sample crucibles. Variations in temperatures from the upper to the lower tiers of samples were probably well within 50° C., because no variation of the interlayer spacing or the average crystallite height of the same sample placed in these positions was observed.

X-ray diffraction patterns were obtained, and interlayer spacings and crystallite heights were calculated following procedures used previously (14). Using these methods, the accuracy of the interlayer spacings was believed to be correct to ±0.0005 A. for the graphitized carbons and to ±0.005 A. for the amorphous carbons. The crystallite heights for all carbons were believed to be correct to ±20%.

Results and Discussion

Chemical Aspects of Condensation of Anthracene. The chemical compounds in the tar were separated using chromatographic techniques. Activated alumina was used as adsorbent, and benzene, n-heptane, toluene, and mixtures of these were used as eluents. Identification of the fractions separated was attempted by comparing their ultraviolet absorption spectra with those of known compounds in the literature. A large number of fractions were obtained with different and apparently characteristic spectra which could not be identified. Among those identified were 9,10-diphenyl anthracene, 1,2,5,6-dibenzanthracene, and anthraquinone.

Anthraquinone was separated only from the 1-hour experiment and, as it was not observed after 5 hours' heating, probably reacted slowly with other molecules in the bomb. No doubt it was formed by the oxidation of anthracene by the small amount of air remaining in the bomb, because when the air was replaced by helium in a second 1-hour run no anthraquinone appeared.

Other unidentified oxygenated products were also isolated. Analyses of two of these fractions are given in Table I. As these products were obtained from the pyrolysis using helium to replace the air in the bomb as well as when the bomb contained air, it is believed that the oxygen was introduced into these molecules after the bomb was opened and the products exposed to air. Many anthracene derivatives (1, 3, 4, 9) readily undergo photooxidation in solution; and it seems probable that this type of reaction occurred, adding to the difficulties of separating and identifying the tar intermediates.

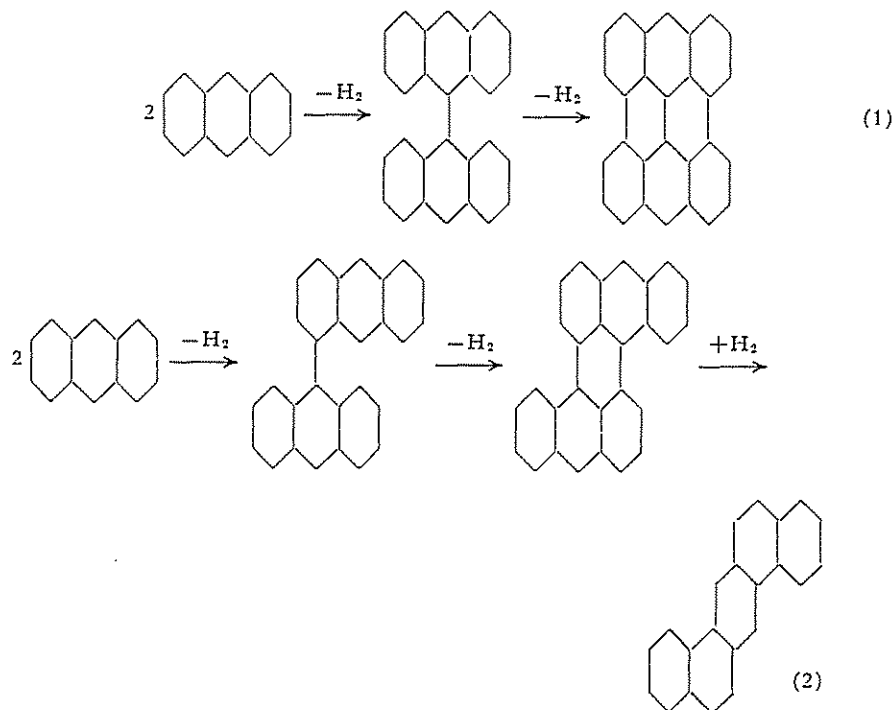The formation of pyrolytic products from anthracene, such as 9,10-diphenyl-

anthracene and 1,2,5,6-dibenzanthracene, must involve cleavage of aromatic rings. Such behavior is not in agreement with the proposals of Brooks (2), Hofmann (7), Sachanen (13), and others who have pictured the charring of an organic compound as a condensation of the carbon structure, with the elimination of hydrogen or other atoms or groups, forming eventually large polynuclear aromatic molecules, which with continued edgewise condensation become the layer planes of the char or carbon.

Starting with the assumption of Brooks that condensation is the main reaction, anthracene would be expected to form 9,9′-bianthryl and/or isomers. 9,9′-Bianthryl has been reported in the pyrolysis of anthracene (10), but in the present investigation it was not identified. A fraction was isolated which had nearly the identical spectrum of 9,9′-bianthryl, but the melting point (232–5° C.) was too low, and a mixed melting point with an authentic specimen was further depressed. Nevertheless, the close similarity of the spectrum with that of 9,9′-bianthryl suggests that the product was an isomeric bianthryl or possibly a mixture of isomers.

On further heating, the bianthryl isomers would be expected to undergo additional condensation with the elimination of hydrogen. 9,9′-Bianthryl and 1,1′-bianthryl should give bisanthene, Reaction 1, and 1,9′-bianthryl should give 1,2,7,8-dibenzoperylene, Reaction 2.

Table II. Parameters of Carbons Prepared from Anthracene 500° C. Chars

Soak Temp., ° C.	d Spacing, A.	L_c, A.	I_v/I_p
A. Heating Rate, 3° C. per Minute			
500	3.44	50	0.77
604	3.44	35	0.79
697	3.43	23	0.72
815	3.44	17	0.73
904	3.45	21	0.81
1000	3.48	24	0.89
2500	3.3643	1030	...
B. Heating Rate, 5° C. per Minute			
508	3.44	39	0.79
600	3.43	23	0.73
700	3.40	23	0.65
800	3.43	18	0.74
900	3.42	20	0.78
1004	3.44	22	0.86
2500	3.3643	1120	...
C. Heating Rate, 10° C. per Minute			
508	3.44	33	0.79
607	3.43	27	0.72
710	3.43	21	0.61
816	3.44	20	0.69
2500	3.3647	1020	...
D. Heating Rate, 45° C. per Minute			
552	3.44	31	0.98
2500	3.3610	1310	...

Table I. Microanalysis of Oxygen-Containing Products in Tar

Band No.	C, %	H, %	O (by Diff), %
3	82.6	7.8	9.6
4	90.7	5.5	3.8

$$2 \quad \xrightarrow{-H_2} \quad \xrightarrow{-H_2} \quad (1)$$

$$2 \quad \xrightarrow{-H_2} \quad \xrightarrow{-H_2} \quad \xrightarrow{+H_2} \quad (2)$$

the d spacings tend to fall to a minimum value slightly below 3.44 A. at 700° C. suggesting that some further ordering including a small amount of three-dimensional crystalline graphite structure occurs.

Above 700° C. the average d spacings tend to become larger, increasing to as much as 3.48 A., with the 1000° C. carbon in the 3° C. per minute series. Perhaps this is due to the development of new crystallites of small height, and hence larger d spacings, from some of the disorganized gaslike carbon rather than an actual separation of the carbon layer planes to a greater distance as the data might imply.

These changes in d spacings are accompanied by a general decrease in the crystallite heights, reaching a minimum at 800° C. in each case. This decrease in L_c could be explained on the basis that new crystallites of smaller average height are being formed in this temperature range; but this does not appear to be a satisfactory explanation because the d spacings also decrease, at least to 700° C. Therefore, it seems probable

Bisanthene and 1,2,7,8-dibenzoperylene were not isolated, but such large seven- and eight-ring aromatics would be strongly adsorbed on the char and, having low solubility in benzene used to extract the tar, would not be efficiently extracted. Consequently, it was assumed that if such intermediates were produced they remained with the char. That crystalline, organic compounds were present in the benzene-extracted, 454° C. char was indicated by the observation of a fairly strong x-ray diffraction peak (6) at 18.8° (2θ), which was not given by the extracted 500° C. chars. No doubt further reaction of these large molecules with anthracene occurred, giving still larger molecules which would have, in relatively few steps, the properties of a char or carbon.

The ring cleavage that produced 9,10-diphenylanthracene and 1,2,5,6-dibenzanthracene may be accounted for by the action of hydrogen produced in the bomb. Orlov (12), for example, has shown that chrysene when heated with hydrogen under pressure to 450° C. yields alkyl derivatives of phenanthrene, naphthalene, and benzene. He gives, as the mechanism, the formation of cycloparaffin rings by the addition of hydrogen followed by the carbon-to-carbon cracking of these rings—a reaction known to occur in preference to the cracking of the corresponding aromatic ring. Support for this mechanism occurring in the pyrolysis of anthracene in the present work may be found in the analysis of band 3 in Table I, in which the percentage of hydrogen is materially higher than in anthracene, 5.6%. The formation of 1,2,5,6-dibenzanthracene from 1,2,7,8-dibenzoperylene is shown in Reaction 2, and that of 9,10-diphenylanthracene by the hydrogenolysis of

9,10-di(9′,9″)anthrylanthracene, in Reaction 3.
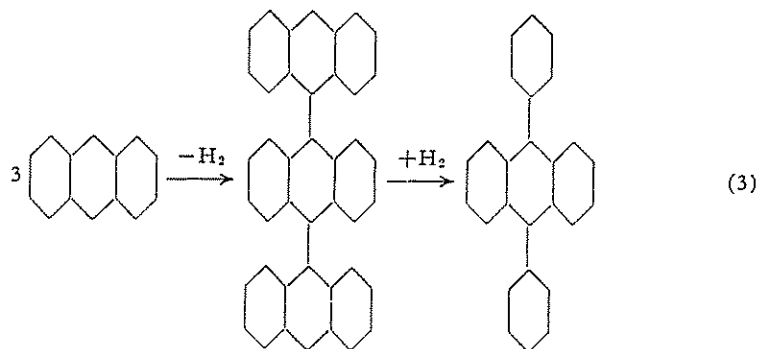
It seems probable that the products isolated and identified from the tar are not necessarily characteristic of the charring process of anthracene but are in part by-products of a secondary reaction, hydrogenolysis, which occurs because of the liberation of hydrogen in the primary reaction, condensation. It also seems probable that anthracene forms a graphitizing char because, when it condenses with itself, multiple links are formed which of necessity lie in one plane as in Reaction 1, for example. These large, planar, aromatic molecules probably continue to grow in the same manner, forming the crystallites described below.

Heat Treatment of Chars. The interlayer spacing of all the initial 500° C. anthracene chars prepared at heating rates of 3° to 45° C. per minute was 3.44 A. (Table II). This is the minimum limiting value of nongraphitic carbons according to Franklin (5) and indicates that the char crystallites have grown in a very regular manner to achieve this condition. When the initial chars are reheated at the same heating rates in a helium stream to higher temperatures,

$$3 \quad \xrightarrow{-H_2} \quad \xrightarrow{+H_2} \quad (3)$$

that some of the initial 500° C. crystallites undergo cleavage into two or more thinner crystallites as they draw into a more crystalline structure, which is indicated by the smaller d spacings. Further confirmation of this interpretation is obtained by comparing the height of the (002) peak with the depth of the valley on the low-angle side on the following basis.

The background intensity of scattered radiation on the low-angle side of the (002) peak is always larger for the poorly organized carbons and for non-graphitizing carbons particularly. For the graphitizing anthracene carbons, the valley is well defined, as shown in Figure 1, which traces the (002) peak of the 5°-per-minute char calcined at 1004° C. The increased amount of background on the low-angle side of a peak is due to many factors, but assuming that large proportions of organized carbon in a sample give large valleys and large proportions of disorganized carbon relatively low valleys, the ratio of the intensity of the valley to the intensity of the peak, I_v/I_p, may be considered to be in part proportional to the

relative amounts of organized and disorganized carbon in the sample.

Values of I_v/I_p obtained for the 500° C. anthracene chars are correlated with d spacings and L_c dimensions in Table II. The decrease of I_v/I_p values upon heating the 500° C. chars to 700° C. was not expected, but this does suggest that disorganized carbon is not converted to new crystallites in this temperature range. Also, if initial crystallites undergo splitting into smaller crystallites, a larger number of smaller crystallites would be expected to increase the scattered radiation, which would decrease I_v/I_p as observed.

Increasing calcining temperatures from 700° to 1000° C. reverses the downward trend of the I_v/I_p ratios, and at 1000° C. they approach 0.9, indicating a large proportion of organized carbon in these samples. The 552° C. char prepared at the highest rate of heating, 45° C. per minute, gave an I_v/I_p ratio of 0.98. This may be somewhat out of line experimentally, but this char gave the most graphitized product at 2500° C., the d spacing falling to 3.3610 A. and the crystallite height growing to 1310 A.

The nongraphitizing behavior of a biphenyl char is shown in Table III. Because of the greater thermal stability of biphenyl, it was charred at 594° C., using the 5° C. per minute heating rate. The char produced had a much greater d spacing than the corresponding 700° C. anthracene char (Table II B) and the crystallite height was somewhat less, indicating a poorer ordering of the carbon. Of particular interest however, was the small I_v/I_p ratio of only 0.22, which appears to show that a large part of the carbon was in a disordered state. At 800° and 1000° C. there was little change in the d spacing or crystallite height, but the increased I_v/I_p ratio indicates that some organization of the disordered carbon took place. On graphitizing this char at 2650° C., the average d spacing fell to only 3.42 A., showing that only a small part of the sample was graphitizable, compared with the highly graphitizable behavior of the anthracene chars. It appears that an initial char, to be easily graphitizable, should have a d spacing approaching 3.44 A. and an I_v/I_p ratio of about 0.75 or above. If it has these properties, crystallite growth appears to take care of itself.

The graphites produced by heating the 3°, 5°, and 10° C. per minute chars to 2500° C. (Table II) have nearly identical x-ray parameters, indicating nearly equal ease of graphitization of these chars. The increased ease of graphitizing the 45° C. per minute char, however, suggests that reactions requiring longer time for completion do not favor the production for the most
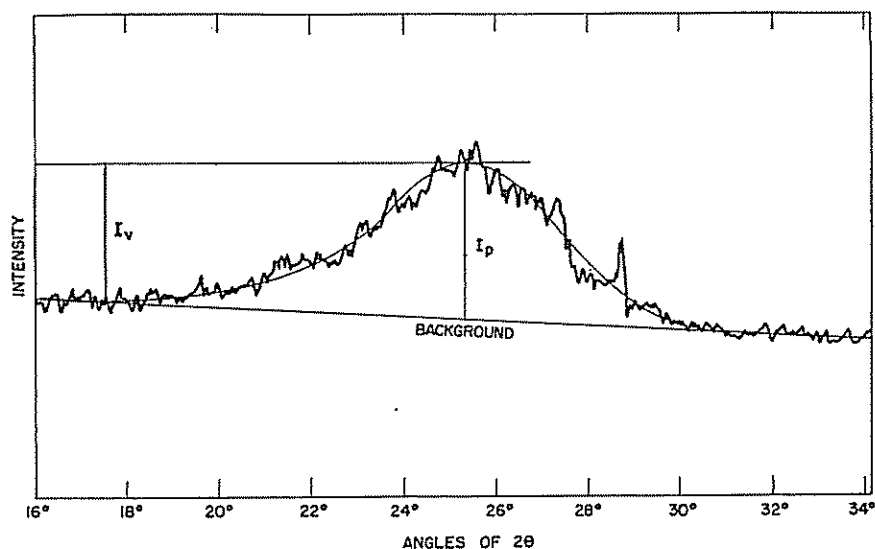
easily graphitized char. Presumably these reactions would be of the stepwise Orlov type described above, involving hydrogenolysis of aromatic rings. Consequently, chars were extracted to remove tar molecules before further heat treatment to ascertain whether this would improve the graphitizability of the chars.

The effect of removing tar is shown in Table IV. The decrease in d spacing below 3.44 A. which was observed for the unextracted chars in Table II was not obtained with either the 500° or 600° C. chars in Table IV, except for the spacing of 3.42 A. for the 506° C. heat-treated carbon, which seems to be too low. A better value would be 3.46 A. which was obtained for the 500° C. char prepared in a helium atmosphere (C, Table IV). If this value is substituted, the d spacings are at a minimum at 700° C. for both series of chars, but the spacings for the 500° C. chars do not rise again, at least up to 1000° C., while the 600° C. chars rise to 3.46 A.

Graphitization of these extracted chars at 2500° C. decreases their spacings to values indistinguishable from that obtained from the 45° C. per minute

char (Table II). It appears that extraction has the same effect in improving the graphitizability of anthracene chars as does a high-heating rate.

Crystallite heights of the extracted chars change with heat treatment (Table IV) in much the same way as the unextracted chars in Table II. The I_v/I_p ratios change in the same way, particularly if the ratio of the 500° C. helium char (C, Table IV) is substituted for that of the 506° C. char (A, Table IV).

Figure 1. X-ray pattern of carbon calcined at 1000° C., copper radiation

Table IV. Parameters of Carbons Prepared from Tar-Free Anthracene Chars at Different Temperatures[a]

Soak Temp., ° C.	d Spacing, A.	L_c, A.	I_v/I_p
A. 500° C. Char			
506	(3.42)	38	(0.69)
600	3.45	32	0.75
700	3.44	29	0.74
800	3.44	19	0.78
1004	3.44	23	0.88
2500	3.3608	1100	...
B. 600° C. Char			
607	3.44	27	0.72
690	3.44	24	0.66
796	3.45	18	0.72
1000	3.46	21	0.82
2500	3.3610	1450	..
C. Special Chars			
454[b]	3.46	22	0.77
450[c]	3.45	24	0.66
500[d]	3.46	38	0.77

[a] Heating rate, 5° C. per minute; all chars extracted with benzene in Soxhlet extractor for 24 hours before heat treatment.
[b] Char yield 1% of anthracene charge.
[c] Anthracene charred at 450° C. for 5 hours instead of 1 hour as in all other cases; yield, 88%.
[d] Air in bomb replaced by helium.

Table III. Parameters of Carbons Prepared from Biphenyl 594° C. Char[a]

Soak Temp., ° C.	d Spacing, A.	L_c, A.	I_v/I_p
690	3.60	17	0.22[b]
800	3.59	15	0.42
1000	3.60[c]	15[c]	0.46
2650	3.42	248	...

[a] Heating rate, 5° C. per minute.
[b] Average from three x-ray diffraction patterns.
[c] See (11).

Although the 2500° C. graphites (A and B, Table IV) are equal in d spacing to that of the 45° C. per minute char in Table II, the I_v/I_p ratios of the former do not approach that of the latter. Consequently, the latter ratio may be partly the result of an experimental inaccuracy.

The effect of decreasing the charring temperature to 450° C. is also shown in Table IV, C. At 454° C. only 1% of the anthracene is converted to benzene-insoluble char in 1 hour. This char has a slightly higher d spacing and lower crystallite height than the 500° C. chars. When reheated to 600° C., d spacings decrease from 3.46 to 3.44 A. Upon charring anthracene for 5 hours at 450° C., the yield of benzene extracted char was increased to 88%. Parameters for this char were similar to those obtained from the 1-hour char, except that the I_v/I_p ratio was noticeably lower.

On graphitizing the benzene-extracted, 1-hour 454° C. char at 2500° C., a markedly inferior graphite was obtained compared with the 506° and 607° C. chars (Table V). This seems to show that a temperature of at least 500° C. is desirable for carbonizing anthracene to produce the best graphitizing carbon.

As the bomb used in this work could not be used safely above 600° C., the experimental procedure was changed to obtain results at higher temperatures. Anthracene has been shown to be nearly completely carbonized at 1 atm. at 1000° C. (8). By passing anthracene vapors in a helium steam through a silica tube at this temperature, two kinds of carbon were obtained in the present work. One was a shiny gray, brittle film on the walls of the tube, and the other was a soft, sooty deposit of carbon black that formed in the gas

phase and settled to the bottom of the tube.

The film deposit, as expected, gave a lower d spacing than either the 508° C. char calcined at 1004° C. or the carbon black (Table VI). The I_v/I_p ratio of the film also indicated a highly organized carbon and on graphitization at 2650° C. gave a spacing approaching that of natural graphite which is 3.3540 A. The crystallite height of this carbon before graphitization, however, was small, an indication that the L_c value of the initial char is not as indicative of a graphitizable carbon as its d spacing, or possibly its I_v/I_p ratio.

The carbon black deposit had a larger d spacing than the film carbon but was surprisingly small for a vapor-phase soot. The crystallite height was also larger than that of the film, and this may have been made possible by the relatively large size of the spherical particles which were found by electron micrographs to be in the range of 0.2 to 0.5 micron in diameter. The I_v/I_p ratio was smaller than either the 508° C. char reheated to 1004° C. or the film carbon (Table VI); on graphitizing at 2650° C., a graphite inferior to either of the other carbons resulted. Consequently, it appears that the higher the temperature of carbonization, the better the graphite produced provided that vapor-phase soot or carbon black formation is avoided.

The effect of change in graphitizing temperature on the parameters of the same anthracene char in the range of 2400° to 2650° C. is shown in Table VII. The interlayer spacing is still decreasing and the crystallite height increasing at 2650° C. Consequently, more complete graphitization of the chars described in previous tables would probably have been obtained had it been possible to raise the temperature to higher levels. However, the data given are indicative of the graphitizing behavior of anthracene chars.

Conclusions

Anthracene chars prepared at 500° C. have interlayer spacings approaching 3.44 A. and I_v/I_p ratios above 0.75, which appear to predict good graphitizing behavior. When the initial chars are calcined in the range of 500° to

1000° C., the d spacing tends to fall slightly to a minimum at 700° C. and then to rise as disordered carbon undergoes ordering. These changes are accompanied by similar changes in the I_v/I_p ratios, indicating that these ratios are related to the amounts of ordered and disordered carbon in the sample. High temperatures, high rates of charring, and/or removal of tars before further carbonization favor the formation of graphitizable chars from anthracene.

Acknowledgment

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