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SOME NEW ASPECTS OF GRAPHITE OXIDATION AT 0°C IN A LIQUID MEDIUM. A MECHANISM PROPOSAL FOR OXIDATION TO GRAPHITE OXIDE

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Abstract—Graphite has been oxidized with the Staudenmaier reagent at 0°C over various periods of time. After dehydration over P_2O_5 the oxidation products have been characterized by chemical analysis, X-ray diffraction and IR absorption spectroscopy. Their thermal decomposition has been studied by thermogravimetry (TG) and differential thermal analysis (DTA). The oxidizing capacities against KI in H_2SO_4 solutions have also been measured. The observations are explained by an oxidation mechanism in three stages leading to graphite oxide.

Key Words—Oxidation, graphite oxide, thermal analysis.

1. INTRODUCTION

The process of graphitization can be studied by means of techniques such as X-ray diffraction, electron microscopy, bromine fixation[1] or potassium intercalculation[2], yielding two different types of graphite intercalation compounds[3]. Another useful technique is the treatment of graphite or graphitizable carbons with strong oxidizing agents in a liquid medium[4]. This kinetic process allows one to discern textural and structural differences between several graphites. Thus López González, Carpenter and Deitz[5] have shown that natural and synthetic graphite exhibit different behaviours. Later more remarkable differences have been observed between intermediate products obtained by cold oxidation from graphites of different origin[6]. Oxidizing treatment of graphite in a liquid medium finally yields graphite oxide (GO), which is a thermolabile compound[7] and a reagent with an oxidizing power similar to PbO_2. Several papers examine these GO properties[8–11], but there is no literature dealing with the oxidizing behaviour or thermal decomposition of partly oxidized graphite. Previously we have published a paper about thermal decomposition[12] and in the present paper we carry out a comparative study of the chemical reduction and thermal decomposition of such intermediate preparations.

2. EXPERIMENTAL

Two different kinds of graphite were used. Both graphite samples were ultrapure and polycrystalline materials, one natural graphite (N) from Degussa (Germany) and the other synthetic (A-graphite) made by Sigri Elektrographit GmbH (Germany). Basically the treatment was the Staudenmaier method[13] using an oxidizing mixture of $KClO_3$, nitric and sulfuric acids. The particle size ranged from 44 to 60 μm and the beaker was kept at 0°C during the reaction. The oxidation attack was interrupted at different times for each sample by dilution with 10 l of distilled water at 0°C. The samples so obtained were washed with dilute HNO_3 and distilled water. Later they were labeled with a letter (N or A) indicating their origin and a number indicating the reaction time in hours. A particle size of 40–60 μm was then chosen for the subsequent experiments.

The oxidation products were kept in a desiccator over sulfuric acid solution (density = 1.24 g/cc, water pressure = 12.7 torr at 20°C) until they attained constant weight, and later in a desiccator with P_2O_5 under vacuum, where some water was lost, until constant weight was regained. Chemical analysis was carried out by means of a Herrmann–Moritz analyzer model EH-64. An oxygen flow at 25 cc/min (purity = 99.998%) was used in all operations performed, taking care that the samples did not deflagrate, so that the non-oxidized graphite was thoroughly burnt. IR spectra were recorded by means of a Pye–Unicam spectrophotometer SP-300, using KBr pellets from a carefully dried spectroscopic potassium bromide.

Samples of 10 mg in equilibrium over the sulfuric acid solution were subjected to thermal analysis (TG and DTA) by means of a Mettler TA-HE 20 analyzer system. The rates of heating were 6°C/min between 25°C and 140°C and then 1°C/min thus avoiding deflagration. Thermal decomposition under inert atmosphere was performed using a helium flow at a rate of 60 cc/min. The gases evolved were analyzed by means of a Hewlett–Packard Chromatograph. Oxidizing capacities were measured by reaction between 80–150 mg of sample dehydrated over P_2O_5 and KI solution (110 g/l) in 1 N sulfuric acid. The reaction progressed for 6 h at 55°C under a slow flow of Ar. Iodine released from solution was condensed in a Dimroth refrigerant. When the reaction was completed, the iodine was titrated, first the amount released in solution and later a small amount which was extracted by HCl ethanol solution. Finally the carbonaceous residue was burnt in a sealed flask previously filled with oxygen. The iodine evolved was collected in alkali solution and completely oxidized to produce iodate by means of bromine. The remaining bromine was removed using a formic acid solution, then an amount of iodine proportional to the initial quantity was regenerated in acid medium with potassium iodide. This amount of iodine was also titrated. So both amounts of iodine, i.e. iodine in solution that includes extracted iodine in HCl–ethanol solution, and retained iodine in the reduced sample were determined. Carbon and hydrogen percentages in the reduced samples were also determined by means of a Carlo Erba 1106 elemental analyzer.

Powder diagrams were obtained by means of a Siemens set model D-500 using Ni filtered CuK$_\alpha$ radiation, and Agfa–Gevaert film Structurix (Model NDT) system, and a Philips PW 1024/30 camera with a diameter of 114.9 mm. Debyeograms were transformed and plotted by a KD-540 microdensitometer.

3. RESULTS

The results obtained from chemical analysis are listed in Table 1 as chemical formulae based on four C atoms. A similar composition to the GOs has been found for the more extensively oxidized samples. The higher oxygen level in strongly oxidized products belonging to the A series has been interpreted by López-González and coworkers[14] as a consequence of a greater concentration of –C = O, –C–O–C– and –C–OO–C– groups. They have also suggested that in these samples more carboxylic groups could be linked to the edges. Powder diagrams of the oxidation products show GO and graphite lines in intermediate samples. No graphite lines were observed for N-56, A-56 and more extensively oxidized samples. From chemical analysis and X-ray diffraction it is possible to deduce that samples N-72, N-84, N-96, N-108, N-120, A-72, A-84, A-96, A-108 and A-120 are graphite oxides.

The very similar IR absorption spectra of N-120 and A-120 correspond to graphite oxides. Hadzi and Novak[15] have shown that it is possible to distinguish between hydroxyl groups inserted between the layers and intercalated molecular water. A very strong band centered at 3430 cm^{-1} is assigned to ν(O–H) of the hydroxyl groups belonging to GO. A shoulder at 3600 cm^{-1} indicates the presence of another kind of hydroxyl group. The position of the medium band at 1700–1710 cm^{-1} is characteristic of non-conjugated carboxylic carbonyl groups. The band at 1610 cm^{-1} is associated with the deformation mode of the intercalated water molecules. The peaks observed at 3250 and 3300 cm^{-1} (stretching modes of water), in dried samples remain relatively hidden in a wide shoulder at the low frequency side of the –OH band which indicates a weak hydrogen bonding. The band at 1360–1410 cm^{-1} may be assigned to the deformation mode of the C–O groups (other than those included in the carboxyl groups). The shoulder at 920–970 cm^{-1} possibly indicates hydroperoxide groups and the band at 820 cm^{-1} supports the presence of the oxygen bridge C–O–C.

Intermediate preparations and slightly oxidized samples exhibit IR absorption spectra where just a few either weak or impossible-to-evaluate bands appear (Fig. 1). IR spectra of samples belonging to the A-series show more bands than samples prepared from natural graphite with an identical oxidation time. This fact indicates that more groups have been produced and confirms that A-graphite is more quickly oxidized than N-graphite due to the different crystallite sizes.

Results of thermal analysis are listed in Table 2 and a selection of DTA curves is shown in Fig. 2. When the more strongly oxidized products were subjected to a heat-

Table 1. The formula before (Initial) and after chemical reduction with KI in sulfuric acid solution (Final)

Sample	Initial	Final	Sample	Initial	Final
N-12	$C_4O_{0.67}H_{0.85}$	$C_4O_{0.64}H_{0.66}$	A-12	$C_4O_{0.29}H_{0.76}$	$C_4O_{0.31}H_{0.19}$
N-24	$C_4O_{1.44}H_{2.15}$	$C_4O_{1.50}H_{1.65}$	A-24	$C_4O_{0.80}H_{0.82}$	$C_4O_{0.44}H_{0.34}$
N-32	$C_4O_{1.24}H_{0.83}$	$C_4O_{0.59}H_{0.56}$	A-32	$C_4O_{1.11}H_{1.01}$	$C_4O_{0.44}H_{0.38}$
N-40	$C_4O_{1.31}H_{1.59}$	$C_4O_{1.12}H_{0.94}$	A-40	$C_4O_{1.07}H_{0.95}$	$C_4O_{0.43}H_{0.29}$
N-48	$C_4O_{1.05}H_{0.87}$	$C_4O_{0.62}H_{0.44}$	A-48	$C_4O_{1.29}H_{0.95}$	$C_4O_{0.40}H_{0.25}$
N-56	$C_4O_{1.44}H_{1.30}$	$C_4O_{0.73}H_{0.31}$	A-56	$C_4O_{1.58}H_{1.20}$	$C_4O_{0.35}H_{0.16}$
N-64	$C_4O_{1.62}H_{1.29}$	$C_4O_{0.57}H_{0.33}$	A-64	$C_4O_{1.86}H_{1.22}$	$C_4O_{0.24}H_{0.11}$
N-72	$C_4O_{2.32}H_{1.55}$	$C_4O_{0.42}H_{0.21}$	A-72	$C_4O_{2.25}H_{1.59}$	$C_4O_{0.23}H_{0.13}$
N-84	$C_4O_{2.09}H_{1.83}$	$C_4O_{0.45}H_{0.21}$	A-84	$C_4O_{2.11}H_{1.68}$	$C_4O_{0.30}H_{0.15}$
N-96	$C_4O_{2.09}H_{1.63}$	$C_4O_{0.40}H_{0.25}$	A-96	$C_4O_{2.12}H_{1.58}$	$C_4O_{0.35}H_{0.14}$
N-108	$C_4O_{1.81}H_{1.50}$	$C_4O_{0.46}H_{0.25}$	A-108	$C_4O_{2.10}H_{1.56}$	$C_4O_{0.49}H_{0.15}$
N-120	$C_4O_{2.15}H_{1.87}$	$C_4O_{0.30}H_{0.32}$	A-120	$C_4O_{2.13}H_{1.65}$	$C_4O_{0.24}H_{0.14}$

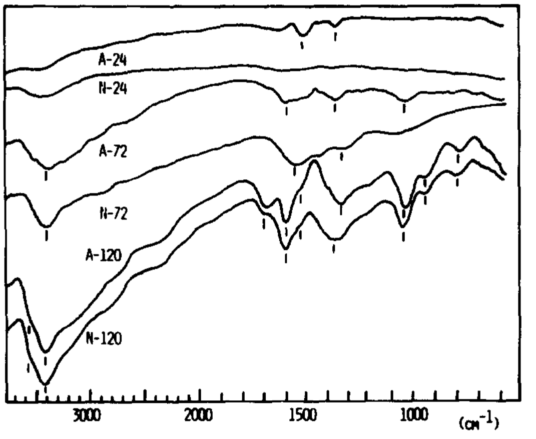

Fig. 1. IR absorption spectra of some graphite oxidation products.

ing rate of 6°C/min they deflagrated spectacularly at 230°C[12]. Deflagration was avoided by a heating rate of 1°C/min. There are then three stages in thermal decomposition. An endothermic first stage is consistent with dehydration, its characteristic temperature ranging from 50 to 85°C. In a second stage (200–240°C) exothermic thermal decomposition of graphite oxide occurs. During this step H_2O, CO and CO_2 are evolved. Finally, combustion of the residue begins in air at temperatures ranging from 650–700°C. Combustions of the intermediate products proceed at lower temperatures (540–650°C) as a consequence of their more disordered states.

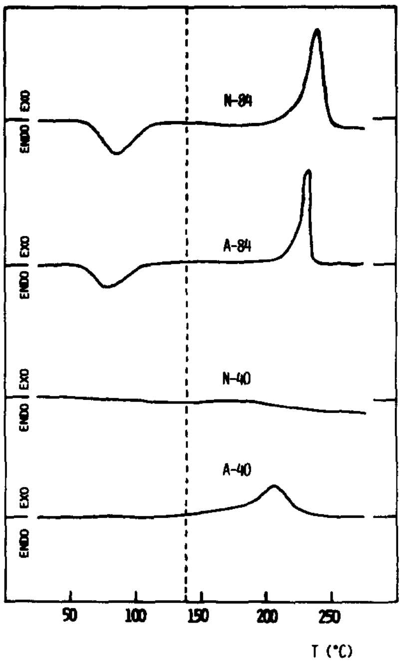

Fig. 2. Thermal differential curves for some graphite oxidation products.

The oxidizing capacities of these preparations are given in Table 3. The values are expressed in millimole of iodine per gram of dehydrated sample. Nearly constant values are observed for N-72, A-64 and the more strongly oxidized samples in both series. For these types of sam-

Table 2. Thermal analysis data of graphite oxidation products

	First Stage		Second Stage	
SAMPLE	W(%)	T(°C)	W(%)	T(°C)
N-12	0.0	--	18.5	---
N-24	2.0	50	20.0	225
N-32	1.5	50	13.5	210
N-40	5.0	75	17.0	200
N-48	4.0	75	16.0	220
N-56	10.0	70	16.5	227
N-64	15.5	85	22.0	225
N-72	14.0	70	27.5	222
N-84	15.5	85	26.5	240
N-96	15.5	80	31.0	225
N-108	15.0	80	26.0	225
N-120	17.0	80	25.0	230
A-12	0.0	--	7.0	195
A-24	9.0	67	15.0	195
A-32	3.0	--	17.5	200
A-40	8.0	70	13.0	205
A-48	12.0	70	15.0	220
A-56	14.5	70	23.5	223
A-64	15.0	75	23.0	227
A-72	17.0	80	26.5	230
A-84	16.0	80	28.0	230
A-96	17.0	75	26.0	235
A-108	16.5	80	27.0	230
A-120	17.0	80	26.0	235

ples, the average amount of iodine is 14.0 (±0.05) mmole/g in the N-samples and 14.8 (±0.05) in the A-samples. Elemental analysis showed that by chemical reduction with KI in an acid medium we obtained products still containing oxygen and hydrogen. The formulae of the reduced samples are listed in Table 1. They are based on four C atoms, so we can compare them to the formulae of the original oxidation products. After reduction the residues have a graphite-like external appearance, but they produce three different types of powder diagrams. The residues from slightly oxidized samples (up to 12–24 h) showed a relatively intense band near the characteristic position of the (002) graphite reflection. For intermediate oxidation (up to 40–56 h), the products showed this band in a split form. The remaining strongly oxidized samples gave residues exhibiting a simple band again which was shifted to lower angles, however.

4. DISCUSSION

It is possible to calculate the iodine which is released in reduction from the change in chemical composition according to

$$\begin{aligned}C_4O_xH_y + [2(x - a) - (y - b)]\ HI \rightarrow\\ C_4O_aH_b + (x - a)\ H_2O +\\ 1/2[2(x - a) - (y - b)]I_2.\end{aligned}$$

The quantities of iodine so obtained are almost lower than the experimental values in Table 3. The above equation is excessively simple and the quantities of iodine must be related to the nature of the functional groups and their distribution in the GO layers. The relations between produced iodine and the oxygen lost in chemical reduction have been calculated. These values are fairly constant in the A-series, but they point to an evolution of functional groups in samples belonging to the N-series. When the group distribution is similar to that of GO, a $I_2/\Delta O$ ratio of 0.7 (±0.05) mole per mole of O is found, but the values are not constant and we can infer that oxidation probably continues even in samples conventionally considered as graphite oxides. In the A-series a value near 0.7 is faster reached than in the N-series in good agreement with the idea that the synthetic A-graphite is more rapidly oxidized than the natural one. There is a further sign of functional evolution in the layers, the IR band at 1700–1710 cm^{-1} (Fig. 1) evolved later than the other bands, after an oxidation period of 72 h. This fact points out that –COOH groups, which are generally considered as peripheric functions bound to the layers, appear in the last stage of the oxidation attack when they are cleaved and separated to a distance characteristic for GO. There are other functional groups inserted and, probably, these materials have already got a puckered layer structure similar to that in GO or CF. Based on the oxidizing capacities shown by the oxidized compounds, X-ray dif-

Table 3. Oxidizing capacities of graphite oxidation products

SAMPLE	I_2 in solution (mmol/g)	I_2 Total (mmol/g)	$I_2/\Delta O$(mol/atmg)
N-6	0.00	0.00	---
N-12	0.17	0.17	---
N-24	1.06	1.07	0.5
N-32	2.20	2.49	0.3
N-40	2.16	2.31	0.8
N-48	5.17	5.69	0.9
N-56	9.24	9.93	1.0
N-64	9.66	10.40	0.7
N-72	12.02	12.63	0.6
N-84	12.28	12.90	0.7
N-96	14.21	14.79	0.7
N-108	13.10	13.74	0.8
N-120	14.05	14.46	0.7
A-6	0.69	0.69	---
A-12	2.01	2.07	---
A-24	4.24	4.41	0.7
A-32	6.19	6.51	0.6
A-40	7.04	7.48	0.8
A-48	8.81	9.27	0.7
A-56	11.33	11.97	0.7
A-64	13.26	13.79	0.7
A-72	13.87	14.25	0.6
A-84	14.72	15.00	0.7
A-96	14.37	14.70	0.7
A-108	14.29	14.63	0.8
A-120	14.42	14.76	0.7

fraction patterns of the reduced samples, and taking into account the kinetic suggestion about carbon fiber oxidation which has been proposed by Donnet and co-workers[16] a three stage mechanism is suggested to explain the oxidation of graphite in liquid medium:

1) An initial period including N-24 in the N-series and A-12 in the A-series. Functional groups are simply attached to the layer edges. The samples have hardly obtained any oxidizing capacity.

2) An intermediate period lasting up to 56 h in the N-series and 40–48 h in the A-series. In this stage, oxidizing capacities increase to the value characteristic for GO (14–15 mmole of iodine per gram of dehydrated sample)[9].

3) A final period which includes the most strongly oxidized samples in both series. Oxygen and hydrogen contents have reached the maximum values in the characteristic range for GOs. But some groups in the layers still undergo transformation into others.

Results from thermal analysis agree with this mechanism. Only the strongly oxidized samples deflagrated on rapid heating. The first and second stages of thermal decomposition occurred at lower temperatures with the intermediate samples than with the most strongly oxidized samples. This fact points to a great strain between the GO and the graphite layers which coexist in these products. On the other hand powder diagrams of residues obtained by thermal decomposition at 270°C[12] show the production of a highly disordered material that not appear when reduction is carried out with a chemical reagent such as KI in H_2SO_4 solution.

5. CONCLUSIONS

Chemical reduction with a KI solution and thermal decomposition at 270°C of products of graphite oxidation yield two different types of solid residues which are incompletely reduced. From a structural point of view, chemical reduction progresses more gently than thermal decomposition. Thus the later produces more disordered materials according to the powder diagrams. Our data indicate a slower oxidation rate for natural than for synthetic graphite in good agreement with reports in the literature. A slower rate can be explained if the larger layers and their more perfect arrangement in natural graphite are taken into account. Consequently graphites with bigger crystallite size should be more appropriate materials to study the cold oxidation of graphite. Based mainly on the results of chemical reduction, an oxidation mechanism in three stages is proposed. This proposal agrees with other results obtained by thermal analysis and IR spectroscopy. Evolution of functional groups probably occurs even in the last oxidation stage. Thus GO characterization by elemental analysis and X-ray diffraction alone is incomplete. It must be supplemented using other techniques such as thermal analysis or IR spectroscopy.

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