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MASS SPECTROMETRY OF GRAPHITE INTERCALATION COMPOUNDS
OF BINARY FLUORIDES OF XENON, XENON OXIDE TETRAFLUORIDE
AND ARSENIC PENTAFLUORIDE

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ABSTRACT

Thermal decomposition of the intercalates of XeF_6 , XeF_4 , XeOF_4 and AsF_5 in graphite has been studied using a molecular beam source mass spectrometer. The product of the hydrolysis of the intercalate of XeF_6 has also been examined. The species liberated at low temperatures ($T < 150^\circ\text{C}$) may be either the ones originally intercalated (XeOF_4 , AsF_5) or the next lower oxidation state (XeF_4 from XeF_6 , and XeF_2 from XeF_4). At higher temperatures (200-400°C) the intercalated XeF_4 , XeF_2 or XeOF_4 attack the graphite lattice, and evolve large quantities of xenon, and subsequently fluorocarbons and/or carbonyl fluoride. In contrast, the intercalate of AsF_5 evolves AsF_5 as the dominant gas over most of the temperature range, with a much lower degree of fluorination of the graphite lattice. The hydrolysis product of the XeF_6 intercalate was similar to the intercalate of XeOF_4 , but the evidence indicates

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that the hydrolysis proceeded well beyond XeOF_4 . The extent of attack upon the graphite lattice correlates well with the oxidizing or fluorinating ability of the intercalated compound

INTRODUCTION

Graphite intercalation compounds with xenon tetrafluoride,¹ xenon hexafluoride,² and xenon oxide tetrafluoride³ are known. While these three compounds react directly with graphite, xenon difluoride intercalates only in the presence of HF to form layer compounds of variable composition containing both XeF_2 and HF.⁴ Wide line NMR measurements using the ^{19}F nucleus as a probe have shown that in the case of xenon tetrafluoride and xenon hexafluoride intercalates, the main species intercalated are actually xenon difluoride and xenon tetrafluoride, respectively. Similarly, Mössbauer spectra have shown that antimony pentafluoride and antimony pentachloride react with graphite with partial reduction to Sb(III) ,⁵ but it is not clear whether the reduced species is intercalated. A graphite intercalation compound of arsenic pentafluoride is also known,⁶ but in this case ^{19}F NMR results show the intercalated species to be pentavalent. The identity of the central atom oxidation state thus appears to be a general problem not limited to intercalated fluorides. Even the "classical" graphite/ FeCl_3 system has been subject of considerable controversy, different physical methods having given widely divergent results as to the $\text{Fe(II)}/\text{Fe(III)}$ ratio of the intercalated species.^{7,8}

Although thermogravimetric data on the xenon fluoride intercalates are available and have been used to deduce the stoichiometry of the various stages, a detailed study of the species evolved as a function of temperature has not yet been reported. Such a study would be helpful to give support to the NMR data and to throw additional light on the chemical processes accompanying intercalation and exintercalation. Particularly, species evolved at or near room temperature would be expected to be characteristic of the oxidation state of the intercalated species. No such claim can be made regarding species evolved at higher temperatures, but these would give additional information on the relative fluorinating powers of compounds vis-a-vis graphite. Previous crude attempts to identify some of the gases evolved by trapping them led to misleading results in some cases. Positive ion mass spectra of the binary xenon fluorides and xenon oxide tetrafluoride have recently been measured using a molecular beam source designed especially for reactive fluorides.⁹ Since the electron impact cracking patterns of these compounds are thus available,^{10,11} the task of analyzing the gases evolved during the thermal decomposition of the intercalates is greatly facilitated.

EXPERIMENTAL

Intercalation compounds were prepared by the exposure of GTA grade Grafoil from the Union Carbide Co. or spectroscopic grade powder (100 mesh) from United Carbon Products to the vapors of the desired compound. Details of

the procedure and preparative apparatus are given in the literature.¹⁻⁴

Samples were loaded into monel ovens in a dry box; the ovens were capped with a 0.02 cm dia. orifice and transported to the molecular beam apparatus without exposing the samples to the atmosphere. The molecular beam path length was 21 cm from the oven orifice to the center of the mass spectrometer ion source. The molecular beam generated by heating the samples was modulated at a frequency of 250 Hz.¹⁰ Phase sensitive detection of the modulated molecular beam allows one to determine whether the beam is composed of more than one component. For example, if both Xe and XeF_4 are being liberated from an intercalate, the Xe^+ ion will be out of phase with the XeF_3^+ ion.

An immediate check for evolution of gases at ambient temperature was always made prior to heating. The ovens were generally heated at a rate of 2°C/min. The mass spectrometer is known to be capable of detecting gases in the oven at pressures as low as 0.02 Torr. The electron energy was held at 60 eV unless the isotopes of doubly charged xenon interfered with any low molecular weight species (COF_2^+ , $m/e = 66$). The electron energy was then reduced to 35 eV and appropriate increases in emission and multiplier voltage were made to keep the total sensitivity at the 60 eV level.

RESULTS AND DISCUSSION

Plots of the signal intensity of an ion characteristic of the gaseous species evolved as a function of oven temperature

are shown in Figures 1 through 4 for the intercalation compounds of XeF_6 , XeF_4 , XeOF_4 with graphite as well as the hydrolysis product of $\text{C}_{19}\text{XeF}_6$. The choice of each ion used to represent a gaseous species was made on the basis of non-interference from previous knowledge of mass spectra. The only exception is CF_3^+ , which is a common ion in the mass spectra of virtually all fluorocarbons. The ion currents are only roughly indicative of the pressure of each species in the source, since no corrections were made for isotopic abundances or ionization cross-sections. The ion currents are reported in arbitrary units, but the same scaling factor is used for all figures. In general, the XeF_6 and XeF_4 compounds share many features, and are naturally distinct from the XeOF_4 compound and the XeF_6 hydrolysis product.

Table I gives the mass spectra of the gases evolved from the intercalates of XeF_6 , XeF_4 and XeOF_4 and those determined from the pure compounds taken on the same apparatus.¹⁰ Tables II and III give the mass spectra of the fluorocarbons evolved from the various intercalates at elevated temperatures.

$\text{C}_{19}\text{XeF}_6$

The XeF_6 intercalate which had previously been pumped on overnight, still liberated XeF_4 at ambient temperatures, with no evidence for XeF_6 . The intensity of the XeF_4 decreased with time at constant temperature, but increased to a maximum at 80°C as shown in Figure 1. Molecular

TABLE I

60 eV Mass Spectra

Ion	XeF ₆ + Grafoil, 25°C	XeF ₄ [*] , 25°C	XeF ₆ [*] , 25°C
Xe	100	65	30
XeF	55	37	27
XeF ₂	59	55	14
XeF ₃	90	100	100
XeF ₄	10	19	28
XeF ₅	-	-	96
XeF ₆	-	-	0.4

Ion	XeF ₄ + Grafoil, 51°C	XeF ₂ [*] , 25°C
Xe	100	100
XeF	36	45
XeF ₂	23	28
XeF ₃	-	-
XeF ₄	-	-

Ion	XeOF ₄ + Grafoil, 25°C	XeOF ₄ [*] , 25°C
Xe	100	100
XeO	7	11
XeF	33	54
XeOF	2	6
XeF ₂	21	21
XeOF ₂	28	36
XeF ₃	16	59
XeOF ₃	29	49
XeOF ₄	-	0.5

*Reference 10.

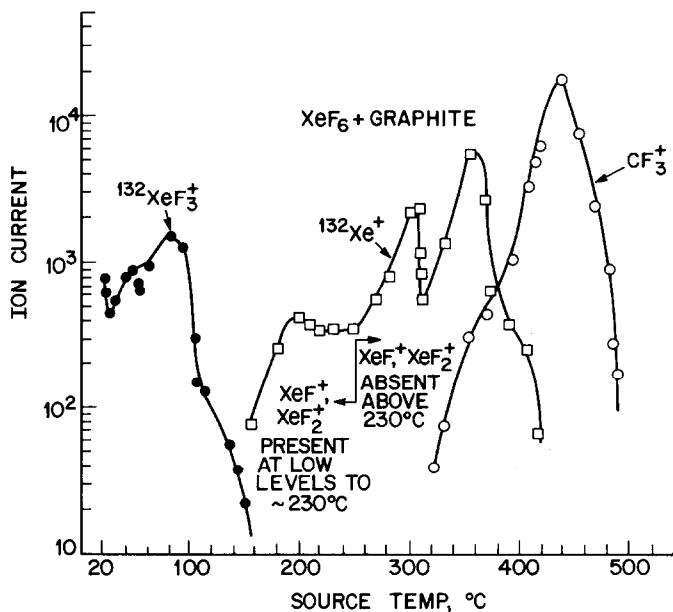


Figure 1. Ion currents characteristic of the gaseous species evolved from the C₁₉XeF₆ intercalate as a function of source temperature.

fluorine and HF were absent over the entire temperature interval. In the region between 150°C and 210°C the mass spectral pattern changed from that of XeF₄ to one which was a mixture of XeF₂ and Xe. Above ~ 230°C, all traces of XeF_n⁺ are gone, only free xenon being liberated. Thus, the Xe⁺ signal below ~ 230°C has some contribution from XeF₂. The apparent double maximum in the Xe⁺ signal resulted from holding the oven temperature constant at 310°C for 20 mins., to see if the xenon evolution would remain at a constant level. The progression in the Xe⁺ signal toward a maximum

value would have been monotonic, had the heating rate been held constant.

The above data correlate well with the results of a thermogravimetric analysis performed previously.^{3,4} The emission of XeF_4 and Xe up to about 250°C is accompanied by relatively minor weight loss, while the more copious xenon and fluorocarbon evolution above that temperature is accompanied by a major decrease in sample weight. ^{19}F NMR measurements² affirm the presence of XeF_4 as the only xenon containing species.

$\text{C}_{40}\text{XeF}_4$

Contrary to previous reports, the intercalate of XeF_4 produced a very weak evolution of XeF_2 at ambient temperature, and some slight evidence of XeF_4 . This is consistent with ^{19}F NMR measurements¹ which show the presence of XeF_2 and XeF_4 in a ratio of about 6 to 1. It must be noted that signal levels at room temperature were near the sensitivity limit of the detector. XeF_2 evolution became easily detectable between 30°C and 100°C, as shown in Figure 2, but the intensity of the signal was an order of magnitude lower than that of the XeF_4 produced by the XeF_6 intercalate. XeF_4 was also detected in this range at about one tenth of the XeF_2 level. The latter is in direct contrast to the XeF_6 intercalate, in which evolution of XeF_6 was not detectable at one part in 250.

Emission of gases between 140°C and 240°C was very abrupt and sporadic. Xenon was detected in some scans and not at all in others. Both xenon and fluorocarbon emission became regular and progressed smoothly to maxima

above 250°C, as shown in Figure 2. The irregular emission of gases between 140° and 240°C was a feature common to all samples of this intercalate.

In a separate experiment on the XeF_4 intercalate, the oven temperature was very rapidly raised to and maintained at 180°C. The evolution of XeF_2 and Xe was very abrupt, and the Xe signal dropped to the noise level after 30 minutes at 180°C. No further evolution of xenon was observed until the temperature was raised to 225°C, whereupon emission of xenon and fluorocarbons occurred from $\sim 240^\circ$ to 500°C as shown in Figure 2.

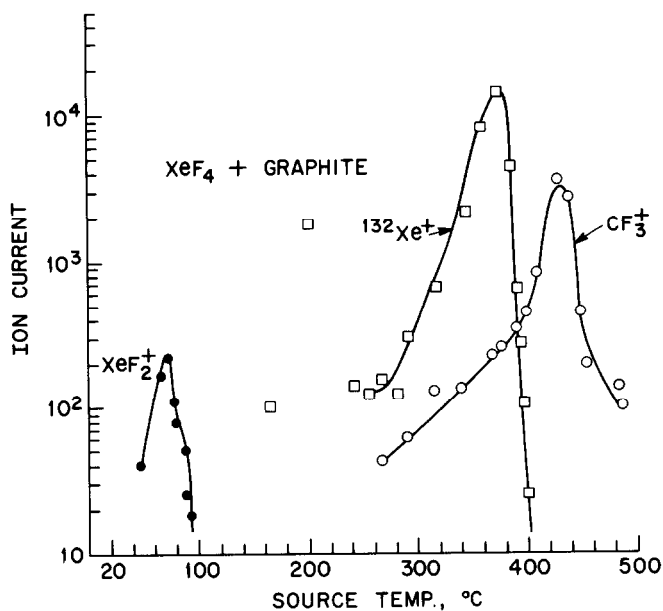


Figure 2. Ion currents characteristic of the gaseous species evolved from $\text{C}_{40}\text{XeF}_4$ as a function of source temperature.

TABLE II

Fluorocarbon Spectra from Intercalates

Ion	Mass	Intercalated Compounds			Lit * (580°)
		XeF ₄ (440°C)	XeF ₆ (415°C)	CF ₁₀ (465°C)	
CF ₃	69	100	100	100	100
C ₃ F ₃	93	3.2	3.6	5.3	40
C ₂ F ₄	100	10	13	11	38
C ₃ F ₄	112	0.8	0.8	0.8	2.1
C ₂ F ₅	119	20	20	9.2	52
C ₄ F ₄	124	0.7	0.8	0.7	2.2
C ₃ F ₅	131	23	28	4.4	37
C ₄ F ₅	143	1.4	1.3	1.2	3.8
C ₃ F ₆	150	1.4	1.3	0.5	4.3
C ₅ F ₅	155	0.6	0.5	0.3	2.2
C ₄ F ₆	162	1.0	1.5	0.2	0.6
C ₃ F ₇	169	3.6	6.7	0.5	4.7
C ₄ F ₇	181	5.2	10	0.4	3.8

* reference 12.

† at 510°C the CF₁₀ spectrum is essentially unchanged.

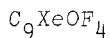
A sample of the XeF₄ intercalate was stored in a Kel-F tube for four months after preparation and pumping to constant weight. Heating this sample in the molecular beam oven produced results virtually identical to those already described and illustrated in Figure 2.

The fluorocarbon spectra obtained from the XeF_6 and the XeF_4 intercalates are substantially the same. These spectra are tabulated in Table II up to mass 181 (C_4F_7^+), along with spectra obtained with our apparatus from a sample of carbon monofluoride (Ozark Mahoning, $\text{CF}_{1.0}$) and one reported in the literature.¹² The major differences between the spectra obtained from the intercalates at higher temperatures and that of $\text{CF}_{1.0}$ are in the temperature at which gas evolution becomes significant and the relative intensities of the C_2F_5^+ and C_3F_5^+ ions.

The results on the intercalation of XeF_6 and XeF_4 with graphite confirm that in the process of intercalation these binary fluorides are reduced to the next lower known oxidation state. A fraction of these binary fluorides can be recovered from the graphite, and their evolution can be ascribed to passage of lower stage compounds to higher stages, as has been demonstrated by crystallographic data on the intercalation compound of XeF_4 . Conversion to still higher stages is not possible, because at higher temperatures the intercalated fluorides cause fluorination of the graphite. This is accompanied by the evolution of xenon and eventually low molecular weight carbon fluorides.

Poly(carbon monofluoride) is stable in air up to at least 600°C , but decomposes under high vacuum¹² between 420 and 580°C . The lower incipient decomposition temperatures and the variations in fragmentation patterns (Table II) indicate that the graphite fluorides resulting in this study are somewhat different in nature from authentic CF_n . Fluorination may be somewhat localized at lattice defects and grain

boundaries, yielding fragments with higher F:C ratios than one obtains from $CF_{1.0}$.



The intercalation of $XeOF_4$ in graphite is distinct from that of XeF_6 or XeF_4 , since appreciable amounts of $XeOF_4$ can be recovered from the graphite between room temperature and $80^\circ C$, as shown in Figure 3. Above $80^\circ C$, there is decomposition and/or reaction of the intercalated $XeOF_4$, and molecular oxygen is liberated in substantial amounts. Smaller amounts of XeO_2F_2 and XeF_2 are also liberated between 80° and $180^\circ C$ and are responsible for the Xe^+ signal

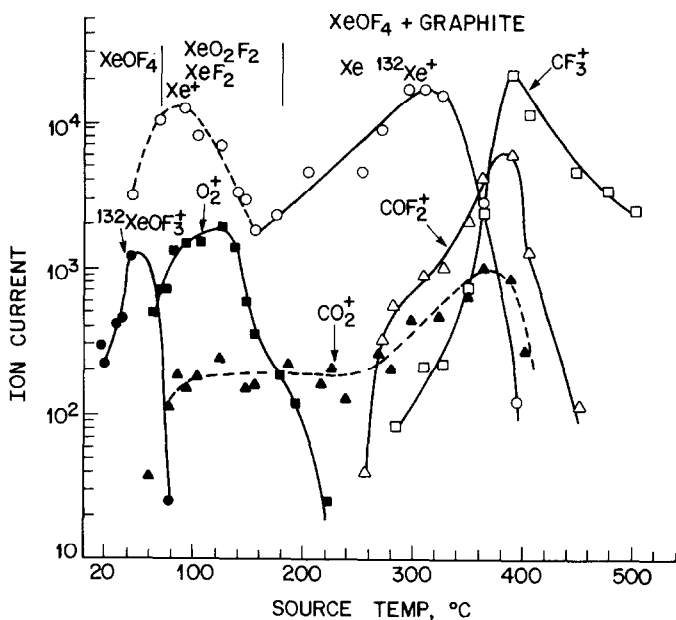
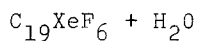


Figure 3. Ion currents characteristic of the gaseous species evolved from C_9XeOF_4 as a function of source temperature.

observed in this region. Above 200°C the O_2^+ , $XeO_2F_2^+$ and XeF_2^+ signals disappear and the Xe^+ signal intensifies to a maximum at $\sim 310^\circ C$. The decrease of Xe^+ above 320°C is accompanied by the evolution of fluorocarbons and a substantial quantity of COF_2 . There is also a persistent low-level emission of CO_2 between 80°C and 280°C. The level of CO_2 then rises to a maximum in coincidence with that of carbonyl fluoride.

The results shown in Figure 3 suggest that $XeOF_4$ reacts above 100°C to yield O_2 (which cannot oxidize graphite to any significant extent below 700°C) and higher stage compounds with intercalated $XeOF_4$, XeO_2F_2 , and xenon difluoride. Intercalated XeO_2F_2 should attack the graphite structure at lower temperatures than either XeF_4 or XeF_2 , owing to its higher reactivity. This is consistent with maxima in the xenon and fluorocarbon evolution occurring 40-60°C lower than for the intercalates of XeF_6 and XeF_4 . Carbonyl fluoride evolution continues significantly beyond the temperatures of cessation of xenon evolution. This may be interpreted as evidence for the presence of a graphite oxyfluoride phase. An ill-defined product of this type has been previously described.¹³



The fate of xenon hexafluoride or xenon tetrafluoride upon hydrolysis has been of concern in previous studies,¹⁻³ mostly from the safety standpoint. Hydrolysis of pure XeF_6 and XeF_4 leads to the explosive XeO_3 . By contrast, the intercalates liberate HF, lose some weight, and eventually

come to constant weight when exposed to moisture-laden air. The residues are neither shock sensitive nor do they explode at higher temperatures. Instead, they deflagrate releasing copious amounts of gas and fine soot upon sudden heating. X-ray powder patterns indicate only graphite lines, but the presence of amorphous matter is not ruled out. The hydrolysis residue is probably not a true intercalation compound.

A sample of the XeF_6 intercalate was exposed to water vapor at ambient temperature for 18 days, and subsequently pumped to constant weight.

The sustained evolution of CO_2 and the lack of evolution of any fluorides of xenon below $\sim 150^\circ\text{C}$ as shown in Figure 4 is a strong indication that the hydrolysis of XeF_6 proceeded beyond XeOF_4 . The evolution of HF between

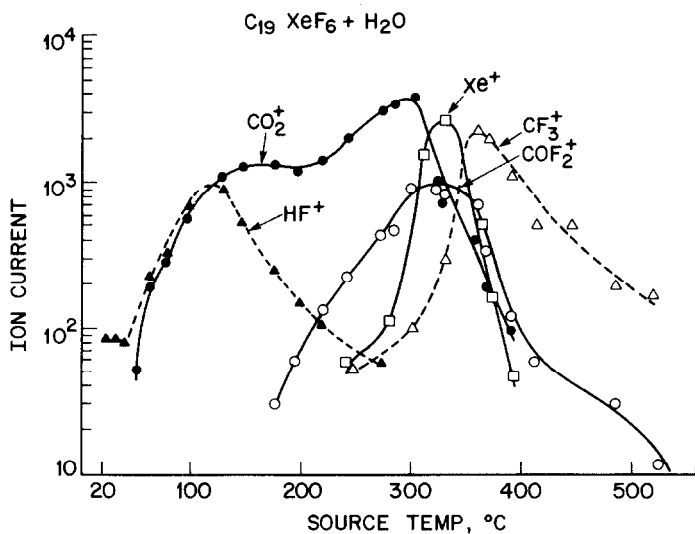


Figure 4. Ion currents characteristic of the gaseous species evolved from the hydrolysis product of $\text{C}_{19}\text{XeF}_6$.

40° and 200°C suggest that the graphite had been locally oxidized to an acidic type structure - one presumably analogous to graphitic acid.¹⁴ Oxidation of the graphite lattice by XeO₃ would also account for CO₂ evolution, but one would also expect atomic xenon to be liberated in coincidence with CO₂.

The emission of COF₂, Xe and fluorocarbons above 240°C is quite similar to the decomposition pattern of the intercalate of XeOF₄, so it is reasonable to conclude that an oxide fluoride of xenon is also present in the graphite. The mass spectra of the gases emitted by the intercalates of XeOF₄ and XeF₆ + H₂O at 390°C are given in Table III.

C₁₀AsF₅

A sample of C₁₀AsF₅ was thermally decomposed in the molecular beam apparatus for comparative purposes. The intercalated AsF₅ is known to form several stages with graphite.⁶ The stable form obtained by pumping the intercalate to constant weight at room temperature has a stoichiometry of C₁₀AsF₅.⁶ Some decomposition of the AsF₅ into AsF₃ occurs at elevated temperatures, but most of the AsF₅ can be recovered as such at low temperatures. Thermogravimetric analyses show that the transition from stage I to stage II is complete at 130°C, and the transition from stage II to stage III is complete at 250°C.

The results obtained on our apparatus are shown in Figure 5. There are three distinct regions of evolution of AsF₅ which correspond reasonably well with the thermogravimetric data.⁶ A careful check on the phases and relative intensities of the AsF₂⁺ and AsF₄⁺ ions showed that evolution of

TABLE III

Fluorocarbon Spectra derived from $\text{XeF}_6 + \text{H}_2\text{O}$ and XeOF_4 Intercalates

		XeOF_4 (393°C)	$\text{XeF}_6 + \text{H}_2\text{O}$ (391°C)
28	CO^+	4	4
31	CF^+	1	2
44	CO_2^+	4	8
47	COF^+	17	11
50	CF_2^+	2	3
66	COF_2^+	28	12
69	CF_3^+	100	100
100	C_2F_4^+	6	4
119	C_2F_5^+	15	11
131	C_3F_5^+	9	6
150	C_3F_6^+	1	1
169	C_3F_7^+	2	2
181	C_4F_7^+	2	2

AsF_3 begins at about 200°C but its intensity is always small compared to the amounts of AsF_5 liberated. AsF_3 evolution at lower temperatures is accompanied by partial fluorination of the graphite lattice, thus accounting for the fluorocarbon evolution observed at higher temperatures. The AsF_3 is liberated as it is formed; separate experiments have shown

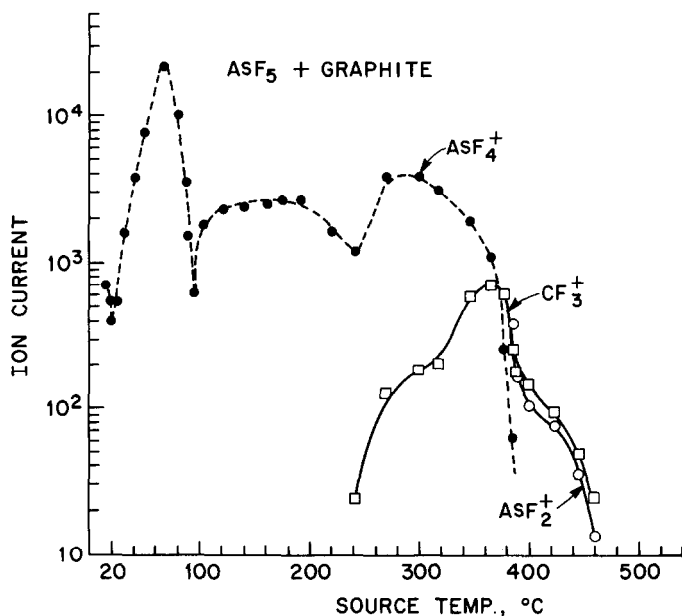


Figure 5. Ion currents showing the evolution of AsF_5 from the intercalate $\text{C}_{10}\text{AsF}_5$.

that AsF_3 does not intercalate into graphite.⁶ Moreover, broadband ^{19}F NMR measurements show the presence of a fluorine signal in the AsF_5 or AsF_6^- region (which unfortunately cannot be distinguished), but not in the AsF_3 region.¹⁵ The fact that not more than 5% AsF_3 is ever evolved during the formation of $\text{C}_{10}\text{AsF}_5$ indicates that the intercalated species is largely AsF_5 . The relative ease with which AsF_5 is recovered over a wide temperature range supports this conclusion, but some AsF_6^- may be present. However, $\text{C}_{10}\text{AsF}_5$ probably is not the same compound, $\text{C}_{10.6}^+\text{AsF}_6^-$, which has been obtained by the oxidation of graphite by $\text{O}_2^+\text{AsF}_6^-$.¹⁶

The question as to whether oxidation of the graphite lattice is a necessary condition for intercalation is still not totally resolved. This study, however, does show in

conjunction with ^{19}F NMR results obtained elsewhere, that some compounds, such as XeF_6 and XeF_4 , intercalate with virtually complete reduction to the next lower oxidation state. The case of AsF_5 appears to be different. Both ^{19}F NMR and mass spectra show that only pentavalent arsenic is incorporated in the graphite lattice, but the small amounts of AsF_3 liberated upon intercalation point to partial oxidation of the graphite.

These differences are no doubt related to the relative fluorinating power of the fluorides which conform to the series $\text{XeF}_6 > \text{XeF}_4 > \text{AsF}_5 > \text{XeOF}_4 > \text{XeF}_2$.

The mass spectra observed in this study show that thermal decomposition of the intercalates occurs in three steps:

1. The evolution of binary fluorides or XeOF_4 with passage to higher stage compounds at comparatively low temperatures. The species liberated may be either the ones originally intercalated (XeOF_4 , AsF_5) or the next lower oxidation state (XeF_4 , XeF_2).
2. Fluorination or oxyfluorination of the graphite lattice accompanied by liberation of xenon (viz. AsF_3).
3. The decomposition of the graphite fluoride (or oxyfluoride) formed in step 2 with the liberation of fluorocarbons with a fragmentation pattern similar to that of authentic graphite fluoride.

In most cases overlap occurs to a certain extent, i.e. they are not distinctly separated as a function of temperature.

Some of the properties of the intercalates studied suggest some interesting applications. Since AsF_5 preserves its integrity upon intercalation, its intercalate might be a useful storage vehicle for the gas. The AsF_5 can be generated upon demand from the intercalate by slight heating, rather than using a high pressure cylinder in which it is sold commercially. The application is not limited to AsF_5 ; in principle, it could be used with any substance that can be recovered from an intercalate without decomposition.

The non-intercalation of XeF_2 in the pure state could serve as a means of purifying XeF_2 contaminated with XeF_4 . This is a difficult separation to achieve by the usual chemical or physical means. However, XeF_2 contaminated with XeF_4 would become depleted in XeF_4 if allowed to be in contact with graphite for some time. Similarly, the intercalate of XeF_6 could be used as a source of pure XeF_4 .

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