

INTERCALATE DISPLACEMENT AND EXCHANGE IN GRAPHITE*

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Summary

The mechanism of intercalate transport in graphite was studied by sequential intercalation of bromine and iodine monochloride. It was found that the transport involved solid-state intercalate displacement such that the first intercalate molecule to enter an interlayer space is the first to reach the center of the graphite sample. Upon exposure of stage-2 graphite-bromine to ICl, the in-plane superlattice diffraction pattern was observed to change from that of graphite-bromine to that of graphite-ICl, while the ICl intercalate distributed itself uniformly at a concentration level above that of the bromine intercalate. This is interpreted as the expulsion of bromine by the in-coming ICl, which dissolved the remaining bromine to form a solid solution with the ICl in-plane structure.

1. Introduction

The question of intercalate transport is important from a technological viewpoint. In batteries, for example, intercalate transport would have a direct bearing on the cell current. Intercalate transport also must be considered in replacement or exchange reactions where the first intercalation compound to be formed is an intermediate to the final compound. Examples of replacement reactions include the formation of transition metal intercalation compounds from alkali metal intercalation compounds [1], and the reaction of aluminum bromide with residue graphite-bromine compounds [2].

The keynote of work pertaining to the mechanism of intercalate transport is Hooley's [3, 4] observation that intercalation begins at the basal edges adjacent to basal surfaces, and that the intercalating species migrate between

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the basal planes. Studies of reaction kinetics can suggest transport mechanisms; it was the observation of the kinetics of the oxidation of intercalated potassium which led Daumas and Hérold [5] to explain staging with the concept of intercalate islands. This concept carries the notion of intercalate displacement by the movement of the intercalate islands. However, most studies of intercalation kinetics have involved vapor phase transport of the intercalate to the sample, and the rate-controlling step in the overall intercalation reaction appears to be at the sample surface. For example, condensation and adsorption appear to be rate-controlling in the intercalation of alkali metals [6] and metal halides [7, 8], while charge transfer and reaction at the surface appear rate-controlling for the intercalation of nitric acid [9] and, in general, in the intercalation of metal dichalcogenide hosts [10]. As a consequence of reaction control at the surface, little information is available pertaining to transport within the graphite. The kinetics of bromine intercalation, on the other hand, appears to be controlled by the diffusion of bromine within the graphite under conditions of both vapor phase and liquid phase intercalation. Furthermore, the diffusion coefficient of bromine as determined during intercalation and desorption [11, 12] is very similar to that observed by Aronson for the self-diffusion of bromine in intercalated graphite [13]. Two diffusion mechanisms are possible; first, the already present intercalation compound can be considered as the reference frame through which fresh intercalate molecules diffuse, as in the case of many oxide films. Second, the intercalate molecules may be considered as diffusing within the graphite, allowing the first molecules to be injected at the crystal edges to be the first molecules to reach the center of the crystal. Measurements of diffusion coefficients generally have implicitly assumed that the second case was correct. By observing the displacement of intercalated bromine by iodine monochloride, we have obtained explicit evidence of this transport mechanism for bromine in graphite.

2. Experimental techniques

We have tried to clarify the intercalation mechanism by sequentially intercalating graphite with bromine and iodine monochloride. Both highly oriented pyrolytic graphite (HOPG, 4 mm × 4 mm) and large single crystal flakes (~ 4 mm dia.) were used. Samples were intercalated in a variety of methods, all of which were carried out at room temperature.

Method 1: A control sample was prepared by partially intercalating HOPG in liquid Br₂, then allowing it to desorb in liquid CCl₄,

Method 2: an HOPG sample and a single crystal flake were partially intercalated in liquid Br₂, and then intercalated in a 2 mol% solution of ICl and CCl₄,

Method 3: an HOPG sample and a single crystal flake were intercalated to completion in liquid Br₂, and then immersed in liquid ICl,

TABLE 1

Mass absorption coefficients of Br, ICl and C

	Br ₂	ICl	C
μ/ρ (cm ² /g)			
Cu K α	92.6	268	4.22
Mo K α	82.2	33.2	0.535
Layer density (g/cm ³)	3.93	3.13	2.27
Stoichiometry at saturation	C ₇ Br*	C ₉ ICl**	—
Stage at saturation	2	1	—

*From ref. 14.

**From ref. 15.

Method 4: an HOPG sample was intercalated to completion in a solution of 50 mol% Br₂ and 2 mol% ICl in CCl₄,

Method 5: an HOPG sample and a single crystal flake were intercalated to completion in a solution of 50 mol% Br₂ and 50 mol% ICl.

Staging in the compounds was determined with a diffractometer using Cu K α radiation and a monochromator. The in-plane structure was observed by the transmission Laue method using Mo K α radiation. The intercalate concentration distribution perpendicular to the *c*-axis was determined by measuring the absorption of monochromatic Cu K α and Mo K α radiation as an intercalated sample was transported through an X-ray beam. Table 1 lists the absorption coefficients and intercalate layer densities for Br₂, ICl and C. The difference in the absorption coefficients at the two wavelengths allowed the mapping of the bromine and iodine monochloride distributions within the graphite. The density used to convert the mass absorption coefficient to a linear mass absorption coefficient was the density calculated for a single intercalate layer. The stoichiometries [14, 15] indicated in Table 1 were used to calculate the density.

It was assumed that the ICl remained a molecular species with little tendency to decompose. With a known initial graphite thickness, the point-wise bromine and ICl concentrations could be determined by the following two equations with two unknowns:

$$\left(\frac{I}{I_0}\right)^{\text{Cu}} = \exp\left[-\mu_{\text{C}}^{\text{Cu}} x_{\text{C}} + \mu_{\text{Br}_2}^{\text{Cu}} x_{\text{Br}_2} + \mu_{\text{ICl}}^{\text{Cu}} x_{\text{ICl}}\right]$$

$$\left(\frac{I}{I_0}\right)^{\text{Mo}} = \exp\left[-\mu_{\text{C}}^{\text{Mo}} x_{\text{C}} + \mu_{\text{Br}_2}^{\text{Mo}} x_{\text{Br}_2} + \mu_{\text{ICl}}^{\text{Mo}} x_{\text{ICl}}\right]$$

where I_0 is the unabsorbed beam intensity, I is the transmitted beam intensity, μ_a^λ is the linear absorption coefficient of component a ($a = \text{C}, \text{Br}_2$, or ICl) at wavelength λ (Cu K α or Mo K α), and x_a is the thickness of component a .

In the succeeding graphs the concentration of a is determined by the ratio of x_a and the product of the initial graphite thickness and the nominal expansion of a first stage compound. In a single-component and single-stage compound, the indicated concentration is the reciprocal of the stage number. The use of Cu $K\alpha$ and Mo $K\alpha$ radiation is particularly appropriate as the bromine absorption coefficient is smaller than that of ICl with Cu $K\alpha$ but larger than ICl with Mo $K\alpha$ radiation. As a consequence, a difference in the distributions of Br and ICl is very clearly evident, even in the raw data. The relative amounts of bromine and ICl can be very accurately determined, but the absolute concentrations cannot. The primary reason for this arises in the measurement of the initial graphite thickness and difficulties in ensuring that the sample is exactly perpendicular to the beam. For these experiments the graphite thickness was measured by X-ray absorption prior to intercalation, and the sample was within 5° of the perpendicular. A further error is possible from the counting statistics, especially in the case of first stage graphite-ICl with Cu radiation. Thus, the absolute concentration values have an uncertainty of $\sim 10\%$, although the relative concentration values are much more accurate.

3. Experimental results

The first curve in Fig. 1 illustrates the distribution of bromine within a sample after a 10 min exposure to Br_2 (Methods 1 and 2). The distribution is

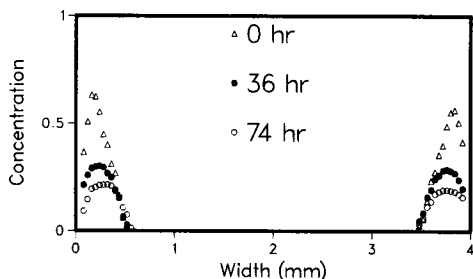


Fig. 1. Distribution of bromine in an HOPG sample after desorption for 0 h (Δ), 36 h (\bullet), and 74 h (\circ).

consistent with the “window-pane” morphology commonly observed in bromine intercalation. The second and third curves indicate the bromine concentration after the subsequent 36 and 74 h in CCl_4 respectively (Method 1). It can be seen that there was virtually no further transport of the bromine into the sample; only desorption of bromine into the CCl_4 occurred.

The behavior on desorption can be contrasted with that occurring when a partially-bromine-intercalated sample is then exposed for 36 h to 2 mol% ICl (Method 2, Fig. 2). The concentration profile (Fig. 2) indicates that the bromine had migrated toward the center of the sample while the edge region

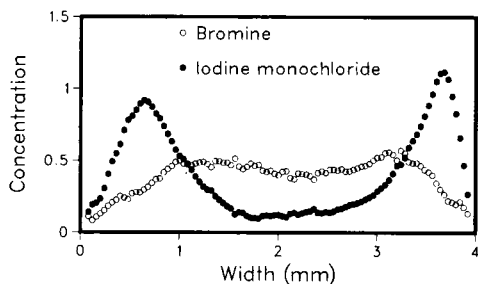


Fig. 2. Distribution of bromine (○) and ICl (●) within graphite flake after partial intercalation in Br_2 , then intercalation in 2 mol% ICl- CCl_4 (Method 2).

contained predominantly ICl. The $00l$ diffraction pattern indicated the presence of both stage 1 and stage 2 compounds. The in-plane diffraction pattern was very similar to that observed for stage 1 graphite-ICl (see Fig. 1 of ref. 15). As discussed below, the same in-plane superlattice was observed when a sample saturated with bromine was exposed to liquid ICl (Method 3) and when a sample was intercalated in a mixture of 50 mol% Br_2 -50 mol% ICl (Method 5).

The concentration profile in Fig. 2 suggested that at short ICl intercalation times the in-plane diffraction pattern should be a superposition of those of graphite-bromine and graphite-ICl. To confirm this, a flake of graphite was immersed in liquid Br_2 for 5 min, and then immersed in liquid ICl for 11 min. Figure 3 shows the transmission Laue patterns obtained from the c -face

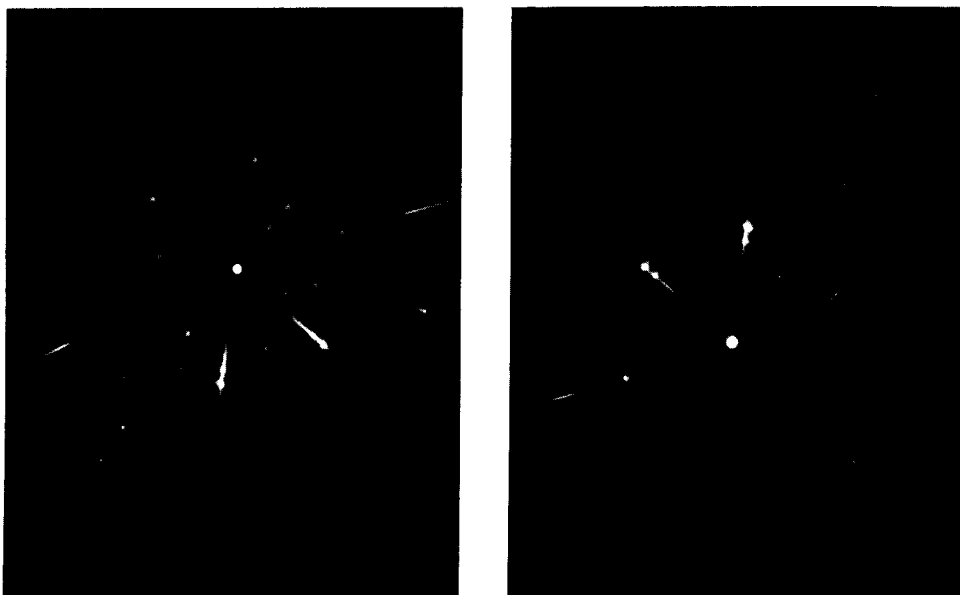
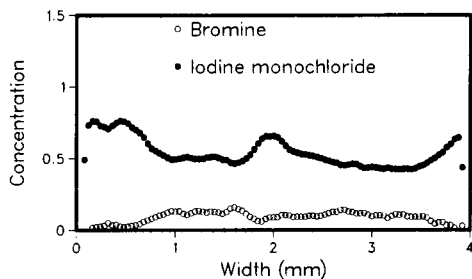


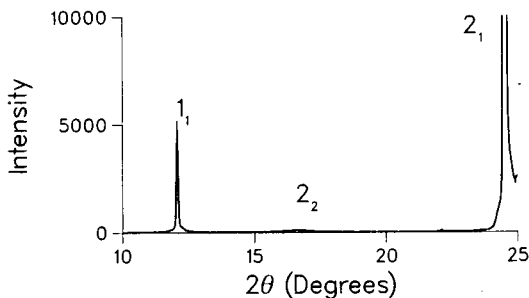
Fig. 3. Transmission Laue photographs taken from (a) the edge, and (b) the center of graphite flake immersed in liquid bromine for 5 min, then immersed in liquid ICl for 11 min.

near the edge and near the center of the flake. Figure 3(a), the pattern obtained near the edge, indicates that both the graphite-bromine and the graphite-ICl in-plane structures were present. Near the center of the flake, however, the graphite-bromine structure was still the dominant phase (Fig. 3(b)).

Figure 4 shows the results obtained when a stage 2 graphite-bromine compound was immersed in liquid ICl (Method 3). Figure 4(a) indicates that,



(a)

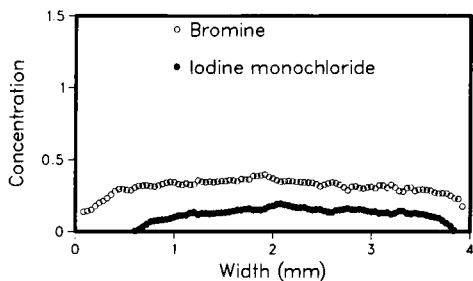


(b)

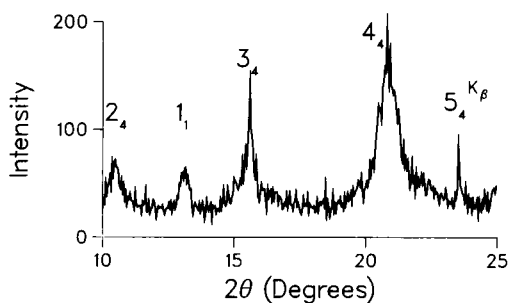
Fig. 4. (a) The distribution of bromine (○) and ICl (●), and (b) the $00l$ diffraction pattern obtained from an initially stage 2 graphite-bromine compound after immersion in liquid ICl (Method 3). The peaks are identified by the l index with the stage number as a subscript.

despite the initial saturation of the sample with bromine, much of the bromine was displaced by the in-coming ICl. This is supported by the diffraction results; the in-plane structure was similar to graphite-ICl and the $00l$ diffraction pattern (Fig. 4(b)) indicates that stage 1 predominated. The apparent expulsion of bromine from the sample in Method 3 can be explained by preferential intercalation by ICl due to a larger reaction energy.

Samples intercalated in a mixture of Br_2 and 2 mol% ICl (Method 4) showed a uniform distribution of bromine and ICl (Fig. 5(a)), and the $00l$ diffraction pattern (Fig. 5(b)) was quite similar to that of a fourth stage graphite-bromine compound, with the exception of a peak where the first stage ICl (001) line may be expected.



(a)



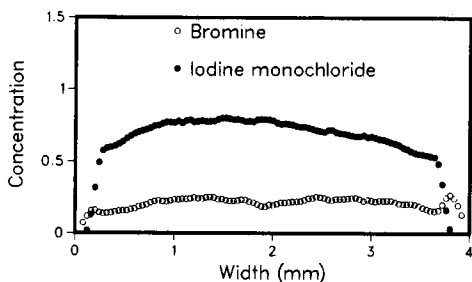
(b)

Fig. 5. (a) The distribution of bromine (\circ) and ICl (\bullet), and (b) the $00l$ diffraction pattern obtained from HOPG intercalated in a solution of 50 mol% Br_2 and 2 mol% ICl in CCl_4 (Method 4).

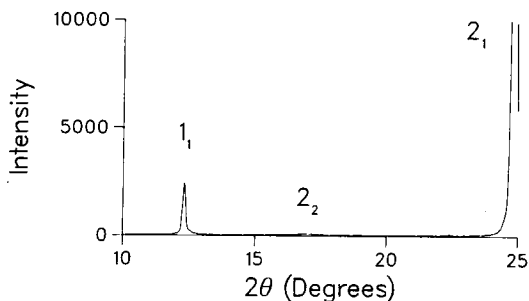
With 50 mol% of ICl in the ICl- Br_2 solution (Method 5), the bromine distribution was relatively uniform (Fig. 6(a)). The $00l$ diffraction pattern (Fig. 6(b)) shows a predominantly first stage pattern, with small amounts of stages 2 and 3. The repeat distance, 7.12 Å, for this first stage compound is the same as that observed after sequential intercalation of ICl into stage 2 graphite-bromine (Method 3). This value is somewhat larger than the repeat distance of 7.06 Å, which was observed in a first stage graphite-ICl compound made by immersion in ICl liquid.

4. Discussion

The evidence in Fig. 3, where both bromine and ICl superlattices are present within the same sample, indicates that initially bromine is displaced by the in-coming ICl toward the central unintercalated region of the sample. This indicates that the presence of an alternative species, ICl, is sufficient to cause bromine to intercalate, even though only desorption occurs if no other intercalate is available. Calculations made by Enriquez *et al.* [16] suggest that the loss of intercalate molecules into the regions between the islands is not energetically favorable. This, in turn, suggests that diffusion may pre-



(a)



(b)

Fig. 6. (a) The distribution of bromine (\circ) and ICl (\bullet), and (b) the 00 l diffraction pattern obtained from HOPG intercalated in a solution of 50 mol% Br₂ and 50 mol% ICl (Method 5).

dominantly be due to the migration of islands rather than the movement of molecules through or between islands. Observations of island boundaries by transmission electron microscopy also suggests that island mobility may be quite high [17]. On the other hand, it is evident that interdiffusion of bromine and ICl between islands occurs, as is shown by the similar repeat distance and in-plane structure observed after sequential intercalation (Method 3), and after intercalation from a Br₂-ICl solution (Method 5). Furthermore, since the in-plane structure appears similar to that observed for graphite-ICl, we suggest that bromine is dissolving into the ICl structure, forming an ICl-rich solution. Since graphite-bromine and graphite-ICl have different in-plane structures, at least two solid solutions are expected — one ICl-rich, with an ICl in-plane structure, and one bromine-rich, with a bromine in-plane structure. The preference observed in this work for the ICl-rich structure is probably due to the high ICl reactivity in the environments used.

Acknowledgements

We thank Professor W. W. Mullins and Dr. D. Ghosh of Carnegie-Mellon University for helpful discussions. We are grateful to Union Carbide Corpora-

tion for providing graphite material. The X-ray diffraction equipment grant from the Division of Materials Research of the National Science Foundation under Grant No. DMR-8005380 is acknowledged. Support from the Materials Research Laboratory Section, Division of Materials Research, National Science Foundation, under Grant No. DMR 76-81561 AO1 is also acknowledged.

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