STUDIES ON PRODUCING GRAPHITIZABLE CARBONS

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Carbonization of pure organic compounds under a variety of conditions is being studied with the objective of understanding how the structure of substances, the physical conditions, and the mechanisms of carbonization affect the graphitizing properties of the carbons produced. Chars prepared for this purpose at 600°C were subjected to further carbonization at 1000°C in a stream of helium before graphitizing at 2500°C to 3000°C, while carbons prepared directly in the range of 900° to 1400°C were graphitized with no additional preparation. Values of d, $\bar{L}_c$, and $\bar{L}_a$ of the different carbons and graphites were obtained from X-ray data. Comparisons of these data show the effects of structure and carbonizing conditions on the graphitizing properties of the carbons.

The variability of the properties of carbons produced from different source materials under different carbonizing conditions is well-known. Not so well-known, however, are the chemical and physical reasons for this variability. Toward a better understanding of some of these problems the following work is directed.

In the first of these studies[1], benzene, naphthalene, anthracene, chrysene and pyrene, were carbonized in the temperature range of 800° to 1100°C to determine the relative carbonizing properties of characteristic aromatic hydrocarbons. Pyrolysis was carried out in both packed and unpacked tubes and a stream of nitrogen was used to carry the hydrocarbons into the heated section. In most experiments, screened metallurgical coke of 16–20 mesh size was used as contact material. Coke packing increased the amount of carbon deposited at a given temperature and usually prevented or at least minimized the formation of soot or carbon black. Most of the carbon deposited was a closely adhering film of silvery gray color. The temperature and the contact time also affected the

relative amounts of the two types of carbon. Contact time varied from about 2 to 45 seconds. In the unpacked tube a film of the silvery gray carbon was deposited on the walls (fused silica) and, depending on the hydrocarbon and the conditions, some sooty black carbon frequently fell to the bottom of the tube or was carried into the first trap. Anthracene, of the five hydrocarbons, was most easily carbonized and possibly for that reason had the greatest tendency to form carbon black.

The effect of structure of the hydrocarbon feed on the quantity of carbon produced from the five hydrocarbons in contact with coke packing in the temperature range of 800° to 1100°C at a contact time of 40 seconds is shown in Figure 1. Benzene is carbonized with the greatest difficulty but at 1100°C is 96% complete. At lower contact times the curve is of course flatter.

Naphthalene is more easily carbonized at higher temperatures than benzene, see Figure 1, but the relative slopes of the two curves suggest that at temperatures below 800°C naphthalene would be the more stable. Chrysene and pyrene, four-ring aromatics, are a little more easily carbonized than naphthalene but the slope of all three

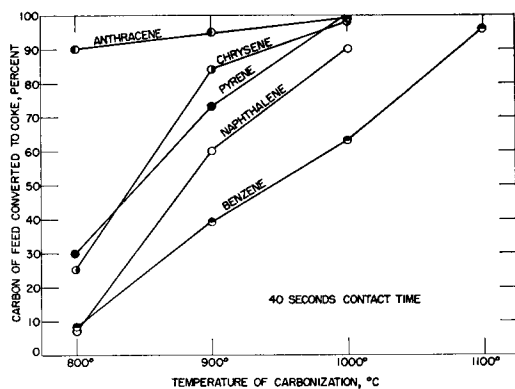[1] C. R. Kinney, and E. DelBel, Ind. Eng. Chem. **46**, 548 (1954).

FIG. 1. Rate of coke formation from aromatic hydrocarbons.

curves is similar. The curve for anthracene is unique. About 90 % is carbonized at 800°C which gives unusual flatness to the curve. Because of this property anthracene is particularly well-adapted to carbonization studies.

In addition to gas-phase carbonizations, liquid-phase carbonizations have been studied searching for a mechanism to account for the effect of structure of the starting material on the character of the carbon produced. Milliken[2] carbonized a number of aromatics including several oxygen derivatives in the liquid state in the temperature range of 475° to 600°C under the vapor pressure of the compound being carbonized and the pressure of the hydrogen evolved under the conditions employed. A small steel bomb was used with the sample placed in a glass liner. The chars produced were then carbonized further by heating them in a stream of helium at 600°, 700°, 800°, 900° and 1100°C. They were also graphitized at 2500° and 3000°C in a nitrogen atmosphere by Mr. W. T. Campbell.[3] The carbons produced were examined by the x-ray diffraction method and the crystallite parameters were calculated from the data obtained. The results are given in

[2] S. R. Milliken, Ph.D. Thesis, The Pennsylvania State University, June 1954; National Carbon Co. Fellow, 1953–1954.
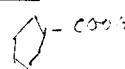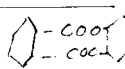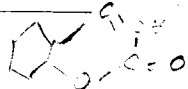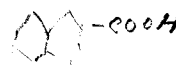
[3] National Carbon Company, Cleveland, Ohio.

Table I. Benzene was not carbonized because of its volatility and resistance to carbonization, but biphenyl and several benzene derivatives were treated.

As is well-known, heat treatment to 1000°C has relatively little effect upon the interlayer d-spacing of carbons, their crystallite height, $\bar{L}_c$, or their diameter, $\bar{L}_a$; see Table I. However, the effect of structure of the starting material is frequently of fundamental importance, but where the structure and the mechanism of carbonization are closely related, little difference is observed. An example of the latter is the behavior of biphenyl and benzoic acid chars. Since benzoic acid is readily decarboxylated to benzene and benzene forms biphenyl at these temperatures, the similar behavior is not surprising. Phthalic acid yields very little char at 500°C, possibly because it first forms its anhydride. Its phenyl ester, diphenyl phthalate, gives a somewhat better yield of char with properties quite similar to those of the biphenyl and benzoic acid chars. Fluorescein, a derivative of phthalic anhydride, gives a char with even poorer crystallite parameters. Very likely this is due to the fact that the fluorescein molecule is biplanar because the two central rings contain a tetravalent carbon atom common to both rings.

A particularly notable example of the effect of structure on the crystallite parameters of carbons heat treated up to 1000°C is that of the anthracene char compared with chars prepared from phenanthrene and anthraquinone. Anthracene and phenanthrene are structural isomers and yet the d-spacings of their carbons differ by 0.1 Å. In the case of anthraquinone, in which two oxygen atoms have replaced two atoms of hydrogen in anthracene, the difference is even greater. The anthracene char is also notable in being obtained in good yield at only 475°C but also that its 500°C char has a d-spacing of only 3.45 Å and an $\bar{L}_c$ dimension of 32 Å.

TABLE I
Properties of Chars Heat Treated at Different Temperatures

Heat Treatment, °C	d-Spacing, Å	L_c, Å	L_a, Å	Heat Treatment, °C	d-Spacing, Å	$\bar{L}_c$, Å	$\bar{L}_a$, Å
Biphenyl, charred at 580°C				Benzoic acid, charred at 600°, 95.5%C, 1.9% H			
600	3.55	10		600	3.55	16	
700	3.45	9		700	3.62	13	
800	3.55	13		800	3.62	15	
900	3.55	11		900	3.60	16	
1000	3.60	15		1000	3.60	16	
2500	3.44	45	150	2500			
3000	3.44	50	160	3000	3.44	74	80
Phthalic acid, charred at 550°C				Phenyl phthalate, charred at 550°C, 93.5%C, 3.4% H			
1000				1000	3.64	14	
2500	3.47	12		2500	3.46	22	
3000	3.44	11		3000	3.44	28	
Fluorescein, charred at 520°C, 90.5%C, 3.7%H				Coumarin, charred at 550°C, 96.5%C, 3.3% H			
600	3.70	12		600	3.55	27	
700	3.77	9		700	3.43	17	
800				800	3.48	18	
1000	3.65	10		1000	3.48	20	
2500				2500	3.37	430	
3000	3.44	55	100	3000	3.36	500	
Naphthalene, charred at 580°C, 96.0%C, 2.3%H				2-Naphthoic acid, charred at 600°C, 95.9%C, 3.1%H			
600	3.70	13		600			
700	3.60	16		700	3.70	11	
800	3.55	16		800			
900	3.55	16		900			
1000	3.51	15		1000	3.50	17	
2500	3.38	460		2500	3.37	430	850
3000	3.36	500		3000	3.36	480	1180
Anthracene, charred at 475°C, 95.6%C, 3.5%H				Anthraquinone, charred at 500°C, 94.5%C, 3.3% H			
500	3.45	32		500	3.68	11	
600	3.44	30		600	3.68	14	
700	3.43	17		700	3.55	11	
800	3.43	16		800	3.60	12	
900	3.43	21		900	3.62	12	
1000	3.43	21	90	1000	3.59	14	
2500	3.37	450	1700	2500	3.44	90	
3000	3.35	520	1900	3000	3.39	130	
Phenanthrene, charred at 550°C, 96.0%C, 3.7% H				Dextrose, charred at 400°C, 84.4%C, 3.9%H			
550	3.54	20		500	3.69	10	
600	3.51	17		600	3.70	12	
700	3.55	18		700	3.77	11	
800	3.55	16		800	3.75	9	
900	3.55	16		900	3.80	11	
1000	3.55	16	60	1000			
2500	3.44	100	160	2500	3.44	33	
3000	3.42	110	200	3000	3.44	47	80

Anthracene char also exhibits a curious behavior first observed when certain coals were carbonized to different temperatures[4]. Examination of the $\bar{L}_c$ values of the anthracene char in Table I shows that increasing the temperature from 500° to 800°C causes a decrease in this value, followed by a slight increase as the temperature is raised to 1000°C. Coumarin and phenanthrene chars show this behavior. The underlying reasons for this behavior are not well-understood and further study is needed.

Naphthalene, which is structurally related to anthracene but having only two aromatic rings, yields a 600°C char that has a relatively high d-spacing of 3.70 Å. On raising the carbonizing temperature this falls more rapidly than with most carbons, reaching 3.51 Å at 1000°C. 2-Naphthoic acid char behaves in a very similar manner. This is expected because of decarboxylation producing naphthalene.

Dextrose 400°C char has been included in Table I so that a char from an aliphatic compound may be compared with chars from aromatic compounds. It will be observed that the d-spacing is large at 500°C and seems to increase as the temperature is raised to 900°C which is not the behavior of the aromatic chars.

Crystallite parameters of the chars heated to graphitizing temperatures of 2500° and 3000°C are also shown in Table I. Again, the affect of structure is outstanding. All of the chars from the benzene derivatives yield 3000°C carbons with d-spacing of 3.44 Å with one exception, coumarin, and this char graphitizes very well indeed. No satisfactory theory has been established to account for this difference, but a prediction of graphitizability appears to be suggested by the smaller d-spacing of 3.48 Å of the 1000°C coumarin char compared with values of 3.60 to 3.65 Å for the chars prepared from

[4] H. E. Blayden, J. Gibson, and H. L. Riley, *"Ultrafine Structure of Coals and Coke"*, p. 176 BCURA, London, 1944.

the other benzene derivatives at this temperature.

As would be expected the crystallite height and diameter of the chars prepared from the benzene derivatives, excepting coumarin, fail to grow appreciably at 2500° to 3000°C. In the case of coumarin char, satisfactory growth occurs, particularly the $\bar{L}_a$ dimension. The chemical mechanism by which this is accomplished in chars of certain compounds but not in others is of fundamental importance, and further study of the mechanism may be made.

Naphthalene char graphitizes a little less well than coumarin char although it might be expected to graphitize better because there is no oxygen to be eliminated. A clue to the mechanism of the carbonization of naphthalene may be found in the fact that binaphthyl and perylene have been identified[1] among the intermediate products (tar). This suggests that naphthalene condenses with itself, eliminating hydrogen atoms in the same way that benzene con-


Naphthalene   1,1'-Binaphthyl
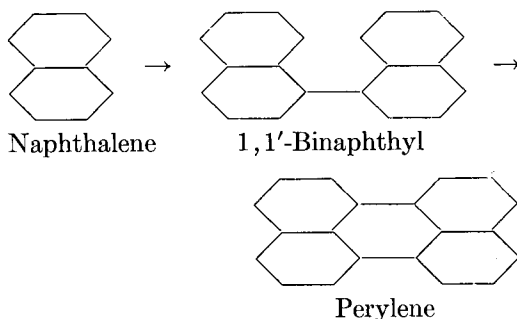
Perylene

denses to biphenyl. If the main intermediate in the formation of naphthalene char is perylene, which has five aromatic rings, it would appear that the formation of large planar sheets of aromatic structure, which would graphitize more readily, could be produced from naphthalene more easily than from benzene (or biphenyl) and with fewer side planes at angles to the main plane being developed, which presumably leads to nongraphitizing carbons.

On the same basis, anthracene should

form an even better graphitizing carbon which is actually observed, see Table I. 9,9′-Bianthryl has been isolated from anthracene pyrolytic tar, but not meso-naphthodianthrene which would be formed if 9,9-bianthryl condensed further in the 1,1′- and 8,8′-positions, as follows.

Anthracene   9,9′-Bianthryl

Meso-naphthodianthrene
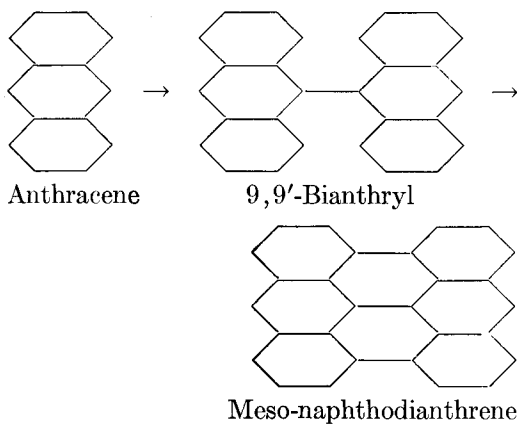
Assuming a condensation of this kind occurs with anthracene, a relatively few steps would be required for the formation of a sheet large enough to have the properties of a char or carbon. Also relatively less of the material would be developed into planes at angles to the main plane as compared with smaller starting molecules. Milliken[2] suggests that the first step in the pyrolysis of anthracene is carbon-to-carbon decomposition at the 9 and 10 carbon atoms. This does not seem as likely for an aromatic hydrocarbon as the mechanism given above—condensation with loss of hydrogen.

Presumably phenanthrene, which has an angular shape, cannot condense into sheets of aromatic structure except by orientation of the molecules in a manner that does not correlate with the preferred chemical behavior of the molecule. Since the chemical behavior probably governs a sufficient number of the condensation reactions to strongly influence the structure of the char formed, a nongraphitizing carbon results. The 3000°C carbon has a d-spacing of 3.42 Å and a crystallite height and diameter of

110 Å and 200 Å, values which are very similar to those obtained from the biphenyl char.

The graphitizability of the chars obtained from the oxygen derivatives of naphthalene and anthracene, are of interest. The char from 2-naphthoic acid graphitizes in a similar manner to that of the naphthalene char which agrees with the hypothesis that napththalene is first formed by the decarboxylation of the acid. Anthraquinone char, however, cannot form anthracene, and because of the strong chemical bond between oxygen and carbon, it is likely that carbon monoxide splits out leaving benzene radicals which condense in a manner similar to that of other benzene derivatives (excepting coumarin). This results in a poorly graphitizing carbon with about the same properties as the benzene-derivative chars.

The nongraphitizing nature of the dextrose char is similar to that of most of the chars prepared from benzene derivatives, Table I. Since aromatization probably occurs during the charing of the dextrose in a manner similar to that of cellulose[5] this is not surprising.

Since anthracene has been established as a substance which yields a graphitizing char when pyrolyzed in the liquid state, Nunn[6] made a more detailed study of the carbonizing properties of this substance. Among these are the decrease in crystallite height as the temperature of carbonization of the char is raised and the effect of heating rate on the carbon produced.

The decrease in crystallite height was confirmed at three heating rates, 3°, 5° and 10°C per minute. The minimum height was observed at 800°C at all three rates. The effect of increasing the heating rate on the

[5] R. C. Smith, and H. C. Howard, J. Am. Chem. Soc. **59**, 234 (1937); B. Juettner, ibid. **59**, 1472 (1937).

[6] R. C. Nunn, Ph.D. Thesis, The Pennsylvania State University, June 1955; Stackpole Carbon Company Fellow, 1954-1955.

crystallite height observed at a given carbonization temperature was to lower the value. For example, at 500°C heights decreased from 50 Å to 33 Å as the heating rate was increased from 3° to 10°C per minute. This decrease became less pronounced as the temperature of carbonization increased and at 700°C and above became negligible. The increase in crystallite height as the carbonizing temperature was raised from 800° to 1000°C was relatively small; at 3°C per minute heating rate, $\bar{L}_c$ increased from 17 Å to 24 Å.

d-Spacings also seem to pass through a minimum, but the minimum seems to be at 700°C instead of 800°C. At a heating rate of 3°C per minute, d-spacings fell from 3.44 Å at 500°C to a low of 3.43 Å at 700°C and rose to 3.48 Å at 1000°C. At 5°C per minute, the values were 3.44 Å, 3.40 Å, and 3.44 Å respectively.

Since 700°-800°C is the temperature at which most of the hydrogen has been evolved from chars, it is assumed that at temperatures below 700°C evolution of hydrogen results in a slight drawing together of the carbon planes with the result that two (or more) crystallites of smaller height are formed from one tall poorly developed crystallite. At temperatures above 800°C, the normal growth of crystallite dimensions, particularly height, appears to occur. The increased disorder evidenced by increased d-spacings above 800°C is more difficult to circumscribe. One possibility is that more oxygen is chemisorbed, when the higher temperature carbons are brought out into the air, which results in further spreading of the planes.

Williford ratios[7] are also of interest in this connection because of a rough correlation, not only between carbons prepared at different carbonizing temperatures, but also between the graphitizability of carbons and their Williford ratio. The Williford ratio is the relative height of the (002) x-ray peak above the background compared with the depth of the valley on the low-angle side. According to Williford this ratio is a measure of the intensity of small-angle scattering and that as the intensity of the scattering increases an increasing number of discrete particles are present. Although there may be some question as to whether Williford's ratio is a measure of low-angle scattering, because this usually does not become important until angles of less than 10° are reached, the relationship of the ratio to the properties of carbons is interesting.

With anthracene char the Williford ratio rises from 1.28 at 500°C to 1.54 to 700°C and then falls to 1.16 at 1000°C (at a heating rate of 5°C per minute). This behavior would be expected if a larger number of discrete particles were produced in the 700°C carbon than at either lower or higher temperatures. The effect of increasing the heating rate seems to increase the ratio. This effect was greatest at 700°C and at this carbonizing temperature the ratios at 3°, 5° and 10°C per minute were 1.43, 1.54 and 1.64. The above ratios are relatively small compared with those obtained from nongraphitizing carbons. For example, biphenyl char carbonized at 700°C gave an average ratio of about 6 (with an uncertainty of the measurements of 2 or 3 integers) and at 1000°C the ratio had fallen to 2.18. These large values indicate a larger number of discrete particles in the nongraphitizing carbon than in the graphitizing carbon. This is perhaps what would be expected, but further work should be done to substantiate this conclusion.

Since anthracene produces a graphitizing carbon and may be considered to be characteristic of hydrocarbons present in coal tar pitch and perhaps in petroleum residues which yield graphitizable cokes, a detailed study of the mechanism of the charring of this hydrocarbon has been made. For

[7] C. L. Williford, "X-Ray Studies of Paving Asphalts", Bulletin 73, Agricultural and Mechanical College of Texas (1943).

this purpose, the effect of temperature and the rate of heating on the properties of the char was determined and a study of the chemical intermediates in the tar made.

Anthracene carbonizes slowly at 450°C under its own vapor pressure in the bomb. In one hour 1% is converted to char (benzene insoluble), but in five hours 88% is charred. At 500°C, 86% is carbonized in one hour, and at 600°C, over 99%. If molecular orientation is required for the production of the best graphitizing carbon, then it must be assumed that the lowest rate of charring, that is lower charring temperatures, would give the best graphite. However, this was not observed experimentally, the best graphitizing char being obtained at 600°C and the poorest at 450°C. On this basis it may be assumed that molecular orientation is not a primary factor in producing graphitizable carbon from anthracene.

The effect of increasing the heating rate from 3° to 5° and to 10°C per minute on chars produced at 500°C was negligible. At a heating rate of 45°C per minute in which the final temperature was 550°C, a better graphite was obtained—comparable to that obtained at a heating rate of 5°C per minute to a final temperature of 600°C. This again suggests that orientation of the molecules is not of fundamental importance.

Small quantities of tar are produced during the carbonization of anthracene, but apparently this material is rapidly converted to benzene-insoluble carbon because its concentration never rises above about 10–15% of the total charge. If these intermediates are extracted from the carbon before graphitization a somewhat better graphite is produced. This suggests that the molecules are adsorbed on the char in such a way, possibly between some of the layer planes, that when it undergoes carbonization a disordering of the crystallites occurs.

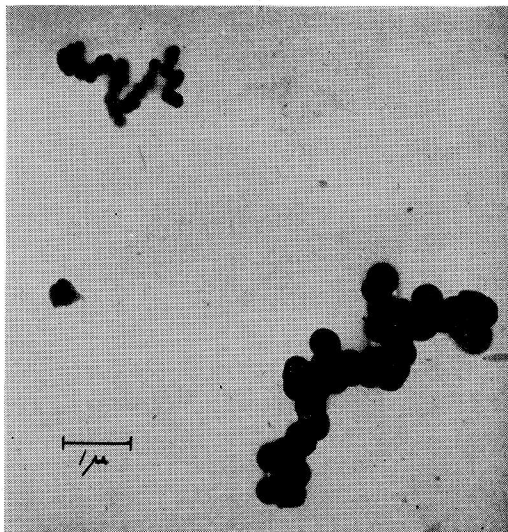Again, a fair agreement was observed

FIG. 2. Electron photomicrograph of B-type carbon produced by carbonization of anthracene at 1000°C.

between the graphitizing properties of these carbons and the Williford ratios calculated from the x-ray diffraction data.

Gas-phase carbonization of anthracene at 1000°C has also been compared with the liquid-phase studies. The usual two kinds of carbons were readily obtained: type A, plated on the walls of the hot tube was hard, brittle and silvery gray in color, and type B, soft, sooty and black in color. An electron photomicrograph reproduced in Figure 2 shows that the B carbon is in spherical form similar to carbon blacks and of about 0.3 microns diameter.

The powdered A carbon gave a d-spacing of 3.46 Å and an $\bar{L}_c$ of 21 Å compared with 3.49 Å and 28 Å, for the carbon black, B type. The spacing of 3.46 Å for the A carbon seems high compared with 3.44 Å obtained from the liquid-phase, 500°C char, and upon mounting a piece of the A carbon film directly on the stage of the x-ray machine, a spacing of 3.43 Å was obtained which seems to be a better value for this material. The Williford ratios of these carbons predict the better graphitizing behavior of the A carbon.

Graphitization of the powdered A sample at 2650°C gave a d-spacing of 3.3567 Å and an $\bar{L}_c$ of 1310 Å, while the B carbon gave 3.3709 Å and 530 Å for the same parameters. On the other hand, the liquid-phase 500°C char, when graphitized at 2650°C, gave a d-spacing of 3.3617 Å and $\bar{L}_c$ of 1250 Å. Comparison of these results show that increasing the temperature of the original charring of anthracene from 500° to 1000°C increases the graphitizability of the carbon, provided the carbon is deposited on a solid surface. When the carbon is produced in the gas phase at this temperature, however, its graphitizability is not as good. Furthermore, it seems obvious that intermediate compounds are formed that condense to fluid droplets which then carbonize while retaining their spherical shape. It is possible that the droplets do not immediately attain the temperature of the surroundings because of the absorption of energy in forming free radicals, ions, etc., and consequently the B-type carbon may be formed at essentially lower temperatures than the A type. In addition, space limitations within the droplet probably affect the growth of the crystallites.

Anthracene carbon black, produced at 1000°C in the gas phase, nevertheless, is a better graphitizing carbon than biphenyl char, for example, carbonized in the liquid phase at 600°C. The biphenyl char, graphitized at 2650°C, gave a d-spacing of 3.42 Å and $\bar{L}_c$ of 250 Å, compared with 3.37 Å and 530 Å for the anthracene carbon black graphitized to the same temperature. These results show the importance of structure of the starting material on the final product, as well as the conditions of treatment.

Current work[8] includes gas-phase studies of aromatic hydrocarbons carbonized in a stream of helium in the temperature range of 900° to 1400°C. Vycor and porcelain tubes were used, and in certain experiments

[8] D. B. Murphy, and W. V. Kotlensky, working under an AEC contract.

fused silica or porcelain rods were used for packing.

Beginning with benzene as the simplest aromatic hydrocarbon a large variety of carbonizations have been made, under different operating conditions, and four physically different appearing carbons have been prepared. The first of these, shown in Figure 3, is the hard gray plated A-type carbon similar in appearance to that described above from anthracene under similar conditions. The second type, shown in Figure 4, is the B-type also similar to that
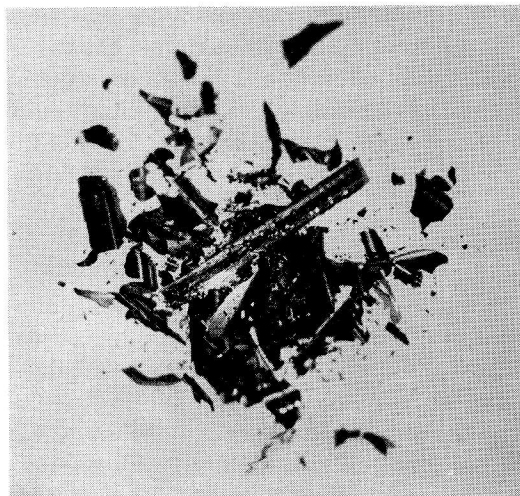

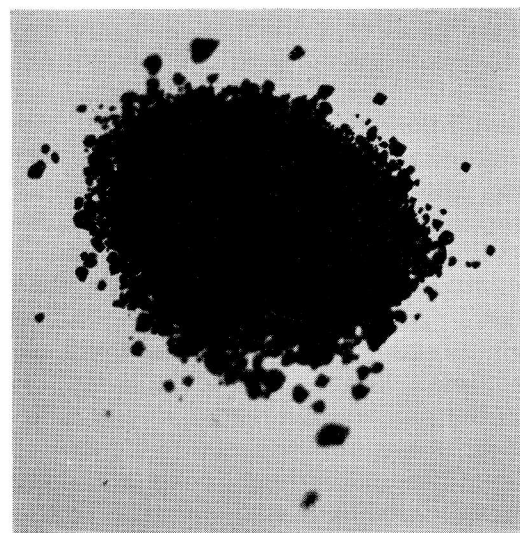
FIG. 3. A-type carbon prepared from benzene

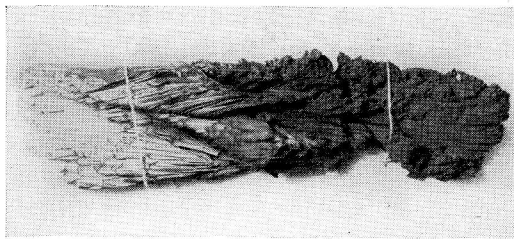FIG. 4. B-type carbon prepared from benzene

FIG. 5 D- and E-type carbon from benzene

FIG. 6. D-type carbon deposited on A-type carbon plates.

obtained from gas-phase pyrolysis of anthracene. Mixtures of the A and B carbons were labeled C and are of no significance in this discussion.

The third and fourth types are shown in Figure 5. These carbons are only formed in the unpacked tube at temperatures of 1200°C or above and when the deposit is allowed to grow until the tube is nearly filled. At these temperatures the carbon deposit is formed rapidly and in a relatively small space. On the upstream side, parallel layers of a feather-like deposit grow out into the gas stream, as shown on the left-hand side of Figure 5. This carbon is designated type D. Apparently this carbon develops from projections which grow out of the plated A carbon if the deposition is continued; notice the rough edge of the large piece of plated carbon shown in Figure 6.

The fourth type of carbon is the deposit downstream from the D carbon and to the right of that deposit in the photograph shown in Figure 5. This deposit, designated
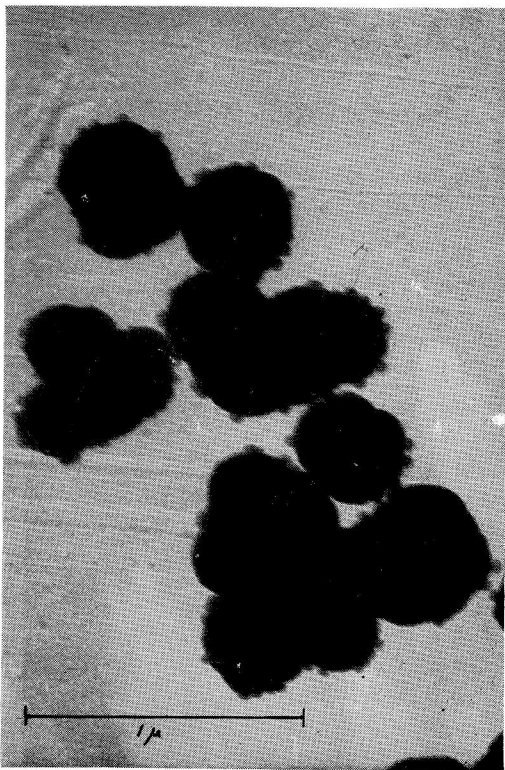

FIG. 7. Electron photomicrograph showing E-type carbon adhering to particles of B-type carbon.

E, is a springy porous material of a brownish black color and with little strength. A remarkable feature of this carbon is shown in the electron photomicrograph shown in Figure 7. From the picture it appears that the carbon black, B-type carbon had been formed in the usual way, but that subsequently, fresh droplets began to form which adhered to the large spheres and were carbonized in place. The unique appearance of this material suggests that it might have industrial specialty applications.

The effect of increasing the carbonizing temperature from 900° to 1400°C on the crystallite parameters of the A carbons was to decrease the d-spacing and to increase the $\overline{L}_c$ and $\overline{L}_a$ values. The d-spacings decreased from a range of 3.54–3.57 Å to 3.43–3.46 Å; the $\overline{L}_c$ average increased from

14–17 Å to 40–45 Å; and the $\bar{L}_a$ increased from 51–62 Å to 58–110 Å.

The effect of increasing the carbonizing temperature on the B carbons was almost nil. The d-spacings remained in the range of 3.60 to 3.73 Å, the $\bar{L}_c$ values from 10–19 Å, and the $\bar{L}_a$ values from 41–65 Å. The D carbons were also little affected by increasing the carbonizing temperature from 1200° to 1400°C. The d-spacings varied within the range of 3.50 to 3.53 Å, the $\bar{L}_a$ values from 28–34 Å, and the $\bar{L}_a$ values from 42 to 53 Å.

The E carbons, which appear to be closely related in appearance to the B carbons showed marked divergence from them in crystallite parameters. The d-spacing decreased from a range of 3.51–3.58 Å to 3.47–3.48 Å as the carbonizing temperature was raised from 1200° to 1400°C. The $\bar{L}_c$ values increased from a range of 18–31 Å to 46–54 Å, and the $\bar{L}_a$ values from 49–65 Å to 60–82 Å.

These variations in crystallite parameters with the temperature of deposition appear to be characteristic of the four types of carbons, and while variations between duplicate preparations are observed, the values fall within the ranges given above. In one experiment all four types of carbon were formed. Since the crystallite parameters of these carbons should be of relative significance they are given in Table II.

The A and E type carbons have remarkably similar parameters, while the B and D carbons are more amorphous. On graphitizing the four types of carbons at 2500°–2600°C, a marked difference in graphitizability was observed, however, as shown in Table II. The A carbon is notable in growing extremely well in the c direction, but not in the a direction. This results in long needle-like crystallites quite different from natural graphite. Again the possibility of specialty graphites is suggested. Better d-spacings have been observed with other carbons of this series, particularly the 1200°C A carbons, which have given values as low as 3.3578 ± 0.0010 Å.

The B, D, and E carbons all graphitize very poorly (Table II). Although the d-spacings fall to 3.39 Å or less and the crystallite heights grow some 5 to 10 times, the carbon layers fail to grow laterally to any appreciable extent. The similarity of these crystallite parameters raises the question of whether a fundamental difference exists between these three 1400°C carbons. However, if these carbons are fundamentally the same, the wide divergence of properties of the A and E 2600°C graphites compared with their similarities at 1400°C is difficult to explain.

The differences in graphitizability of carbons, reported in this paper, are seen to be due to many factors. Carbonization temperatures, rate of heating, catalytic solid surfaces, physical state of the substance being carbonized, and particularly the chemical structure of the substance, all affect the character of the carbons produced. Thus for example, anthracene low-temperature char graphitizes very well indeed compared with chars from many simple benzene derivatives. However, under suitable conditions, such as high temperatures and surface catalysts, graphitizable carbons can be prepared from even benzene. As yet not enough information is available to formulate mechanisms for these different carbonizing behaviorisms.

TABLE II

Crystallite Parameters of the Four Types of Carbons Prepared at 1400°C. and Graphitized at 2600°C.

Carbon Type	1400°C. Carbons			2600°C. Carbons		
	d-Spacing	$\bar{L}_c$	$\bar{L}_a$	d-Spacing	$\bar{L}_c$	$\bar{L}_a$
A	3.46	45	58	3.3646	2900	220
B	3.60	16	47	3.3913	220	54
D	3.52	30	53	3.3889	159	72
E	3.47	46	60	3.3848	220	75