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Synthesis of main-group graphite fluoroanion salts with chlorine-assisted oxidation by Lewis-acid fluorides

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Abstract

Graphite intercalation compounds of main-group acid fluorides have been prepared for the first time utilizing Cl_2 as an oxidizing agent The reactions of several acid fluorides (GeF_4, PF_5 and BF_3) with graphite and either Cl_2 or $Cl_2 + HF$ can produce intercalation salts similar to those obtained by the action of elemental fluorine and the acid fluoride on graphite. These reactions have been followed by X-ray powder diffraction, IR spectroscopy and elemental analysis The vacuum-stable products of all these reactions are graphite intercalation salts of fluoroanions containing only traces of chlorine. The reaction enthalpies for the appropriate reduction half-reactions have been calculated and found to correlate closely with the extent of intercalation observed These results are compared with those obtained previously on reactions which generate graphite fluorometallate salts, and are discussed in terms of a simple thermodynamic model for graphite intercalation

Introduction

Graphite fluoroanion salts of main-group metal fluorides have been studied extensively [1, 2] since graphite was found to react with SbF_5 in 1973 [3]. Spontaneous interactions of the metal fluoride and graphite occur for SbF_5 and AsF_5, where the self-disproportionation:

$$2e^- + 3MF_5 \longrightarrow 2MF_6^- + MF_3 \qquad (1)$$

is sufficiently oxidative to facilitate intercalation to provide a 1st- and 2nd-stage salt, respectively. This disproportionation for the fluoride PF_5 is not sufficiently energetic to spontaneously oxidize graphite, but the combination of elemental fluorine with this and other fluoroacids such as GeF_4, BF_3 and SiF_4 become powerful oxidizers for which the appropriate half-reaction is:

$$e^- + MF_y + \tfrac{1}{2}F_2 \longrightarrow MF_{y+1}^- \qquad (2)$$

This combines the fluoride-ion affinity of the acid fluoride ($F^- + MF_y \longrightarrow MF_{y+1}^-$) for which enthalpy values (kJ mol^{-1}) [4] range from -385 (BF_3) to -477 (AsF_5), and the electron affinity of F_2($e^- + \tfrac{1}{2}F_2 \longrightarrow F^-$), which is 251 kJ mol^{-1}. Thus, these acid fluorides with F_2 provide powerfully oxidizing combinations that spontaneously gen-

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erate graphite salts (F_2 with GeF_4 [5], and F_2/BF_3 [6], form 1st-stage salts, but F_2/SiF_4 forms a 2nd-stage salt [7]). A variety of oxidative species, including ClF [8], NO_2^- [9], O_2^+ [10], and Hg_2^{2-} or Hg^{2+} [11] have also been shown to facilitate the formation of graphite fluoroanion salts.

While there is evidence [12] that Cl_2 adsorbed on graphite does interact with it, neither liquid not gaseous Cl_2 alone will bring about the intercalation of chlorine at ambient temperatures. However, Cl_2 can act as an oxidizing agent in the intercalation of metal chlorides·

$$e^- + MCl_v + \tfrac{1}{2}Cl_2 \longrightarrow MCl_{v+1}^- \qquad (3)$$

Well-studied examples include $AlCl_3$ and $FeCl_3$ [1] In addition, the oxidizing action of Cl_2 can facilitate the intercalation of transition element fluorometallate anions into graphite. Intercalation compounds produced by the reaction of Cl_2 with NbF_5 [13], TaF_5 [13] and TiF_4 [14] have been reported. The products of these reactions were found to be pure fluorometallate salts containing only small amounts of chlorine. It seemed likely, therefore, that the interaction of Cl_2 with main-group acid fluorides, if sufficiently oxidative, might also produce fluoroanion salts.

The widespread interest in graphite fluoroanion salts stems in part from the very high conductivities realized [15]. The use of fluorine as an oxidative reactant however, can result in direct C–F bonding, which has been demonstrated to greatly decrease the conductivity of the salts produced [16, 17]. In this respect, new methods of generating these salts without the use of F_2, such as these chlorine-assisted reactions, are of considerable practical interest.

Experimental

GeF_4 was prepared by the cautious oxidation of Ge metal (Aldrich, 99.999% purity) with F_2 (Matheson). PF_5 (Ozark-Mahoning) was purified by trap-to-trap distillation to remove the less-volatile impurities. BF_3 (Ozark-Mahoning), SiF_4 (Matheson) and Cl_2 (Matheson, 99.96% purity) were used as supplied Anhydrous HF (AHF) was dried over SbF_5, which reacts with water to form the low-voltaility salt $H_2O^+SbF_6^-$. The purity of all gaseous reagents was checked by IR spectroscopy prior to reaction. SP-1 graphite (Union Carbide, spectroscopic powder, average particle diameter = 100 μm) was repeatedly flamed to red heat in an evacuated quartz tube prior to use.

Manipulation of volatile materials was carried out in a pre-passivated metal vacuum line equipped with high-pressure metal valves (Autoclave Engineering). Solid products were handled under a dry argon atmosphere in a Vacuum Atmospheres Dri-Lab Reaction cells of 10 ml nominal volume consisted of Pyrex or quartz for low-pressure reactions ($\leq$5 atm total pressure), #316 stainless steel for higher pressure, or FEP Teflon for reactions involving HF, and were capped with Whitey valves.

Reactions were conducted at ambient temperatures for two days or longer and periodically agitated to ensure product homogeneity. Unless otherwise noted, Pyrex, quartz and Teflon reaction cells were placed outdoors and exposed to direct sunlight.

In low-pressure reactions, the volatile acid fluoride ($\cong 2$ atm, 0.8 mmol) and Cl_2 ($\cong 2$ atm, 0.8 mmol) were placed over SP-1 graphite (60–100 mg, 5–8 mmol). High-pressure reactions involved 6 or more atm each of the acid fluoride and Cl_2. In either case, it was confirmed, either by the use of a large excess of the acid fluoride and Cl_2 or by employing several reaction cycles, that the reaction had proceeded fully. When AHF was used as a reagent, a large molar excess was employed such that a liquid phase (typically < 1 ml) was present. IR spectra of the residual gas in the cells were obtained on a Nicolet 5DX FTIR spectrophotometer. Gaseous samples were admitted in low pressure (5–100 torr) to a pre-passivated Monel gas cell fitted with AgCl windows (pathlength = 8 cm). X-ray powder diffraction photographs of the solid products were recorded by the Debye–Scherrer method using Ni-filtered Cu Kα radiation. Samples were examined after brief (10–30 min) venting to a dynamic vacuum and again after long-term ($\cong 24$ h) evacuation.

Results and discussion

The nature of the solid reaction products given in Table 1 were deduced from X-ray powder diffraction photographs, the volatiles having been characterized by IR spectroscopy. Detailed observations follow for each of the systems investigated.

$C_x + GeF_4 + Cl_2$

For low-pressure reaction conditions (see Experimental) *without* exposure to sunlight, 4th-stage salts with I_c (gallery height, defined as the

TABLE 1

Observed stages and gallery heights of fluoroanion salts for reactions involving Cl_2 reduction

Reaction	Lowest observed stage/gallery height (Å)	
	Brief evac.	24-h evac.
$C_x + GeF_4 + Cl_2$	2nd/7.8, 8.1	3rd/7.8
$C_x + PF_5 + Cl_2$		no reaction
$C_x + BF_3 + Cl_2$		no reaction
$C_x + HF + Cl_2$		no reaction
$C_x + GeF_4 + Cl_2 + HF$	4th/8.1	5th/7.9
$C_x + PF_5 + Cl_2 + HF$	2nd/7.8	4th/8.0
$C_x + BF_3 + Cl_2 + HF$	4th/7.2	6th/7.6
$C_x + SiF_4 + Cl_2 + HF$		no reaction

distance along the c-axis between the two C atom sheets enclosing an intercalant layer) = 8.1–8.3 Å were obtained after brief evacuation. Long-term evacuation resulted in a 5th-stage salt ($I_c = 7.8$ Å). The reaction was promoted by exposure to direct sunlight, suggesting that the rate-determining step involved cleavage of the Cl–Cl bond. Under these conditions a metallic blue, 2nd-stage salt was obtained by a low-pressure reaction followed by brief evacuation. X-ray diffraction data indicated that two 2nd-stage phases, with gallery heights of 7.8 and 8.1 Å, were present. The 7.8 Å phase appeared more crystalline, general (*hkl*) diffraction lines being present for this phase only.

IR spectra of the residual gases from these reactions (see Fig. 1) showed two new multiplets, near 750 and 480 cm^{-1}, in addition to the GeF_4 peak at 800 cm^{-1} (ν_3, asymmetric Ge–F stretch). These new peaks were not observed when GeF_4 and Cl_2 were combined under similar conditions without grapite being present, and are coincident to Ge–F and Ge–Cl stretching vibrations*, respectively, of the mixed chlorofluorogermanes

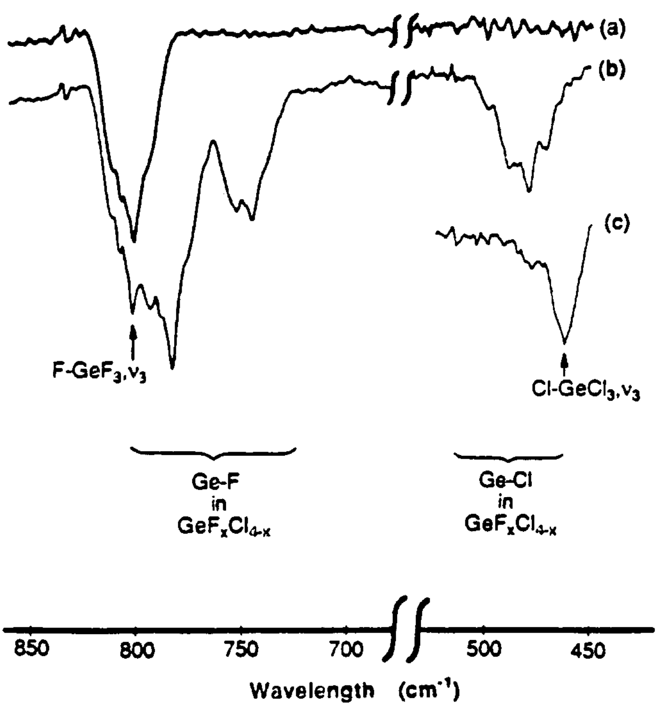

Fig. 1. IR absorbance spectra for (a) GeF_4 (g), (b) the residual gas after reaction of GeF_4 and Cl_2 with graphite, and (c) $GeCl_4$, produced by reaction of GeF_4 (s) with a large excess of Cl_2 (some mixed halides are visible).

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*Ge–F stretches are found in the range 725–800 cm^{-1}, Ge–Cl stretches from 380–480 cm^{-1} [19].

GeF_3Cl, GeF_2Cl_2 and $GeFCl_3$. Ligand exchange between GeF_4, $GeCl_4$ and the three mixed halogenogermanes is known to occur with low activation energy [20].

The relatively large gallery height of 8.1–8.3 Å seen after brief evacuation is in agreement with the polymeric nature of GeF_5^-, which can form a polyanion by fluorine bridging [21]. Elemental analysis of the salt obtained indicates a composition of $C_{24}GeF_{5.1}$, the F/Ge ratio is therefore close to that expected for a GeF_5^- salt. Analysis showed Cl to be absent.

While monomeric fluoroanions can nestle their fluorine ligands [22, 23] into the C_6 rings of the carbon layers, resulting in gallery heights of ~7.6 Å, polyanions such as $(GeF_5)_n^{n-}$ are less likely to be commensurate with the hexagonal carbon lattice and therefore less likely to nestle. They are, therefore, more likely to require the relatively large I_c noted here.

The initial reaction of graphite with GeF_4 and Cl_2 is therefore likely to be:

$$1/n C_x + 2\,GeF_4 + \tfrac{1}{2}Cl_2 \longrightarrow 1/n C_x^{n+}(GeF_5)_n^{n-} + GeF_3Cl \qquad (5)$$

and involves the oxidation of graphite coupled with the following reduction half-reaction:

$$e^- + 2\,GeF_4 + \tfrac{1}{2}Cl_2 \longrightarrow 1/n(GeF_5)_n^{n-} + GeF_3Cl \qquad (T1)$$

A homogeneous phase, noticeably darker in color, was obtained by long-term evacuation (several days at 10^{-3} torr). X-ray diffraction data indicated a 3rd-stage product with small gallery height ($I_c = 7.8$ Å) elemental analysis gave a composition of $C_{30}GeF_{5.4}$. The only volatile was GeF_4. When exposed to fresh GeF_4, the well-evacuated 3rd-stage salt did not change stage, but the gallery height increased to 8.1 Å. These observations are consistent with partial dismutation of a $(GeF_5)_n^{n-}$ polyanion under vacuum to GeF_4, the monomeric anion GeF_6^{2-} and monomeric GeF_5^- each of which nestles. The simultaneous formation of monomeric GeF_5^-, separated by GeF_6^{2-}, fits the elemental analysis:

$$3/n(GeF_5)_n^{n-} \longrightarrow GeF_6^{2-} + GeF_5^- + GeF_4\uparrow \qquad (6)$$

The addition of GeF_4 presumably reconstitutes the polymeric $(GeF_5)_n^{n-}$ to some extent.

$C_x + GeF_4 + Cl_2 + HF$

Since the bond energy difference between the 'HCl' and HF $\{E(\text{H–F}) - E(\text{H–Cl}) = 569-431 = 138\ \text{kJ mol}^{-1}\}$ is not large and HCl is highly volatile, the addition of HF as a reactant might contribute favorably to the formation of fluoroanionic species associated with the intercalation process.

A brief evacuation of the product after two cycles of reaction at low pressure yielded a 4th-stage salt ($I_c = 8.1$ Å). Further, longer term evacuation resulted in a 5th-stage salt ($I_c = 7.85$ Å). An IR spectrum of the residual volatiles from the first reaction shows GeF_4, HF and the absorption bands characteristic of GeF_xCl_{4-x}. Volatiles from the second evacuation showed only GeF_4 and HF. No HCl appeared in the volatiles at any time.

The addition of HF to the $C_x/GeF_4/Cl_2$ system did not influence the oxidation reaction. The presence of mixed chlorofluorogermanes and the absence of HCl in the residual volatiles when HF was included indicates that the reduction half-reaction (T1) is the appropriate one here also. It is possible however, that the half-reaction (T5):

$$e^- + GeF_4 + \tfrac{1}{2}Cl_2 + HF \longrightarrow 1/n(GeF_5)_n{}^{n-} + HCl \qquad \text{(T5)}$$

with the subsequent reaction of HCl with GeF_4 (7):

$$GeF_4 + HCl \longrightarrow GeF_3Cl + HF \qquad (7)$$

could be responsible for the oxidation of graphite in this system. The enthalpy for reaction (7) is (see Table 2) $\Delta H^0{}_{298}$ (reaction T1) $-\Delta H^0{}_{298}$ (reaction T5) $= -493-\{-489(25)\} \cong 0$ kJ mol^{-1}. To test whether reaction

TABLE 2

Calculated enthalpy changes for half-reactions involving the reduction of Cl_2 and generation of fluoroanions[a]

Reduction half-reaction	$\Delta H^0{}_{calc,298}$ (kJ mol^{-1})
$e^- + 2MF_y + \frac{1}{2}Cl_2 \longrightarrow MF_{y+1}{}^- + MF_{y-1}Cl$	
(T1) $e^- + 2GeF_4 + \frac{1}{2}Cl_2 \longrightarrow GeF_5{}^- + GeF_3Cl$	−493[b]
(T2) $e^- + 2PF_5 + \frac{1}{2}Cl_2 \longrightarrow PF_6{}^- + PF_4Cl$	−426[c]
(T3) $e^- + 2BF_3 + \frac{1}{2}Cl_2 \longrightarrow BF_4{}^- + BF_2Cl$	−389 (25)[d]
(T4) $e^- + 2HF + \frac{1}{2}Cl_2 \longrightarrow HF_2{}^- + HCl$	−226
$e^- + MF_y + \frac{1}{2}Cl_2 + HF \longrightarrow MF_{y+1}{}^- + HCl$	
(T5) $e^- + GeF_4 + \frac{1}{2}Cl_2 + HF \longrightarrow GeF_5{}^- + HCl$	−489 (25)
(T6) $e^- + PF_5 + \frac{1}{2}Cl_2 + HF \longrightarrow PF_6{}^- + HCl$	−489 (33)
(T7) $e^- + BF_3 + \frac{1}{2}Cl_2 + HF \longrightarrow BF_4{}^- + HCl$	−456 (25)
(T8) $e^- + SiF_4 + \frac{1}{2}Cl_2 + HF \longrightarrow SiF_5{}^- + HCl$	−364

[a] Fluoride ion affinities (kJ mol^{-1}) for the acid fluorides were taken to be $GeF_4 = 418$ (25) [4], $PF_5 = 418$ (25) [4], $BF_3 = 385$ (25) [4], $SiF_4 = 293$ [7] and HF = 155*.

[b] Calculation based on the average Ge–X bond energy (kJ mol^{-1}) in GeX_4 (Ge–F = 472 [29], Ge–Cl = 339 [30]). Using diatomic bond strengths (Ge–F = 485 (31) (5) [31], Ge–Cl = 343 (21) [32]) gives $\Delta H^0{}_{calc.298} = -485$ (38).

[c] Calculation based on the average P–X bond energy (kJ mol^{-1}), in PX_5 [18] (P–F = 460 P–Cl = 255). Using diatomic bond strengths (P–F = 439 (96), P–Cl = 288 (42) gives $\Delta H^0{}_{calc,298} = -477$.

[d] Based on $\Delta H^0{}_{f,298}$ (BF_2Cl) = −890 (4) kJ mol^{-1} [28].

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*The half-reaction enthalpy for: $e^- + \frac{1}{2}F_2 + HF \longrightarrow HF_2{}^-$, $\Delta H^0{}_{calc.298} = -406$ kJ mol^{-1} [24] is sufficient to generate a 1st-stage bifluoride salt. Oxidation with F_2 actually proceeds to generate the very highly-charged planar-sheet graphite fluorides [2].

(7) is feasible at ambient temperatures, GeF_4 (1 atm) and HCl (1 atm) were allowed to react in a Teflon cell. An IR spectrum of the gases taken after 1 day confirmed the presence of both HF and mixed chlorofluorogermanes. Thus, the possibility of the involvement of HCl in the oxidation process cannot be excluded, although the net oxidation process is still represented by half-reaction (T1). This type of reaction is far less likely for systems involving PF_5 or BF_3 because of the greater difference in M–F and M–Cl bond energies with these halides [18].

An interesting observation is that the evacuated products are of lower stage when HF is not included in the reaction, although the net redox process appears to be similar in each case. This is probably a consequence of the incorporation of neutral HF within the oxidized galleries during intercalation and its subsequent removal upon evacuation. The significant decrease in intercalant volume would be expected to increase the stage of the salt upon this loss of neutral species.

$C_x + PF_5 + Cl_2$

No intercalation was observed in low-pressure reactions in this system. X-ray diffraction data of the solid product showed only a crystalline graphite pattern identical to that of the starting material. High-pressure reactions sometimes yielded 3rd or higher-stage salts (with I_c varying from 7.6 Å to 8.0 Å); in several reactions, however, no interaction was observed. Corrosion of the stainless steel cells was clearly seen after these high-pressure reactions, and IR spectra of the residual gases showed both HF and HCl to be present. No peaks which can be ascribed to a P–Cl stretch were observed in these spectra, although the region from 400 to 600 cm^{-1} is partially obscured by both PF_5 and POF_3 bands.

The hydrogen halides observed in the residual gas after high-presure reactions are apparently generated via the corrosion of the reaction cell (perhaps involving the very rapid attack on hydroxy groups by PF_5: $PF_5 + M\text{–}OH \longrightarrow POF_3 + MF + HF$). The addition of stoichiometric quantities of HF to the PF_5 and Cl_2 combination (discussed in the following section) does result in the oxidation of graphite and the generation of HCl, and it appears that the small amount of HF produced by corrosion is responsible for the intercalation occasionally observed in these reactions.

Since no PF_xCl_{5-x} can be detected in the residual gas, the reduction half-reaction:

$$e^- + 2PF_5 + \tfrac{1}{2}Cl_2 \longrightarrow PF_6^- + PF_4Cl \qquad (T2)$$

does not appear to be sufficiently energetic to provide for the oxidative intercalation of graphite.

$C_x + PF_5 + Cl_2 + HF$

Brief evacuation of the product of low-pressure reactions yielded a blue-black 3rd-stage salt ($I_c = 7.6\text{–}8.0$ Å). IR spectra of the residual gases indicated that HCl was generated in significant quantities. A small peak due to HCl was observed under similar conditions when graphite was not included in the cell, but the peak intensity was far less than in the intercalation reactions. Long-term evacuation resulted in a 6th-stage salt ($I_c = 7.6$–8.0 Å), elemental analyses indicated that Cl was present in the solid product in trace quanities only (0.08% by weight). The half-reaction involved in graphite oxidation is therefore identified as:

$$e^- + PF_5 + \tfrac{1}{2}Cl_2 + HF \longrightarrow PF_6^- + HCl \qquad (T6)$$

After a second cycle of low-pressure reaction and long-term evacuation, a 5th-stage salt was obtained; a 3rd cycle followed by long-term evacuation produced a 4th-stage salt ($I_c = 8.0$ Å). The decrease in the vacuum-stable stage by additional reaction cycles indicates that equilibrium may not have been achieved in the allowed reaction time.

A high-pressure reaction, after brief evacuation, yielded a mixture of 2nd- and 3rd-stage salts. Long-term evacuation then resulted in a 6th-stage salt ($I_c = 8.0$ Å).

The evacuation of graphite fluoroanion salts often results in the increase in stage from $n \longrightarrow n+1$ due to the removal of neutral acid fluorides from the galleries. In these reactions, however, a much greater increase in stage was observed, stages corresponding to $n+3$ and $n+4$ appeared after evacuation. This appears to indicate the initial presence of a high concentration of volatile neutrals in the graphite gallery which are subsequently removed under long-term evacuation. These neutral species have, in most cases, a large dielectric effect and greatly diminish the repulsive interactions of the intercalated anions. The consequences of this effect on lattice stabilization energies will be further discussed below.

$C_x + BF_3 + Cl_2$

X-ray diffraction data of the solid product after low-pressure reaction followed by a brief evacuation showed a crystalline graphite pattern identical to that of the starting material. An IR spectrum of the residual gas indicated only BF_3. Similar results were obtained after a reaction with high-pressure reagents. The reduction half-reaction:

$$e^- + 2BF_3 + \tfrac{1}{2}Cl_2 \longrightarrow BF_4^- + BF_2Cl \qquad (T3)$$

evidently does not provide for graphite oxidation under the experimental conditions applied.

$C_x + BF_3 + Cl_2 + HF$

X-ray diffraction data on the black solid obtained at low-pressures followed by brief evacuation indicate a 4th-stage product ($I_c = 7.24$ Å). A strong IR absorption due to HCl is observed in the residual gas. Long-term evacuation yielded a 6th-stage salt ($I_c = 7.65$ Å). The product remained 6th-stage ($I_c = 7.7$ Å) after a second cycle of reaction followed by long-term evacuation. The reduction half-reaction which accompanies graphite oxidation is therefore identified as:

$$e^- + BF_3 + \tfrac{1}{2}Cl_2 + HF \longrightarrow BF_4^- + HCl \qquad (T7)$$

$C_x + SiF_4 + Cl_2 + HF$

X-ray diffraction data obtained on the product after low-pressure reaction exhibit a diffraction pattern identical to that of crystalliine graphite. An IR spectrum of the residual gas shows SiF_4 and HF only. The reduction half-reaction:

$$e^- + SiF_4 + \tfrac{1}{2}Cl_2 \longrightarrow SiF_5^- + HCl \qquad (T8)$$

does not permit graphite oxidation under the conditions employed.

$C_x + HF + Cl_2$

X-ray diffraction data obtained on the products after low-pressure and high-pressure reactions showed only a crystalline graphite pattern. A flow reaction system with Cl_2 bubbled through a mixture of graphite in liquid HF was investigated; again no reaction was observed, even when the system was irradiated by a mercury vapor UV lamp.

The aim of these reactions was to synthesize graphite bifluoride salts via Cl_2-assisted oxidation. The calculated reduction enthalpy (see Table 2) for the half-reaction:

$$e^- + \tfrac{1}{2}Cl_2 + 2HF \longrightarrow HF_2^- + HCl \qquad (T4)$$

is considerably less exothermic than for half-reactions involving metal fluorides ($\Delta H^0_{\text{calc},298} = -226\ \text{kJ mol}^{-1}$); however, the gallery of the bifluoride salts is smaller than that of fluorometallate salts (≈ 6 Å compared with ≈ 8 Å) and therefore can provide greater lattice energy (see below) [24].

The enthalpy for half-reaction (T4) does not appear to be sufficient to permit intercalation by the bifluoride anion. Although not examined in this study, the generation of the mixed $HClF^-$ anion via:

$$e^- + \tfrac{1}{2}F_2 + HCl \longrightarrow HClF^- \qquad (8)$$

has also been suggested as a route to graphite intercalation compounds [25].

Thermodynamic model

A thermodynamic model has been successfully employed to explain a large number of experimental data on the reactivity of graphite with liquid or gas-phase species [1, 23, 26]. The formation of an intercalation salt by graphite and a reactant (or combination of reactants), and the degree of intercalation which can be achieved, is related to four enthalpic terms as indicated in Fig. 2. (The model is, however, restricted to cases where the entropic terms for the intercalation reactions are similar.) In the case of oxidative intercalants, these are (1) the decrease in van der Waals interaction energy between carbon sheets that are separated by intercalant, (2) the energy required to remove electrons from the carbon

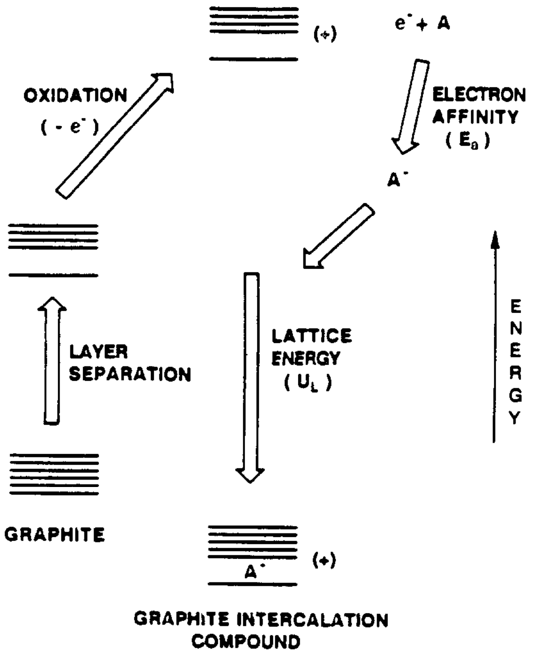

Fig. 2. A Born–Haber cycle for the oxidative intercalation of graphite.

sheet π-system (this is sometimes called the work function and its magnitude depends on the positive charge borne by carbon), (3) the electron affinity (or oxidizing strength) of the reactant(s) involved in graphite oxidation, and (4) the lattice stabilization energy of the intercalation salt produced. Terms (1) and (2) are dependent on the nature of the graphitic carbon sheets, and should not be affected by the particular reactant(s) utilized. It follows that the degree of intercalation attained can be related to the oxidizing strength of the reactants and the lattice energy of the salt produced.

A set of reactions of graphite with closely-related oxidants, the 3rd-row transition-metal hexafluorides (MF_6; M = W, Re, Os, Ir, Pt), was examined earlier [1, 23]. In these intercalation reactions:

$$C_x + MF_6 \longrightarrow C_x{}^+MF_6{}^- \tag{9}$$

where the intercalant species ($MF_6{}^-$) are of like charge and similar effective size, the lattice stabilization energies of the graphite salts must be nearly the same. The intercalation reaction should therefore be dependent on a single energetic term, the oxidizing strength of the metal hexafluoride. Experimental results obtained on this series of reactions support this conclusion. When graphite is exposed to WF_6 (electron affinity = 389 kJ mol^{-1}) it does not react, ReF_6 (e.a. = 447 kJ mol^{-1}) is either unreactive or produces a high-stage (*i.e* slightly intercalated) salt, and the more oxidatively-robust hexafluorides of Os, Ir and Pt produce highly-intercalated, 1st-stage salts.

Graphite salts of the main-group acid fluorides, unlike those of the 3rd-row transition-metal hexafluorides, are not immediately seen to be a related set. Species of different geometries are involved, and the metal tetrafluorides may form either mono- or divalent anions, MF_5^- or MF_6^{2-}. Nevertheless, a strong correlation between oxidizing strength and degree of intercalation reaction has been noted with these intercalants [1, 23, 25]. A closer look at the lattice stabilization energies of these salts will be helpful in explaining this correlation.

The lattice energetics of graphite fluoroanion salts primarily consist of the electrostatic attraction between the positive carbon sheet and intecalated anions and the repulsion of neighboring anions within the same gallery. The gallery height of a graphite salt indicates the distance separating the positive carbon sheets from the anions, and therefore can be correlated to the attractive component of the lattice energy. Anion–anion repulsion depends on the concentration of anions within the intercalated galleries as well as the presence of neutral intercalants (which can act as dielectric spacers and mitigate repulsive forces).

Accurate structural and compositional data have been obtained for several graphite fluoroanion salts. It is notable that gallery heights for all graphite fluoroanion salts, except fluoroborates*, are nearly identical. Prior to removal of the neutral species under vacuum, gallery heights are close to 8.0 Å and decrease by 0.2–0.4 Å upon evacuation and removal of neutral species from the galleries. The approximate constancy of the gallery height is a consequence of the effective thickness of octahedra or tetrahedra being that of a double layer of close-packed F-ligands, thus the thickness of an octahedron is ≅ 4.7 Å and tetrahedron ≅ 4.4 Å [22, 27]. The compositions of several vacuum-stable (neutral-free) graphite fluorometallates have been determined, and again show a marked similarity. These data indicate that lattice energies are similar for many main-group fluoroanion salts of similar composition and stage. As a result, a single factor dominates the degree of intercalation obtained in graphite fluorometallates: it is the oxidizing power of the reactant(s). It should also be noted that the gallery height and concentration of intercalant within the gallery are not greatly affected even if the stage of the salt is changed. It follows that the lattice energy *per intercalant anion* may be considered to be relatively independent of the nature of the fluoroacid mono-anion, or the stage of the salt produced.

Calculated reduction enthalpies for the half-reactions explored in this study are provided in Table 2. In Fig. 3, a pictorial summary of these

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*The influence of lattice energetics has been observed [27] in the reaction of $C_x^+PF_6^-$ with BF_3. Although the fluoride-ion affinity of PF_5 exceeds that of BF_3 by 35 kJ mol^{-1}, a quantitative displacement to produce the fluoroborate salt and PF_5 occurs. The smaller gallery height and consequent superior lattice stability of the fluoroborate salt must provide the driving force for this displacement.

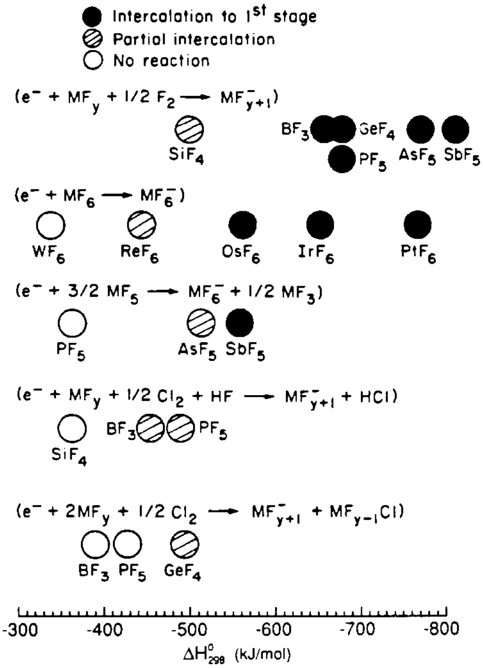

Fig. 3. Reduction enthalpy and degree of intercalation realized for reactions involving the insertion of fluoroanions into graphite.

results, along with those obtained previously [23] on the intercalation of metal fluorides and metal fluorides with F_2, demonstrates the excellent correspondence of the new results with earlier work. The new information more clearly defines a range of reduction enthalpies, lying roughly between -439 and -502 kJ mol^{-1}, where partial intercalation of graphite by fluoroanions occurs. Reagents more oxidative than these will form fully intercalated (1st-stage) compounds, those with reduction enthalpies less exorthermic than -439 kJ mol^{-1} do not react with graphite. The simple model of an oxidative threshold towards graphite intercalation has thus been expanded by the present study.

A refinement of this thermodynamic model will require a quantitative assessment of the effect of the nature of the intercalants on lattice energetics. A significant lattice energy effect noted in this study is the dielectric effect of neutral species within the galleries which must considerably benefit the lattice energy, by reducing the anion–anion repulsion.

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