Reversible Intercalation of Graphite by Fluorine: a New Bifluoride, $C_{12}HF_2$, and Graphite Fluorides, C_xF ($5 > x > 2$)

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A blue-black first-stage graphite fluoride, C_xF ($5 > x > 2$), in which the planar carbon-atom sheets of graphite are preserved, is made by intercalation of graphite with fluorine in the presence of liquid hydrogen fluoride, at *ca.* 20 °C, the oxidation (which is electrochemically reversible for $x > 2.6$) proceeding *via* a highly conductive second stage salt: $C_{12}{}^+HF_2{}^-$.

The recent discovery[1] in these laboratories that the intercalation of graphite by AsF_5, in the presence of elemental fluorine, resulted in the incorporation of 'extra' fluorine to a limiting composition $C_xAsF_6\cdot\frac{1}{2}F_2$ has prompted an examination of the factors which govern the intercalation of graphite by fluorine itself. It is common knowledge that graphite is not intercalated spontaneously by fluorine at room temperature and ordinary pressures, but that interaction between these elements does occur at higher temperatures (usually *ca.* 400 °C) to yield fluorides such as $(CF)_n$ and $(C_2F)_n$, in which the F atoms are covalently bound to tetrahedral carbon.[2,3] However, more than thirty years ago, Rüdorff and Rüdorff[4] had discovered that graphite does intercalate fluorine spontaneously, at room temperature, in the presence of gaseous hydrogen fluoride to yield a first-stage graphite fluoride C_xF with x values ranging from 3.57 to 4.03 which they termed 'tetracarbon monofluoride'. *X*-Ray diffraction data showed that the carbon-atom layers in their C_xF materials were planar and that the F ligands were covalently bound to carbon atoms. Our work has shown that the Rüdorffs' species is part of a more extensive system of true intercalation compounds including hydrofluorides, a second-stage bifluoride $C_{12}HF_2$, and a first-stage compound C_xF ($5 > x > 2$). For much of this composition range the intercalation has proved to be reversible. The materials are sufficiently conductive to facilitate reversible electrochemical oxidation or reduction over the range $C_{2\cdot6}F$ to graphite. The intercalation compounds are synthesised principally by using anhydrous HF and F_2 (2 atm), or alternatively, using electrochemistry to *ca.* $C_{2\cdot6}F$, the latter method being impracticable for $x < 2.6$ owing to their very low conductivity.

With anhydrous liquid HF and gaseous F_2 (2 atm), at 20 °C, graphite† intercalation to the second-stage salt, of approximate composition $C_{12}{}^+HF_2{}^-$, occurs within two hours. A third-stage salt has been observed as a major phase after only several minutes of interaction. A less impure sample of the

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† Union Carbide SP 1, or powdered HOPG interacts in the time stated. For larger HOPG pieces the required interaction times increase markedly with size.

Table 1. Structural data for second- and third-stage graphite bifluorides.

Compound	Hexagonal unit cell parameters/nm	Non-intercalated C-atom sheet to C-atom sheet separation/nm	Intercalated C-atom sheet to C-atom sheet separation/nm	Closest approach of F atoms to C-atom sheets/nm
$C_{12}HF_2$	$a_0 = 0.2456(3)$ $c_0 = 1.888(1)^a$	0.342(4)	0.602(4)	0.28(1)
$C_{18}HF_2$	$a_0 = 0.2456(3)$ $c_0 = 1.281(3)$	0.337(4)	0.607(4)	0.29(2)

[a] For the 00*l* data $l = 2n$, but observed *hkl* reflexions require this doubling of c_0. The stacking sequence of the carbon-atom sheets required to fit the observed line intensities is AB|BA|AB.

third-stage salt has been prepared by interaction of the second-stage salt with graphite in the presence of HF. Its composition lies within the range $C_{18-24}HF_2$. Both of these salts are dark grey solids (similar in appearance to graphite itself). They give sharp *X*-ray powder data to high Bragg angles and the analysis of that data, summarized in Table 1, indicates that the F atoms of the guest species (assumed to be HF_2^-) are approximately mid-way between the enclosing carbon-atom sheets of the host. The distance between adjacent carbon-atom sheets without intercalant is 3.4 Å in each salt, a value not significantly different from that observed in graphite itself (3.348 Å).[5] The identity of the *d* spacings of the *hk*0 diffraction data in these salts with the same data for graphite indicates that the average C–C nearest-neighbour distances within the carbon-atom sheets have not changed significantly with the intercalation. The increased separation of the sheets which accompanies intercalation (*ca.* 2.6 Å) is appropriate for the accommodation of ions with the size of bifluoride (*ca.* 2.6 Å). In accord with the increase in the number of positive holes in the valence band which the $C_x^+HF_2^-$ formulations suggest, each of these salts is an *ab* plane electrical conductor superior to graphite itself. The ratios at 20 °C of the specific conductivity‡ relative to that of the pristine graphite from which the salts were made ($\sigma:\sigma_{\text{graphite}}$) are for second stage, 1.5:1, and third stage, 4.0:1.

All efforts to prepare a first-stage bifluoride have failed.[6] Indeed, as intercalation of fluorine proceeds beyond the second stage, $C_{12}HF_2$, a first stage material, C_xF, is observed to be in admixture with it. In order to define the permissible values for *x* the interaction has been carried out using gaseous HF and fluorine, thus slowing the reaction. From such studies the maximum value for *x* in first-stage C_xF has been found to be between 5 and 6. At this and subsequent points in the reaction sequence the recovery of HF employed in the preparations is almost complete. It appears that the co-operative localisation of charge, by placement of HF_2^- on each side of a carbon-atom sheet, renders the first-stage bifluoride unstable with respect to C_xF and HF. However species such as HF_2^- may continue to have a role in the intercalation of fluorine which continues, over a period of two days, to yield a material of approximate composition C_2F. (The hydrogen content of 'C_2F' could be as high as that required for $C_{12}HF_2{\cdot}4F$ but HF recovery and analytical data indicate that it is probably less.)

Table 2. Some physical properties of C_xF.

Ratio	Parameters of hexagonal unit cell		Resistivity
C/F	a_0/nm	c_0/nm	$\rho/(\Omega\ \text{cm})$
5.2[a]	0.2456(3)	0.522(2)	$>8 \times 10^{-3}$
3.67	0.2459	0.536	8×10^{-1}
3.20	0.2456	0.545	3×10^{0}
2.70	0.2460	0.571	2×10^{1}
2.49	0.2457	0.590	1×10^{3}
2.42	0.2459	0.602	1×10^{3}
2.15	0.2468	0.622	1×10^{7}
1.94	0.2466	0.645	2×10^{7}

[a] Contains some $C_{12}HF_2$ which is highly conductive.

The first-stage C_xF ($5.4 > x > 1.9$) solids are black. Some of their physical properties are set out in Table 2. Although the *X*-ray diffraction data for C_xF are not of the high quality found for the bifluorides they are indicative of hexagonal symmetry and the *hk*0 *d* spacings have nearly the same values as in graphite itself over the full range of *x* values. The *d* spacings for the 00*l* data indicate a smooth increase in I_c (which increases sharply for $x < 3$). The 00*l* data are few however, usually only 001 and 002 being observed. Moreover the powder lines are rather broad. This suggests that the inter-carbon-atom sheet spacing varies somewhat, either as a consequence of occasional guest–guest abutment or variation in the guest concentration within a gallery. The resistivity increases by ten orders of magnitude from graphite to C_2F. The latter is an insulator. For values of $x > 2.4$, however, the conductivity is sufficient to permit electrochemical reduction (using HF containing NaF as electrolyte and graphite as counter electrode) to higher-stage bifluorides.§ Moreover, it has been possible to prepare C_xF with *x* as small as 2.6 by electrochemical fluorination of graphite using HF containing NaF as electrolyte, PbF_2 with lead as the other electrode, and a driving potential of 3.0 V. Open circuit voltages of C_xF against lead have been determined as follows (*x* in parentheses): (3.7), 2.03; (2.7), 2.2; (2.5), 2.38 V.

Although the *d* spacings for the *hk*0 diffraction data for C_xF (Table 2) are nearly the same as in graphite, the relative intensities are not. It appears that the carbon-atom sheets must eclipse one another {in the [001] direction} and that the F atoms must also eclipse carbon atoms. However, the relative weakness of 002 relative to 001 shows that the F atoms cannot be near the mid-point between the enclosing carbon-atom sheets. Evidently each F atom makes a close approach to one carbon atom (on the *c* axis), and the attachment to carbon does not cause that atom to move out of the plane defined by its neighbours.¶

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‡ Measurements made in collaboration with Dr. T. E. Thompson of SRI International, Menlo Park, CA.

§ Some (5—10%) $C_{5-6}F$, identified by its 001 diffraction line, usually remains in the electrochemically reduced C_xF.

¶ The available *X*-ray diffraction data are insufficient to prove the coplanarity of the carbon atoms. If the carbon atoms linked to F atoms are not coplanar with their neighbours the carbon to carbon bond distances projected into the *ab* plane are required to be coincidentally the same as the in-plane pristine graphite distances. This is not the case[3,6] for either $(CF)_n$ or high-temperature C_2F.

Table 3. XPS binding energies for $C_{2\cdot5}F$ and comparison materials.

Compound	C 1s, eV	F 1s, eV	Reference
$C_{2\cdot5}F$	284.6	686.6	Present work[a]
C_2F	$\left\{\begin{matrix}288.5\\290.4\end{matrix}\right.$	689.3	3
$(CF_2)_n$	291.8	689.1	7
LiF		684.9	7
Graphite	284.2		7

[a] The recording of the XPS spectra and the reduction of data were carried out by Dr. K. D. Bomben and Prof. W. L. Jolly.

From the *X*-ray photoelectron spectroscopy (XPS) binding energies given in Table 3 the F ligands of C_xF are seen to be intermediate in character between the F in LiF and F in Teflon, whereas the F ligands in C_2F prepared by Watanabe and his co-workers[3] appear to be more akin to F in Teflon. Evidently the F in $C_{2\cdot5}F$ is semi-ionic in character, yet the bulk of the carbon closely resembles carbon in graphite. The ease with which the F ligand can be moved electrochemically is compatible with the semi-ionic nature of the C–F bond in C_xF. Transmission i.r. spectra obtained from a chip of $C_{2\cdot5}F$ {made thin by grinding perpendicular to the [001] axis} showed a strong absorption between 1050 and 1150 cm^{-1}. This agrees with the observations[8] of Lagow *et al.* for C_4F and is lower in frequency than the C–F stretch noted by Watanabe and his co-workers[3] for $(CF)_n$ and $(C_2F)_n$ (1219 and 1221 cm^{-1}).

Semi-ionic C–F bonding in C_xF is also supported by the long (2.1—2.2 Å) C–F bond lengths suggested by structural models for C_5F, C_3F, and C_2F. In these packing models the carbon- and fluorine-atom van der Waal's radii are taken as 1.67 and 1.33 Å, respectively. The fluorine atoms are distributed evenly over the carbon atoms of the planar eclipsed sheets and the C–F bond length varies to produce the observed *c*-spacing.

It might be that the fluorine is attached to the carbon in three-centre four-electron F–C–F bonds. The bonding molecular orbital for such a three-centre set has the symmetry appropriate for π-bonding to its graphite environment. Also, the non-bonding orbital has no carbon orbital component. The long, highly ionic C–F bonds, the pseudo-graphite inter-sheet bonding, and the marked increase in resistivity,** as the composition C_2F is approached, are thus accounted for.

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6 W. Rüdorff (*Z. Anorg. Allg. Chem.*, 1947, **254**, 319) reported a first-stage hydrofluoride of composition $C_{24}HF_2.4HF$, with an I_c of 8.06 Å, prepared by interaction of graphite with liquid HF and F_2 in quartz apparatus. Such materials have never been observed in the present studies. It may be that the quartz is an essential ingredient for the first-stage material observed by Rüdorff.

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** Although the bonding three-centre CF_2 orbital provides for π-bonding to the three C-atom neighbours, it is unlikely that such a π-system would provide for the passage of a current carrier (hole or electron). The pair of electrons in the orbital, because of its σ-bonding role in binding the two F ligands, is more localized than the π-pair of electrons of the precursor graphite system. The CF_2 and attendant three carbon atoms, C_3CF_2, would therefore act as insulating islands. Composition C_3CF_2 (*i.e.* C_2F) would be an insulator.