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Graphite oxides which had been prepared from three different size graphite particles by the modified Brodie method were observed with the electron microscope. The thermal decomposition products of the oxides, obtained by heating them at 240° and 300°, were observed using the electron microscope and x-ray diffraction.

Graphite oxide was seen (using the electron microscope) to consist of flexible, irregularly shaped sheets. The decomposition products were observed as irregularly shaped sheets, somewhat folded, torn or split, and at higher temperatures as amorphous carbon.

X-ray diffraction patterns of the decomposition products allow the qualitative evaluation of the change in the composition of

the various samples. The level of oxidation obtained is due to the original graphite particle size and to the number of oxidation steps to which a sample is subjected. At the higher temperature the decomposition products consist of unoxidized graphite and amorphous carbon.

APPLICATION OF ELECTRON MICROSCOPY AND X-RAY DIFFRACTION TO GRAPHITE OXIDE AND ITS DECOMPOSITION PRODUCTS

by

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INTRODUCTION

Graphite oxide has been known since 1859 but it is still of contemporary interest (9, p. 249-259). It has been recently patented as a component in rocket fuels (17, p. 25, 832), and it is finding some use as a component in anti-knock additives for gasoline (15, p. 16, 812). Although a century of experimentation has resulted in some modern industrial uses for this substance, its structure still has not been explicitly defined.

One of the early investigators, M. Balbiano (2, p. 191-203), prepared graphite oxide from three types of graphite using two different methods of synthesis. He dried these samples over H_2SO_4 in vacuo and then analyzed the decomposition products. He determined an empirical formula of $C_{14}H_4O_7$ or $C_{13}H_4O_7$. This attempt (1815) is indicative of the problems which were to be encountered in subsequent investigations. There are two factors which increase the difficulty in establishing a consistent empirical formula. One of these is the fact that graphite oxide is hydrophilic and absorbs water into its interlamellar spacings, thus making it difficult to obtain a thoroughly anhydrous sample. A second factor which contributes to this problem is that there is considerable disagreement about the temperature to which graphite oxide can be heated without decomposition. These two factors account for much of the variance in the results which have been reported. For a comparison of these results refer to Table I (1, p. 131-140).

Graphite oxide is known to consist of lamellar layers of hexagonal carbon rings (12, p. 468-469). To most of the carbon atoms an oxygen-containing group is thought to be bonded. These oxygen-containing groups are believed to consist of at least three different types. The C-OH, C-O-C, and C=O (1, p. 131-140; 12, p. 468-469) groups are the three most often reported. The presence of these groups is substantiated by infra-red absorption spectra of the graphite oxide.

From Table I it can be seen that the C:0 ratio never attains the value of two, considering the H to be present as OH. This suggests that double bonds are inherent in the nature of graphite oxide. There are two structural formulas proposed for this substance, both of which incorporate double bonding. One is an idealized formula which was originally suggested by Ruess (16, p. 381-417). This formula, shown in Figure I, does not consider the keto-enol tautomeric forms which have been proposed by various investigators. Ruess's formula has a C:0 ratio of 2.67 and is

Table I. Composition of Graphite Oxide*

Formula	% C	% H	% O	Author and Date
$C_{11}H_4O_5$	61.11	1.85	37.03	Brodie (1860)
$C_{11}H_4O_6$	56.9	1.72	41.38	Gottschalk (1865)
$C_{11}H_4O_7$	53.22	1.61	45.16	Balbiano (1916)
$C_6(OH)_3$	58.54	2.44	39.02	Thiele (1930-1937)
$C_6O_{1.6}OH$	62.83	0.87	36.30	Ruess (1946-1947)
C_4O_2H	59.26	1.23	39.51	Franklin (1953)
$C_7O_4H_2$	56	1.33	42.67	DeBoer & Van Doorn (1954)
$C_8O_2(OH)_2$	59.26	1.23	39.51	Hoffmann _et al_ (1957)

* Source: (1, p. 131-140)

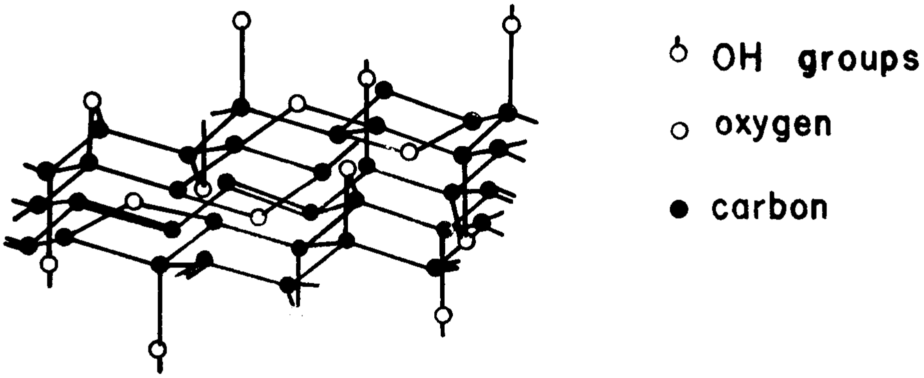
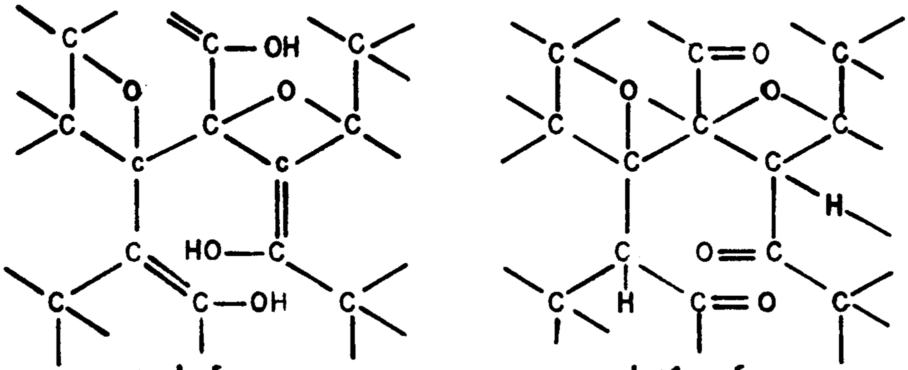


Figure I Structure of Graphite Oxide as suggested by Ruess (16, p. 381-417)



enol form keto form

Figure II Structure of Graphite Oxide as suggested by Clauss et. al. (11, p. 205-220) written as $C_8O_2(OH)_2$. It exhibits the puckered ring structure which has been proposed by other investigators (4, p. 141-147). The second structural formula is that proposed by Clauss et al (11, p. 205-220). The existence of the keto-enol forms is predominant in this formula as can be seen in Figure II. It should be noted that the existence of the keto-enol tautomeric forms is observed by Clauss et al and also by DeBoer and Van Doorn (6, p. 160-169), whose conclusions were arrived at by different methods of experimental examination.

X-ray diffraction studies are capable of yielding only a limited amount of information because of the highly disorganized nature of the graphite oxide structure. The interlamellar distance of dehydrated graphite oxide is 7.0 Å (10, p. 1222) and the hexagonal structure of the layers has a 1.44 Å (7, p. 242-252) C-C distance. X-ray studies which have been used to observe changes in the spacings upon adsorption of various liquids are rather extensive. Changes in the spacings which have been reported by Ruiz and MacEwan are summarized in Table II (10, p. 1222).

The electron microscope has been used by a number of experimentalists (7, p. 242-252; 3, p. 929-935; 14, p. 44-45; 5, p. 119-127) to observe the surface character of graphite oxide. They concur that the graphite oxide forms flexible sheets which

Table II. Interlamellar spacings of graphite oxide.*

Substance	d(001)	Δ**
Dried over conc. sulphuric acid	7.0	---
Water in excess	10.9	3.9
Ethylene glycol	9.6	2.6
Glycerol	10.0	3.0
Acetone	9.0	2.0
Phenol in aq. sol.	10.5	3.5
Acrylic nitrile	8.0	1.0
Propionic acid	9.2	2.2
Amyl nitrite	7.5	---
Nitrobenzene	8.8	1.8
m-Nitroaniline in aq. sol.	11.0	4.0
Carbon disulphide	7.7	---
Benzene	7.3	---
Ethylamine	8.7	1.7
isoButylamine	16.8	9.8
Aniline	18.5	11.5
Aniline in aq. suspension	23.1	16.1
Pyradine	11.1	4.1

---

* Source: (10, p. 1222).

** Indicates increase in d(001) spacing upon adsorption.

can be observed as folds with the electron microscope. Graphite does not display this phenomena and it is seen as rigid, flat sheets. Beckett and Croft (3, p. 929-935) attribute this change to a modification in the character of the bonds that exist between the planes. They propose that the strongly directional bond of order 1.5 for C-C is altered by the formation of covalent oxygen bonds to a reduced order for the C-C bond. This is what would be expected if a number of double bonds had disappeared during the oxidation process. Thus the planar sp^2 hybridized character of graphite has been changed to the sp^3 hybridized character of a six-membered carbon ring. This graphite oxide six-membered ring is pictured in the Ruess structure as being in the chair configuration. The addition of a keto-enol tautomeric effect within this structure is the description which is arrived at upon examination of the literature.

It should be noted here that samples of graphite which had undergone varying degrees of oxidation were available to this investigator. It was felt that the electron microscope might show a significant trend in the changes of surface character of the graphite oxide upon increased oxidation. Another area of investigation which has received only small recognition by previous investigators is the examination of the decomposition products. Therefore the application of the electron microscope and of x-ray diffraction to the decomposition products will be the subject of this paper.

EXPERIMENTAL

Graphite oxide sample preparation

The graphite oxide samples used in this study were prepared by E. V. Vander Zanden (18, p. 5). They were prepared from three grades of graphite, numbers 1, 3, and 5, which were of coarse, medium, and small particle size respectively. The modified Brodie method of oxidation was used (9, p. 244-259). This consists of adding potassium chlorate to a mixture of red, fuming nitric acid and graphite which is cooled in an ice bath. To obtain samples which had undergone varying degrees of oxidation, one fifth of the total product of the first oxidation step was set aside and the other four fifths used for the second step and so forth up to five oxidation steps. Labeling these samples was accomplished by indicating the graphite particle size as a superscript and the method of oxidation as a subscript, followed by the total number of oxidation steps. An example would be C_B^5-3, indicating small size graphite particles oxidized by the Brodie method through three steps. These samples were purified by electrodialysis and centrifugation.

The decomposition products were obtained by heating the various graphite oxide samples in a temperature controlled electric oven to 240° and 300°.

Electron microscope sample preparation

A 0.4% solution of collodion in reagent grade amyl acetate was used as the solution medium for the preparation of the collodion supporting films. This was accomplished by dipping a 1 x 3 inch microscope slide into a beaker of the solution, lifting it out and allowing the amyl acetate to evaporate. The film was then placed on a water surface by scoring the sides of the microscope slide with a razor blade and breathing on the slide to cause the condensation of water vapor on the film. The slide was then lowered into the water at approximately a 30° angle. After the film lifted off onto the water surface, the slide was pulled from under the film and removed from the recepticle. Commercially prepared copper grids were used to support the collodion films. These were placed, face down, on the collodion films as they were supported on the water surface. After three to five of these grids had been placed upon a film, it was swept off the water with another microscope slide. This was done by holding the slide above the film, lowering the slide down to the film and then pushing the film under the surface and at the same time inverting the slide so the film and grids were supported on the upper surface of the slide. As the slide, grids and film were allowed to dry, the collodion adhered to the glass surface, fixing the grids to the glass and making them easy to handle.

The sample to be placed on the grid was ground in a mortar and pestle. This was transferred to a bottle containing either water or xylene. A suspension was achieved and this was sprayed upon the grid using a glass atomizer. It was found that water gave the best suspension, but, due to its high surface tension, agglomerated the particles upon evaporation. The xylene worked well, except it was difficult to obtain an adequate suspension of the sample.

Electron microscope experimental work

An electron microscope, model R.C.A. EMU-2D, was used in the experimental work. Using this instrument, it was determined that the particle size of the sample was very critical. The particles have to be small, 1-10 microns, and thin, transparent to the electron beam, before a picture can be taken at an appreciable magnification without collapse of the supporting film.

Samples of C_B^3-Series 1-5 were used primarily and electron micrographs of these particles, which had been water suspended, were taken. Also, electron micrographs of xylene suspended samples of C_B^3-1 and 2 were obtained. Electron micrographs of samples of C_B^1-Series 1-5 and C_B^5-Series 1-5 were attempted, but due to the inappropriate particle size, pictures were not obtained from any but C_B^5-1, 3, and 5.

Electron micrographs of graphite and of carbon black were used as comparisons. Also a blank was taken of the sample grids, which had no sample placed on them, to detect the level of contamination.

Electron micrographs of the decomposition products were taken of the samples decomposed at 240°. Pictures were obtained for C_B^1-1, 2, 4, and 5 and also for C_B^3-5. Also, of the 300° decomposition products, pictures were obtained for only C_B^3-2.

It should be noted here that in these electron microscope pictures which were obtained, there were four levels of magnification used. This was done because of the variation in the particle size of the samples which were used. The graphite oxide pictures were taken at a magnification of 10,200 X, the 300° decomposition products at a magnification of 19,200 X and the 240° decomposition products at a magnification of 1,200 X, 6,000 X and 10,200 X.

Shadow casting with carbon was attempted on one set of pictures which was taken. The limited amount of additional information which was obtained from this technique was not sufficient to warrant the extra labor.

X-ray experimental work

The samples used in the x-ray diffraction were ground in a mortar and pestle and then fixed to a 1 x 1-3/4 inch microscope slide with collodion. This was done by preparing a thin paste of the sample in the mortar and pestle using a collodion and amyl acetate mixture. The paste was placed on the slide, smoothed out and then allowed to dry.

A General Electric XRD-5 x-ray diffraction machine was used in this experimental work. A spectrogoniometer coupled with a Speedomax G recorder were the devices used in recording the data. The x-ray machine was fitted with a vacuum chamber which was capable of obtaining a vacuum of approximately 5 microns of pressure (see Figure III). The x-ray scans were made at the rate of 2°/min. The slit arrangement was adjusted to yield the optimum balance of resolution and intensity.

X-ray scans were made of the following samples:

C_B^1 1-5 at decomposition temperatures of 240° and 300°.

C_B^3 1-5 at decomposition temperature of 240°.

C_B^5-1 at decomposition temperature of 300°.

C_B^5 2-5 at decomposition temperature of 240°.

Amorphous carbon, Spheron 6 (1000°) from Cabot Carbon

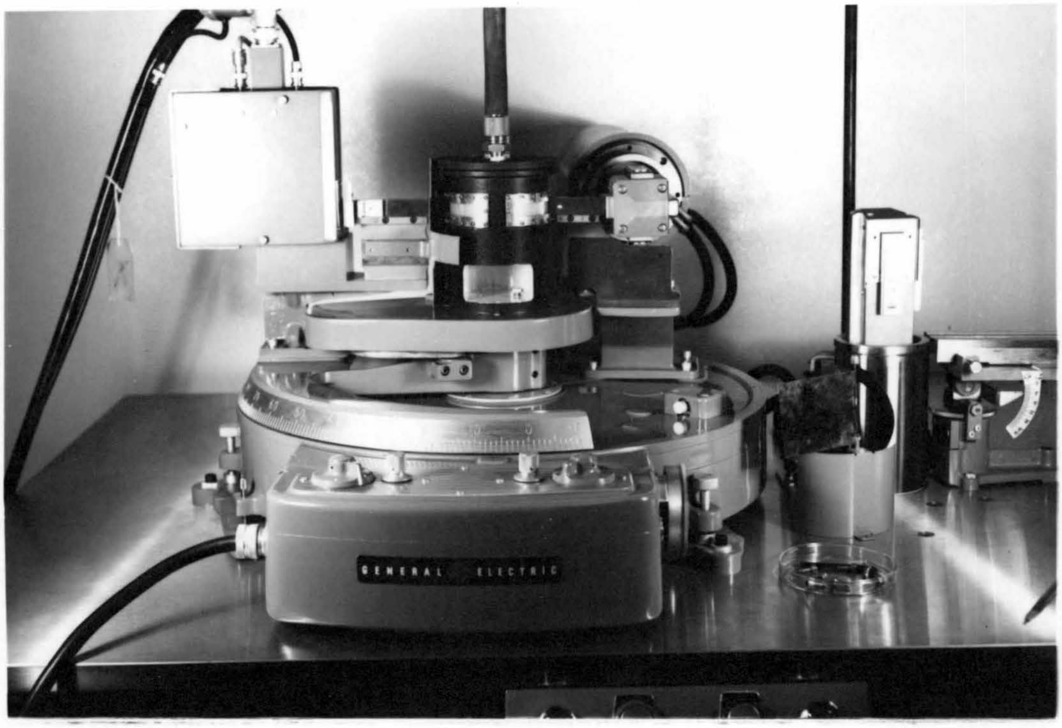


Figure III. X-ray diffraction spectrogoniometer and vacuum chamber.

Blacks.

Graphite number 3.

The x-ray scans were made at atmospheric pressure and again under evacuation in instances where additional information might be obtained.

RESULTS AND CONCLUSIONS

Electron Micrographs

At the beginning of this discussion, it should be pointed out that a large number of particles must be observed to establish a trend of change in the surface character of a substance. It should also be noted that a method of sampling must be adopted which will allow typical particles to be observed as well as those which are exceptional.

As has been pointed out in the description of the experimental work, these two goals were not achieved. Only a very select size and type of particle was observed. This was due primarily to collapsing collodion supporting films when particles of various sizes and types were examined under increased magnification.

A trend of change in surface character could not be observed upon increase in oxidation of the sample particles. Thus, the only value which can be obtained from these micrographs is some insight into the nature of graphite oxide.

Figure IV is of a sample of graphite which was deposited from a xylene dispersion onto the sample grid. The long straight lines in this picture are due to folds in the graphite platelets. These folds are relatively large and quite rigid. These are not normal

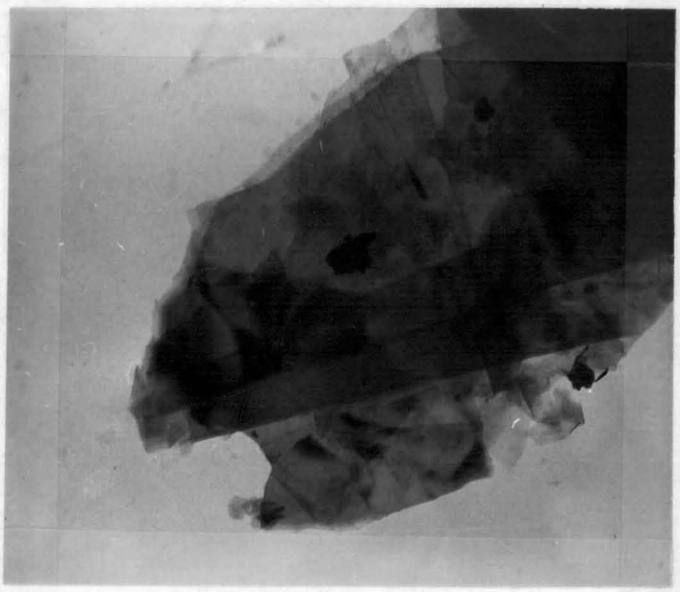


Figure IV. Graphite No. 3 X10,200

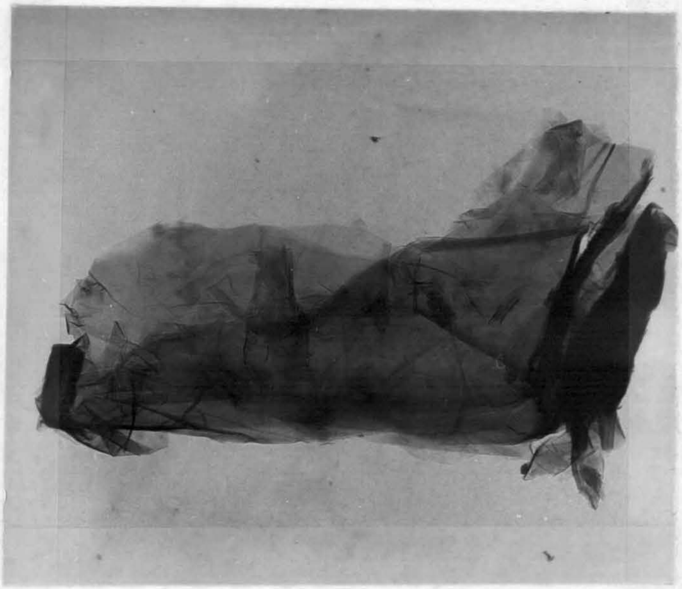


Figure V. C_B^3-1, xylene X10,200

edges because it can be seen that the exterior edges are rough and irregular.

It is interesting to note here that the folded character of graphite oxide has been used as evidence to indicate that it is unique. Samples of graphite and of graphite oxide have been prepared using water dispersions. The graphite appears as flat and the graphite oxide appears folded. However, graphite is hydrophobic as opposed to graphite oxide, and an alkaline water suspension of graphite would not tend to cause the separation of sheets that is observed in graphite oxide Because of this difference in colloidal character, it would appear that the same results could not be expected from the same method of sample preparation for graphite and graphite oxide

Micrographs of graphite oxides prepared with xylene (Figures V and VI) and with water (Figures VII and VIII) show this difference in degree of layer dispersion. Note that there is no axis to which the folds in these particles are parallel. The width of the folds in the xylene and water samples are different. In the xylene samples the width of the layer folds is as large as approximately 0.8 microns whereas the water dispersed particles have folds as large as approximately 2.4 microns. This would indicate that the water

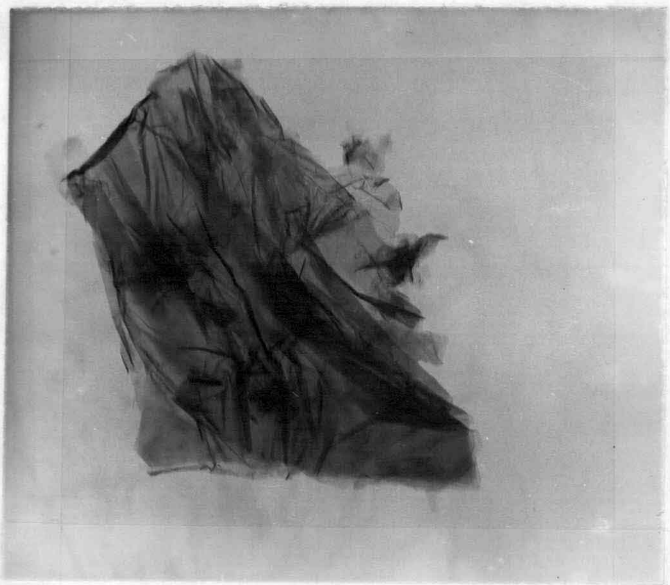


Figure VI. C_B^3-2, xylene X10,200

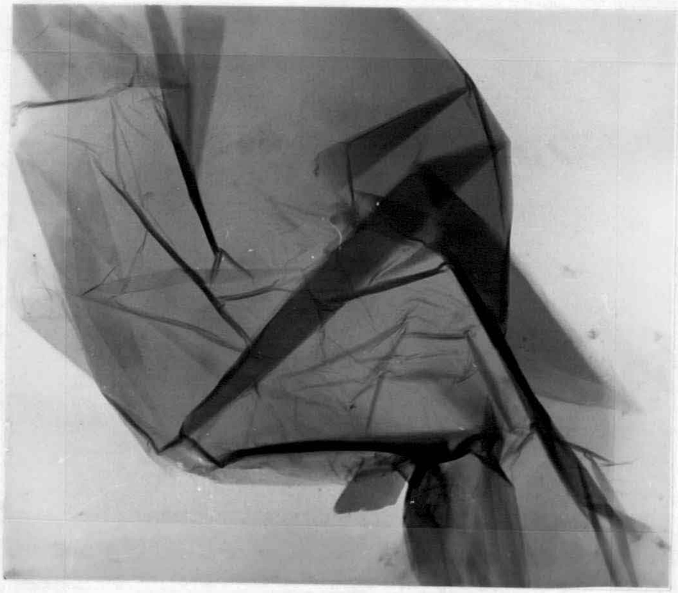


Figure VII. C_B^3-3, water X10,200

Figure VIII. C_B^3-5, water X10,200

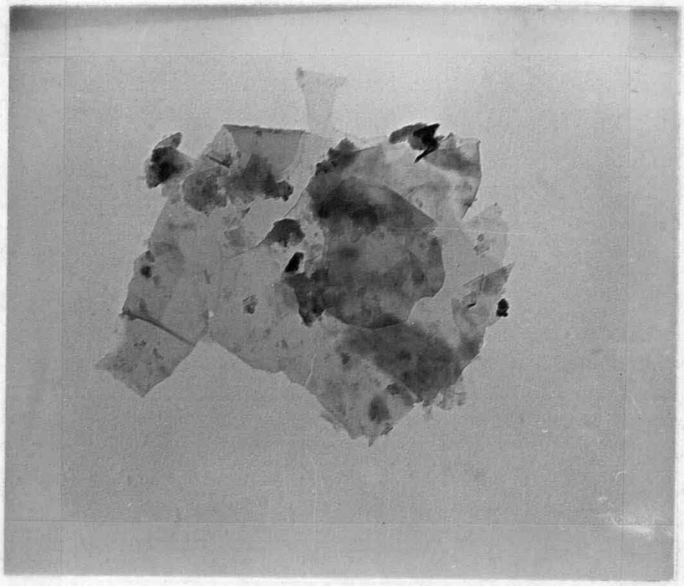


Figure IX. C_B^1-1 (240°), xylene X10,500 dispersed samples were of lesser thickness than the xylene samples. This is what would be anticipated upon evaluation of the hydrophilic nature of graphite oxide and the method of sample preparation. It appears that differences in the character of graphite oxide samples, as observed from the micrographs taken, are due largely to the differences in the method of sample preparation.

Figures IX, X and XI were taken of samples of graphite oxide which had been decomposed at 240°. It is noted that there is disorder in the arrangement of the particles. Also the sheets are split in irregular lines. The amount of folding has decreased and the particles appear to be either thicker or more opaque to electrons.

Figure XII was made from a graphite oxide sample which was decomposed at 240°. This micrograph was shadowed with carbon to obtain the illusion of depth. This technique is used either to observe particles which are transparent to electrons or to estimate particle thickness. By knowing the angle of elevation of the carbon electrode above the sample and measuring the unshadowed portion at the edge of a particle, the thickness can be estimated using geometrical relationships. This technique of calculating thickness is not applicable here due to the flexibility of the collodion supporting film.

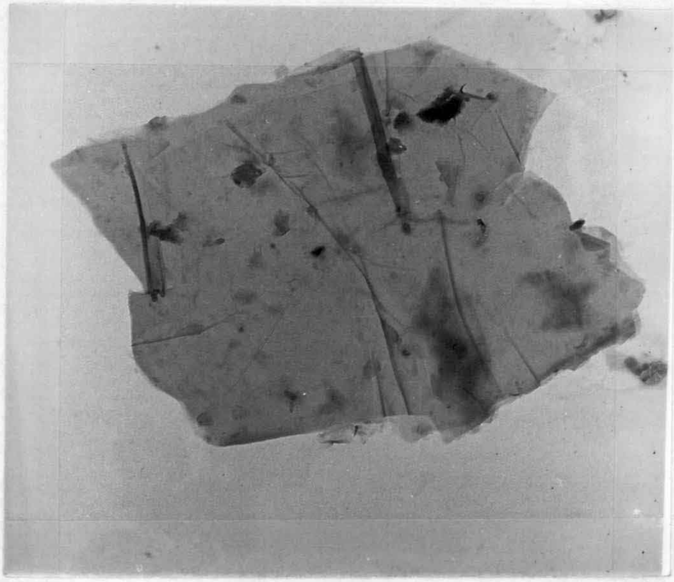


Figure X. C_B^1-2 (240°), xylene X10,500

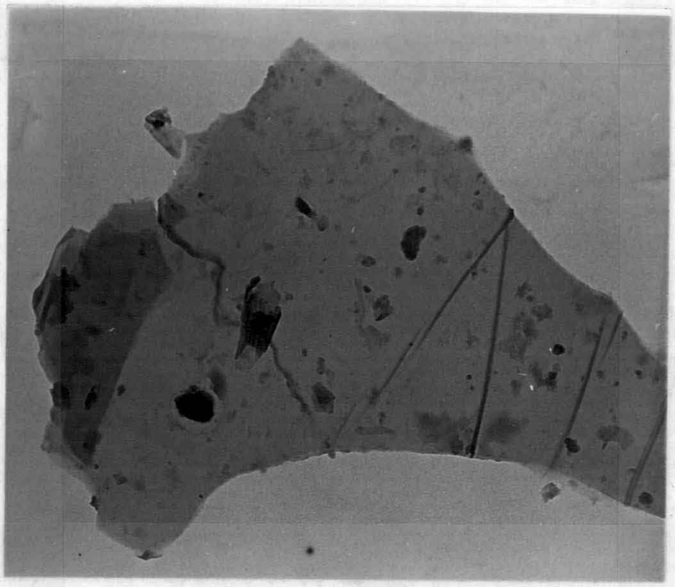


Figure XI. C_B^1-5 (240°), xylene X10,500

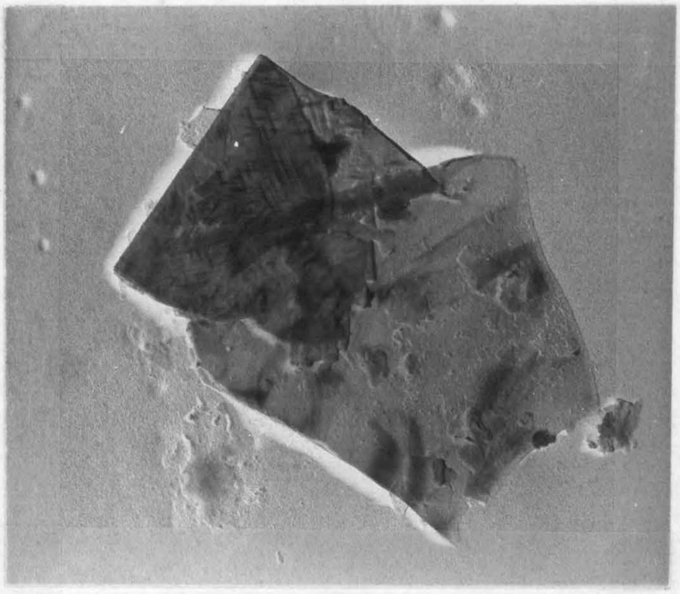


Figure XII. C_B^3-5 (240°), xylene X10,200, shadowed

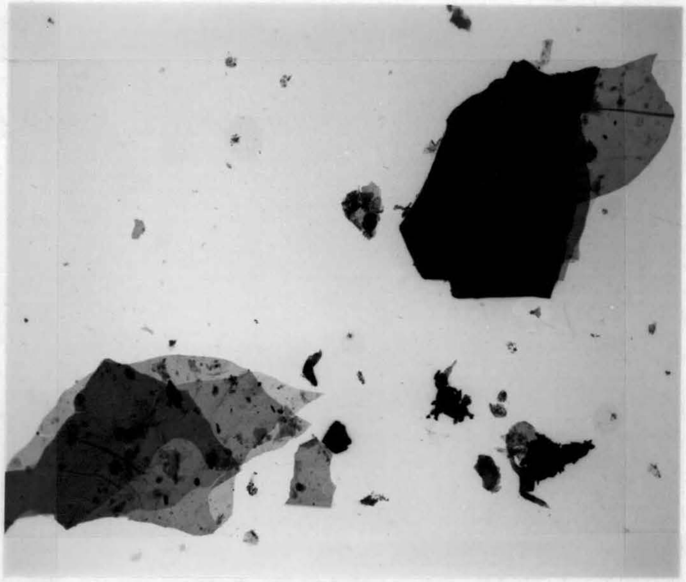


Figure XIII. C_B^3-5 (240°), xylene X1200

Figures XIII and XIV illustrate variations in magnification. Folding can be observed in the sheets of these particles and several layers can be seen as is indicated by the various shades of gray. The presence of particles of many shapes and sizes can also be observed. Note that in Figure XIV the collodion film has begun to decompose. This is indicated by the appearance of the torn collodion film and the small holes that are formed. This type of phenomena was also observed with the graphite oxide. It is relevant in that it indicates that the forces (thermal or electrostatic) which cause decomposition of the collodion film do not affect the sample.

Figures XV and XVI are of graphite oxide which has been decomposed at 300°. Figure XV shows the very flexible films that are present in samples that have been decomposed at this higher temperature. Figure XVI shows the amorphous carbon which is formed at this decomposition temperature. The appearance of some orientation in Figure XVI is caused by the evaporation of xylene as it was placed upon the sample grid. The gray areas represent clusters of amorphous carbon particles as is revealed by increased magnification. It is of interest to note that these pictures were taken at the maximum magnification of the electron microscope.

Figure XIV. C_B^3-5 (240°), xylene X6000

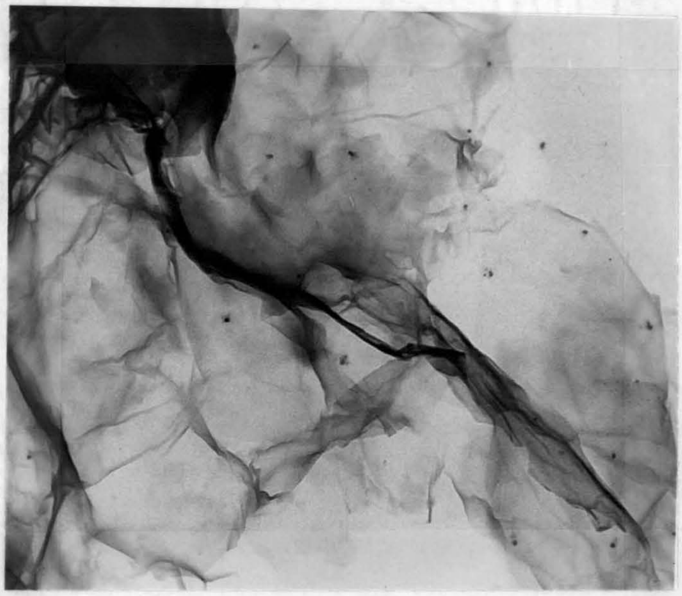


Figure XV. C_B^3-2 (300°), xylene X19,200

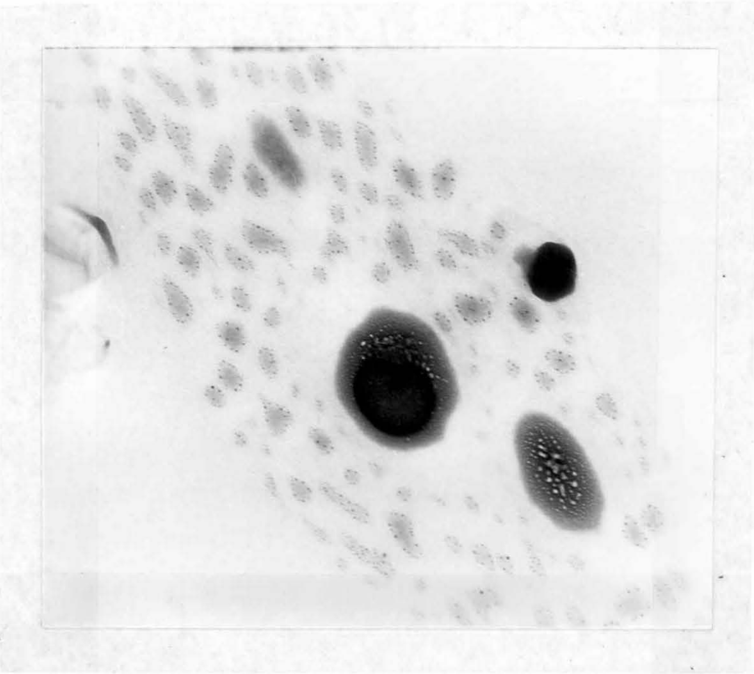


Figure XVI. C_B^3-2 (300°), xylene X19,200

X-ray diffraction

The amount of information which can be obtained from x-ray diffraction scans is limited because of the highly disordered nature of the structure (12, p. 468-469). From the electron micrographs of graphite oxide and of its decomposition products, it appears that the decomposition products are even more disordered. The only x-ray peaks that are observed in the decomposition products are those of residual graphite oxide and of graphite. The only sharp peak that is observed in the diffraction pattern is that of graphite. The graphite oxide peaks which are observed are small and diffuse.

The samples scanned and the peaks observed are listed in Table III. Because the graphite oxide decomposition products are of highly disordered structure, the peaks observed can be evaluated only qualitatively.

From Table III it can be seen that the series C_B^1 1-5 (240°) contains the c-spacing of the graphite peak, 26.4° (2θ) (8, p. 416), in its diffraction pattern. The $C_B^1$2-5 (240°) series contains a peak which varies from 19.6 to 20.2°(2θ). In all cases this peak was small and diffuse. For this reason, it is believed that the variation of 0.6° is not significant. The series C_B^1 1-5 (300°) shows no residual graphite oxide peak and retains the 26.4° graphite peak. The

Table III. X-ray diffraction angles (2θ)

Sample	Decomp. temp.	Evacuated	Amorphous carbon	Graphite Oxide peak	Graphite peak
C_B^1-1	240°	No		--	26.5
"	"	Yes		--	26.5
C_B^1-2	"	No		20.0	26.43
"	"	Yes		20.0	26.5
C_B^1-3	"	No		19.65	26.4
"	"	Yes		19.85	26.4
C_B^1-4	"	No		19.7	26.4
"	"	Yes		20.2	26.4
C_B^1-5	"	No		20.1	26.5
"	"	Yes		20.1	26.5
C_B^1-1	300°	No		--	26.5
"	"	Yes		--	26.55
C_B^1-2	"	No		--	26.4
"	"	Yes		--	26.4
C_B^1-3	"	No		--	26.4
"	"	Yes		--	26.4
C_B^1-4	"	No		--	26.4
"	"	Yes		--	26.4
C_B^1-5	"	No		--	26.42
"	"	Yes		--	26.5
C_B^3-1	240°	No		--	26.4
"	"	Yes		--	26.4
C_B^3-2	"	No		19.3	26.3
"	"	Yes		19.55	26.4
C_B^3-3	"	No	x	--	--
"	"	Yes	x	--	--
C_B^3-4	"	No	x	--	--
"	"	Yes	x	--	--
C_B^3-5	"	No	x	--	--
"	"	Yes	x	--	--
Graphite No. 3		No		--	26.5
C_B^5-1	300°	No	x	--	--
C_B^5 Series 2-5	240°	No	x	--	--
Amorphous C Spheron 6	1000°	No	x	--	--

C_B^3-1 (240°) sample shows only the graphite peak and the C_B^3-2 (240°) sample shows both a 19.2° - 19.5° graphite oxide peak and a 26.4° graphite peak. The remainder of the series, C_B^3 3-5 (240°) shows only an amorphous carbon diffraction pattern. This is characterized by a fairly straight line which has no peaks. The amorphous carbon pattern is all that is observed for the series C_B^5 1 (300°), 2-5 (240°).

Samples of an amorphous carbon, Spheron 6 (1000°) and graphite number 3 were scanned as a reference.

A qualitative evaluation of these diffraction patterns yields the following results. The larger graphite particles, graphite number 1, are difficult to oxidize. Thus C_B^1-1 (240°) has either decomposed to amorphous carbon and residual unoxidized graphite or to regenerated graphite and residual unoxidized graphite. An x-ray scan of C_B^1-1 does show a peak for both graphite and graphite oxide. The remainder of the series C_B^1 2-5 (240°) has achieved only a limited degree of oxidation. This intermediate amount of oxidation allows the graphite oxide in the decomposition sample to remain partially undecomposed at 240°. There is residual unoxidized graphite remaining in all of the C_B^1 1-5 (240°) series. This is due to the difficulty in oxidizing large particles of graphite.

The C_B^1 1-5 (300°) series shows that the small amount of graphite oxide which had not decomposed at 240° contains enough oxygen to be unstable at 300°. The only peak remaining at 300° for this series is the graphite peak. The C_B^3 1-5 (240°) series shows this same trend. C_B^3-1 (240°) shows both the graphite oxide and graphite peaks. C_B^3-2 (240°) shows both the graphite oxide and graphite peaks. C_B^3 3-5 (240°) shows only a graphite peak. Thus C_B^3-1 (240°) has achieved a limited amount of oxidation which is unstable at 240°, C_B^3-2 (240°) has achieved an intermediate stage of oxidation which is stable at 240°, and C_B^3 3-5 (240°) have achieved a high degree of oxidation which is unstable at 240°. The graphite number 3 consists of medium size particles which are intermediate in ease on oxidation. Being cognizant of the relationship between particle size and ease of oxidation, it can be seen that there is a similarity which can be observed in the x-ray patterns of the two series.

Graphite number 5 is of small particle size and undergoes oxidation readily. The series C_B^5 2-5 (240°) shows only an amorphous carbon diffraction pattern. This indicates that all of the graphite had obtained a level of oxidation which would be unstable at 240°. The C_B^5-1 (300°) sample had to be heated to the temperature of 300° to obtain observable decomposition. Thus it might be presumed that this sample is of an intermediate level of oxidation.

SUMMARY

In conclusion it can be said that the following results were achieved in this research. The electron microscope pictures contributed to the further illumination of the surface character of graphite oxide and its decomposition products. Graphite oxide was seen to consist of flexible, irregularly shaped sheets. The decomposition products are observed as irregularly shaped sheets, somewhat folded, torn or split and at higher temperatures as amorphous carbon.

The x-ray diffraction patterns of the decomposition products allow us to evaluate qualitatively the change in the composition of the various samples. At 240°, the decomposition products contain residual graphite oxide.

It is indicated clearly that the ease of oxidation of graphite is dependent upon particle size. The large particles achieved only limited oxidation throughout the five oxidation steps. This limited degree of oxidation allows the C_B^1 (240°) series to retain a diffuse graphite oxide peak which disappears at 300°. The medium size particles achieve a degree of oxidation similar to the C_B^1 series in samples C_B^3 1 and 2. C_B^3 3-5 achieve a higher degree of oxidation which is unstable at 240°. The smaller particles, graphite number 5, are easily oxidized and thus allows the C_B^5 2-5 series to achieve a degree of oxidation which is unstable at 240°.

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