

INTERCALATION OF BROMINE INTO NATURAL GRAPHITE

THE EFFECT OF OXIDATION AND RESIDUAL BROMINE ON
THE RATE AND AMOUNT OF UPTAKE

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Abstract—Intercalation of bromine at 20°C into spectroscopic grade SP-1 natural graphite flakes oxidized previously to four levels of burn-off has been studied. The threshold pressure, equilibrium amounts taken up at relative pressures up to 0.95, and the diffusion coefficient for bromine uptake are little affected by graphite oxidation at all burn-offs studied (up to 46.1%). However the time after bromine exposure at the threshold pressure at which rapid bromine intercalation commences monotonically decreases with increasing burn-off. It is suggested that during this initial time period, bromine entering the graphite is essentially fully ionized, whereas bromine entering later, and rapidly, is not ionized. Oxidation affects the subsequent thermal stability of the intercalated bromine and the composition of the residue compound formed following heating to 950°C. Rates of uptake and amount of bromine intercalated subsequently on the residue compounds are dependent upon their Br/C ratio and how the residual compounds were formed.

1. INTRODUCTION

Extensive studies have been conducted on the intercalation of bromine into carbons[1]. There has been interest in such diverse aspects of the phenomenon as: (i) the fraction of the molecular intercalate which is ionized[2], (ii) what relation exists between the Fermi level in the carbons and amount intercalated[3], and (iii) the effect of perfection of the carbon structure on the threshold pressure required for intercalation[4], rate of intercalation[5] and nature of the residue compounds[6]. In this study, the effect of oxidation (etching) of a highly crystalline natural graphite on some of these phenomenon has been studied.

2. EXPERIMENTAL

2.1 Materials

The carbon used was spectroscopic grade natural graphite powder, grade SP-1, supplied by Union Carbide Corporation. Its surface area, calculated from the physical adsorption of N₂ at 77°K, was 1.8 m²/g. From the chemisorption of oxygen, it is estimated that 3.3% of this total area was active area located primarily at the edges of the flake-like particles[7]. The flake-like particles had an average diameter of 20 μm and a thickness of 0.5 μm[7]. From X-ray diffraction measurements, the interlayer spacing was found to be 3.3541 Å at 15°C. Following slight oxygen etching at the crystallite boundaries, the average crystallite diameter was estimated at 10 μm. Crystallite alignment within the particles was high.

The bromine used was a reagent grade, having a purity

of >99.8%. Oxygen used for etching was extra dry grade, having a purity >99.6%.

2.2 Oxidation of graphite

The original SP-1 graphite was oxidized at atmospheric pressure in a stream of oxygen at 600°C to four levels of burn-off. Upon oxidation to 10% burn-off, the specific surface area, calculated from nitrogen adsorption at 77°K, increased from 1.8 to 3.6 m²/g. The area remained essentially constant with additional burn-off.

2.3 Bromine uptake

The apparatus used is described in detail elsewhere[8]. Briefly, uptake of bromine was monitored gravimetrically using a fused quartz spring (sensitivity of 2 mm/mg). A cathetometer, used to measure spring extension, could accurately measure a change in length of 0.01 mm. This combined with the sensitivity of the spring enabled detection of weight changes of the order of 5 × 10⁻⁶ g. The sample temperature was controlled within ±0.1°C by circulating water from a constant temperature bath. The bromine temperature (determining its vapor pressure) was also controlled within ±0.1°C.

Prior to an adsorption run, the sample was outgassed for 2 hr at 950°C. A 24 hr equilibration time was allowed for each adsorption point on the isotherms. Desorption was carried out by first closing off the valve to the bromine bath, then connecting the system to a liquid nitrogen trap for 30 min. The sample was then outgassed using a combination of mechanical and mercury diffusion pumps until constant weight was attained.

2.4 Calculation of diffusion coefficient

Using an approach similar to Dowell[5], apparent diffusion coefficients, D_{app} , were calculated from the

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equation

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{D_{\text{app}}}{r^2} \right)^{1/2} (t - t_0)^{1/2} \quad (1)$$

where M_t is the mass increase at time t and M_∞ is the mass increase at $t = \infty$ (24 hr), and r is the average radius of the graphite flake. Values of time, t_0 , were determined by extrapolating the linear portion of plots of M_t/M_∞ vs $t^{1/2}$ to $M_t = 0$.

The average radius (r) of the original unoxidized SP-1 graphite particle was 10 μm . Values of r for the oxidized samples were estimated by assuming that the fractional volume decrease of the particle upon burn-off was equal to the fractional weight decrease and that the volume decrease occurred entirely through attack at the prismatic surfaces. Such assumptions are reasonable for graphites where crystallite alignment is very high, as previously shown[9]. Under these assumptions

$$r_2 = (1 - \text{B.O.})^{1/2} r, \quad (2)$$

where r is the initial particle radius and r_2 is the particle radius after some fractional burn-off (B.O.).

3. RESULTS AND DISCUSSION

3.1 Equilibrium studies

3.1.1 *Effect of oxidation of graphite on bromine uptake.* Assuming hexagonal close packing of bromine upon its physical adsorption on the graphite surface at 20°C [10], it is calculated that its molecular area would be 21.5 Å^2 . Taking the area of the SP-1 graphite as 1.8 m^2/g , it is calculated that for monolayer adsorption of bromine on the outer surface of the graphite the bromine/carbon atom ratio would be 0.3 Br/1000 C. As will be seen, this amount of bromine is small compared to that intercalated, even at the threshold pressure.

Table 1 summarizes results for the uptake of bromine at 20°C on samples of graphite oxidized to varying levels of burn-off. A threshold relative pressure† close to 0.1 was found for all samples. Over the relative pressure range from 0.1 to 0.95, there was little effect of burn-off on bromine uptake. This result suggests that extensive oxidation did not introduce a significant number of trapping states into the graphite compared to the original

Table 1. Uptake of bromine (as Br/1000 C) on graphite samples of various burn-off at 20°C and different relative pressures

Burn-off	Relative pressures				
	0.1	0.2	0.4	0.8	0.95
0.0	11.6	55.1	83.0	116.6	118.9
4.4	12.4	53.8	83.5	111.9	114.9
9.7	13.2	54.8	83.4	112.5	116.4
21.4	12.2	53.3	81.5	111.2	116.0
46.1	12.3	54.0	80.5	109.1	114.0

†Threshold pressure is the critical pressure at which intercalation first starts, the amount of uptake at this point is extremely small. For all practical purposes, the threshold pressure quoted here is slightly above this pressure.

number of carriers present and, hence, alter the Fermi level noticeably[3].

A Br/1000 C ratio of 125 corresponds to C_8Br , which represents the maximum intercalation of bromine that has been found[1]. Since in this compound there is one layer of bromine for every two layers of carbon, it is estimated that each bromine molecule occupies 21.0 Å^2 between the basal planes. This is in close agreement with the area calculated previously assuming hexagonal close packing. Such agreement is expected since it has been concluded that the fraction of molecular bromine intercalate which is ionized when forming C_8Br is only about 0.02[2].

3.1.2 *Effect of oxidation of graphite on nature of residue compounds.* On desorption following intercalation at 20°C, a residue compound was always obtained. The extent of oxidation of the graphite did not affect the amount of bromine residue obtained at 20°C. However, the amount of bromine remaining in the residue increased with an increase in the sorption pressure at which the intercalate was initially prepared. The residue compound was thermally unstable. For example, outgassing at 950°C reduced the bromine content from 15 Br/1000 C (residue obtained at 20°C following desorption from a relative pressure of bromine of 0.95) to 3 Br/1000 C for the unoxidized sample. The thermal stability of the residue compound decreased with increasing amount of previous oxidation of the graphite. Thus on heating the residue compound of the 46% burn-off graphite sample at 950°C following its formation at a relative pressure of 0.95 at 20°C, only 1 Br/1000 C remained. The smaller amount of bromine retained in the case of the oxidized sample suggests that enlargement of the defect size in the parent graphite through gasification facilitated bromine removal at elevated temperatures. A similar effect of oxidation has been found for the enhanced thermal release of radioactive krypton and xenon from graphite, following their being imbedded in the graphite as a result of nuclear fission.

3.1.3 *Subsequent intercalation on residue compounds.* Uptake of bromine was studied at 20°C and a relative pressure of bromine of 0.1 on samples containing residual bromine. Residue compounds were prepared by first intercalating bromine at a relative pressure of 0.95 and then degassing, first at 20°C and then at 950°C. Results are summarized in Table 2. Comparison of results in

Table 2. Bromine uptake on residue compounds at 20°C and a relative pressure of 0.1

Burn-off	Residue Br/1000 C	New bromine Br/1000 C	Total Br/1000 C
0.0	15.0	22.3	37.3
	3.2	23.0	26.2
4.4	12.3	21.9	34.2
	1.6	23.8	25.4
9.7	15.0	24.8	39.8
	1.5	23.6	25.1
21.4	15.0	24.6	39.6
	1.5	23.8	25.3
46.1	14.5	24.6	39.1
	1.0	22.4	23.4

Table 2 with those in Table 1 shows that the total amount of bromine, as well as the new bromine taken up by the residue compounds at a relative pressure of 0.1, far exceeds total uptake on the original samples. However, the new bromine taken up remained almost independent of the bromine content of the residue or the extent of burn-off given the graphite.

By contrast, at relative adsorption pressures of 0.2 and greater, the new bromine taken up on the residue compounds was always such that the total uptake (residue plus new bromine) was quite close to the amount of bromine sorbed by the original graphites at the corresponding relative pressures. This agrees with observations reported by Hooley [11] and Marchand *et al.* [12].

Thus the most interesting feature of the sorption studies on the residue compounds was observed at a bromine relative pressure of 0.1. Bromine in the residues obtained following intercalation at a relative pressure of 0.95 would be expected to be present to some extent between all alternate basal planes of graphite, as is found in C_6Br . The presence of this bromine obviously facilitated subsequent intercalation of bromine, at a relative pressure of 0.1, between basal planes which were not accessible in the original graphite samples at a comparable pressure.

3.1.4 Effect of temperature on bromine uptake. Sorption studies of bromine on unoxidized SP-1 graphite were carried out at 30, 40 and 50°C, in addition to 20°C. The threshold relative pressure at which intercalation started increased with increasing sorption temperature from 0.10 at 20°C to 0.16 at 50°C. Using the Clausius-Clapeyron equation, a heat of sorption of 10.2 ± 0.2 kcal/mole is calculated for bromine intercalation at threshold conditions. Heats of sorption were also calculated at constant levels of intercalation between 25 Br/1000 C and 65 Br/1000 C; values found were 10.6 ± 0.2 kcal/mole. Hooley previously reported a value of 11.7 ± 0.3 kcal/mole for bromine intercalation into natural graphite flakes from the variation of threshold pressure with temperature [13]. For comparison, the heat of condensation of molecular bromine at 15°C is 7.0 kcal/mole, and the heat of adsorption is 11.1 ± 1.1 kcal/mole [13] and 11.4 kcal/mole [14] on graphitized carbon black and charcoal, respectively. The closeness of the values for the heat of adsorption and the heat of intercalation of bromine suggests that interaction of bromine with the carbon surface is similar in the two processes. Hooley came to the same conclusions [13]. This supports the conclusion that the fraction of bromine which ionizes upon intercalation is very low [2].

Not only did temperature affect the threshold pressure but also did the existence of a residue compound. For example, following a sorption run at 30°C up to a relative pressure of 0.8, the sample was outgassed at 30°C. In a subsequent sorption run at 30°C, the threshold relative pressure was 0.10 compared to 0.12 on the original graphite.

3.2 Kinetics of bromine intercalation at 20°C

3.2.1 Rate of uptake on virgin graphite. Figure 1 and Table 3 summarize the results of graphite samples taken

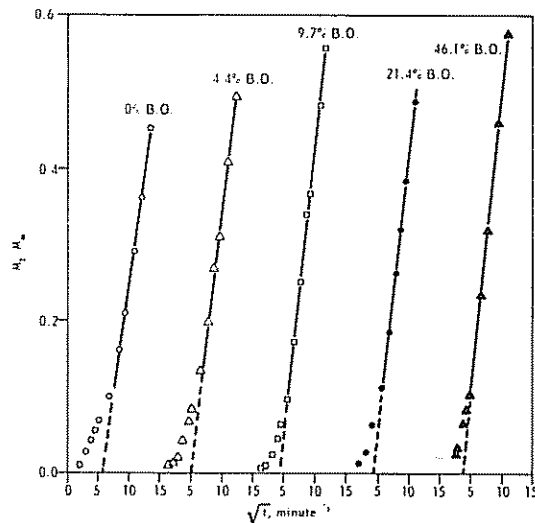


Fig. 1. Effect of level of burn-off given graphite on kinetics of subsequent bromine uptake at 20°C and the threshold relative pressure (0.1).

Table 3. Diffusion coefficients for bromine intercalation at 20°C and a relative pressure of 0.1 for graphites of different burn-off

Burn-off	D_{app} ($cm^2/sec \times 10^{12}$)
0.0	4.4
4.4	5.5
9.7	6.2
21.4	4.6
46.1	4.5

to different levels of burn-off. As reported by Dowell [5] and others, the M_t/M_∞ vs $t^{1/2}$ plots can be divided into three regions. At early times uptake is slow and the plot usually non-linear; this is followed by an extended linear region to large fractional uptakes and finally followed by a region of decreasing slope. The last region is not shown in Fig. 1. Extrapolation of the linear plots in region 2 to the abscissa yields values of t_0 . Values of t_0 decrease monotonically from 31 to 14 min with increasing graphite burn-off. Previously, Dowell found for a series of graphites ranging from highly oriented pyrolytic to Thornel fibers that t_0 increased as the mean *c*-axis strain (measured from X-ray) increased [5]. This finding suggests that oxidation may have preferentially removed the more highly strained regions in the graphite particles used in this study, that is, material closest to the prismatic surfaces.

The amount of bromine taken up before Region 2 commences remained essentially independent of the extent of previous burn-off given the graphite; it amounted to about 1 Br/1000 C. This is thought to be of significance from the standpoint of mechanism of intercalation. That is Blackman *et al.* [15] have shown that the intercalation of about 1 Br/1000 C produced a major decrease in the electrical resistivity of their graphite, whereas further addition of bromine resulted in little additional decrease in electrical resistivity. They conclude that the first bromine which intercalates is fully ionized by abstracting

electrons from the π -band of the graphite. By contrast, they conclude that the bromine which intercalates, following the addition of about 1 Br/1000 C, to be non-ionized. This again suggests that the fraction of the total bromine intercalate (of C_6Br) which is ionized in the SP-1 graphite is low, in agreement with the conclusion of Dresselhaus and Dresselhaus[2].

It is seen from Table 3 that low carbon burn-offs resulted in an increase in diffusion coefficients for bromine intercalation over the value found for the unoxidized sample. This would be expected to the extent that initial burn-off preferentially occurred at non-basal screw dislocations and crystallite boundaries in the graphite. Such attack would result in creating additional prismatic carbon surface for intercalation and thereby decrease the average diffusion distance between basal planes. Interestingly, the diffusion coefficient went through a maximum with increasing carbon burn-off, with the value following 46.1% burn-off being the same as that for the original graphite. The reason for this is not understood, but the same behaviour was found when diffusion studies were conducted at a relative bromine pressure of 0.4.

As just indicated, diffusion measurements were also made at a relative pressure of bromine of 0.4. Values for t_0 were markedly reduced when working at this higher bromine pressure. For example, for the unoxidized graphite t_0 decreased from 31 min (at a relative pressure of 0.1) to 0.6 min (at a relative pressure of 0.4). Also diffusion coefficients for bromine intercalation in region 2 were substantially higher than those reported in Table 3. For example, for the unoxidized sample the diffusion coefficient at 20°C was 1.5×10^{-10} cm²/sec. The rate of bromine intercalation was also studied close to saturation vapor pressure (that is at a relative pressure of 0.95). Further decreases in the values of t_0 were noted, but diffusion coefficients were essentially unchanged from values found at a relative pressure of 0.4.

The magnitude of the diffusion coefficients reported in this paper are much lower than those reported by Dowell[5] for intercalation of bromine close to its saturation pressure into a 1.0 cm dia. sample of highly oriented pyrolytic graphite (that is, 2.4×10^{-8} cm²/sec at 30°C). Perhaps the effective diffusion distance (r) in the pyrolytic graphite was somewhat less than the radius of the cylinder, which was assumed by Dowell to be the value of r when solving eqn (1). Significant transport of bromine down non-basal dislocations[16] would decrease the diffusion distance (r) between basal planes for intercalation to occur, leading to consideration of three-dimensional diffusion as discussed by Marchand *et al.*[12].

3.2.2 Rate of uptake on residue compounds. Rates of bromine uptake in region 2 at a relative pressure of 0.1 at 20°C on samples containing residue bromine of about 15 Br/1000 C, following desorption at 20°C from a relative pressure of 0.95, showed significant increases over uptake rates on the original graphite samples. For example, for the unoxidized sample the diffusion coefficient increased from 4.4×10^{-12} cm²/sec to 30.9×10^{-12} cm²/sec. As previously, the diffusion coefficient

went through a slight maximum with increasing carbon burn-off of the graphite samples studied. The diffusion coefficient for intercalation of bromine into the maximum burn-off sample (46.1%) was only slightly higher than that for the original unoxidized graphite (that is, 35.0×10^{-12} cm²/sec).

X-Ray diffraction measurements showed that the interlayer spacing of the residue compound (15 Br/1000 C) was 3.367 Å compared to 3.354 Å for the original unoxidized graphite. Equilibrium measurements, previously discussed, showed that bromine uptake on the residue compound, at a relative pressure of 0.1, was considerably in excess of the bromine taken up by the original graphite at the same relative pressure. Further, the threshold pressure was lower for the residue compound. Possibly the residual bromine affects the mode of bromine penetration between basal planes, such as the profile of bromine concentration in the radial direction of the particle as a function of time[17]. Indeed, the use of Fick's law of diffusion to describe the intercalation process has recently been brought into question, since intercalation does not start simultaneously at all graphite interspaces[18].

Rates of bromine uptake were also studied at 20°C and a relative pressure of 0.1 on the residue compounds (~3 Br/1000 C) formed from the unoxidized graphite. This amount of residue was obtained in two different ways. Residue compound A was obtained by desorption from a sorption partial pressure of 0.95 at 20°C (maximum uptake 118.9 Br/1000 C) and subsequent heating at 950°C *in vacuo*. This compound had a composition of

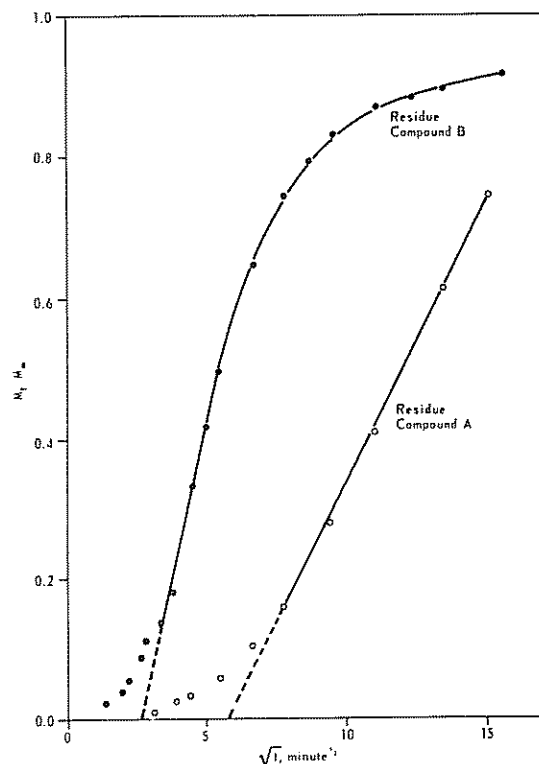


Fig. 2. Rate of bromine uptake at 20°C and relative pressure of 0.1 on residue compounds having a composition ~3 Br/1000 C made by different techniques.

Table 4. Effect of the method of preparation of residue compounds on the amount and rate of subsequent bromine uptake at 20°C and a relative pressure of 0.1

Compound	Residue Br/1000 C	Total uptake Br/1000 C	D_{app} (cm ² /sec × 10 ¹²)
A	3.2	26.2	6.4
B	3.4	12.6	30.4

3.2 Br/1000 C. Residue compound B (3.4 Br/1000 C) was obtained by desorption at 20°C from a sorption partial pressure of 0.1 at 20°C (maximum uptake 11.6 Br/1000 C). Rates of bromine uptake on these residue compounds are plotted in Fig. 2 and results are summarized in Table 4. Striking differences are seen. In the case of residue compound A, t_0 was essentially the same as found for sorption of bromine on the original graphite (that is, 33.6 min compared to 31 min). By contrast, on residue compound B, t_0 was sharply reduced to 6.8 min. Further, the amount of bromine taken up at equilibrium on residue compounds A and B were markedly different—26.2 Br/1000 C compared to 12.6 Br/1000 C. Clearly in the case of residue compound A bromine was intercalating between basal planes which were not accessible for intercalation in the case of residue compound B. Total uptake in the case of residue compound B closely paralleled that found on the original graphite as seen in Table 1.

Despite the larger total uptake on residue compound A at equilibrium, the rate of attaining this equilibrium was smaller for this compound. That is, as seen in Table 4,

the diffusion coefficients in region 2 for bromine intercalation were 6.4×10^{-12} cm²/sec and 30.4×10^{-12} cm²/sec on residue samples A and B.

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