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THE EFFECT OF FLAKE SIZE ON THE COMPOSITION OF GRAPHITE FERRIC CHLORIDE*

J. G. HOOLEY and R. N. SONIASSY†
Department of Chemistry, University of British Columbia, Vancouver 8, Canada

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Abstract—A method of preparing stage 1 graphite ferric chloride with 97 per cent of the theoretical composition of $C_{6\cdot1}FeCl_3$ is described. The solvent action of acetone on the product has been shown to completely empty a certain fraction of the spaces. This fraction is a negative exponential function of the thickness of the original flake of graphite. Various theories to explain this are proposed and related to the general process of intercalation.

1. INTRODUCTION

Graphite ferric chloride has usually been prepared by heating the anhydrous reactants in a sealed tube, chilling the product and either subliming off excess $FeCl_3$ or washing it away in a solvent[1–3]. Rudorff and Schulz [2] originally reported a $C_{10}FeCl_3$ below 309° and a $C_{30}FeCl_3$ between 310° and 410°C both independent of flake diameter from 250 to 550 μ, and of the solvent used for removal of excess $FeCl_3$. We define flake diameter as the minimum cross dimension and take it as equal to the diagonal on the sieve opening. Rudorff and Landel[4] later reported some variation with flake diameter. One at 330–1400 μ gave $C_{10\cdot3}FeCl_3$ whereas a finer graphite of unstated size gave $C_{12\cdot3}FeCl_3$. However, Barker and Croft[3] reported a $C_{10\cdot4}FeCl_3$, after washing, which was independent of both diameter from 60 to 400 μ and of temperature from 200° to 350°C. Cowley and Ibers[5] showed by X-ray and electron diffraction that a $C_{10\cdot9}FeCl_3$ from 60 μ dia. flakes was 17 per cent free graphite. The remainder contained in each layer space a single layer of $FeCl_3$ at 92 per cent of the density of bulk $FeCl_3$. They pointed out that if every space was filled at the same density as in bulk $FeCl_3$ the product would be $C_{6\cdot1}FeCl_3$.

Lazo and Hooley[6] found that a $C_{12}FeCl_3$ from Acheson graphite would not exchange radioactive iron with an HCl solution of $FeCl_3$. Hooley and Bartlett[7] measured the isotherm of $FeCl_3$ vapor on a fine natural graphite Spec C-SP1. At 300°C they found one pressure independent composition of C_7FeCl_3 and at 350°C, two-of C_{12} and C_7FeCl_3.

Brusset *et al.*[8] found that repeated washing would not remove all the $FeCl_3$ from a $C_{14}FeCl_3$ made from flakes $< 120\,\mu$. They found that both agitation and successive washing and drying increased the percentage lost but even after 27 cycles in 6 M HCl for 150 days the composition was $C_{26}FeCl_3$. They also followed the change in X-ray diffraction pattern during 9 cycles for each of 6 solvents and concluded that complete layers of $FeCl_3$ are randomly removed, leaving a structure with less order in the '*c*' direction and containing a certain amount of graphite.

The above review shows that the C_7FeCl_3 in near saturated vapor at 315°C loses $FeCl_3$ on chilling and solvent treatment. Complete layers of $FeCl_3$ are randomly removed leaving

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a number of nearly filled layers which are impervious to further attack. Although there are suggestions that the fraction of layers emptied is greater for finer flakes, there has been no systematic study of the effect of flake diameter and thickness on the composition of the initial and final washed product. We have done this for natural flakes from 2 to 2600 μ in diameter and from < 1 to 175 μ in thickness. We used a two temperature system for preparation so that the initial product would contain no condensed $FeCl_3$. The effect of subsequent washing on the intercalated $FeCl_3$ could then be determined.

2. PROCEDURE

Madagascar and New York flakes were HCl and HF washed and sieved. In Table 1, the diameter is the average of the diagonals on the screens or, for the 2 and 25 μ sizes, it has been estimated from microscopic examination. For the sieved material, the range is ± 15 per cent. Certain sieve fractions (15–22) were then further separated into fractions of different thicknesses. This was done by suspending a few grams in a 2 meter flowing air column 3 cm in diameter. The thinnest flakes were collected from a horizontal platform surrounding the top end of the tube. A butterfly valve about 10 cm above the porous disc at the bottom was closed as the air current was stopped. When no more sample could be collected from this valve or from the top, the thickest flakes were collected from the disc and a fresh sample was introduced. The rate of air flow was held constant at a value which put about one third of the original amount in each category. For all samples larger than 250 μ across, the thickness of each of 30 flakes was determined with a dial gauge of sensitivity 1 micron. The distribution showed a standard deviation from the average of about 20–40 per cent. However, this average thickness takes no account of the weight of the flake. It is therefore not used in Table 1 where the relationship to composition is of interest. Instead, a weighted average thickness is calculated from the above distribution, using the fact that for a given diameter, weight is proportional to thickness. Specifically, $\Sigma n_i t_i^2 \div \Sigma n_i t_i$ is listed in Table 1 for flakes larger than 250 μ across. For the smaller ones that had not been separated into thickness fractions we relied on Salzano's claim[9] that thickness is proportional to diameter. The ratio of weighted average thickness to diameter was taken as 0·03 which is the value found for larger flakes.

About 1 g of graphite weighed in a glass boat was placed in a glass tube with 20 per cent more iron wire than required to give both C_6FeCl_3 and 760 Torr. of Fe_2Cl_6 vapor at 310°C. The open ends were sealed and the tube was evacuated through a side tube to 10^{-4} Torr. Dry Cl_2 was admitted to 760 Torr. and the Fe wire was alternately heated and cooled until completely converted to $FeCl_3$. This required about 10 cycles because a coating of product would stop the reaction. If conversion is not complete it has been shown [10] that the $FeCl_2$ content of the product is increased. The cold tube was evacuated, sealed off and then heated in a horizontal furnace in which the graphite half was maintained at 315°C and the other half at 310°C both $\pm 0{\cdot}5$°C. The vapor pressures at these two temperatures are 840 Torr. and 650 Torr.[11] so that the partial pressure over the graphite is 0·78. After 24 hr or more, the glass tube was cooled in such a way that the non-graphite end cooled first, thereby minimizing the condensation of $FeCl_3$ on the flakes. The increase in sample weight was assumed to be intercalated $FeCl_3$ even though it has been shown by Mössbauer spectroscopy that a few per cent is present as $FeCl_2$[10]. This initial composition is shown in Table 1.

The $C_{x_1}FeCl_3$ in the boat was then washed completely to a weighed filter crucible with acetone, washed with five 10 ml portions, dried at 100°C and reweighed. A second series of washings removed only a few mg. and a third series removed less than a mg.

Two samples from runs 4 and 12 were soaked in acetone for an additional 15 days and then 50 days with no weight change. The final column in Table 1 is the fraction of filled spaces which must have been completely emptied to account for the initial and final values of x.

Finally, the densities of the 6 washed products in Table 2 were determined by noting the fraction that floated in mixtures of CH_2Br_2 and CCl_4 of known density. They all showed a distribution of densities over 0·05–0·10 g cm^{-3} with about 50 per cent floating in a liquid of the density shown in column 2. The calculated density is shown for two cases—D_1 for complete removal of $FeCl_3$ from the number of spaces required by the value of x_2 and D_2 for partial removal from all spaces and no contraction of the expanded separation of 9·4 Å[5].

3. RESULTS AND DISCUSSION

For flakes from 25 to 500 μ across and from 1–40 μ thick, the chilled product after 24 hr in 650 Torr. Fe_2Cl_6 at 315° has 6·28 ± 0·13 C atoms per $FeCl_3$ molecule. Because there is no trend with flake size, we believe this represents an equilibrium composition. For larger flakes, this value was reached for the 650 μ dia. flakes in 72 hr but was not reached for the 2600 μ flakes in 191 hr. This is at least partly caused by the longer diffusion path but may also be caused by a possible greater number of imperfections in larger flakes[9]. This could either slow the reaction or decrease the final $FeCl_3$ content by closing certain regions to intercalation.

Because the composition of the chilled product is independent of flake size within the above range, we believe that during the chilling process no $FeCl_3$ could have condensed on the product. If it had, the amount gained would surely have varied with flake size and so have lead to a variation in final composition. Furthermore, if the graphite ferric chloride in contact with near saturated vapor at 315°C had any $FeCl_3$ condensed in the capillary regions between flakes it must all have been lost on pressure reduction. Otherwise, again, the final composition would have varied with flake size. Hence the compound in equilibrium with the near saturated vapor at 315°C must have had a $FeCl_3$ content at least as high as in $C_{6\cdot3}FeCl_3$. The difference between this and the isotherm value of C_7FeCl_3 must be experimental error.

The value of 6·3 is remarkably close to a theoretical value of 6·1 calculated on the assumption that every space is filled with one layer of $FeCl_3$ with the same Fe–Fe separation as in bulk $FeCl_3$ at 20°C. The one layer consists of two hexa coordinated Cl layers sandwiching an Fe layer. Although there is electron transfer to the iron in these layers [10] it is apparently not sufficient to appreciably change the structure away from that of bulk $FeCl_3$. In other words, epitaxy is negligible and the X-ray work of Cowley and Ibers[5] confirms this.

The 2 × 0·1 μ sample in Table 1 is Spec C-SP1 ball milled 112 hr. It intercalated less Br_2 than normal (12), no CrO_2Cl_2 (12) and apparently less $FeCl_3$ than did larger flakes. These differences may be partly caused by size and partly by imperfections introduced during grinding and should be further studied.

When the chilled equilibrium product is washed with acetone, the weight loss reaches a constant value for a given flake size. This suggests that we are dealing with a residue compound similar to the one produced by, say, pressure reduction of Br_2 around graphite-bromine. In that case, Saunders *et al.* [13] have shown that the process involved the emptying of whole layer spaces and produced, for a given Br_2 pressure, a collection of full and of empty spaces. This is, indeed, also true for the washed products as can be seen from the densities in Table 2 and from the X-ray data of Brusset *et al.*[9] and of Cowley and Ibers[5]. The fraction of spaces that must have been emptied to account for

Table 1. Composition as a function of flake size

Sample number	Diameter (μ)	Thickness (μ)	Time (hr)	$C_{x_1}FeCl_3$ initial	$C_{x_2}FeCl_3$ washed	$1-\frac{x_1}{x_2}$
1	2	0·1	120	7·20	194	0·96
2	25	1	24	6·34	13·68	0·54
3	90	3	24	6·21	11·71	0·47
4	190	6	24	6·21	8·88	0·30
5	275	10	24	6·38	8·54	0·25
6	425	19	24	6·40	8·70	0·26
7	650	25	24	6·60	8·17	0·19
8	650	25	48	6·42	7·81	0·18
9	650	25	72	6·30	7·56	0·17
10	650	61	120	6·42	7·30	0·12
11	1100	91	72	6·54	7·15	0·09
12	1300	72	120	6·58	7·13	0·08
13	2600	164	120	6·70	7·00	0·04
14	2600	175	191	7·00	7·26	0·03
15	190	thin	24	6·14	12·29	0·50
16	190	thick	24	6·15	9·55	0·35
17	275	1	24	6·09	9·60	0·36
18	275	12	24	6·18	8·15	0·24
19	425	10	24	6·54	8·42	0·23
20	425	40	24	6·40	7·90	0·19
21	475	6	24	6·20	8·51	0·27
22	475	21	24	6·34	7·60	0·17

Note: 10, 12, 13, and 14 are New York flakes and all others are Madagascar flakes

Table 2. Density of $C_{x_2}FeCl_3$

Sample number	X_2	D (50% floats)	D_1 calcd. graphite $+C_{6·3}$ FeCl$_3$	D_2 calcd. no contraction
15	12·29	2·44	2·39	1·69
16	9·55	2·45	2·43	1·94
17	9·60	2·46	2·43	1·94
18	8·15	2·50	2·46	2·14
21	8·51	2·44	2·45	2·08
22	7·60	2·50	2·47	2·24

the composition change is in the last column of Table 1. It is plotted against the log of the thickness in Fig. 1 and it is apparent that at least for flakes thicker than a few microns, the relationship is a linear one. The thickness of very thin flakes is not well known and hence, for them, the linearity is a conjecture. It is apparent, however, that a flake can be so thin that most of the $FeCl_3$ is removed—96 per cent in one case. This dependence of fraction lost on thickness easily explains the distribution of densities associated with each sample of Table 2. Thus, even a sieved and air column separated sample has been shown to have a distribution of thicknesses and therefore of fractions lost and therefore of densities.

The fraction removed may also be a func-

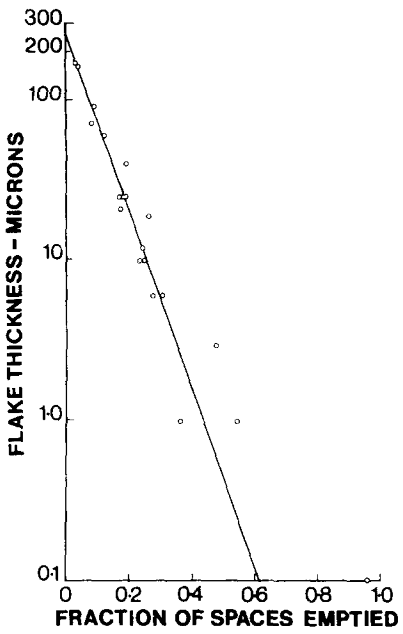

Fig. 1.

tion of diameter but it was not possible to study this because the range of diameters available for a given thickness is too limited. This is because average thickness increases with average diameter[9] and although grinding and air suspension can change the ratio, they cannot change it sufficiently to allow study. The effect, if any, is much less than that of thickness as is shown by the 3 pairs 17–22. Here, only thickness is changed for each of 3 diameters and the resultant 3 slopes are in line with that for the full range of sizes in Fig. 1. If there were a diameter effect, then holding diameter constant should produce a slope or thickness effect different from that observed for samples 2–14 where both diameter and thickness increase together.

It is intriguing that both the fraction of spaces emptied by acetone and the threshold pressure for the intercalation of Br_2 in pyrolytic graphite[14] are exponential functions of thickness. The reason for this may become apparent when other properties of graphite are studied as a function of thickness. In the meantime we can only make the following conjectures about the mechanism of the solution process. If it further resembles intercalation in pyrolytic graphite, it starts at the two outer spaces of the layer plane system and proceeds toward the center[14]. What, however, is the ordering of the emptied spaces? The X-ray data of Brusset *et al.*[8] show a random distribution but this may be deceiving. Thus, the sequence of emptied spaces may be uniform in a given flake but the actual sequence may be a function of thickness. Now every sample of graphite used by us and by Brusset had a distribution of flake thicknesses. The X-ray would interpret this collection of various ordered sequences as a loss of order in the '*c*' direction. If the emptied spaces are indeed in an ordered sequence in each flake, then the process does resemble intercalation except for the effect of flake thickness in the solution case. Intercalation stages, defined by the number of carbon layers between adduct layers, have never been reported to vary with flake size and appear to be the same for both the entry of adduct and its exit from the graphite. This problem may be resolved by diffraction work on single flakes of various thicknesses.

There are three other mechanisms that should be considered. In one, the solution process starts at the opposite basal plane spaces and proceeds toward the center by emptying every one of the first *n* spaces, leaving the core intact. The fraction emptied would be less for thicker flakes and this may be associated with their greater rigidity. Although this mechanism is consistent with the observed densities, it cannot explain the X-ray data of Brusset[8].

A second possibility is that the solvent makes a random selection of the spaces to be emptied. Such a process could show a thickness effect if the minimum number of emptied spaces left between full ones was an increasing function of thickness. It would be in accord with both the density data and the X-ray data of Brusset. However, neither this nor the preceding mechanism could explain the stages often produced during the removal of adduct from an intercalated system.

Thirdly, there is the solution mechanism proposed by Rudorff[2]. This involves loss of $FeCl_3$ from the periphery of the flake. The remaining adduct in the core is protected from further attack by a sheath of graphite layers at their normal spacing. Flakes of smaller diameter lose a greater per cent of their $FeCl_3$ in arriving at this state and so a size effect is predicted on the basis of diameter rather than thickness. Our work shows that thickness has a greater effect than diameter. However, his mechanism will explain the density data and perhaps the X-ray data of Brusset if the zone between peripheral graphite and the core is diffuse. It would not explain stages if applied to intercalation, and the dished shape of the carbon layers is not appealing. It would require changes in bond angle and distance with only the weak attraction between carbon layers as a driving force.

4. CONCLUSIONS

When graphite ferric chloride is prepared at 315°C and a partial pressure of Fe_2Cl_6 vapor of 0·8, the equilibrium composition is independent of flake cross section from 25 to 650 μ and of thickness from 1 to 60 μ. The value of $C_{6\cdot 3}FeCl_3$ corresponds to 97 per cent filling of all spaces with single layers of $FeCl_3$ at the same density as in the solid. From this compound, acetone removes a certain fraction of the adduct. The density of the product shows that spaces end up either full or completely emptied of $FeCl_3$. The distribution of emptied spaces through the flake is not known but is believed to be regular on the basis of the known behaviour of certain other adducts when they are being removed from graphite. The fraction of spaces emptied by acetone is a negative exponential function of the thickness of the original flake. This fact could explain the variety of compositions previously reported for graphite ferric chloride. It shows that graphite metal chloride compounds should be prepared at an adduct pressure somewhat below saturation so that a solvent is not needed to remove any condensed adduct.

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