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INTERCALATION OF HALOGEN FLUORIDES INTO GRAPHITE

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ABSTRACT

IF_7 intercalates into graphite accompanied by the partial fluorination of the graphite host. The intercalated species was identified as IF_5 by IR and ^{19}F nmr spectroscopies. Mass spectrometric analyses of the gases evolved from the intercalate showed only IF_5 and fluorocarbons. Iodine pentafluoride intercalates only in the presence of HF, yielding a compound with the stoichiometry C_8IF_5 and no fluorination of the graphite host. Careful elimination of even traces of HF resulted in no intercalation. Evolved gas analysis showed that the only species recovered from the intercalation was IF_5. The remaining interhalogens, ClF_5, ClF_3, BrF_5 and BrF_3 all intercalate into graphite with extensive fluorination of the lattice. In the case of these four compounds, the intercalate proved to be more difficult to characterize, e.g. stoichiometry was often variable, and ^{19}F nmr yielded resonances that did not agree with any known halogen fluorides. Thermal decomposition of these intercalates showed little or no gas evolution until relatively high

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*Permanent Address: Hebrew University, Jerusalem, Israel temperatures were reached, whereupon Cl_2 or Br_2 was evolved, followed by fluorocarbons.

INTRODUCTION

The ability of graphite to form compounds with volatile inorganic fluorides has been amply demonstrated in recent years [1]. Classes of compounds which have been subjected to particularly intensive investigations are the noble gas fluorides [2-6], the halogen fluorides [7,8], as well as the fluorides of the main group V elements, AsF_5 and SbF_5 [9-12]. The intercalation compounds of the latter two have drawn special attention, because it has been shown recently that their graphite intercalates display high electrical conductivity on par with metallic conductors such as copper and silver [11,13].

In the case of the noble gas compounds it has been shown that some (XeF_6 and XeF_4) intercalate with reduction of the xenon to the next lower valence state [14], others intercalate with little or no reduction ($XeOF_4$), while XeF_2 appears to intercalate only in the presence of HF [5,15]. In the case of the halogen fluorides, it is not clear to what extent HF is required for intercalation to occur. Some (BrF_3 and IF_5) have been reported to intercalate in the neat state [7], while with others (ClF_3) acids such as HF [8] and SbF_5 [9] have been used to promote intercalation.

We have now investigated the intercalation with graphite of several halogen fluorides, particularly IF_5 and IF_7. In a previous study [16], the behavior of intercalation compounds with noble gas fluorides as well as with AsF_5 was studied by mass spectrometry. The present study includes the application of this technique to the halogen fluoride intercalates as well as that of antimony pentafluoride.

EXPERIMENTAL

The intercalation compounds were prepared by exposure of GTA grade Grafoil from Union Carbide Co. or spectroscopic grade powder (100 mesh) from United Carbon Products (U.P.), or native graphite from BDH to the vapors of the volatile fluoride. Details of procedure and apparatus have been given elsewhere [16]. The inorganic fluorides were obtained from the following suppliers: IF_7 - Alfa Inorganics, IF_5 and BrF_5 - the Matheson Co. and SbF_5 - Ozark-Mahoning.* Particular attention was devoted to purification of these materials, especially from HF. Purity and absence of HF were checked by mass spectrometry.

Mass spectra were obtained by generating a modulated molecular beam which traversed the mass spectrometer ion source. Details of the molecular beam source and sample loading technique have been given in previous publications [16]. The quadrupole mass spectrometer on the instrument described in reference [18] has been replaced with a 21 cm radius magnetic instrument, with a constant resolution of 1000. All other conditions and procedures for obtaining mass spectra are essentially the same as those reported in reference 16.

Fluorine NMR measurements were done on a Varian WL 112 spectrometer with radiofrequencies between 15 and 35 MHz supplied by an external frequency synthesizer. A 35 Hz sinusoidal modulation of the magnetic field was employed, with peak-to-peak amplitudes less than or equal to 25% of the observed signal linewidth. Chemical shifts were measured with respect to an external CF_3COOH standard.

Where applicable, infrared spectra of intercalated Grafoil samples were performed on a Perkin-Elmer Model 283 spectrophotometer using the ATR technique with KRS-5 windows.

The determination of the elemental composition of the samples presented problems which were not completely solved in all cases. The intercalates were subjected to microchemical analysis. Although in most cases duplicate analyses yielded reproducible results, the determination of halogens

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*ClF_5 was prepared in this laboratory according to a method described in the literature [17].

other than fluorine remained unsatisfactory. This situation may result from the peculiar nature and reactivity of the intercalates. In the case of reactions with IF_7, the compositions of the intercalate could be determined independently by the following procedure. The intercalation of IF_7 into graphite proceeds with simultaneous reduction to IF_5 according to the scheme

$$xC + yIF_7 \rightarrow C_x(IF_5)F_{2y} + (y-1)IF_5$$

The amount of IF_5 formed in the reaction could be determined by weighing, after separating it from the excess IF_7 left after the reaction by fractional distillation through a cold trap at -23°C (CCl_4 slush). The value 2y corresponding to additional fluorine bonded covalently to the graphite can thus be determined, while the amount of IF_5 intercalated in the graphite is determined by subtracting the weight of 2yF from the total weight increase of the graphite. Separate experiments showed that no fluorine is lost as either the element or as fluorocarbons. The identity of the intercalated species as IF_5 was confirmed by infrared and ^{19}F NMR spectroscopies. In cases where intercalation proceeds with little or no reduction, the composition is best determined by assuming that the weight increase is solely due to the intercalating species, as is true for IF_5. The compositions of intercalates formed by reaction of graphite with BrF_3, BrF_5, ClF_3, and ClF_5 have not been fully resolved to our satisfaction.

RESULTS AND DISCUSSION

Intercalation of IF_5

An intercalate of graphite with IF_5 of composition $C_{18}IF_5$ has been previously reported [7]. Later work [2] appeared to confirm this, suggesting that a first stage compound of approximate composition $C_{8.7}IF_5$ existed as well.

It appears now that IF_5 intercalates only in the presence of at least traces of HF. Prolonged contact of graphite with IF_5 that was free from traces of HF yielded little or no reaction. If traces of HF are added, reaction occurs after a short induction period. The reaction is accompanied by swelling of the graphite and the development of a small amount of iodine color. However, most of the weight increase can be attributed to IF_5. The samples lost weight slowly at room temperature. If extrapolated to zero pumping time, a composition C_8IF_5 is obtained. Figure 1 shows the evolution of IF_5 from two intercalates as well as weight loss as a function of temperature. There was no detectable evolution of fluorocarbons, nor of HF, H_2 and F_2, although HF was necessary to initiate the reaction. The absence of fluorocarbons shows that little reduction of IF_5 occurs, in agreement with the liberation of only minor amounts of iodine. The mass spectra indicate that IF_5 evolution occurs in discrete steps, which probably correlate with passage to higher stage compounds.

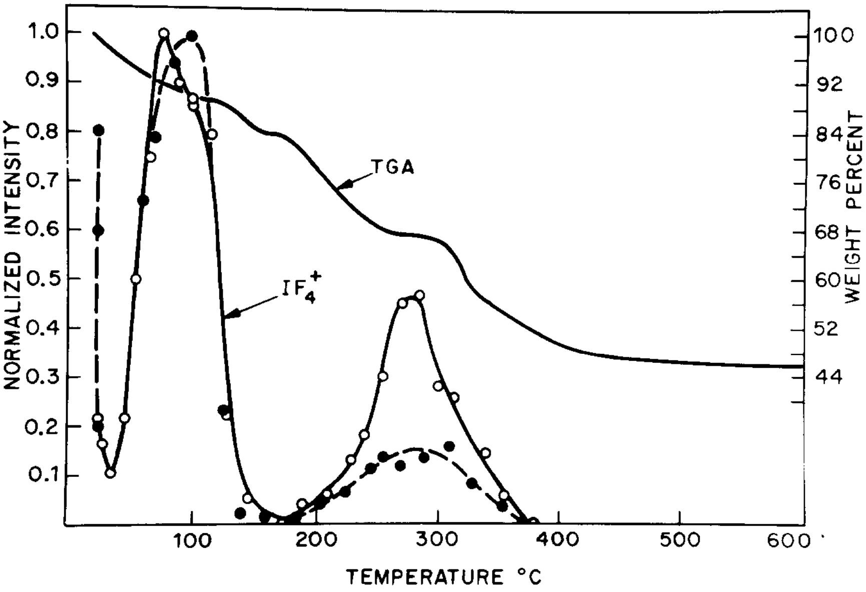

Fig. 1. Ion currents characteristic of gaseous species evolved from the C/IF_5 intercalate as a function of temperature. Two different sample curves are shown. The TG curve is also shown.

Samples of graphite powder and of Grafoil gave the same results. Attempts to identify the intercalated species more directly by ^{19}F NMR led to inconclusive results. A new signal appears for the intercalate at $\delta_{CF_3COOH} = (-146 \pm 10)$ ppm. The narrowness of the peak indicates motional narrowing due to translation and/or rotation. The chemical shift does not correspond to any known pentavalent iodine fluoride species. Thus, IF_5 has a doublet-quintet pattern at $\delta_{CF_3COOH} = -86$ and -136 ppm [19], while the IF_6^- ion has been reported to have shifts at +33.5 and -80 ppm [20]. It is interesting to note, however, that in many complexes of IF_5, such as with $HCON(Me)_2$ [21] and in IF_5-py [22], only single sharp resonances have been observed in the IF_5 doublet region. These have been attributed to exchange collapse [22]. No direct clues as to the nature of the intercalated species exist, except for the evolution of IF_5 in the mass spectrum near ambient temperatures. The NMR signal could be due to exchange with small amounts of IF_6^- formed upon liberation of the iodine.

Intercalation of IF_7

In contrast to IF_5, IF_7 intercalates into graphite in the absence of HF. The stoichiometries of the resulting intercalates vary considerably and are listed in Table I. They were calculated on the basis of the indirect analysis described above. It is evident that in the process of intercalation IF_7 partially fluorinates the graphite liberating IF_5, some of which is retained in the lattice.

Although there is no significant variation in the stoichiometry of graphite powder or of Grafoil, there are marked differences in the appearance of the intercalates. Powder intercalated with IF_7 is almost unchanged in appearance, but the shiny black Grafoil turns completely white upon intercalation. This is reminiscent of graphite fluoride which becomes lighter with increasing fluorine content, finally becoming completely white at $CF_{1.12}$ [23]. The stoichiometry of carbon to excess fluorine in our product is approximately $CF_{0.5}$, however.

TABLE I

Reactions of graphite with IF_7

Type Graphite	Wt. Taken (gm)	Wt. Increase (gm)			Stoichiometry
		Due to F_2	Due to IF_5	Total	
Grafoil	0.1967	0.1400	0.1431	0.2740	$C_{27.1}IF_{17.2}$
Powder (U.C.)	0.2930	0.2138	0.1545	0.3683	$C_{35.1}IF_{21.2}$
Grafoil	0.1784	0.1367	0.1537	0.2904	$C_{21.5}IF_{15.4}$
Grafoil	0.3148	0.2813	0.1726	0.4539	$C_{33.7}IF_{24.0}$
Grafoil	0.3183	0.2549	0.1913	0.4462	$C_{30.8}IF_{21.6}$
Powder (BDH)	0.428	0.1466	0.354	0.501	$C_{22.4}IF_{9.8}$
Powder (BDH)	0.387	0.1399	0.321	0.461	$C_{22.3}IF_{10.1}$
Powder (BDH)	0.472	0.264	0.345	0.609	$C_{25.3}IF_{13.9}$

X-ray diffraction patterns of the intercalate show the complete absence of the strong 3.36 Å line of graphite and the appearance of a new pattern with d-spacings at 6.2 Å and 4.0 Å.

The identity of the intercalated iodine species has been determined by ^{19}F nmr and infrared spectroscopies. A broadline nmr spectrum [14] shows two signals: S_1 = -86 ppm and S_2 = -128 ppm with an intensity ratio $S_1/S_2 \approx 4$. These are very close to those observed for neat IF_5 [19]. Most of the observed features of the infrared spectrum can also be assigned to IF_5 and are given in Table II. The spectrum is a property of the bulk matter as it is identical to one obtained from an interior face of a split foil. The IR spectrum is shown in Figure 2.

Table II

Infrared spectrum of $C_{33.7}IF_{24.0}$

Frequency (cm^{-1})	Assignment	Reference
310	IF_5 $\nu_3(a_1)$	24
370	IF_5 $\nu_8(e)$	24
470	IF_5 $\nu_5+\nu_9$? $\nu_6+\nu_9$	24
563	IF_5 $\nu_4(b_1)$	24
620 650	IF_5 $\nu_7(e)$	24
700	IF_5 $\nu_1(a_1)$	24
770	IF_5 $\nu_4+\nu_8$?	24
	C-F deform	26
1110	C-F sym. str.	23
	C_4F ?	23
1215	C-F tert C-F str.	23

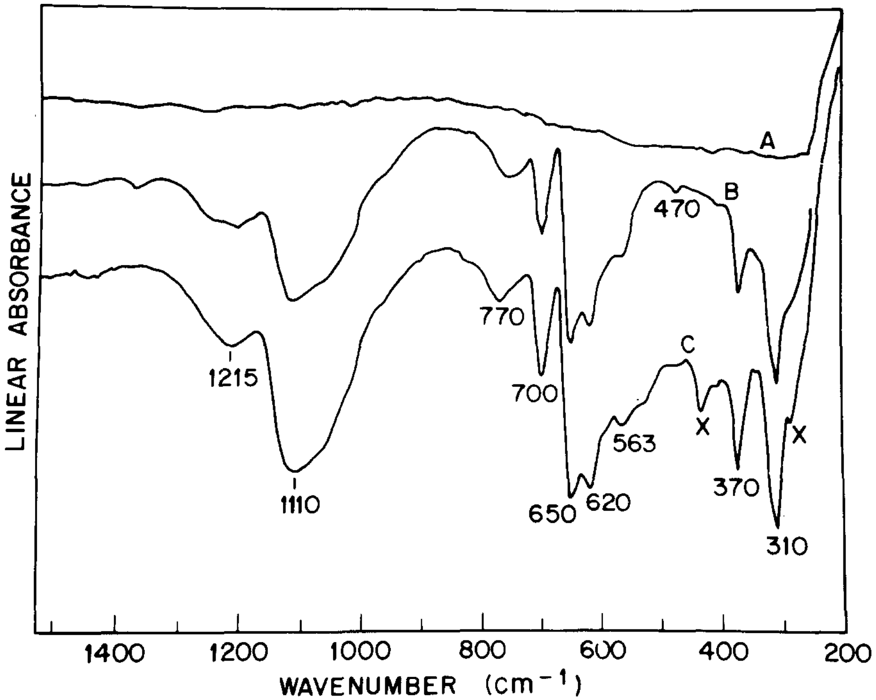

Fig. 2. ATR-infrared spectra of C/IF_7 intercalate. A. Original graphite; B. Intercalate; C. Intercalate after heating in vacuum at 350°C. The peaks labeled X resulted from reaction with the KRS-5 windows.

Both frequencies and relative intensities correspond closely to those observed for a spectrum of the vapor [24]. It is also noteworthy that the spectrum persists even for a sample heated in vacuum for 16 hours at 350°. This is consistent with results of an evolved gas analysis (EGA) as a function of temperature (Fig. 3). It is evident from comparison with Figure 1 that IF_5 evolution from the IF_7 intercalate has a markedly different temperature dependence than does the IF_5 intercalate. The higher temperature required to drive off the IF_5 (Fig. 3) is probably due to reduced mobility in the fluorinated host. Since fluorinated graphite has covalently bonded fluorines pointing both above and below the graphite skeleton, these could present a steric barrier to migrating IF_5, though permitting rotation, thus accounting for a relatively narrow line width in the nmr spectrum. Mass spectra of evolved gases showed no traces of IF_6^+, which is one of the

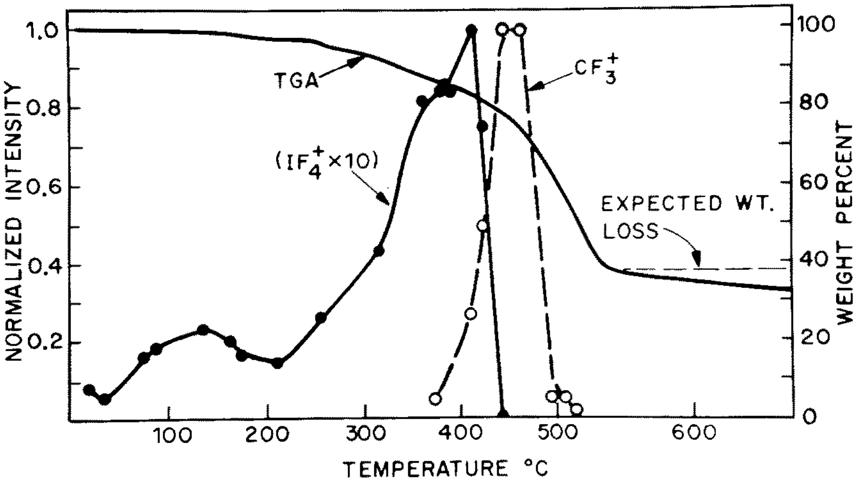

Fig. 3. Ion currents characteristic of gaseous species evolved from the C/IF_7 intercalate as a function of temperature. The TG curve is also shown.

dominant species in an IF_7 mass spectrum. Fluorocarbon evolution occurred in the same temperature range as it did for the intercalates of binary noble gas fluorides [6,16]. The cracking pattern of the fluorocarbons was essentially identical to that obtained from graphite fluoride [25].

Intercalation of other halogen fluorides

A number of intercalates have been prepared with other halogen fluorides. These have been less well characterized, particularly because their compositions are uncertain on account of the difficulties encountered in their analysis.

Intercalation of ClF_5

Chlorine pentafluoride reacts readily with graphite with simultaneous intercalation and fluorination. Chemical analyses were not reproducible, but a typical stoichiometry was $C_{7.6}ClF_{4.3}$. X-ray patterns showed the absence of the characteristic strong graphite line at 3.36 Å and the appearance of a new pattern with d-spacings at 7.5 Å, 5.7 Å, and 2.1 Å. While the intercalated powder is grayish in appearance, the intercalated Grafoil becomes almost white as is the case with IF_7. The ClF_5 intercalate is, however, considerably more reactive, and hence infrared spectra obtained by the ATR method were less reliable because of reaction with the KRS-5 windows. Strong peaks were observed at 1050 and 1220 cm^{-1} in the C-F region. Other bands were observed at 320 (s), 640 (s), 710 (m) and 740 (w) cm^{-1}. The spectrum is somewhat reminiscent of ClF_3 [27], and in fact, mass spectra taken as a function of temperature support the presence of ClF_3 in the intercalate. Gas evolution did not occur at ambient temperature but between 60° and 115° weak signals due to Cl_2 and ClF_3 were observed. Gas evolution resumed only at 180°, at which point Cl_2 and ClF were observed. The evolution of ClF was not sustained, but the molecular chlorine signal continued to intensify as the temperature increased, reaching a maximum between 310° and 380°C. Fluorocarbons were evolved beginning about 320°C and continued to 500°. The ^{19}F nmr spectrum showed a strong signal at $\delta = (-180\pm20)$ ppm. While the signal cannot be reconciled with any known chloride fluorides [28], it is of interest that above room temperature ClF_3 exhibits a broad singlet at about -140 ppm, this being due to exchange collapse [29].

Intercalation of ClF_3

Chlorine trifluoride reacts with graphite with simultaneous partial fluorination of the graphite lattice. Chlorine monofluoride is released in the process. The products do not differ markedly in appearance from the original graphite. Analyses were not reproducible, but a typical stoichiometry was $C_{31}ClF_8$. The product was very reactive, and infrared measurements did not yield meaningful results. Examination of mass spectra as a function of temperature showed that chlorine evolution began at about 80°C. This Cl_2 evolution increased steadily to a maximum at $\sim$370°C, decreasing rapidly thereafter. Fluorocarbon emission began at around 350°C, reaching an intense maximum near 425°C. No chlorine fluoride species were observed at any time in contrast to the thermal degradation of the ClF_5 intercalate.

Although ClF_3 intercalation in the presence of HF had been reported previously [8], it is evident that HF is not necessary for intercalation to occur. The intercalated species is probably in the form of a fluoride, because the existence of a graphite/chlorine compound is still highly questionable [1]. It is also unlikely that elemental chlorine would persist to the high temperatures at which Cl_2 has been observed in the mass spectra.

Intercalation of BrF_5

Reaction of graphite with BrF_5 was accompanied by evolution of bromine vapor. The resulting materials are dark green in color and X-ray patterns show the absence of the 3.36 Å line of graphite and appearance of a new pattern with d-spacings at 7 Å, ∿5 Å and 2.1 Å. Analytical results were relatively reproducible and gave approximate stoichiometries $C_{25}BrF_{12}$. The compound is relatively reactive and it was not possible to obtain an infrared spectrum. ^{19}F nmr spectra showed a strong signal at (-205±20) ppm which differs from that of any known bromine fluoride species. TG and EGA analyses showed that neither weight loss nor gas evolution occurred till about 350°C. Molecular bromine was then evolved and continued to intensify until 440°C. At this point gas evolution was so intense that the experiment was discontinued. No species other than Br_2 and fluorocarbons were observed at any point.

Intercalation of BrF_3

Bromine trifluoride has been previously reported to intercalate with graphite giving a compound of stoichiometry $C_{8.9}BrF_3$ [7]. Our results indicate that a similar stoichiometry is indeed obtained based solely on weight increase of the graphite. However, considerable amounts of bromine are evolved upon intercalation. This, combined with microchemical analyses, show that excess fluorine is present in the graphite. Although results were not reproducible, a stoichiometry

$C_{24}BrF_{13}$ may be considered representative. This is not very different from the products obtained with BrF_5. In fact, mass spectrometric examination of species evolved as a function of temperature shows almost identical results as those obtained with the BrF_5 intercalates. This is confirmed by TG analyses of the intercalates which do not begin to lose weight substantially until about 350°. This is in sharp contrast to previous reports that BrF_3 is completely desorbed at about 180° [7]. A ^{19}F nmr spectrum gave a signal at (+15±20) ppm, strongly shifted from that of neat BrF_3 (-54.3 ppm). It appears that the products in these two studies are not identical and experimental conditions including types of graphite used may play a decisive role in governing the course of intercalation.

Intercalate of SbF_5

The intercalation of SbF_5 has been treated in previous publications [12,13,30]. For the sake of completeness, we report here results of a mass spectrometric study as a function of temperature, similar to previous reports on the AsF_5 intercalate [16]. As in the former case, SbF_5 appears to intercalate with very little reduction. This appears to contradict results of Mössbauer measurements (31) which show the presence of unspecified amounts of Sb(III) in intercalated SbF_5. Experience with other compounds, where intercalation has been accompanied by reduction, has shown that in such cases fluorocarbons are emitted at higher temperatures. This is not observed for SbF_5. Moreover ^{19}F nmr spectra [14] show a single resonance line at (+42±7) ppm in the Sb(V) region, but not in the Sb(III) region. On the basis of the above results it is estimated that as in the case of AsF_5 less than 5% of the trivalent compound is formed during the intercalation. Figure 4 shows the evolution of SbF_5 from C_6SbF_5 (powder). The sample had previously been brought to constant weight by pumping on it overnight. The SbF_4^+ intensity vs. temperature indicates three stages of intercalation. Dimeric ions, $Sb_2F_{10}^+$, were easily detected at the first maximum (60°).

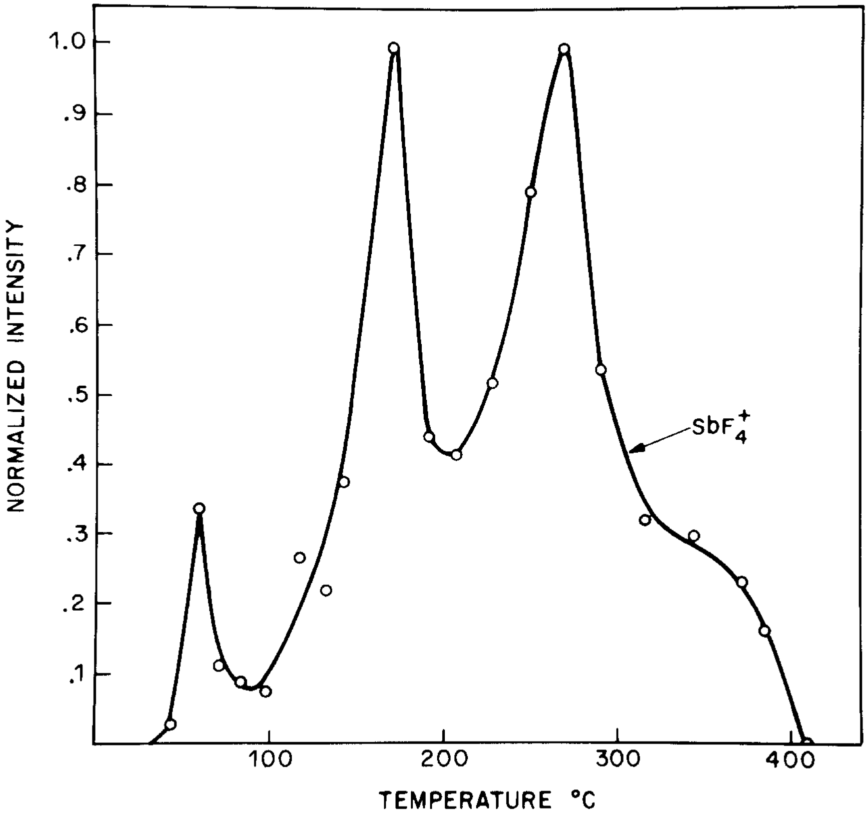

Fig. 4. Ion currents characteristic of gaseous species evolved from C_nSbF_5 intercalate as a function of temperature. Dimer ions are not shown (see text).

Moreover, the intensity ratio of the dimers to monomers was the same (0.4) as that observed for SbF_5 vapors in equilibrium with liquid SbF_5. Above 100°, only monomeric ions were observed. It is not possible to tell whether the associated species were actually intercalated or whether they form upon release from the graphite.

In summary, it may be stated that, except for the IF_7 intercalate, the characterization of intercalated species of other halogen fluorides remains highly elusive.

Since current theories of the ^{19}F nmr chemical shift are not as yet on a firm theoretical foundation [28], it would clearly be speculative at best to interpret ^{19}F nmr spectra of the intercalates. However, since the new signals observed are relatively narrow, it is probable that they arise from fluorines bonded to halogen rather than fluorines bonded covalently to the graphite matrix.

It would be highly desirable to bring other physical techniques such as Mössbauer and NQR spectroscopies to bear on these compounds in attempts to elucidate their nature.

The rule established with the xenon fluoride intercalates [16] that the less reactive species do not intercalate at all or only in the presence of HF, appears to hold also for the halogen fluorides. Such is the case with IF_5 as well as ClF. The latter also intercalates only in the presence of HF. On the other hand, we have found that even concerted action of PF_5 + HF on graphite does not lead to intercalation.

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