THE INTERCALATION OF BROMINE- AND IODINE FLUOROSULFATE DERIVATIVES IN SOLUTIONS OF FLUOROSULFURIC ACID

BY

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ABSTRACT

The oxidative intercalation of halogen fluorosulfate derivatives such as $I(SO_3F)_3$, $Br(SO_3F)_3$, $BrSO_3F$, $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$ from solutions in fluorosulfuric acid into graphite (SP-1 and to a lesser extent HOPG) is studied. In addition, the intercalation of solvated cations of the type I_2^+ and NO^+ is included in this research as well.

The results, supported by microanalysis, X-ray powder diffraction data, Raman frequency shifts, Solid state ^{19}F-NMR spectroscopy and UV-visible optical spectra of the supernatant solutions support three different courses of the intercalation reactions:

a) At very high intercalant concentrations (about a five fold excess over the stoichiometrically required quantity) $Hal(SO_3F)_3$ and the anion $[Hal(SO_3F)_4]^-$, with Hal = I or Br, intercalate without noticeable solvent cointercalation.

b) At intermediate concentrations, solvent intercalation is observed.

c) When low intercalant concentrations are used, the only intercalate is found to be the solvent HSO_3F.

In all the intercalation reactions except the $NO^+_{(solv)}$ promoted synthesis, first stage compounds are formed. These stage one GIC's with c-axis layer repeat distance $I_c \sim 8.0$ Å are found for the intercalants $I_2^+{}_{(solv)}$, $I(SO_3F)_3$, $BrSO_3F$ and $Br(SO_3F)_3$ with compositions $C_{32}SO_3F.3HSO_3F.0{\cdot}2I$, $C_{22}I(SO_3F)_3$, $C_{11}HSO_3F.0{\cdot}5SO_3F.xBrSO_3F$ ($x \leq 0.025$)

and $C_{26.8}$ Br.$4SO_3F$ respectively. $K[Hal(SO_3F)_4]$ (Hal = Br, I) in HSO_3F gave first stage products with formulae $C_{84}Br.11 \cdot 22SO_3F$ and $C_{86}I.10 \cdot 51SO_3F$.

The $NO^+_{(solv)}$ induced reaction leads to a stage two compound with $I_c \sim 10.6$ Å, and a general composition of $C_nxSO_3F \cdot yHSO_3F$ is proposed for the product which is compositionally inhomogeneous. In addition, the basal plane electrical conductivity enhancements are measured for the graphite-$I_2^+{}_{(solv)}$ and graphite-$I(SO_3F)_3$ systems employing a contactless radio frequency induction method.

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GLOSSARY

Acceptor Intercalation Compounds - Compounds formed from electron acceptor intercalants such as Br_2 and AsF_5.

Bounding Layers - the carbon layers adjacent to an intercalate layer.

Charge Transfer Factor(f) - the extent of electron removal from the graphite lattice due to oxidation.

Deintercalation - the process that occurs at elevated temperatures which produces the initial intercalant(s) as well as other volatile decomposition products.

Donor Intercalation Compounds - compounds synthesized from electron donor intercalants like K and Cs.

Exfoliation - the collapse of the layer structure due to an intercalation-deintercalation cycle.

Hexagonal Graphite - infinite sheets of hexagons, formed by carbon atoms, and stacked together in an ABAB.... sequence along the c-axis direction.

Intercalant(s) - molecules, ions or atoms capable of insertion between the vacant sites of the host lattice material.

Intercalate(s) - the species actually present inside the lattice after the process of intercalation.

Intercalation - the insertion of ions, atoms or molecules generally into a layer structure, and specifically between carbon layers of the graphite lattice.

Interior Layers - the carbon layers not in direct contact with the intercalate layer.

Limiting Composition - during the intercalation reaction, intercalation will not proceed after reaching a limiting composition. This composition may differ from stage one composition, e.g. the GIC $C_nPF_6(CH_3NO_2)_y$ refers to a stage two limiting composition product.

Residual Compound - the solid material left after deintercalation.

Stage Index - the number of carbon layers separating two nearest intercalate layers.

Staging - the regular alternation of intercalate layers and empty lamellar spaces along the vertical or c-axis direction.

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CHAPTER 1

INTRODUCTION

1.1 General Comments

Research on graphite intercalation compounds (GIC's) has undergone explosive and rapid growth during the last 25 years. The synthesis and characterization of GIC's have drawn many specialists from varying fields such as inorganic, physical and solid state chemistry, solid state physics, material science and electrical engineering to work together, and to reach a better understanding of the chemical, structural and electronic properties of this potentially very useful group of compounds. The use of graphite intercalation compounds as electrical storage systems and planar conductors[1-3] has made them prime candidates in industrial applications. The utilization of graphite as the host material or matrix in heterogeneous catalysis[4] has also contributed to the popularity of intercalation compounds in basic and industrial research.

Detailed review articles summarizing past and recent advancements by Henning[5] and Rudorff[6], Herold et al.[7] (1965), Ebert[8] (1975), Herold[9] and Fischer[10] (1970), Selig and Ebert[11] (1980) and more recently by Forsman et al.[12] (1983) respectively have appeared during this period. The following observation, made by a specialist in graphite intercalation, summarizes the major, initial challenge to the synthetic chemist: "The synthesis of lamellar compounds poses the following fundamental question to the chemist: which reagents are capable of insertion and under what conditions?"[13]

More recently, new problems regarding the nature of the intercalated species once intercalation has occurred, the mechanism by which it

occurs and the extent of electron transfer between the guest or intercalate and the host, the graphite lattice, have emerged, providing sufficient stimulus for researchers.

1.2 Historical Review

The first lamellar or intercalation compound was made by Schafheautl in 1840 and 1859[20] by reacting graphite with oleum resulting in oxidative intercalation. Covalent graphite compounds were also known as early as 1859[14]. These compounds, generally called graphite oxide or graphite acid, are synthesized by strongly oxidizing systems such as solutions of sodium nitrate or permanganate in sulfuric acid reacting with graphite[15] to produce compounds of formula $C_8O_2(OH)_2$[16] or $C_8O_4H_2$[18,19]. It is hence interesting to note that sulfuric acid as a reaction medium played an important role in the discovery of both the first GIC and the first covalent graphite compound.

Research on graphite intercalation compounds first reached a peak during 1959-1960 with the vast majority of the effort directed towards their synthesis.

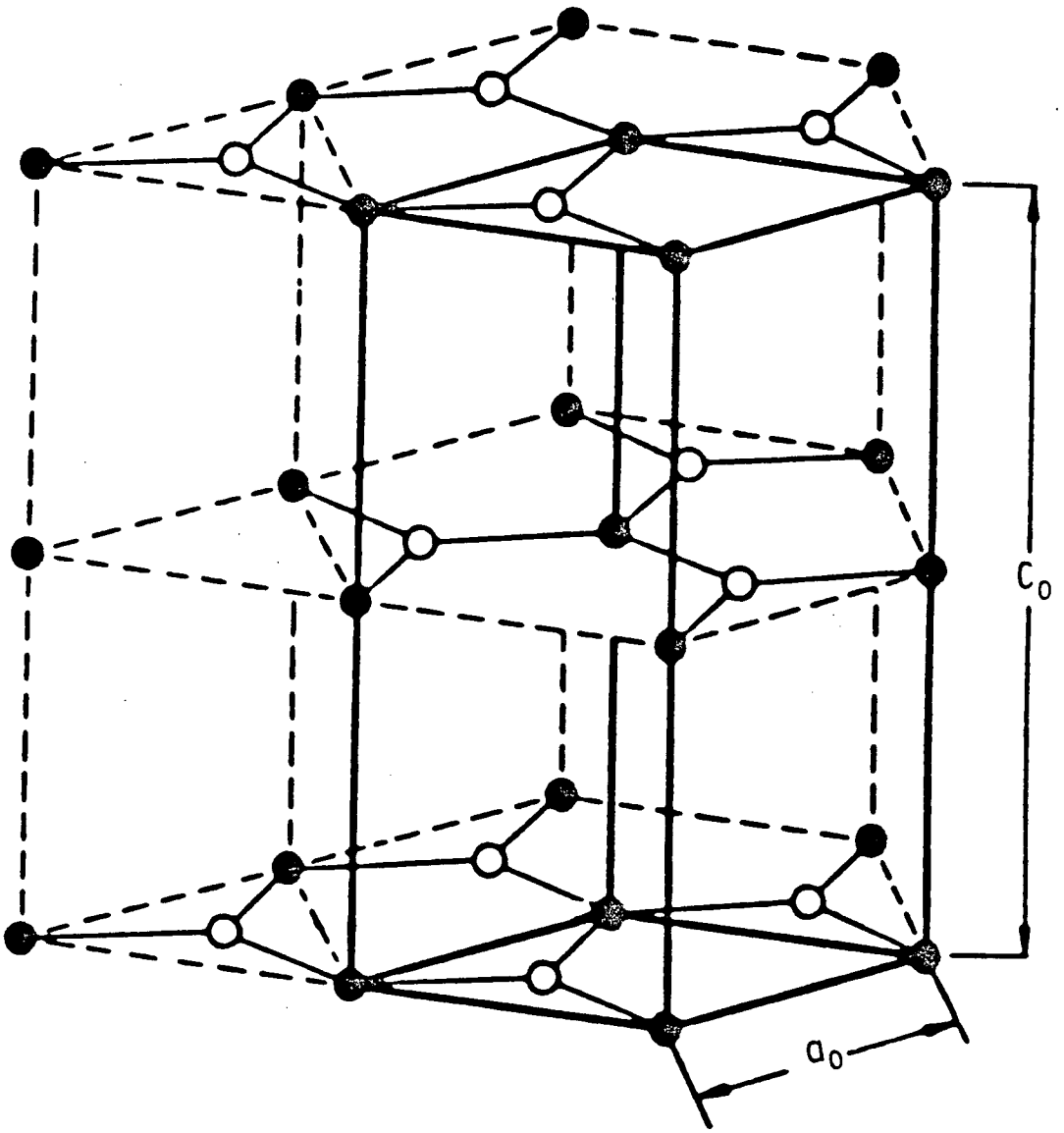
In the late 1970's, mechanistic studies and the use of physical methods in the structural elucidation of GIC's became prominent. At present, intense research activity on the electronic structure and two dimensional physical properties, novel synthetic routes and mechanistic pathways in their preparation continue as the cause of potential application of GIC's becomes increasingly wider. In 1959, Henning[5] listed

about three dozen known compounds which spontaneously form intercalation or lamellar compounds. Today, the metal chlorides alone claim a large number of intercalation compounds, and the total of all known intercalants and their products is now several times larger than in 1959.

Looking back, it appears that research on GIC's has evolved from an obscure field, reminiscent of alchemy in the Middle Ages, into a highly challenging, multifaceted scientific endeavour. Much of the credit for this achievement must go to the development of chemically pure, highly ordered, and uniform synthetic graphite, resulting in a greater reproducibility of results than had been possible with natural graphites. Some important aspects of graphite itself will now be discussed in the following section.

1.3 Graphite

The structure of hexagonal graphite, the most common polymorphic form, is shown in Fig. 1.1. Infinite planar sheets of hexagons, formed by carbon atoms, are stacked together to give a layer structure to the graphite lattice. The intralayer C-C bond distance is 1.42 Å, which is slightly less than the C-C distance of 1.54 Å in diamond. Planarity within the layers and bond angles of 120° suggest the involvement of carbon sp^2 hybrid orbitals to form σ-bonds. The remaining valence electrons reside in atomic orbitals perpendicular to the infinite sheets and hence contribute to delocalized π-bonds to produce a polyaromatic system. It is this π-electron density in the valence bond which is



$a_0 = 1.42A^0$
$C_0 = 6.70A^0$

Figure 1.1: The Unit Cell Dimensions of Hexagonal Graphite.

responsible for the two dimensional metallic conductance in the basal plane. The interlayer spacing in the lattice is 3.35 Å, much too long for covalent bond formation but consistent with the view that these carbon planes are held together by relatively weak Van der Waals forces. As seen from Fig. 1.1, the carbon layers in hexagonal graphite are not directly superimposable and show an ABAB..... stacking sequence. The weak nature of the interlayer forces in graphite is responsible for its use as a solid, high temperature lubricant, where the layers can slide easily in a horizontal direction.

A second form of graphite, called rhombohedral graphite, differs in the layer stacking sequence, which is ABCABC. This polymorphic form is rare and has not been used extensively as a host species in graphite intercalation. All work described in this thesis will involve hexagonal graphite only.

Graphite used in intercalation reactions differs from graphite used as electrode material in industrial electrolysis, in nuclear reactors as moderators or as combustion material. It must meet the requirements of high purity and order. For practical purposes, graphite may be classified into two broad groups: natural graphite and synthetic or pyrolytic graphite. Both have been used extensively in graphite intercalation, but the disadvantage in using natural graphite is its uncertain and variable purity. Usually iron, calcium, and other minerals such as silicates and carbonates are present as impurities and, in addition, many natural graphites have crystal defects, which could interfere with both the intercalation process[21] and the interpretation and reproducibility of results. Nevertheless, natural graphite which has been sub-

jected to extensive purification processes finds use in intercalation reactions. Pyrolytic graphite is a monolithic graphite material with a high degree of preferred crystallographic orientation of the c-axis. It is made by pyrolysis of small hydrocarbons and subsequent heat treatment at temperatures above 2100 K or by the chemical vapor deposition-method.

Application of high pressure and temperatures (above 2800 K) produces so called Highly Oriented Pyrolytic Graphite (HOPG)[22]. HOPG, which is available in plates, exhibits a highly ordered structure with nearly parallel carbon layers in the basal plane. This form has been used extensively in intercalation reactions, and it was used during this study in order to measure enhanced electrical conductivities.

As can be seen from Table 1.1, natural and synthetic graphite exhibit quite different physical properties in a- and c-axes. The anisotropy ratio (σ_a/σ_c) is fairly low for natural graphite as compared to synthetic graphite.

SP-1 graphite (spectroscopic grade), which was used in all our synthetic reactions, is a highly purified natural graphite of grain size about 50-100 microns. It is made from Madagascar graphite and treated with HCl and HF to remove basic impurities. A Cl_2 stream at high temperature is then applied to remove any metallic components present.

1.4 Graphite Intercalation

A number of terms unique to graphite chemistry are now introduced.

Table 1.1 Anisotropy factor for various types of graphite*.

Material	T(K)	σ_c ($ohm^{-1}\ m^{-1}$)	$(\frac{\sigma_a}{\sigma_c})$
Natural graphite (Ceylon, Mexico)	300	8.3×10^4	100
Natural graphite (Ceylon)	300	10^4	100
Natural graphite (Ticonderoga)	300	$1.5\text{-}2.3 \times 10^4$	100-170
Natural graphite (Ticonderoga)	300	2×10^4	130
Natural graphite (Ticonderoga)	300	3.3×10^4	80
Kish graphite	300	$1.3\text{-}1.5 \times 10^4$	-
Pyrolytic carbon +(T_d = 2200°C)	300	125	5500
Pyrolytic carbon +(T_d = 2500°C)	300	83	5000
Pyrolytic graphite •(HTT = 3000°C)	300	385	5200
HOPG (annealed 3500°)	300	590	3800

* from reference 89.

\+ T_d = Deposition temperature.

• HTT = Heat Treatment Temperature.

and defined. **Intercalation** refers to the insertion of ions, atoms or molecules generally into a layer structure and specifically between carbon layers of the graphite lattice[11,12]. The planarity of the layers in the host lattice is retained in the intercalation process. The stacking order, interlayer separation, and to a far lesser extent intralayer bond distances may all be changed due to intercalation.

Molecules, ions or atoms capable of such insertion are termed **intercalants**. The species actually present inside the lattice after intercalation has taken place is called **intercalate**. Depending on the nature of the 'guest-host' interaction, intercalant and intercalate may differ in their electronic structure, electronic charge, molecular structure and even in their chemical identity.

A classification of GIC's may be based on the nature of the guest-host interaction: **Donor GIC's** are formed by electron donor intercalants such as potassium and cesium. **Acceptor compounds** are synthesized from electron acceptor intercalants such as Br_2 and AsF_5. In donor intercalation compounds, the intercalant is an effective reducing agent, while acceptor GIC's are formed by relatively mild oxidizing agents, i.e. Br_2. When a strong oxidizing agent such as F_2 is used as the intercalant, the polyaromatic character of the graphite is lost, the planarity of the carbon layers is destroyed and covalent C-F bond formation occurs with bonding described by sp^3 carbon hybrid orbitals.

The resulting **covalent graphite compounds** are insulators, often white or grey in color and have compositions of ~CF. A sheet-like non-planar structure exists in these compounds with F.....F intralayer contacts.

The chemical nature of the intercalants determines the direction of charge transfer during intercalation, resulting in acceptor or donor GIC formation.

In acceptor intercalation compounds formed by oxidative intercalation, covalent bond formation (as in CF) is seen as the limiting case in oxidation. In contrast to covalent bond formation, intercalation is partially reversible. The compounds thus formed by intercalation are usually sensitive to water and organic solvents, whereas covalent compounds are stable under these conditions.

Heating of covalent compounds produces volatile low molecular weight molecules such as CO_2 and CF_4, while intercalation compounds undergo **deintercalation**. This process, occurring at elevated temperatures, produces the initial intercalant as well as other volatile decomposition products. The solid material left (termed 'residue compound') has a composition which is dependent on the deintercalation temperature and may be different from graphite, e.g. deintercalation of C_nAsF_5 may result in a residue compound with a small fluorine content. These residue compounds are usually poorly understood and rarely investigated. In the case where intercalation is reversible, an interesting technical application results: an intercalation-deintercalation cycle will lead to a collapse of the layer structure (called exfoliation) yielding graphite with a larger surface area. This brings up another interesting aspect. Mere adsorption of the intercalant, termed capillary condensation, on the GIC surface can occur which again is a limiting case. Application of a dynamic vacuum will usually remove such excess surface adsorbed intercalants.

A final comment is given below regarding the two contrasting types of intercalation, i.e. oxidation and reduction. Oxidation will generate usually C_n^+-positively charged graphite layers (and reduction, C_n^--negatively charged layers). The extent of electron removal is termed the **charge transfer factor** (f), and represents a characteristic quantity for a given GIC. The reduced electron density in the valence bond (carrier density) results in a lowering of the Fermi level and p-type conductance enhancement. Filling interstitial space with oppositely charged, generally molecular intercalate anions will increase the anisotropy of electrical conductance, with enhanced conductance in the ab-plane and reduced conductance in the c-axis direction.

Conversely, reducing agents are commonly atoms (e.g. Li, K) which will donate electrons into the empty conductance bond causing a rise in the Fermi level and n-type conductance enhancement with reduced anisotropy of conductance due to the atomic nature of the intercalate anion.

Interestingly, donor GIC's have found extensive use as model reducing agents, whereas research on acceptor GICs has focussed more on the resulting electronic features.

1.5 Donor Intercalation Compounds

While not directly pertinent to this study, this brief summary serves two purposes:

a) to illustrate the unpredictable nature of intercalation, and

b) to introduce the important concept of staging.

Lithium, potassium, rubidium and cesium (and their vapors) react with graphite to give donor type intercalation compounds[23,24] with interlayer separations of 5-6 Å. However, sodium does not intercalate, and a satisfactory explanation is still to be found. The reaction between potassium and graphite produces a compound with a limiting composition of C_8K, which is called a first stage compound, implying all galleries in the graphite lattice are filled. Higher stage compounds with stoichiometries of $C_{12n}M$ ($n>1$) could be synthesized by either controlling the intercalation time, temperature or intercalant concentration or by partial deintercalation via controlled heating.

The graphite-lithium reaction under extreme conditions yields a GIC of formula $C_{6n}Li$[25,26]. In intercalated donor compounds, the interlayer separation distances tend to be smaller than that of acceptor compounds. This is due to the fact that donor intercalants are usually microatomic while acceptor intercalants are molecular aggregates by nature.

The concept of staging in graphite intercalation implies that intercalation compounds at equilibrium favour a situation where the interlaminar regions or galleries are either completely filled or totally empty[12]. A classical view of staging is shown in Fig. 1.2. An intercalant will fill or vacate a given layer or gallery in the graphite lattice before another layer is either attacked, opened up and filled or vacated. This will result in a regular alternation of intercalant layers and empty lamellar spaces.

The stage index, denoted by n, is defined as the number of carbon layers separating two nearest intercalant layers. Hence a stage index

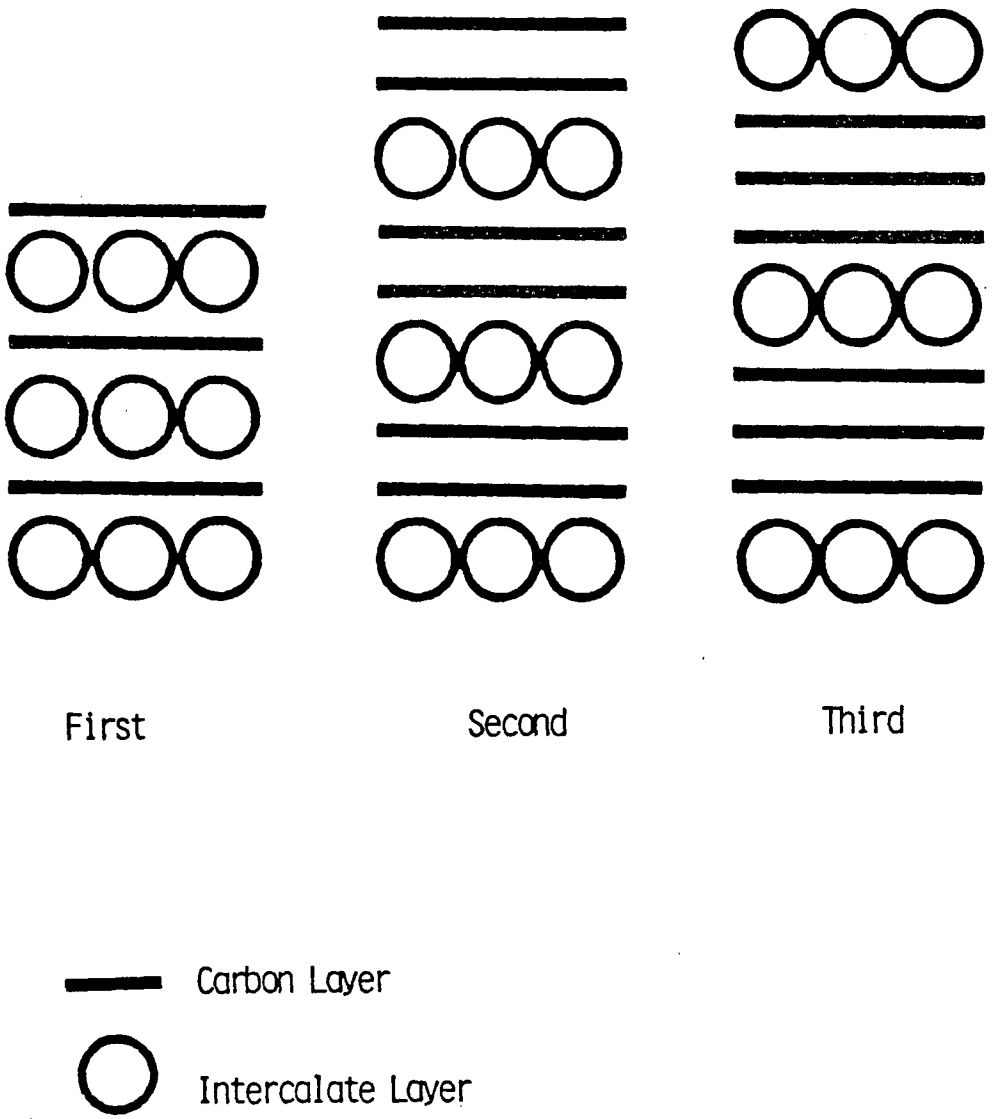


Figure 1.2: Staging in Graphite Intercalation.

of 1 implies the highest possible intercalant concentration, the lowest carbon content of the compound and a single unique interlayer separation distance along the c-axis I_c, which is characteristic of the intercalate's space requirement. Intercalation compounds with higher stage indeces imply a lower intercalant to carbon ratio. With interlayer separations in empty layers = 3.35 Å as in graphite itself, the interlayer separation for a stage n compound becomes I_c + (n-1) 3.35 Å, with I_c the interlayer separation in the corresponding first stage compound. Due to intercalation, some ordering takes place in the graphite layers as well. The carbon layers adjacent to an intercalate layer are called **bounding layers**, while the other layers, not in direct contact with the intercalate are termed **interior layers**. The latter layers have the ABAB layer repeat pattern, which is similar to the graphite lattice arrangement, but the bounding layers may have ABAB, AAA or a mixture of both these repeat sequences[27].

In practice, however, the infinite regular stacking of layers with intercalate layers inserted in every nth intercarbon layer space along the c-axis, which is implied by the classical model, may not be observed. The ability of intercalate species to distribute between the graphite layers will result in the formation of mixed stage compounds. In order to accommodate this macroscopic distribution of intercalate species, Daumas and Herold proposed a domain (or pleated layer) model for the layer stacking pattern in intercalated compounds[28] (Fig. 1.3). The host carbon and intercalate layer stacking arrangement for compounds of stage one, two and three are shown in Fig. 1.3. The basic advantage of this concept is that it becomes easier to explain stage transfor-

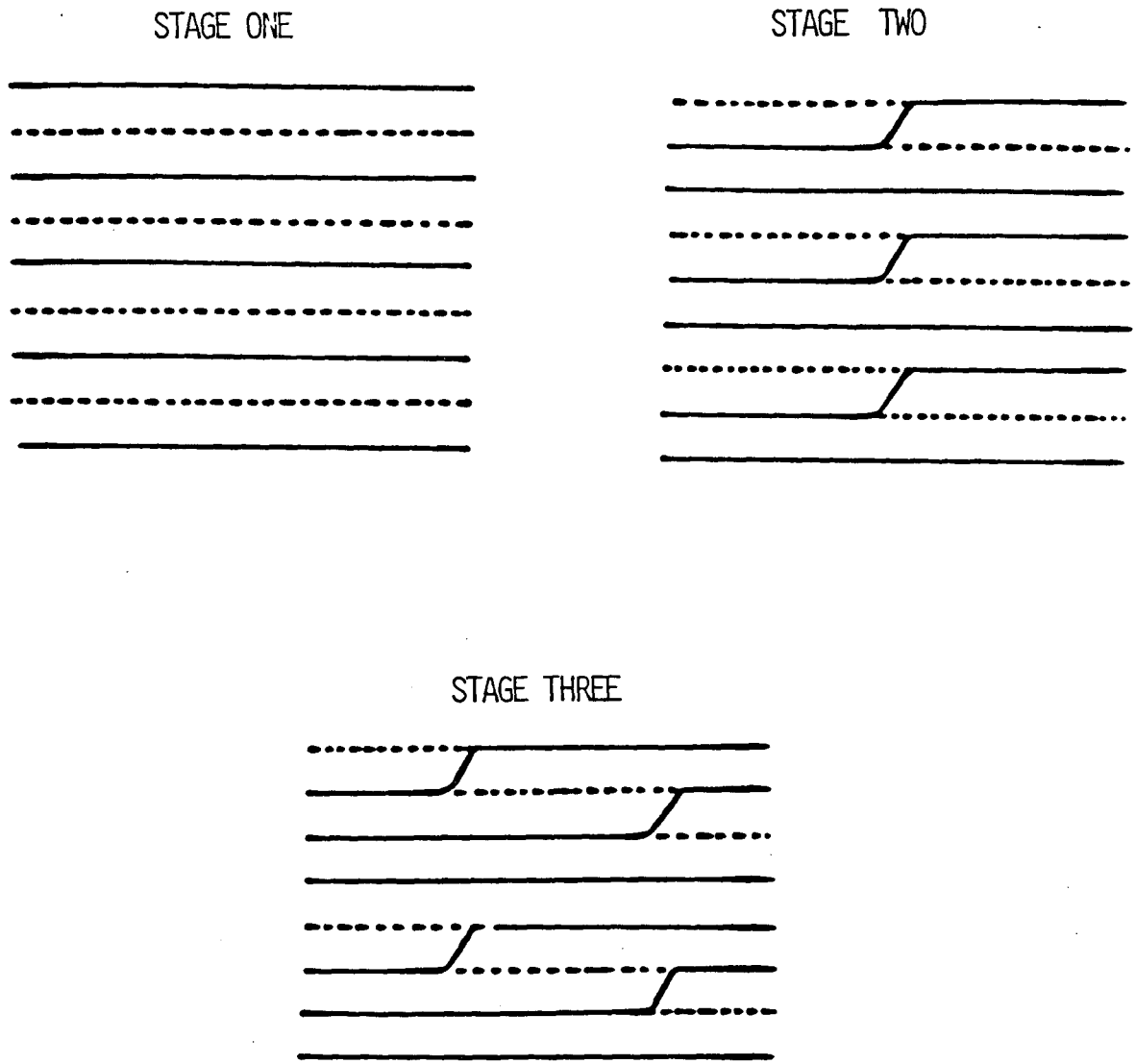


Figure 1.3: **The Daumas-Herold Model for Staging.**

mations which, according to this model, involve movement of intercalate islands. These islands are formed by the non-continuous occupation of all the interlayer regions by the intercalate species. As shown by theoretical studies[29,30], the intercalate molecules or atoms between the same two carbon layers will exert an attractive force to form two dimensional islands while those between different pairs of carbon layers will repel each other. This will eventually lead to the formation of domains of intercalates with macroscopic sizes. This formation of domains along the c-axis could be termed as staging, which explains the existence of mixed stages. Mixed stage formation takes place when a mixture of domains, each of them purely formed, is observed along the c-axis of the graphite lattice.

The X-ray diffraction method, used widely to determine the stage(s) of an intercalated compound, usually gives statistically averaged information on typically $(0.1\ mm)^3$ crystals and can generally reveal their average stage ordering[31]. Presentday high resolution electron microscopy, supported by computer simulations, could be used to image and locate intercalated species directly[32].

1.6 Acceptor Intercalation Compounds

These comprise a rather large group of compounds, and some more relevant members of this group will be introduced in a subsequent section. A few general comments in order to better characterize this group will be summarized. Unlike donor intercalants, which are basi-

cally restricted to metals, acceptor intercalants span a wider range and variety. The following differences as compared to donor GIC's, contribute to their extensive chemistry and practical interest.

Acceptor intercalants are: a) molecular - resulting in a greater anisotropy with typical I_c values of about 8 Å; b) oxidizers - this leads to p-type conductance with the Fermi level lowered rather than raised. Intense practical interest in these types of materials have been shown; c) capable frequently of direct intercalation on account of their physical and chemical properties. This makes them suitable systems for mechanistic studies (e.g. graphite-Br_2 system).

The intercalate in acceptor GIC's may or may not differ from the intercalant in its molecular structure. Two examples are given below to illustrate this difference:

1. $S_2O_6F_2$, bis(fluorosulfuryl)peroxide generates $^{\bullet}SO_3F$ radicals, which in turn act as one electron oxidizer and produce the SO_3F^- ion on intercalation.
2. AsF_5, arsenic(V) fluoride intercalates into graphite to give a compound of limiting composition C_8AsF_5[33]. However, the intercalate appears to be described by the equilibrium $3AsF_5 + 2e \rightleftharpoons 2AsF_6^- + AsF_3$. Therefore, in this system the extent of oxidation, the equilibrium position and the exact concentrations of the various intercalate species are subject to much controversy, and are not easily deduced from the stoichiometric composition.

1.7 Methods of Intercalation

The principal methods used in graphite acceptor intercalation synthesis could be classified as: direct intercalation; oxidation by an external chemical species which will not itself intercalate; anodic oxidation of graphite (modification of method 1.7.2); intercalate exchange and substitution; intercalate oxidation or reduction. A brief summary of each technique is given below:

1.7.1 Direct Intercalation

This method is the most common and most general type used for the synthesis of graphite intercalation compounds and applies well to both acceptor and donor compound preparation. The method could be illustrated by the very simple equation:

$$nC_{(s)} + X_{(l,g,\ solution)} \longrightarrow C_nX_{(s)}$$

Compounds such as $S_2O_6F_2$, HNO_3 and $BrSO_3F$ could act as the intercalant X to yield the C_nX product.

Some implications are: 1. Solutions require the presence of a suitable solvent, and hence solvent co-intercalation may occur. 2. Temperature, pressure, concentration, and reaction time are all factors controlling the extent of intercalation; 3. Following intercalation by weight becomes the simplest method of product analysis,

termed gravimetry. This method may be unreliable in the case of solution intercalation due to co-intercalation taking place. 4. Strictly physical criteria are used to characterize intercalants, i.e. an intercalant must be a gas, a liquid or a solid with a measurable vapor pressure or capable of dissolving in order to intercalate into graphite.

Finally, the composition of the GIC C_nX is influenced by the physical dimensions of X and the degree to which interlamellar spaces are filled.

1.7.2 Oxidation by an External Chemical Species

Three contrasting examples are presented below to indicate the scope of this technique:

1. Gaseous oxidizer - Cl_2 aided intercalation of $AlCl_3$ [34];
2. Solid molecular oxidizer - CrO_3 acts as the oxidizer in H_2SO_4 intercalation[35];
3. Ionic oxidizer - NO_2^+ allowing intercalation of MF_6^- ion[36]; M = P or Sb.

In all the above systems, the oxidizing species will generally not intercalate into graphite. It facilitates the intercalation of neutral molecules and anions by giving the graphite lattice a positive charge.

$AlCl_3$ vapor reacts with graphite only in the presence of Cl_2 gas,[34] and a stage one compound, $C^+_{30}AlCl_4^-.2AlCl_3$ is obtained. The role of Cl_2 as the oxidizer is evident in the following mechanism[37,38]:

$$Cl_{2(g)} \rightleftharpoons Cl_{2(ads)}$$

$$1/2\ Al_2Cl_{6(g)} \rightleftharpoons AlCl_{3(g)} \rightleftharpoons AlCl_{3(ads)}$$

$$AlCl_{3(ads)} + Cl_{2(ads)} \rightleftharpoons Cl^+\ AlCl_4^-(ads)$$

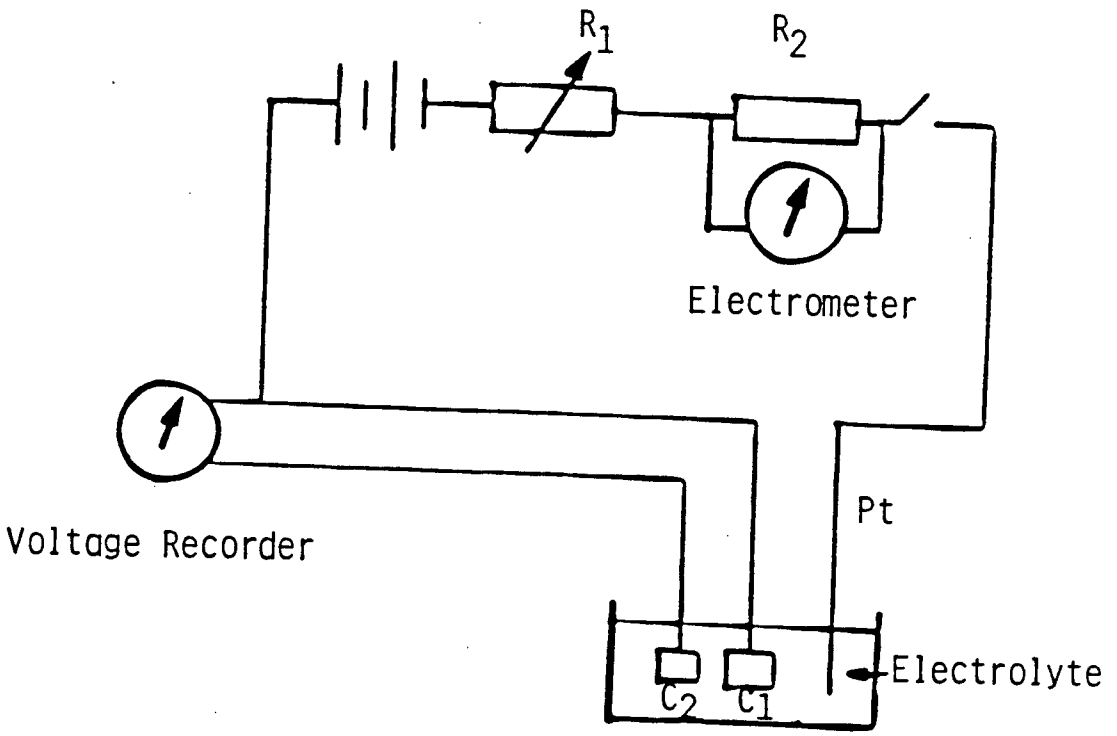
$$C_n + Cl^+.AlCl_4^-(ads) + mAlCl_{3(g)} \longrightarrow C_n^+AlCl_4^-.mAlCl_3 + Cl^\bullet(ads)$$

$$2Cl^\bullet(ads) \longrightarrow Cl_{2(ads)} \longrightarrow Cl_{2(g)}$$

In H_2SO_4 intercalation, CrO_3 reacts initially with graphite and compounds of general formula $C^+_{24n}.HSO_4^-.2H_2SO_4$ are synthesized[35]. Strong acids such as $HClO_4$ and CF_3COOH could be intercalated in a similar manner, using CrO_3 or other oxidants such as $KMnO_4$, MnO_2 and PbO_2. As shown by Billard et al.[36] NO_2^+ ion, coming from NO_2SbF_6 or NO_2PF_6, oxidizes the graphite in a nitromethane solution, and a product with formula $C^+_{23n}MF_6$ (CH_3NO_2) could be obtained (M = Sb or P). The value of Y is given as between 1.7 and 2.5.

1.7.3 Anodic Oxidation of Graphite (Electrochemical Method)

This method is primarily used for the intercalation of protonic acids when graphite acts as the anode (Fig. 1.4). C_1 denotes the graphite anode and the voltage drop between C_1 and C_2 and is monitored continuously during the intercalation process. A non-aqueous protonic



C_1& C_2 are Graphite Electrodes

R_1& R_2 are Resistances

Figure 1.4: Apparatus for the Electrochemical Synthesis of Intercalation Compounds.

acid such as H_2SO_4 or HSO_3F functions as electrolyte in the (electrolysis) cell. As intercalation proceeds, anions and neutral acid molecules will insert into the graphite anode, and a build-up of voltage takes place with time.

For the two protonic acids CF_3SO_3H and H_2SO_4, the following reactions could be written[39]:

$$26C + (x + 1)\ CF_3SO_3H \longrightarrow C^+_{26}CF_3SO_3^-.xCF_3SO_3H + 0.5\ H_2 \qquad (x = 1.63)$$

$$24C + (x + 1)\ H_2SO_4 \longrightarrow C^+_{24}HSO_4^-.xH_2SO_4 + 0.5\ H_2 \qquad (x = 2.42)$$

An interesting comment concerns the anodic oxidation in HSO_3F. This acid dissociates to give SO_3F^- as well as $H_2SO_3F^+$. The anion SO_3F^- can be oxidized to $SO_3F^\bullet$ or $S_2O_6F_2$ according to:

$$2SO_3F^- \longrightarrow S_2O_6F_2 + 2e^-$$

Hence, the anodic oxidation just discussed may be interpreted as intercalation of $S_2O_6F_2$ in the presence of an excess amount of HSO_3F.

Some conditional systems where anodic oxidation is used to synthesize GIC's involve metal chlorides such as $BiCl_3$ and $TeCl_4$, where their melts function as electrolytes[40] or lithium salts such as $LiPF_6$, $LiAsF_6$ and $LiSbF_6$, which give compounds of general formula $C^+_{24}X^-.4$ (solvent). These are electrolyzed in protic donor solvents[41].

1.7.4 Intercalate Exchange and Substitution

This method was first used in the conversion of $C^{+}_{24}HSO_4^{-}$ to the corresponding perchlorate product, according to[42]:

$$C^{+}_{24}HSO_4^{-} + \text{excess } HClO_4 \longrightarrow C^{+}_{24}ClO_4^{-} + H_2SO_4$$

Recent work done by our group has provided some additional examples of intercalate exchange reactions[43]:

$$C_7SO_3F + \text{excess } HSO_3CF_3 \longrightarrow C_{12}SO_3CF_3 + ...$$

$$C_7SO_3F + \text{excess } SbF_5 \longrightarrow C_8SbF_6 + ...$$

$$C_{12}BrSO_3F + \text{excess } HSO_3CF_3 \longrightarrow C_{12}SO_3CF_3 + ...$$

Substitution reactions are generally rare and even when they occur, interpretation of results could be difficult since equilibrium mixtures could form at certain stages of the reaction: for example, when $C_{8n}AsF_5$ was treated with NO_2SbF_6, the resulting product showed the following intercalates: SbF_6^{-}, AsF_6^{-}, SbF_5, AsF_5 and AsF_3[44].

1.7.5 Intercalate Oxidation or Reduction

This method is illustrated by studying the redox reaction of the

graphite-$FeCl_3$ system. The intercalated $FeCl_3$ could be reduced either to $FeCl_2$ by treating the intercalated product with H_2[45] or to Fe_2O_3 by heating in an oxygen stream[40]. Attempts to reduce the intercalated metal halides to pure metal, where the resulting product in turn could be used as potential catalysts, have not been successful so far[46].

Intercalate oxidation has also been observed in graphite-fluorosulfate compounds. When $C_{12}BrSO_3F$ was reacted with $S_2O_6F_2$, a compound of composition $C_{16}Br(SO_3F)_3$ was obtained[43]. This product may later undergo intercalate reduction, to yield the initial compound, i.e. $C_{12}BrSO_3F$, in the following manner:

$$3C_{16}Br(SO_3F)_3 + 3Br_2 \longrightarrow 4C_{12}BrSO_3F + 5BrSO_3F$$

1.8 Review of Selected Acceptor Intercalation Compounds

A brief summary of some of the graphite acceptor systems which are relevant to this work is given in the following section.

1.8.1 Graphite-Halogen and Interhalogen Compounds

Of the diatomic halogens, only bromine, Br_2 and possibly chlorine, Cl_2 are known to intercalate into graphite to give true intercalation compounds. The bromine intercalation compounds of graphite have been known since 1933,[47] and the composition $C_{4n}Br$ ($n \geq 2$) has been found for

these compounds[48]. It is interesting to note that the limiting composition corresponds to a stage two compound. Although formulae such as $C^+_nBr^-.3Br_2$ were given to early intercalation products[49], efforts to identify species such as Br^- or Br_3^- in the lattice have proven fruitless, and later research indicated that there is very little charge transfer between the intercalant and the host lattice in Br_2 intercalation[50]. Intercalation of chlorine led to compounds of formula $C_{4n}Cl$ ($3 \leq n \leq 5$) with interplanar spacing of about 7.0 Å[51].

Intercalation compounds of interhalogens such as ICl and IBr have been known for sometime [49], whereas ternaries such as $C_nBr_xCl_{1-x}$ have only recently been characterized[52].

The graphite-BrCl system is rather complicated since BrCl can disproportionate readily: $2BrCl \rightleftharpoons Br_2 + Cl_2$. When reacted with graphite, a product of formula $C_8Br_{0.55}Cl_{0.45}$ for the richest compound was found[52].

With increasing coordination, polarization of the X-Y bond is usually accentuated, and hence polyatomic interhalogens have stronger oxidizing abilities. BrF_3, ICl_3 and IF_5 all undergo appreciable auto-ionization in the liquid phase[53]: $2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$; $I_2Cl_6 \rightleftharpoons ICl_2^+ + ICl_4^-$; $2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$.

Oxidation of the graphite lattice, for example, may be carried out according to[12]:

$$2nC + 2ICl_2^+ \rightleftharpoons 2C_n^+ + ICl + \frac{1}{2} I_2Cl_6$$

The observation that in IF_5 intercalation, HF[54] or BF_3[11] catalyses the reaction led to the possible IF_4^+ anion formation mechanism[12],

$$IF_5 + mHF \rightleftharpoons IF_4^+H_mF^-_{m+1}$$

or

$$IF_5 + BF_3 \rightleftharpoons IF_4^+BF_4^-$$

This could take place more easily than by autoionization, and intercalation compounds of IF_5 may, therefore, contain HF_2^- or BF_4^- ions in addition to the molecular pentafluoride.

1.8.2 Graphite-Fluorosulfate Compounds

This group consists of three types of intercalation compounds:

a) Graphite fluorosulfates - C_nSO_3F.

b) Graphite acid fluorosulfates - $C_nSO_3F.(HSO_3F)$, and

c) Graphite bromine fluorosulfates - $C_nBr(SO_3F)_m$, m = 1, 3 and $C_{20}BrF(SO_3F)_2$.

These compounds will be briefly reviewed in the following subsections. Our research group has been actively involved in the re-investigation of group a) and b) graphite compounds, while all GIC's in group c) were reported by us for the first time[43]. In all instances, complete characterization by gravimetry, microanalysis and physical methods such as X-ray powder diffraction, ^{19}F-NMR, ^1H-NMR and Raman

spectroscopy, leaves little doubt regarding their compositions[43].

1.8.2a Graphite-Fluorosulfates

The oxidative intercalation of bis(fluorosulfuryl)peroxide, $S_2O_6F_2$ into graphite was first undertaken by Bartlett et al.[55]. A first stage compound of composition C_8SO_3F was reported by this group, but later research carried out by Hooley[56] using gas phase intercalation of $S_2O_6F_2$ into various types of graphite showed a limiting composition of C_7SO_3F. Synthesis performed by our group, in both liquid and gas phases[43], confirmed the above results. The bonding model for C_7SO_3F has been proposed, and a number of conversion reactions are reported[43] and have been mentioned in earlier sections.

1.8.2b Graphite-Acid Fluorosulfates

It has generally been recognized that fluorosulfuric acid, HSO_3F, by itself does not intercalate well, producing only a fifth stage material[57]. Hence the formation of lower stage compounds would have to involve an oxidizing agent. Electrochemical oxidation, first reported by Ubbelohde and coworkers[42] and later by Herold et al.[58] is said to produce a first stage intercalation compound formulated as $C^+_{24}.SO_3F^-.mHSO_3F$, with m = 2.0-2.5. Some evidence for the formation of a "C_{12}^+ compound" by overoxidation is found in the same study where the

following sequence is proposed:

$$C^{+}_{24}SO_3F^{-}.mHSO_3F \longrightarrow C^{2+}_{24}.2SO_3F^{-}.(m-1)HSO_3F + H^{+} + e^{-}$$

With CrO_3 as an oxidizer, a first stage compound of formula $C_{5\pm1}HSO_3F$ is said to be obtained[57], and the results of a Raman study of this compound[59] were interpreted in terms of tightly packed acid molecules in the lamellar spaces.

Yaddaden et al.[60] used HSO_3F and SO_3 or CrO_3 as oxidizing agents and carried out synthetic reactions between the acid solutions and Madagascar graphite. Although SO_3 was used as an oxidant, additional SO_3 would always be present whenever HSO_3F is used due to the equilibrium.

$$HSO_3F_{(l)} \rightleftharpoons SO_{3(g)} + HF_{(g)}$$

First stage compounds were obtained for reactions between graphite and HSO_3F/SO_3, with compositions $C_{10}HSO_3F$ to C_5HSO_3F. These values show a pronounced deviation from the values given by other authors for chemical oxidation[59,57].

When dilute solutions of SO_3 in HSO_3F were used, the main intercalant was found to be SO_3. For the case where the acid was relatively free of SO_3, CrO_3 had to be used as the oxidizing agent to yield first stage intercalation products. This study clearly shows that the purity of the acid could play an important role in the intercalation of HSO_3F into graphite.

The intercalation process carried out in fluorosulfuric acid may, therefore, have major limitations and could lead to difficulties when one attempts to explain possible compositions and mechanistic pathways. In order to avoid impurity based problems, the acid used in our work was purified by three successive distillations and hence made SO_3 free as much as possible. Research performed earlier in our group[43] showed that HSO_3F intercalation could be carried out rather conveniently by a successive intercalation method. The initial stage two intercalation product, for example $C_{14.1}SO_3F$, which was synthesized using graphite and $S_2O_6F_2$ vapor, was reacted with excess HSO_3F to give a stage one ternary product with composition $C_{14}SO_3F.1.05$ HSO_3F. The simultaneous intercalation of HSO_3F and $S_2O_6F_2$ indicated only very small amounts of acid present in the product. This is due to the greater ability of $S_2O_6F_2$ to undergo oxidative intercalation.

1.8.2c Graphite-Bromine Fluorosulfates

When graphite was reacted with $BrSO_3F$ at ambient temperature, an intercalated stage one product with composition $C_{12}BrSO_3F$ was obtained[43]. The reaction between graphite and $BrSO_3F$ at elevated temperature (105-110°), however, gives a different product with stoichiometry $C_{20}BrF(SO_3F)_2$[43].

The room temperature reaction is assumed to take place as:

$$12C + BrSO_3F \longrightarrow C_{12}BrSO_3F$$

The high temperature reaction sequence is proposed as follows:

$$3BrSO_3F \rightleftharpoons Br_2 + Br(SO_3F)_3$$

followed by,

$$Br(SO_3F)_3 \xrightarrow[\text{decomposition}]{\text{Partial}} BrF(SO_3F)_2 + SO_3$$

$$20C + BrF(SO_3F)_2 \longrightarrow C_{20}BrF(SO_3F)_2$$

The reaction of $C_{12}BrSO_3F$ and excess $S_2O_6F_2$, as shown earlier, gives an oxidative intercalation compound of formula $C_{16}Br(SO_3F)_3$. However, both stoichiometric and ^{19}F-NMR evidence suggest that some unintercalated $Br(SO_3F)_3$ is still present[43], and this excess material may be chemi-absorbed on the intercalation product.

In summary it seems that synthetic approaches to both fluorosulfate and halogen derivatives of graphite have relied extensively on the direct intercalation of Br_2, Cl_2, ICl, IBr or BrCl, $S_2O_6F_2$, $BrSO_3F$ and to a lesser degree, on oxidation of graphite in HSO_3F (via a chemical oxidizer or the electrochemical technique) or the oxidative conversion of a GIC, as exemplified by the synthesis of $C_{16}Br(SO_3F)_3$.

In order to widen the scope of the more useful direct intercalation method, for example to iodine fluorosulfates or perhaps I_2 itself, it becomes necesssary to consider direct intercalation with the intercalant dissolved in a suitable solvent.

Two general types of solvent promoted intercalation systems have been described and will now be considered:

1. The use of non-protonic solvents,
2. HSO_3F and other protonic acids as solvents.

These two systems will be discussed below as part of the review on selected intercalation compounds.

1.8.3 Graphite-Intercalation Compounds in Non-protonic Solvents

Two intercalation studies, carried out by Herold et al.[36] and Forsman et al.[61], will be illustrated in this section. Of the two works, the first mentioned gives more details on possible compositions and the nature of the intercalated species. NO_2^+ ion is a common oxidizer in both systems. It was shown by Herold et al.[36] that nitryl salts such as NO_2BF_4, NO_2PF_6 and NO_2SbF_6 (or the nitrosyl salt $NOSbF_6$) when dissolved in dry nitromethane, CH_3NO_2, produced NO_2^+ (or NO^+ from $NOSbF_6$) ions, which were able to oxidize graphite to give intercalation compounds.

Fluoroanions of salts such as BF_4^-, PF_6^- and SbF_6^- were intercalated into pyrographite, and by chemical analyses and X-ray methods, the GIC's were shown to have the ideal composition $C^+_{23n}MF_6^-(CH_3NO_2)_y$, where n is the stage and y = 1.7-2.5.

^{19}F and ^{31}P NMR studies have been carried out on the second stage product of PF_6^- in order to establish the nature of the intercalated species. The main reaction is thus given as:

$$NO_2PF_6 + nC \longrightarrow NO_2 + C_n^+PF_6^-$$

The second study by Forsman et al.[61], noticably lacking in chemical and spectroscopic evidence, shows the intercalation of SbF_6^- or BF_4^- into graphite. NO_2SbF_6 and NO_2BF_4 were dissolved in tetramethylene sulfone (sulfolane) to give the above anions. Neutral solvent molecules together with the anions and possibly NO_2BF_4 or NO_2SbF_6 molecules are believed to intercalate into graphite. No information on the actual composition of the products was given. It was however observed that the reactions at 40°C gave different products from those run at room temperature. This is explained by assuming that the amount of solvent (together with the anions and the neutral molecules) that inserts may depend on the intercalation temperature.

Solvent-cointercalation has also been noted by Hooley, where nitromethane was found as an intercalate during the solution intercalation of $FeCl_3$[62].

1.8.4 Graphite-Intercalation Compounds in Protonic Solvents

The two solvent systems that are to be described in this section are:

a) Oxidizing acids (e.g. HNO_3) and graphite systems

b) Solutions of oxidizing agents in protonic acids and graphite systems.

1.8.4a Graphite-Nitric Acid Compounds

On account of its strong oxidizing ability, HNO_3 is unique in acting both as a solvent and an oxidizing agent towards graphite. Only gaseous or liquid nitric acid is involved in the reaction with graphite[63]. This system provided useful information regarding the role played by the solvent in intercalation reactions.

As suggested by Forsman, the active species in intercalation by HNO_3 is the nitronium ion[37,38]. NO_2^+ is generated in the liquid phase by the self-dissociation of HNO_3. In vapor phase intercalation, it is observed as a surface adsorbed species.

The following mechanism is proposed for the vapor phase intercalation[38]:

$$HNO_{3(g)} \rightleftharpoons HNO_{3(ads)}$$

$$2HNO_{3(ads)} \rightleftharpoons NO_2^+{}_{(ads)} + NO_3^-{}_{(ads)} + H_2O$$

$$C_n + NO_2^+{}_{(ads)} \longrightarrow C_n^+ + NO_{2(ads)}$$

$$NO_{2(ads)} \longrightarrow NO_{2(g)}$$

$$C_n^+ + NO_3^-{}_{(ads)} + mHNO_3 \rightleftharpoons C_n^+.NO_3^-.mHNO_3$$

The number of neutral acid molecules m in the product is stated as 4.5 and 4.3[64], respectively, with m dependent on the partial pressure of

HNO_3, P_{HNO3}, resulting frequently in stage transformations. The initial intercalation of HNO_3 into graphite takes place along the basal planes[69]. This observation is similar to the one made earlier by Hooley during the intercalation of bromine[66,67].

The following conclusions can be drawn from the above discussion:

a) HNO_3 is unique in providing both the oxidizer (NO_2^+) and the intercalates (NO_3^- and HNO_3).

b) Gas phase intercalation occurs by a complex mechanism, but a strong similarity to the intercalation by $Br_{2(g)}$ is noted.

c) Co-intercalation of acid molecules takes place with removal of HNO_3 being relatively easy.

1.8.4b Graphite-Solutions of Oxidizing Agents in Protonic Acids

Since the focus of this thesis is on the synthesis of acceptor GIC's in fluorosulfuric acid, a closer look at some related systems is now necessary.

When considering intercalation into graphite using solutions of strong protonic acids, two quite distinct objectives emerge:

1) Intercalation of acid anions, possibly with concomitant cointercalation of the neutral acid molecules aided by suitable oxidizing agents:

$$nC + \text{excess } HX + \text{Oxidizer} \longrightarrow C_nX.mHX$$

This is the general route to acid salts, and, as shown earlier, anodic oxidation in strong acids may be treated as a special case within this group.

2) The intercalation of acceptor compounds, which will not intercalate by themselves for physical reasons, dissolved in protonic acids acting as ionizing solvents: the objective now is to intercalate the solute Y, with possible acid cointercalation according to

$$nC + Y_{(solv)} \longrightarrow C_nY$$

The latter category of reactions is of interest to us while the first group has already been reviewed[35,68].

Graphite intercalation in chlorosulfuric (HSO_3Cl) and fluorosulfuric (HSO_3F) acids was first reported by Herold et al.[69,70]. Chlorosulfuric acid was used as the solvent in one system, and elemental chlorides such as $CuCl_2$, $ZnCl_2$, $PbCl_2$, $AlCl_3$, BCl_3, $SbCl_5$, and $AuCl_3$ were dissolved, and the resulting solutions were exposed to graphite[69].

Although no chemical analyses or mechanisms were shown, the following conclusions are reported for the intercalated products:

a) Insertion of acid only is quoted for most of the halides, i.e. $CuCl_2$, $ZnCl_2$, $MnCl_2$, $PbCl_2$, $FeCl_2$, PCl_5, $NbCl_5$, etc., and an interlayer separation I_c of ~8.03 Å was observed with stages ranging from 3 to 5.

b) Formation of ternary BCl_3 + HSO_3Cl compounds with I_c ~8.36 Å (stage 3) was found for BCl_3.

c) Two phase systems were shown to be present: one graphite-HSO_3Cl

phase (I_c' = 8.10 Å), one graphite-$AuCl_3$ or $SbCl_5$ or $SbCl_3$ phase.

In all cases, the X-ray diffraction technique was used as the sole means of product characterization.

A similar study was carried out using HSO_3F and metal fluorides CuF_2, NiF_2, AlF_3, FeF_3, NbF_5, SbF_5 etc. by the same authors[70]. No mechanisms were given for any reactions, and chemical analyses were shown only for the first stage graphite-SbF_5 compound. In most cases, the temperature had to be kept at ~60°C for intercalation to proceed. For all the halides other than SbF_5, only HSO_3F was found as the intercalate. Interplanar distances were about 7.90 Å to 8.03 Å, with stages of 2 to 4 for these intercalated products. For the reaction between SbF_5 and graphite, a first stage ternary compound with general formula $C_7(HSO_3F)_{X'}(SbF_5)_{1-X'}$ was proposed[70], where X and X-1 represent the fractional proportions of HSO_3F and SbF_5 in the free starting mixtures. The many possible complex associations between HSO_3F and SbF_5 is cited as the primary cause which makes accurate interpretation of data difficult. In summary, these studies are rather fragmentary, and the resulting products are poorly characterized. It is unclear from these studies whether oxidative intercalation occurs or not, whether the acid or its anion intercalate or perhaps even both, and in what oxidation state and molecular form intercalated solute is present.

1.9 Intercalation in Fluorosulfuric Acid

The use of fluorosulfuric acid, HSO_3F, in our study as the solvent was considered advantageous for several physical and chemical reasons.

HSO_3F is commercially available, easily purified by distillation at atmospheric pressure and will not etch glass at room temperature when pure. Some physical properties of the acid are summarized in Table 1.2. The acid's broad liquid range is an asset which permits the study of reactions over a very wide temperature range.

The low viscosity of HSO_3F compared to H_2SO_4 simplifies many operations such as filtration or vacuum transfer and enhances ion mobility. Also, excess acid can be removed at room temperature via a dynamic vacuum, which makes it possible to obtain GIC's free of surface adsorbed fluorosulfuric acid.

As discussed previously, HSO_3F does not intercalate by itself well[57], and hence ideally functions as an uncomplicated solvent medium in graphite intercalation. It is also an excellent ionizing solvent on account of its high dielectric constant. Moreover, the high acid strength makes it an ideal solvent for non-volatile, often solid or viscous intercalants in GIC synthesis. Since almost all the compounds used in this work undergo ionization to varying degrees in fluorosulfuric acid, most solutes show basic behavior resulting in increased SO_3F^- ion formation. In addition, HSO_3F is transparent over the visible and near UV region, which should allow monitoring intercalation of absorbing solutes via UV-visible spectroscopy. Another reason for using HSO_3F in our research is that all the compounds used have a common anion, i.e.

Table 1.2: Physical and Thermochemical Properties of Fluorosulfuric Acid*

Property	Value	Temperature (°C)
Boiling point (°C)	162.7 164.4	
Freezing point (°C)	-88.98	
Density (D_4^{25})	1.726 1.728	25 25
Viscosity (centipoise)	1.56 1.72	25 25
Dielectric constant	~120	25
Specific conductance ($ohm^{-1}\ cm^{-1}$)	1.08×10^{-4}	25
Heat capacity ($cal\ deg^{-1}\ g^{-1}$)	0.28	25
Latent heat of vaporization ($kcal\ mole^{-1}$)	8.4	
Heat of formation of gas, (from elements) ($kcal\ mole^{-1}$)	181.9	
Heat of formation of liquid, (from elements) ($kcal\ mole^{-1}$)	190.3 184	
Heat of formation of gas from gaseous SO_3 and HF ($kcal\ mole^{-1}$)	23.2	

* from reference 71.

SO_3F^-, with respect to HSO_3F. Due to this, the intercalants form relatively simple ions in a solution of fluorosulfuric acid. The extensive use of the acid in synthetic reactions by our group and others, as well as its compatibility with oxidizing agents such as $S_2O_6F_2$ (which has been studied previously with regard to intercalation[43]) justifies its use as a solvent in GIC synthesis.

However, some complications do occur in this solvent system. Many solutions of HSO_3F are exceedingly complex, and if these solutions are used as intercalants, interpretation of results may lead to difficulties; e.g. SbF_5-HSO_3F in graphite intercalation[70]. Fluorosulfuric acid is sensitive to moisture, which makes it necessary to carry out solvent manipulation and synthetic reactions under vacuum or inert atmosphere conditions. Additionally, in the presence of oxidizing intercalants, co-intercalation of HSO_3F may take place and as a consequence, ternary intercalation compounds are generally formed. In such instances, H-microanalysis results could give an indication of the extent of acid intercalation.

In addition, there are two principal equilibria in HSO_3F to consider[71].

(a) Self-ionization or autoprotolysis:

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^-, \quad K_{ap} = 3.8 \times 10^{-8} \text{ mole}^2 \text{ kg}^{-2}$$

The $H_2SO_3F^+$ ion is termed acidium ion and SO_3F^-, base ion.

(b) Self-dissociation:

$$HSO_3F \rightleftharpoons HF + SO_3, \quad K_{sd} < 3 \times 10^{-7} \text{ mole}^2 \text{ kg}^{-2}$$

The SO_3 thus produced can aid oxidative intercalation, but at room temperature the extent of dissociation can be considered negligible.

In order to extend intercalation studies to cationic iodine species and iodine as well as bromine fluorosulfate compounds, HSO_3F becomes the solvent of choice for the following reasons:

(a) Iodine cations, in particular I_3^+ and in spite of limited dissociation I_2^+, are stable in this solvent, and their UV-visible spectra are known.[72] They may be generated in HSO_3F by the reaction,

$$nI_2 + S_2O_6F_2 \xrightarrow{HSO_3F} 2I_n^+(solv) + 2SO_3F^-(solv)$$

where n = 2 or 3.

(b) $I(SO_3F)_3$ and $Br(SO_3F)_3$ behave as non-electrolytes in HSO_3F, which implies that dissociation is extremely slight.[94,97]

(c) The anions $I(SO_3F)_4^-$ or $Br(SO_3F)_4^-$ may be obtained by dissolution of $K[I(SO_3F)_4]$ or $K[Br(SO_3F)_4]$ in HSO_3F.

1.10 Enhanced Electrical Conductance in Intercalated Compounds

For a few compounds, the enhanced electrical conductivities were measured using the contactless radio frequency method[82]. Since the main goal of this thesis is the synthesis of new acceptor intercalation compounds, only a few samples were used to obtain basal plane conductivities. Nevertheless, an explanation of this phenomenon is necessary, since the practical application of GIC's is largely based on their enhanced conductance in the basal plane.

Enhanced electrical conductivity in intercalated graphite samples can be explained by studying the electronic density of states for graphite (Fig. 1.5). In an isolated carbon layer, the bonding (π) and antibonding (π^*) bands are formed from ρ orbitals of the carbon atoms, with an overlap energy of about 30-40 meV[88]. Due to this band separation or gap, electrons can move from the valence (π) band to the conduction (π^*) band. This process creates positive holes in the valence band. These holes as well as electrons in the conduction band are the basic carriers of charge in the graphite lattice.

Although this model does not take into consideration the interaction between the graphite layers, it is not "ideal", since the interlayer forces (Van der Waals type) are quite weak by nature[89].

Donor type intercalants would add electrons and acceptor intercalants would remove electrons from the conduction (π^*) band and valence band (π) respectively. Therefore, in donor GIC's the enhanced electrical conductivity in both a-and c-axis directions is due to the presence of additional electrons. However, in acceptor compounds, holes, which

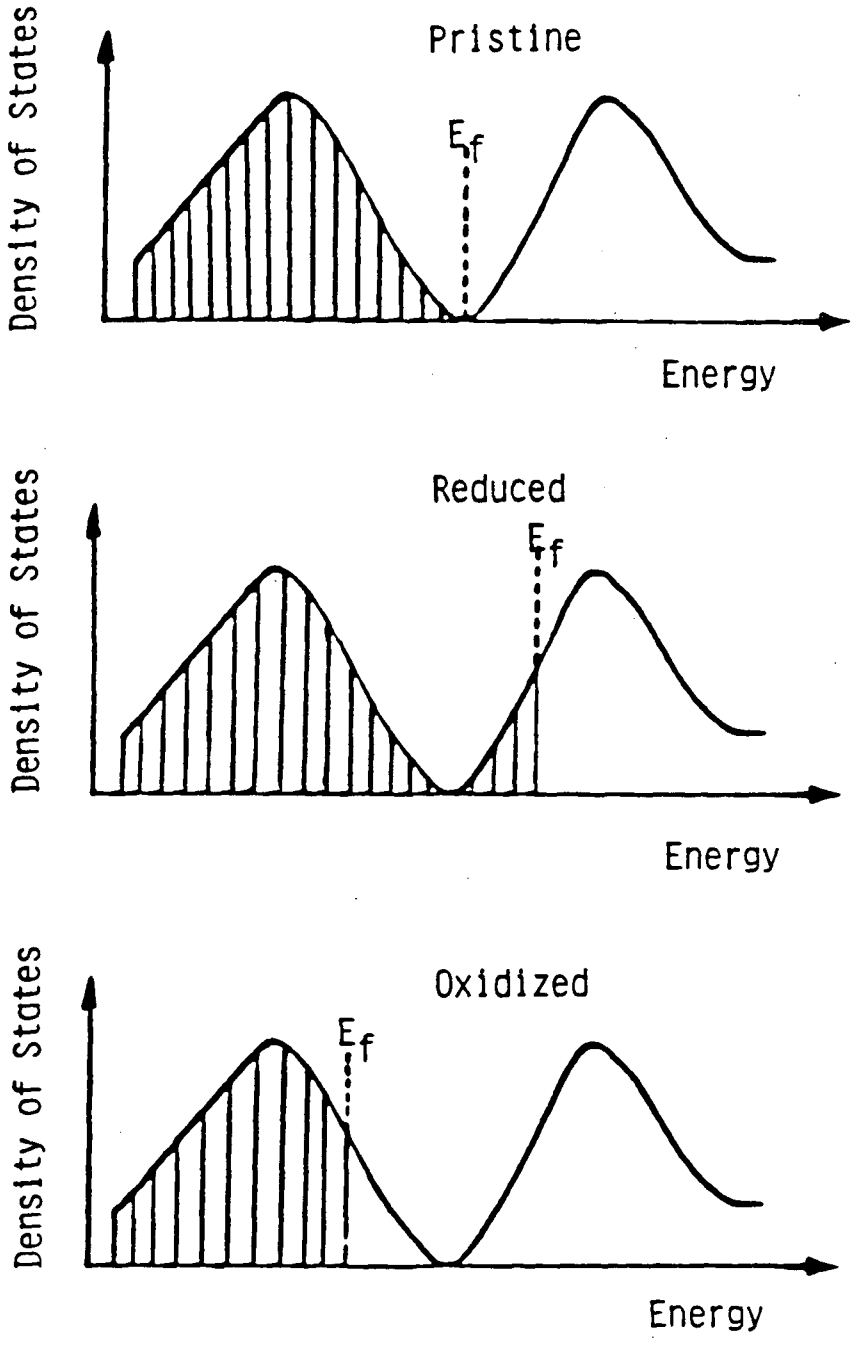


Figure 1.5: Density of States in Pure, Reduced and Oxidized Graphite According to the Band Model.

are formed by the loss of electrons, would increase the conductance along the basal plane. Another factor which contributes to high basal plane conductivity in acceptor GIC's is the charge localization around the intercalate species. This process will effectively minimize any interaction between the carbon layers, hence giving the compounds extreme 2D characteristics[90-92].

1.11 Purpose of This Study

The reasons that initiated this research leading to the synthesis of new acceptor graphite intercalation compounds can be summarized as follows:

a) Synthetic aim to intercalate iodine-fluorosulfate compounds or iodine itself by utilizing $I_2^+{}_{(solv)}$ as precursor.

b) Comparative study of the intercalation of $BrSO_3F$ reported previously with HSO_3F as solvent, and with extension to $Br(SO_3F)_3$, hopefully providing a better route to synthesis of $C_nBr(SO_3F)_3$.

c) An attempt will be made to ascertain reaction conditions, which would lead to the formation of GIC's where acid cointercalation is eliminated or minimized.

d) Utilization of $NO^+ + e^- \longrightarrow NO$ couple to intercalate SO_3F^- in fluorosulfuric acid, and a comparison of this synthetic route to direct intercalation of graphite by $S_2O_6F_2$. This system will also be compared to the NO^+ promoted intercalation systems in non-

protonic solvents.

e) Exploratory reactions of non-intercalated halogen fluorosulfates, which are pertinent to intercalation chemistry, will be investigated.

CHAPTER 2

EXPERIMENTAL SECTION

EXPERIMENTAL

General Comments

Since most compounds used in this research were moisture sensitive, care was taken at all stages to avoid any contact with moist air. The synthetic reactions were performed in well ventilated fumehoods and transfers of materials were carried out in a dry box filled with purified nitrogen or argon. All volatile compounds were handled in glass vacuum lines mounted on metal frameworks inside fumehoods.

2.1 Apparatus

2.1.1 Glass Vacuum Line

Standard high vacuum techniques were used in all the synthetic reactions. The high reactivity of the compounds towards moisture made it necessary to keep the pressure at 0.001 torr. The main manifold of the pyrex vacuum line was 600 mm in length and 20 mm O.D. Five outlets fitted with Kontes teflon stem stopcocks were used to attach reactors and other apparatus through B10 ground glass cone and socket joints. The vacuum line was connected to a Welch Duo-seal mechanical pump (model 1405) via a liquid nitrogen cold trap to prevent any corrosive volatile

materials being drawn through the pump. Pressures measured in the manifold using a mercury manometer showed values from 0.5 torr to 1 atmosphere. Transfer of liquids and other volatile material from one reaction vessel to another was carried out using a T-connecting bridge, which was attached to the vacuum line via a B10 cone.

2.1.2 Metal Fluorine Line

In the $S_2O_6F_2$ preparation (Fig. 2.7), the fluorine line and the flow apparatus were built using copper or monel tubing (1/4 inch, O.D.) attached to a metal frame work. The valves used were from Whitey Research Tool Co., California; Hoke Inc., New Jersey and Autoclave Engineering Inc., Pennsylvania respectively. All connections in the line were either silver soldered or made with Swagelock fittings.

2.1.3 Dry Atmosphere Box

The manipulation of all air sensitive compounds were carried out in a Vacuum Atmosphere Corporation "Dri-Lab", model HE-43-2, fitted with dry and purified nitrogen or argon. P_2O_5 was kept in an open container inside the dry box to remove any residual moisture and to act as an indicator. The dry box was equipped with a "Dri-Train" model HE-93B recirculating unit for constant circulation of nitrogen or argon over molecular sieves. A Mettler P160 top loading balance was used inside

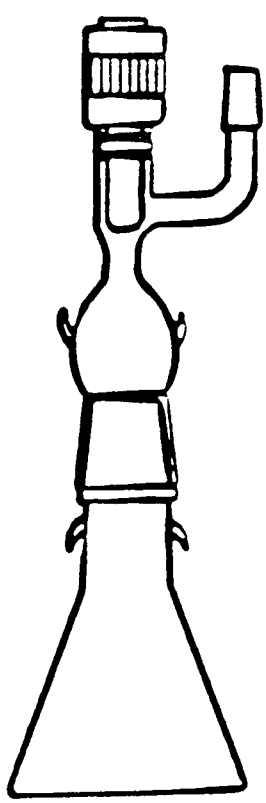
the dry box in order to weigh hygroscopic materials.

2.1.4 Reaction Vessels

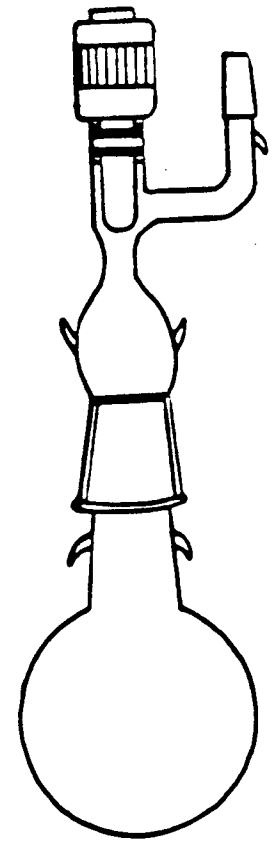
Primarily two types of pyrex vessels were used.

a) Two Part Glass Reactor

The reaction flask used was either a 50 ml Erlenmeyer flask or a round bottom flask with a standard B19 ground glass cone. The reactor top consisted of an adapter with a Kontes teflon stem stopcock sandwiched between a B19 socket and a B10 ground glass cone, for attachment to the glass vacuum line (Figs. 2.1(A) and 2.1(B)). The flat bottom Erlenmeyer flask had the advantage of exposing a larger surface area of graphite for intercalation reactions. Obvious disadvantages of using a flat bottom apparatus in vacuum line work were the small volume of the reactions and the fact that during the reactions HSO_3F and more so $S_2O_6F_2$ raised the internal pressure at room temperature to at least 5 torr. Also, the addition of reagents and HOPG plates was much more easily carried out in a two part glass reactor than in a single part reactor. The obvious disadvantage was the possible contamination of products due to fluorocarbon grease (or its reaction products) which had to be applied at the ground glass joints to maintain leakproof connections under vacuum. Quite obviously, two part reactors are particularly useful in exploratory intercalation studies.



(A)



(B)

Figure 2.1: Two Part Reaction Vessels.

(A) "Flat Bottom" Reactor.

(B) "Round Bottom" Reactor.

b) One Part Glass Reactors

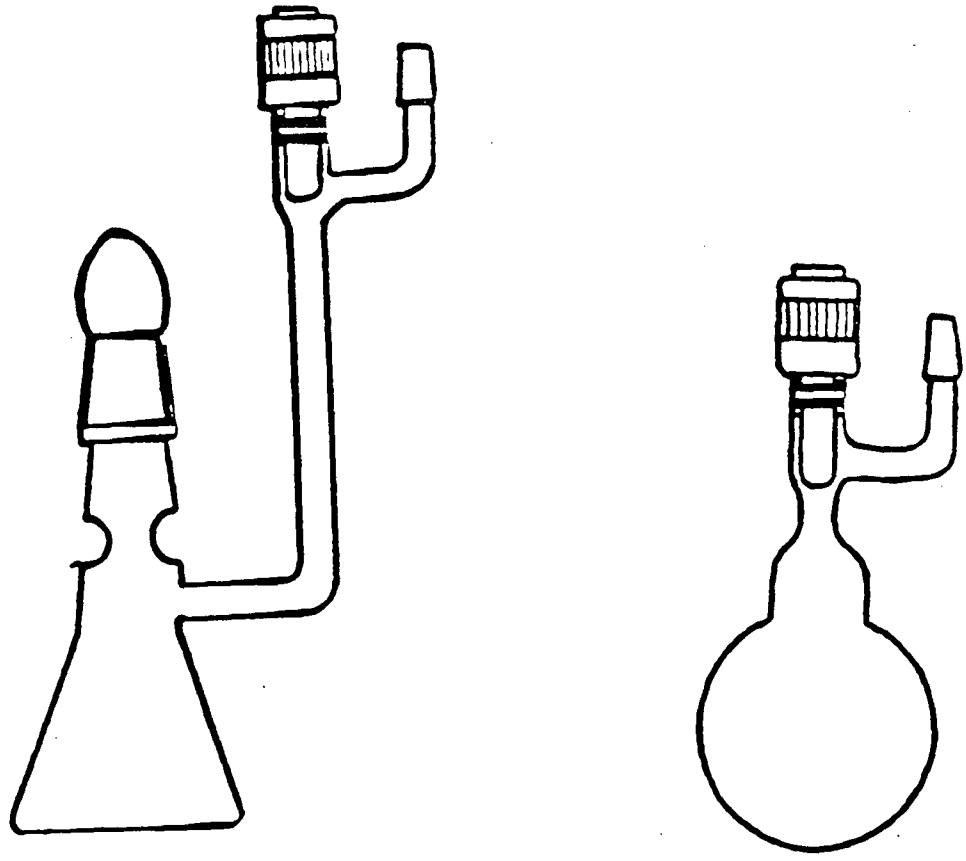
To avoid grease contamination altogether, single part reaction vessels were used wherever necessary (Figs. 2.2 and 2.3). The seal-off one part reactor (Fig. 2.2(A)) was made up of either a pyrex Erlenmeyer flask or a round bottom flask (50 ml), with a constriction and a B19 cone. The side arm of the reactor was fitted with a Kontes teflon stem stopcock, and a B10 cone. Once the reagents were added in the dry box, the capped reactor could be flame sealed at the constriction. The addition of liquid reactants was carried out via distillation through the side arm.

Both single part reaction vials (Fig. 2.3) and reaction vessels with a round bottom flask (Fig. 2.2(B)) were also used. The addition of SP1 graphite and solid or liquid reagents could be done with relative ease in these types of reactors. Teflon coated magnetic stir bars (10 mm x 3 mm) were used in order to mix solid and liquid phases in intercalation reactions as well as in primary synthesis reactions.

2.1.5 Miscellaneous Glass Apparatus

a) $S_2O_6F_2$ Addition Trap

When stoichiometric amounts of $S_2O_6F_2$ were needed for a reaction, an addition trap was used (Fig. 2.4). Exact volumes of up to 0.50 ml could be distilled using this device. The trap was made up of a pipette

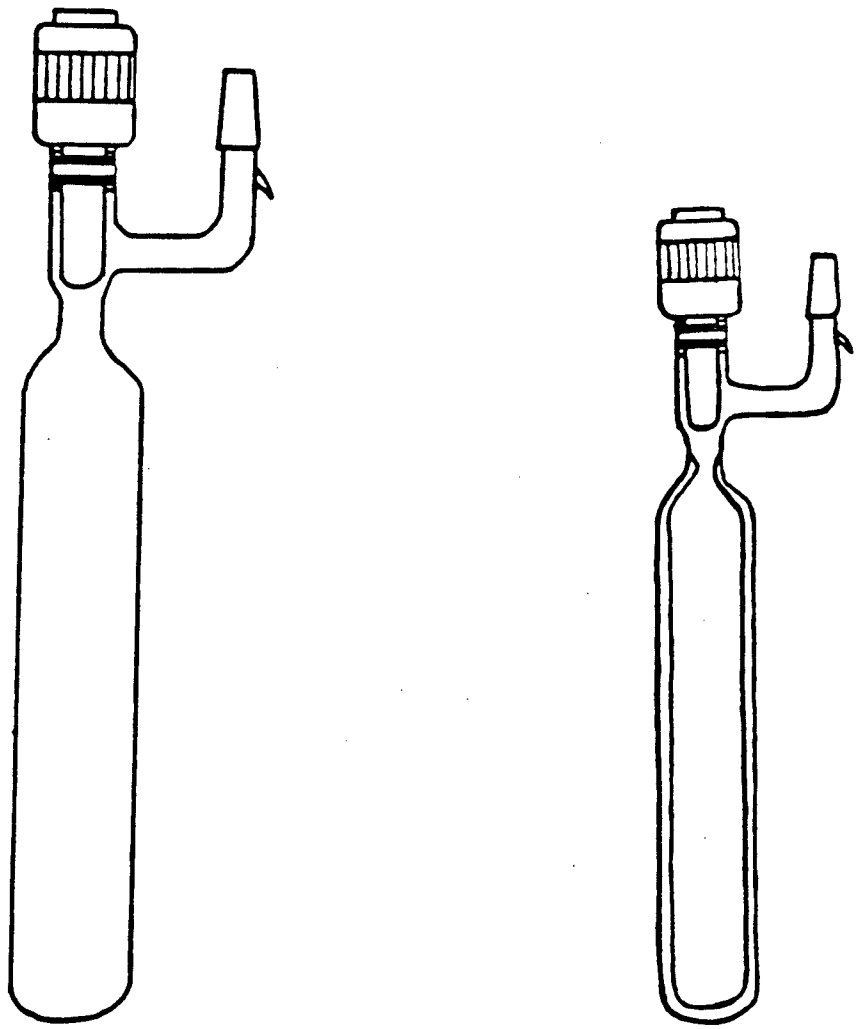


(A) (B)

Figure 2.2: One Part Reaction Vessels,

(A) "Seal off" One Part Reactor.

(B) "Round Bottom" One Part Reactor.



(A) (B)

Figure 2.3: One Part Reaction Vials.

(A) "Medium Walled" Reactor.

(B) "Thick Walled" Reactor.

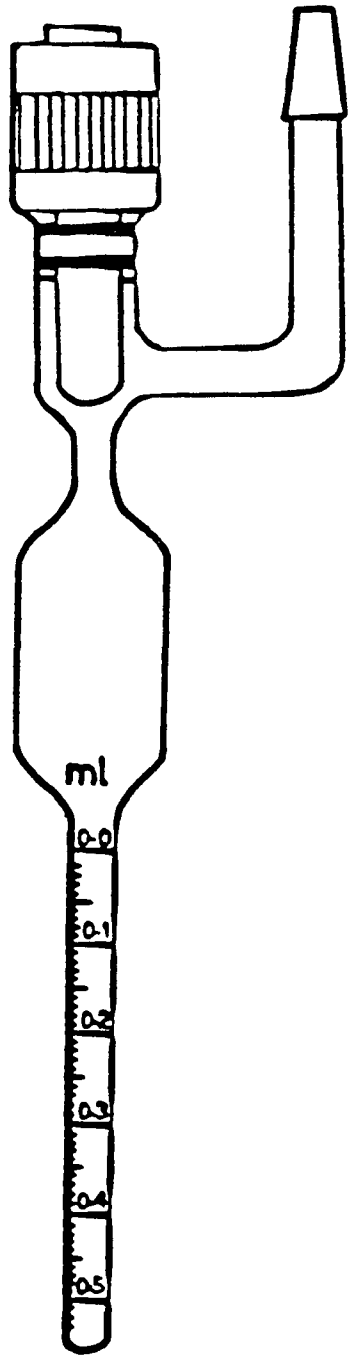


Figure 2.4: $S_2O_6F_2$ Addition Trap.

(0.00-0.50 ml) fitted with a 20 mm long (10 mm O.D.) pyrex bulb to which a Kontes teflon stem stopcock was attached. A side arm extension ended with a B19 ground glass cone. The compact nature of the trap made it easy to weigh in an analytical balance, thus providing another method to check the amounts added. For addition of larger amounts of $S_2O_6F_2$, a similar type of trap, with a 4.00 ml capacity pipette, was used.

b) Vacuum Filtration Apparatus

In order to separate a solid from a liquid in a reaction mixture, a vacuum filtration apparatus (Fig. 2.5) as described in Shriver[87] was used. The apparatus consisted of a 25 mm O.D. pyrex glass tube in which a medium coarseness glass frit was set about one third from the bottom. The top of the tube ended in a B19 cone and the bottom in a B19 socket. Between the glass frit and the B19 socket, a Kontes teflon stem stopcock was connected. The side arm of the apparatus also had a similar stopcock, above which a B19 ground glass cone was attached. Once the B19 socket was fitted with a 100 ml round bottom flask, the whole apparatus could be evaporated. The filtration was then carried out in the dry box.

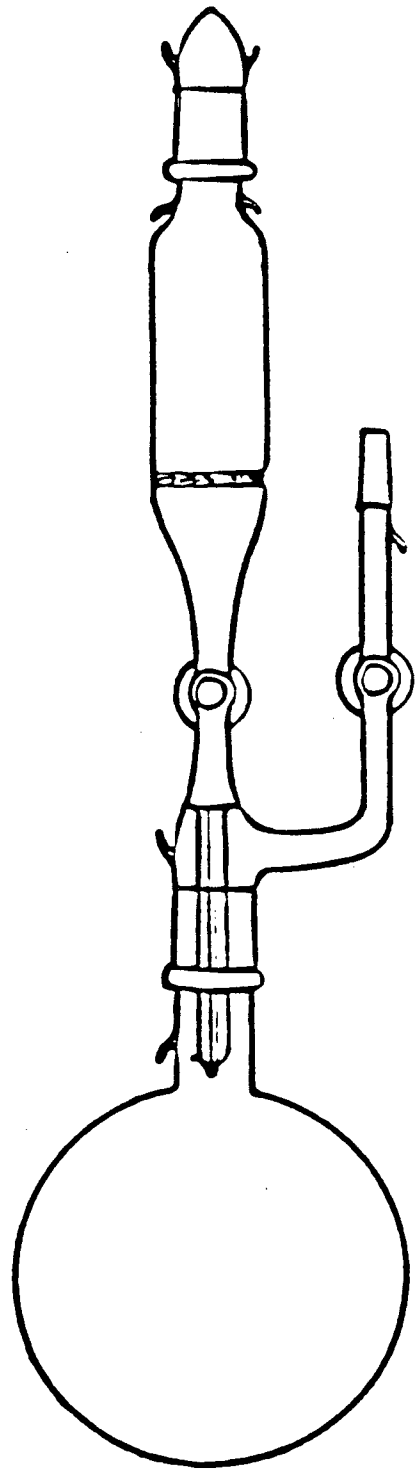


Figure 2.5: Vacuum Filtration Apparatus.

2.2 Analytical Equipment

2.2.1 Visible and Ultraviolet Spectrophotometer

A Cary 17D double beam spectrophotometer was used to obtain room temperature U.V. and visible spectra in the range of λ = 750-300 nm. The wavelength range of the spectrophotometer was 186-2650 nm and the spectral band width 0.1 nm. Samples were filled in 1.00 mm cell path quartz optical cells obtained from Thermal Syndicate Ltd., England, and kept airtight with teflon stoppers. All solutions were made and transferred in the dry box.

2.2.2 Infrared Spectrophotometer

Infrared spectra were recorded using a Perkin-Elmer 598 grating spectrophotometer, in the wavelength range of 4000-200 cm^{-1}. Since the compounds used were highly reactive and moisture sensitive, AgBr windows were used without a mulling agent. The samples were prepared in the dry box and spectra recorded as soon as possible. Gaseous I.R. spectra were taken using a monel metal cell, which was fitted with vacuum tight AgCl windows (0.042 inch thickness). A polystyrene film was used as a reference for all spectra, and the optical windows were obtained from the Harshaw Chemical Co., Ohio.

2.2.3 Nuclear Magnetic Resonance Spectrometer

A Bruker CXP-200 FT-NMR spectrophotometer was used to record solid state ^{19}F spectra. The spectrophotometer was operated at 188.15 MHz. NMR tubes of 30 mm length and 5 mm O.D. were used. The powder samples were loaded inside the dry box and flame sealed. Freon-11 was used as an external reference. High resolution ^{1}H spectra of liquid samples were taken using a Varian EM-360, at a frequency of 60 MHz. Tetramethylsilane (TMS) was used as an external reference. ^{19}F spectra of liquids were recorded on a Varian EM-360, operated at 56.45 MHz. HSO_3F and Freon-11 were used as internal and external references respectively. All spectra were taken at room temperature.

2.2.4 Raman Spectrophotometer

Room temperature Raman spectra were recorded using a Spex Ramalog-5 spectrophotometer, and the excitation wavelength was the green line at 514.5 nm, emitted by a Spectra Physics 164 argon ion laser. Since graphite intercalation compounds have a very high reflectivity as well as absorption, a back-scattering arrangement was used[80]. This geometry minimizes the loss of laser power at the quartz windows and also prevents any polarization change in the incident beam (Fig. 2.6). A teflon cell, with quartz windows, was used to hold the samples. All sample manipulations were done in the dry box, and spectra were taken as soon as the sample preparation was over.

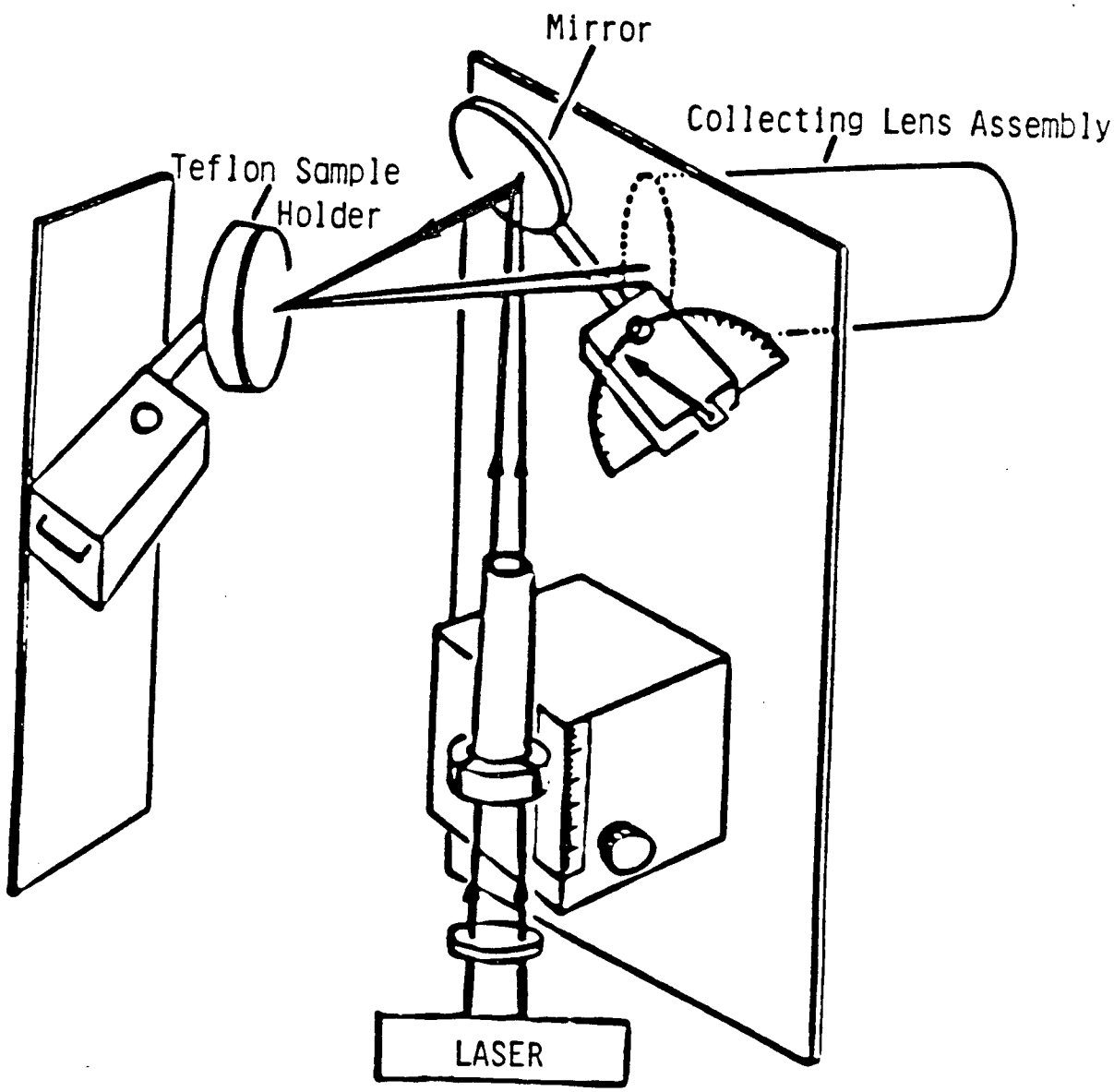


Figure 2.6: Back-scattering Arrangement Used for Raman Spectra.

2.2.5 X-ray Powder Diffraction

X-ray powder photographs were taken using a Phillips powder camera of 57 mm radius, having a conventional Straumanis loading arrangement. Cu-K_α X-ray radiation (λ = 1.5405 Å) was used with a nickel filter to reduce K_β radiation. The time of exposure depending on the nature of the samples, ranged from 8-12 hrs. The powder samples were loaded into 0.5 mm Lindemann glass capillaries in the dry box and flame sealed. Kodak NS-392 T type films were used to obtain X-ray powder photographs. The diffraction lines were measured on a film illuminator, which was made up of a meter stick to which a measuring slide assembly, containing a Vernier and a magnified cross-hair for location of the diffraction lines, was attached. The accuracy of the measurement is ±0.03 Å.

2.3 Elemental Analyses

Carbon, hydrogen, and nitrogen analyses were done by Mr. P. Borda at the Microanalytical Laboratory of the Chemistry Department, The University of British Columbia. A flash oxidation method, using a Carlo Elba model 1106 elemental analyzer, was used for this purpose[81]. Elemental sulfur and halogens were analyzed by Analytische Laboratorien, Gummersbach in West Germany. All samples used for microanalysis were loaded into glass tubes (6-7 mm O.D.) in the dry box and flame sealed.

2.4 Electrical Conductivity of Intercalated HOPG Samples

A contactless radiofrequency induction technique[82] was used to measure the room temperature electrical conductivity of intercalated HOPG samples. A circular ferrite core of 60 mm diameter was used to insert the sample tubes. The thickness of the sample and the surface area were measured using a travelling microscope and a toolmaker's micrometer. The system was calibrated using metal samples with known electrical conductivities. The overall relationship is given by:

$$\Delta V = kts^2\sigma$$

where,

ΔV = output voltage (mv)

k = constant

t = thickness of the sample (cm)

s = surface area of the sample (cm^2)

σ = electrical conductivity of the sample ($ohm^{-1}\ cm^{-1}$)

Some other useful relationships are as follows:

σ/σ_g = specific conductivity. (σ_g = conductivity of HOPG).

k/k_g = specific conductivity (normalized) per plane of graphite.

= $\Delta V/\Delta V_g$.

t/t_o = increase in thickness.

$\therefore \sigma/\sigma_g = (k/k_g)/(t/t_o)$.

2.5 Other Techniques

Mass spectra were obtained with a Kratos MS50 mass spectrometer operated at 70 eV. A Thomas Hoover capillary melting point apparatus was used to get the melting points.

2.6 Preparation and Purification of Reagents

2.6.1 $S_2O_6F_2$

Bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, was prepared (in several kilogram quantities) by the reaction of fluorine and sulfur trioxide using a AgF_2 catalyst at a temperature of ~180°C [83,84]. The experimental set-up for this preparation is shown in Fig. 2.7. This method is a modified version of the general synthetic route as described in the literature. Pressure regulated fluorine was passed through a stainless steel cylinder containing NaF. This trap is necessary to remove any HF impurities from the fluorine gas. HF free fluorine was then allowed to react with sulfur trioxide, which was carried to the AgF_2 catalytic reactor by a stream of dry nitrogen. Excess flow of fluorine was detected using a fluorolube oil bubble counter.

To improve the yield of the reaction, sulfur trioxide was heated using a heating mantle to 50°C, and the overall reaction temperature was maintained at ~180°C. The products generated were collected by condensation in the dry ice traps A, B and C, kept at -78°C. Excess

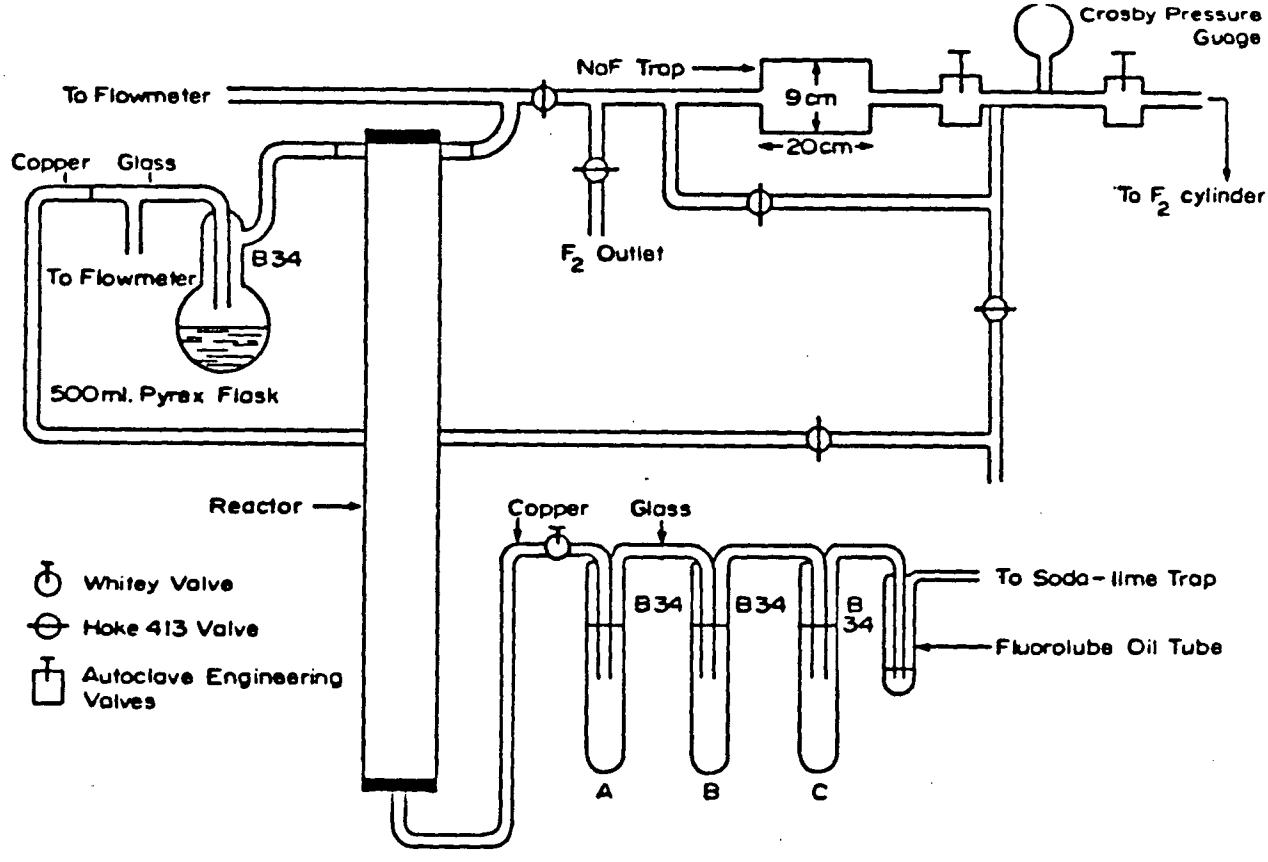


Figure 2.7: Apparatus for the Preparation of $S_2O_6F_2$.

fluorine and by-product FSO_3F were carried to a soda lime reactor, hence rendering them inactive. The condensed colorless liquid was extracted with 96-98% H_2SO_4 to remove any unreacted sulfur trioxide. This purified $S_2O_6F_2$ was then vacuum distilled into pyrex storage vessels. Gas phase infrared spectroscopy and liquid ^{19}F NMR were used to confirm the purity of the $S_2O_6F_2$ obtained.

2.6.2 HSO_3F

Technical grade fluorosulfuric acid was obtained from commercially available sources and was purified by a double distillation technique described by Thompson and Gillespie[85,86]. The apparatus used for this method is shown in Fig. 2.8. The entire system was first flame dried to remove any moisture, and nitrogen was flushed through for about 15 h. Distillation was carried out under a blanket of dry nitrogen at atmospheric pressure, and the first fraction collected was made HF free by a counterflow of nitrogen. The constant boiling second fraction was then collected at 163°C. The storage container was evacuated and the acid stored in the dry box to protect it from any contamination.

2.6.3 I_2^+(solv)

Preparation of this reagent was carried out according to the method described by Gillespie and Milne[72]. 1.1057 g of I_2 and 0.4298 g of

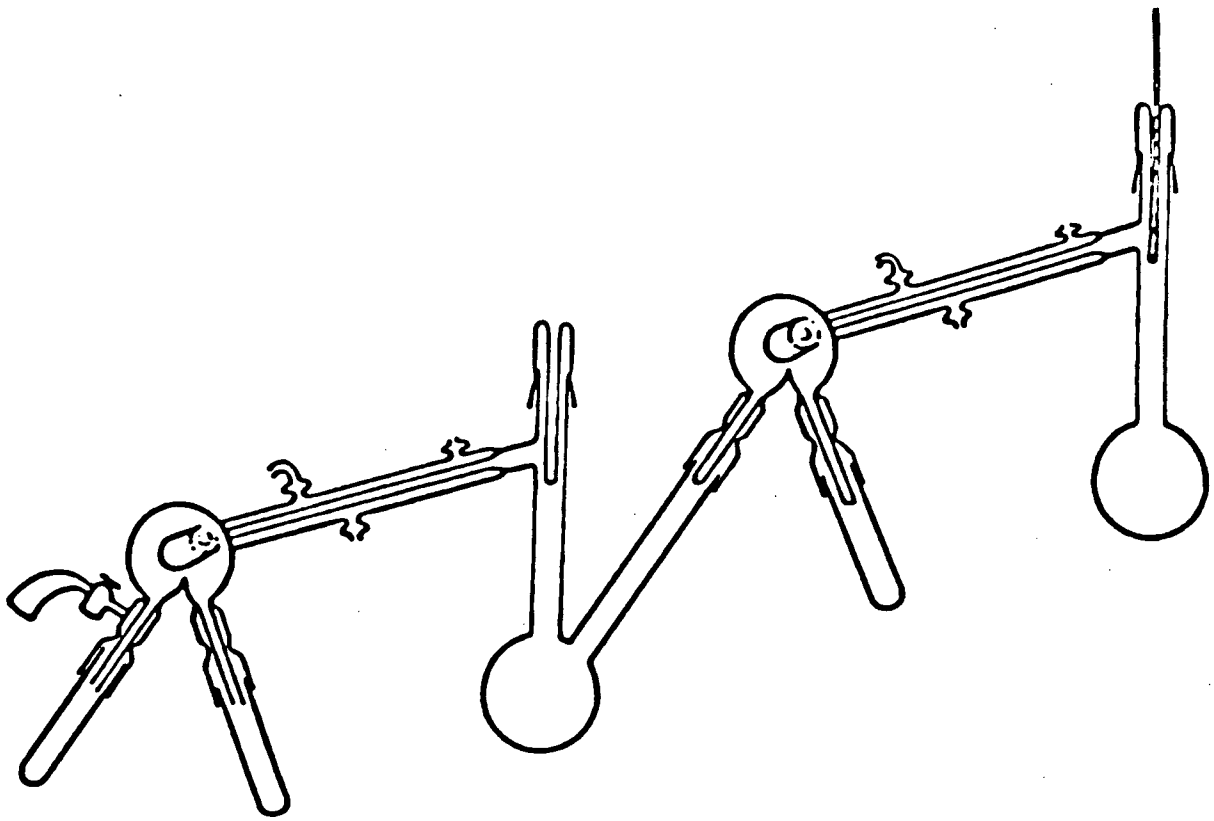


Figure 2.8: Fluorosulfuric Acid Distillation Apparatus.

$S_2O_6F_2$ were used, and the reaction took place according to the equation,

$$2I_2 + S_2O_6F_2 \longrightarrow 2I_2^+ + 2SO_3F^-$$

The mole ratio of I_2 to $S_2O_6F_2$ was kept very close to a value of 2:1, and the reaction was allowed to take place for 18 h, at room temperature. The solution was used immediately for intercalation.

2.6.4 $I(SO_3F)_3$

This reagent was made from I_2 and excess $S_2O_6F_2$ as shown by Roberts and Cady[73]. 1.1952 g of I_2 was used, and when the reaction had warmed to room temperature, 4.003 g of yellow viscous $I(SO_3F)_3$ was obtained. The excess $S_2O_6F_2$ was removed by vacuum.

$$I_2 + 3S_2O_6F_2 \longrightarrow 2I(SO_3F)_3$$

The solutions of $I(SO_3F)_3$ were used for intercalation with HOPG and SP-1 graphite.

2.6.5 ISO_3F

Synthesis was carried out using a mole ratio of $S_2O_6F_2$ to I_2 of 1.05. The method is described by Aubke and Cady[74]. 1.4096 g of I_2 and

1.1506 g of $S_2O_6F_2$ were used, and a dark brown solid product was obtained according to:

$$I_2 + S_2O_6F_2 \longrightarrow 2ISO_3F$$

The product was used immediately for intercalation reactions.

2.6.6 IBr_2SO_3F

Preparation was done according to the technique published by Wilson and Aubke[75]. A large excess of dried and purified bromine was distilled in vacuo onto pre-weighed ISO_3F, contained in a single part reaction vessel. The product was stored under nitrogen in the dry box since IBr_2SO_3F is extremely moisture sensitive.

$$ISO_3F + \text{excess } Br_2 \longrightarrow IBr_2SO_3F$$

2.6.7 $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$

Two synthetic methods were used.

a) An excess of $S_2O_6F_2$ (~3.00 ml) was distilled onto about 1.00 g of dried KI, to obtain $K[I(SO_3F)_4]$ or onto KBr to synthesize $K[Br(SO_3F)_4]$,

according to the method described by Lustig and Cady[76]. Since the two phases of $S_2O_6F_2$ and the potassium halides did not give a homogeneous mixture, the reaction took approximately 3 weeks to achieve completion.

$$KI + 2S_2O_6F_2 \longrightarrow K[I(SO_3F)_4]$$

$$KI + 2S_2O_6F_2 \longrightarrow K[Br(SO_3F)_4]$$

A novel alternative route was tried to overcome this problem.

b) Dried KI (~0.532 g) was added to a one part reactor, which was in turn connected to the vacuum line via a T-bridge. The salt was kept under dynamic vacuum for 30 min. to remove any residual moisture. A sufficient amount of HSO_3F (~2.00-3.00 ml) was then distilled onto the KI reactor, which was kept at liquid nitrogen temperature. In a similar manner, an excess of $S_2O_6F_2$ (~3.00 ml) was distilled into the reactor. Upon warming to room temperature, a mild exothermic reaction took place, and the resulting solution was light yellow in color. The reaction went to completion after about 2 h. The excess HSO_3F and $S_2O_6F_2$ were removed by slow pumping under vacuum.

$$KI + \text{excess } S_2O_6F_2 \xrightarrow{HSO_3F} K[I(SO_3F)_4]$$

The reaction was monitored by weight, and about 1.568 g of the product was obtained. An identical technique was used to synthesize

$K[Br(SO_3F)_4]$.

2.6.8 $Br(SO_3F)_3$

Bromine(III) fluorosulfate was made according to the reaction[73].

$$Br_2 + \text{excess } S_2O_6F_2 \longrightarrow 2Br(SO_3F)_3$$

An excess of $S_2O_6F_2$ was distilled onto about 1.59 g of Br_2 contained in a two part reactor, and the mixture allowed to warm to room temperature. The excess $S_2O_6F_2$ was then pumped off, leaving about 1.539 g of light yellow solid. The reaction was followed by weight, and checked for purity by I.R. spectroscopy.

2.6.9 $BrSO_3F$

Bromine(I) fluorosulfate was prepared according to the method of Aubke and Gillespie[77] by using a mole ratio of $S_2O_6F_2$ to Br_2 ~1.018.

$$Br_2 + S_2O_6F_2 \longrightarrow 2BrSO_3F$$

The small excess of $S_2O_6F_2$ was necessary to get a much improved yield of $BrSO_3F$. In the intercalation reaction with SP-1 graphite, about 0.790 g of the red-brown liquid was used.

2.6.10 $NOSO_3F$

Nitrosonium fluorosulfate was prepared using a slight excess of NO and $S_2O_6F_2$, according to the method published by Qureshi et al.[79]. About 1.236 g of NO gas and ~2.00 ml of $S_2O_6F_2$ were distilled into a one part reactor, which was kept at liquid N_2 temperature. About 4.20 g of white solid $NOSO_3F$ was obtained, and the product was checked for purity using I.R. Spectroscopy.

$$2NO + S_2O_6F_2 \longrightarrow 2NOSO_3F$$

The product was weighed in the dry box and used for intercalation with SP-1 graphite.

2.7 Commercially Available Chemicals

2.7.1 Graphite

Two kinds of graphite, SP-1 graphite and HOPG were used, but most reactions were carried out using SP-1 graphite only.

SP-1 graphite (spectroscopic grade, purified natural graphite) of 50-100 μ grain size was obtained from Union Carbide Ltd., Parma, Ohio, and from Dr. J.G. Hooley, Department of Chemistry, University of British Columbia. HOPG (Highly Oriented Pyrolytic Graphite) was purchased from Union Carbide Ltd., Parma, Ohio.

The HOPG was primarily used to synthesize GIC's for electrical conductivity studies, but SP-1 graphite was used for all other reactions. To obtain an efficient mixing of graphite and liquid phase intercalant, small amounts of graphite (~150 mg) were used.

2.7.2 Other Chemicals Obtained from Commercial Sources

The following table lists chemicals purchased from commercial sources with their suppliers.

Table 2.1:

Chemical	Source	Remarks
HSO_3F (tech.)	Allied Chemicals, Morristown, New Jersey	Doubly distilled (2.6.2)
SO_3 (sulfan)	Allied Chemicals, Morristown, New Jersey	
F_2	Matheson of Canada Ltd.	98% pure, passed through NaF to remove HF.
Br_2	Mallinckrodt Inc. St. Louis, Missouri	Analytical reagent, stored over P_2O_5 to remove moisture and KBr to remove Cl_2.
I_2	American Scientific and Chemical, Seattle	Reagent grade, used as obtained.
KI	Fischer Scientific Co. New Jersey	Dried at ~70°C to remove any moisture.
KBr	Fischer Scientific Co. New Jersey	Dried as in KI.
NO	Matheson of Canada Ltd.	Passed through silica gel (--198°C) to remove moisture and NO_2.

CHAPTER 3

SYNTHETIC REACTIONS

SYNTHETIC REACTIONS

General Comments

All the synthetic reactions described in this work were carried out under vacuum or nitrogen atmosphere conditions. The manipulation of reagents and reactants was done in the dry box, and all volatile compounds were transferred from bulk vessels into reactors by vacuum distillation. SP-1 graphite (spectroscopic grade) was used for all the intercalation reactions, and X-ray and microanalysis data were obtained for the products thus synthesized. The few intercalation compounds synthesized from HOPG (Highly Oriented Pyrolytic Graphite) were used solely for electrical conductivity measurements.

Unless otherwise mentioned, all the reactions were performed at ambient temperature. The elemental analysis values shown indicate weight percentage compositions for the various elements. Prior to any use of the graphite in the reactions, the powder reactant bulk was dried for about one hour in a dynamic vacuum. Magnetic stirring of the reaction mixtures was carried out to obtain phase homogeneity and hence an accelerated intercalation rate. When HOPG plates were used, the reaction mixture was kept undisturbed in order to salvage intact intercalated graphite plates.

3.1 Intercalation of $I_2^+(solv)$ into Graphite

The $I_2^+(solv)$ was prepared by using I_2 and $S_2O_6F_2$, the ratio being 2:1. 6.0 ml of HSO_3F was used as the reaction medium, and the estimated intercalant amount was about 1.530 g (4.34 mmol). The dark blue solution of I_2SO_3F was then reacted at room temperature with 0.5123 g of graphite. To obtain good phase homogeneity, the reaction mixture was stirred magnetically, and the reaction was allowed to proceed for 18 h. At the end of this time period, the suspension was observed to be reddish brown in color. The intercalated graphite product was then dried in a dynamic vacuum for about 3 h. The product had the characteristic metallic blue tint, and about 0.468 g weight increase was noticed. The intercalated graphite grains showed size expansion by a factor of about two. The synthesis was repeated four times to obtain consistent data.

A similar procedure was followed in the case of HOPG intercalation, but the solution mixture was allowed to stand without stirring in order to keep the HOPG plates intact.

The composition of the product, $C_{32}SO_3F.3HSO_3F.0{\cdot}2I$, agrees with the microanalysis results.

Compound: $C_{32}SO_3F.3HSO_3F0{\cdot}2I$

Microanalysis data:

Element	C	H	I
Calculated	47.5	0.37	3.14
Found	47.2	0.37	3.10

X-ray diffraction values of the sample suggest a compound with a c-axis layer repeat distance I_c of 7.99±0.03 Å. When the intercalated HOPG samples (0.1746 g) were heated at 200°C for 4 h, small amounts of I_2 were observed inside the one part reactor. The HOPG plates appeared to be exfoliated after the thermal decomposition process.

3.2 Intercalation of $I(SO_3F)_3$ into Graphite

The concentration of $I(SO_3F)_3$ in HSO_3F was varied, and the products obtained were analyzed for composition.

3.2.1 High Concentration of $I(SO_3F)_3$: (~1.20 M)

Reaction was carried out using 4.103 g (9.443 mmol) of light yellow and viscous $I(SO_3F)_3$ as the intercalant. Freshly made $I(SO_3F)_3$ was dissolved in 8.10 ml of HSO_3F in a two part reactor inside the dry box. The homogeneous solution had a slight red tint. 0.523 g of graphite was added to the $I(SO_3F)_3$ solution, and a green blue color of the solution was noted immediately. The reaction was allowed to proceed for 18 h. When dried in a dynamic vacuum for 3 h, the surface of the product appeared dark blue. The filtrate had a green blue color. The weight of the graphite had increased by 0.7942 g. The synthesis was repeated four times, and all the products were analyzed for composition, which was shown to be $C_{22}I(SO_3F)_3$. When HOPG plates were used, about five plates,

with an average weight of 0.0949 g, were reacted with 3.6411 g (8.589 mmol) of $I(SO_3F)_3$ for two days. 0.1765 g weight increase was observed for the products.

Compound: $C_{22}I(SO_3F)_3$

Microanalysis data:

Element	C	H	I	S	F
Calculated	38.37	0.0	18.46	13.95	8.28
Found	37.90	0.0	18.60	14.01	8.14
Mole ratio			1 :	2.99 :	2.93

X-ray powder data indicated a c-axis repeat layer distance I_c of 7.94 ± 0.03 Å.

3.2.2 Low Concentrations of $I(SO_3F)_3$

Since the product obtained from the reaction between concentrated solutions of $I(SO_3F)_3$ and graphite had a composition of $C_{22}I(SO_3F)_3$, stoichiometric amounts of $I(SO_3F)_3$ and graphite were reacted in HSO_3F, and the products were analyzed for carbon, hydrogen and iodine contents respectively. 3.3465 g (7.894 mmol) of freshly made $I(SO_3F)_3$ was dissolved in 20.00 ml of HSO_3F, and the stock solution thus prepared had a concentration of 0.395 M.

For a typical reaction between graphite and $I(SO_3F)_3$, (44C:0.5

$I(SO_3F)_3$)), 0.1510 g of graphite and 0.0606 g (0.1429 mmol) of $I(SO_3F)_3$, which was obtained from 0.362 ml of the stock solution, was allowed to react in a two part reactor. A blue-green color solution mixture was observed, and the reaction was allowed to proceed for 24 h. The product was dried in a dynamic vacuum for 3 h. The filtrate was bluish green in color, and the dried product showed a typical metallic blue surface lustre.

The following table summarizes the results, obtained for various mole ratios of carbon and $I(SO_3F)_3$ in HSO_3F.

Table 3.1:

Amount Graphite (g)	Amount $I(SO_3F)_3$ (g)	Mole ratio $C:I(SO_3F)_3$	Elemental Analysis C	H	I*
0.1510	0.0606 (0.1429 mmol)	44:0.5	47.48	0.35	0.0
0.2934	0.0424 (0.100 mmol)	73.33:0.3	47.74	0.34	0.0
0.1502	0.1544 (0.3642 mmol)	27.5:0.8	47.43	0.27	0.0

* Iodine was absent in all the samples.

3.3 Intercalation of $K[I(SO_3F)_4]$ into graphite

In a typical synthesis, 0.1145 g of graphite was allowed to react with 0.7320 g (1.302 mmol) $K[I(SO_3F)_4]$. The creamy white powder of $K[I(SO_3F)_4]$ was first dissolved in 6.0 ml of HSO_3F and the solution, which was very light green yellow in color, was then added to the graphite powder contained in a two part reactor. The solution mixture turned green, and the reaction was allowed to proceed for 18 h.

When the product was filtered in vacuo, the filtrate was observed to have a green color. The powder product obtained was dried in a dynamic vacuum for 3 h, and when completely dry, showed a metallic blue color.

The following composition was obtained for the sample by micro-analysis.

Compound: $C_{86}I.10 \cdot 51\ SO_3F$.

Microanalysis:

Element	C	H	I	S	F
Calculated	46.92	0.0	5.76	15.32	9.08
Found	46.09	0.0	5.55	14.74	8.80
Mole ratio				1 :	1.0

3.4 Intercalation of $Br(SO_3F)_3$ into Graphite

For a typical preparation, 0.1502 g of graphite was used to react with $Br(SO_3F)_3$. The pale yellow solid $Br(SO_3F)_3$ (4.5287 g; 2.015 mmol) was dissolved in 8.0 ml of HSO_3F, and the solution formed, which was golden yellow in color, was allowed to react with graphite in a two part reactor. Total reaction time was 24 h and the filtrate still had the golden yellow color. The intercalated product was vacuum dried for 3 h, and the powder product surface showed a bluish tint. The composition of the sample was shown to be $C_{26.8}Br.4SO_3F$.

Compound: $C_{26.8}Br.4SO_3F$.

Microanalysis:

Element	C	H	Br	F
Calculated	40.33	0.0	10.02	9.53
Found	39.94	0.0	10.56	10.30
Mole ratio			1 :	3.95

X-ray diffraction data gave a GIC with c-axis layer repeat distance I_c of 7.88 ±0.03 Å.

3.5 Intercalation of $K[Br(SO_3F)_4]$ into Graphite

In a typical synthesis, 1.0325 g (2.005 mmol) of white creamy

powder $K[Br(SO_3F)_4]$ was dissolved in 6.0 ml of HSO_3F, which gave a golden yellow solution. 0.1268 g of graphite was then added to this solution, and a suspension of dark black color was formed immediately. The reaction was allowed to take place for 18 h. The powder product was filtered in vacuo and dried in a dynamic vacuum for about 3 h. The filtrate still had the golden yellow color, and the intercalated graphite product showed a distinct blue tint. The microanalysis of the sample gave the composition as $C_{84}Br.11.22.SO_3F$.

Compound: $C_{84}Br.11\cdot22SO_3F$.

Microanalysis:

Element	C	H	I	S	F
Calculated	45.85	0.0	3.63	16.36	9.69
Found	45.63	0.0	3.63	16.42	9.68
Mole ratio				1	: 0.995

3.6 Intercalation of $BrSO_3F$ into Graphite

For a typical preparation, 4.00 g (22.36 mmol) of the red-brown liquid $BrSO_3F$ was allowed to react with 0.1159 g (9.66 mmol) of graphite in a one part reactor. The amount of HSO_3F used was about 6.0 ml. $BrSO_3F$ and then the acid was transferred to the reactor via vacuum distillation. A black-green suspension was observed upon warming to room temperature. The mixture was allowed to react for 18 h, and the

intercalated product was separated by vacuum distillation at the end of this time period. A reddish brown filtrate was observed, and the dried powder product was metallic blue in color.

The intercalated sample was analyzed for its composition, and the following values were obtained.

Compound: $C_{11}HSO_3F.0{\cdot}5SO_3F.x\ BrSO_3F.$ $(x \leq 0.025)$.

Microanalysis:

Element	C	H	Br	F	S
Calculated	46.16	0.35	0.69	10.13	17.10
Found	46.30	0.30	0.67	9.19	15.80
Mole ratio				1	: 1.02

The c-axis layer repeat distance for the sample, as indicated by X-ray powder diffraction data, gave a value of 8.22 ±0.03 Å.

3.7 Intercalation of $NOSO_3F$ into Graphite

For a typical synthetic reaction, 0.1443 g (12.03 mmol) of graphite and 1.305 g (10.12 mmol) of white solid crystalline $NOSO_3F$, which was freshly made, were transferred into a one part reactor inside the dry box. 7.0 ml of HSO_3F was then distilled in vacuo into the reactor, and the reaction was allowed to take place for several days at room temperature.

The volatile products from the reaction were collected by vacuum distillation. For this purpose, the reaction tube was kept at dry ice temperature and the collection vessel at liquid N_2 temperature. The products thus collected were then analyzed by mass spectroscopy. The intercalated graphite product was filtered and vacuum dried for 3 h.

Microanalyses of the samples (several preparations) gave varying amounts of carbon and hydrogen, indicating inhomogeneous sample compositions.

Table 3.2: Typical Microanalysis data

Sample	Amount NO (mmol)	Amount Graphite (mmol)	Reaction time	Composition C	H	N
A	25.93	13.34	10 d	67.49	0.28	0.0
				70.62	0.0	0.0
B	15.20	12.07	18 h	69.30	0.20	0.0
C	43.49	12.03	10 d	76.0	0.30	0.0
				77.0	0.16	0.0

The X-ray diffraction values obtained showed a compound with c-axis layer repeat distance $I_c = 10.59 \pm 0.03$ Å. The mass spectra analysis gave primarily peaks related to SiF_4. NO could not be identified in these spectra. The amounts of carbon and hydrogen as analyzed by

microanalytical methods, did not vary significantly when the reaction time or reactant concentrations were changed.

3.8 Intercalation of IBr_2SO_3F into Graphite

Approximately 3.50 g (9.07 mmol) of brick red solid IBr_2SO_3F was dissolved in 7.0 ml of HSO_3F. The black brown solution thus formed was mixed with 0.1432 g (11.93 mmol) of graphite in a two part reactor. When the graphite was added, the solution turned almost black. The reaction was allowed to go on for 2 days. The intercalated product was then vacuum filtered and dried in a dynamic vacuum for 3 h. The dried powder had the characteristic metallic blue color, and when analyzed, gave the following composition.

Microanalysis data:

Element	C	H
Found	47.15	0.0

3.9 Reactions of Halogen Fluorosulfates

3.9.1 Attempted Oxidation of $K[I(SO_3F)_4]$

0.2697 g of $K[I(SO_3F]_4$ was transferred to a one part reactor inside

the dry box, and 6.0 ml of HSO_3F and excess $S_2O_6F_2$ were vacuum distilled into the same reactor. Upon warming to room temperature the reaction mixture showed a yellow color. Magnetic stirring for 5 h did not give any observable change. The reactor was then heated using a water bath, and the temperature was kept constant at 75°C for 18 h. Since no color change was detected, the temperature was raised to 90°C, and the reaction allowed to proceed for one day.

The reactor was then cooled to room temperature and the excess HSO_3F and $S_2O_6F_2$ were removed via vacuum. The reactor was kept under dynamic vacuum for several hours, and a viscous red colored liquid was obtained as a product. The reaction was monitored by weight.

3.9.2 Reaction of $K[I(SO_3F)_4]$ with Excess Br_2

$$K[I(SO_3F)_4] + \text{excess } Br_2 \xrightarrow[2 \text{ days}]{\text{R.T.}} 2\ BrSO_3F + K[IBr_2(SO_3F)_2]$$

Approximately 0.6322 g $K[I(SO_3F)_4]$ was added to a one part reactor, and excess Br_2 was then vacuum distilled into the same vessel. A dark brick red color was observed in the reaction tube. The reaction was allowed to proceed for 2 days at room temperature.

The volatile byproducts of the reaction were collected via vacuum distillation and were analyzed by ^{19}F-NMR. The color observed for the volatile(s) was still brick red. The solid product, which was light red brown in color and crystalline, was analyzed by I.R. Spectroscopy. The

reaction was followed by weight as well.

3.9.3 Reaction of $I(SO_3F)_3$ with Excess Br_2

$$I(SO_3F)_3 + \text{excess } Br_2 \longrightarrow IBr_2SO_3F + 2BrSO_3F$$

3.4699 g of $I(SO_3F)_3$, which was freshly made in a one part reactor, was allowed to react with excess Br_2 at room temperature for 2 days. The reactor was then heated using a water bath (~65°C) for 5 h. A dark red viscous liquid was observed. The reaction vessel was then evacuated under a dynamic vacuum for 48 h while being kept at about 0°C. The product obtained was still a dark red very viscous liquid, and attempts to obtain a solid product by cooling at liquid N_2 temperature did not prove to be successful. The reaction was followed by weight.

CHAPTER 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

General Comments

This chapter is intended to rationalize the observations and results presented in the previous sections of this thesis. In order to maintain a logical sequence, the chapter is divided into the following subsections:

4.1 Intercalant Preparation in Fluorosulfuric Acid and Related Studies

The synthesis of various fluorosulfate species which are used as intercalants and their physical and chemical behaviour in HSO_3F will be discussed. In addition to previously reported reactions and properties, miscellaneous attempted reactions of halogen fluorosulfates, pertinent to intercalation chemistry, are to be included in this section.

4.2 Intercalation of Iodine Containing Species

Solution intercalation of I_2^+, $I(SO_3F)_3$, $K[I(SO_3F)_4]$ and ISO_3F is considered, and the results are discussed.

4.3 Intercalation of Bromine Containing Compounds

The following compounds and their intercalated products are to be discussed: $BrSO_3F$, $Br(SO_3F)_3$, $K[Br(SO_3F)_4]$, IBr_2SO_3F.

4.4 Nitrosonium Ion (NO^+) Promoted Intercalation of SO_3F^-

A comparative study of NO^+ intercalation in HSO_3F and in non-protonic solvents will be made in this section.

4.5 General Comments on HSO_3F and Conclusion

4.1 Intercalant Preparation in Fluorosulfuric Acid and Related Studies

Section A

The system I_2-$S_2O_6F_2$ allows one to generate the following iodine containing species:

a) Solvated ions formed in strong protonic acids such as I_2^+, I_3^+ and possibly I_5^+, with non-integer oxidation states of iodine. Of the strong protonic acids available, HSO_3F is sufficiently acidic to stabilize I_2^+, but on account of its oxidizing ability the existence of I_5^+ in this medium is questionable.

b) Binary fluorosulfates of iodine, i.e. ISO_3F and $I(SO_3F)_3$, which are formed in the absence of acid. Other binary, iodine rich species like I_3SO_3F and I_7SO_3F have been identified,[74,106] but this study will concentrate on ISO_3F and $I(SO_3F)_3$. Finally, ternary $K[I(SO_3F)_4]$ is also included as a potential intercalant in addition to the other two binary fluorosulfates.

4.1.1 I_2^+(solv)

I_2^+ ions can best be generated reasonably quantitatively in HSO_3F by the method reported by Gillespie and Milne.[72] The ion has an intense blue color in solution and an optical spectrum can be obtained. In addition magnetic susceptibility measurements and resonance Raman spectra are used in the study of these species.[98] For the synthesis of I_2^+(solv), the mole ratio of I_2:$S_2O_6F_2$ has to be maintained close to 2:1, since in addition to the principle reaction

$$2I_2 + S_2O_6F_2 \xrightarrow{HSO_3F} 2I_2^+(solv) + 2SO_3F^-(solv)$$

other cations of iodine such as I_3^+ or species like $I(SO_3F)_3$ can be formed, either by the oxidation of excess iodine or by the use of excess $S_2O_6F_2$ at room temperature. Absorption studies of I_2^+(solv) give three sharp peaks in the optical spectrum at 640, 490, and 410 nm, assigned to I_2^+ (Fig. 4.1). The small peak at 300 nm in the 2:1 solution is due to the I_3^+ ion, which is formed according to:

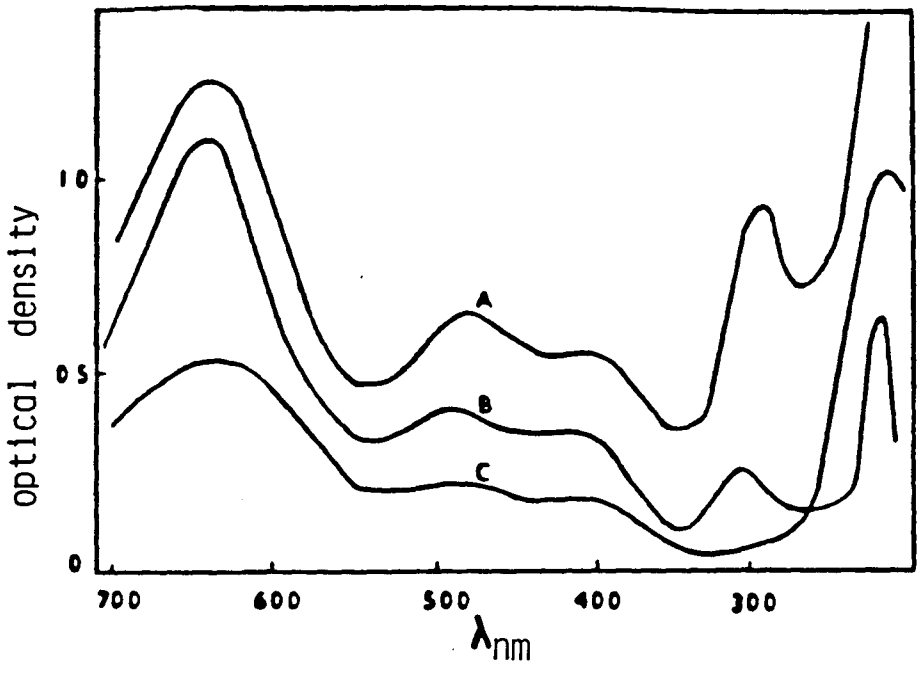


Figure 4.1: Absorption Spectra of 1:1 and 2:1 $I_2/S_2O_6F_2$ Solutions: A, 2:1 $I_2/S_2O_6F_2$, m_{I_2} = 0.164, path length = 0.005 cm; B, 2:1 $I_2/S_2O_6F_2$, m_{I_2} = 0.372, path length = 0.01 cm; C, 1:1 $I_2/S_2O_6F_2$, m_{I_2} = 0.0186, path length = 0.01 cm. from reference 72.

$$8I_2^+ + 8SO_3F^- \rightleftharpoons 5I_3^+ + 5SO_3F^- + I(SO_3F)_3$$

However, in HSO_3F, this equilibrium produces only very small amounts of I_3^+ at lower concentrations. Therefore, it can be safely assumed that the 2:1 $I_2/S_2O_6F_2$ solution is predominantly made up of I_2^+ ions. To avoid the presence of I_3^+, low concentrations were used in the preparative synthesis.

4.1.2 ISO_3F

Iodine(I) fluorosulfate is synthesized using nearly equimolar (1:1.05) amounts of I_2 and $S_2O_6F_2$.[74] When the initial crude product is heated to 60°C for ~1 h, a dark blackish brown hygroscopic solid of composition ISO_3F is obtained. When added to HSO_3F, ISO_3F dissolves readily to form a blue color solution due to I_2^+ ions. The optical spectrum of ISO_3F in HSO_3F is shown in Fig. 4.2. ISO_3F was found to be diamagnetic, thereby indicating covalent bonding.[74] Since the compound is a very strong oxidizer and hygroscopic, solutions of it in HSO_3F had to be used immediately for the reactions with graphite. If the samples become even partially hydrolyzed, green solutions are observed due to the formation of some I_3^+ ions.

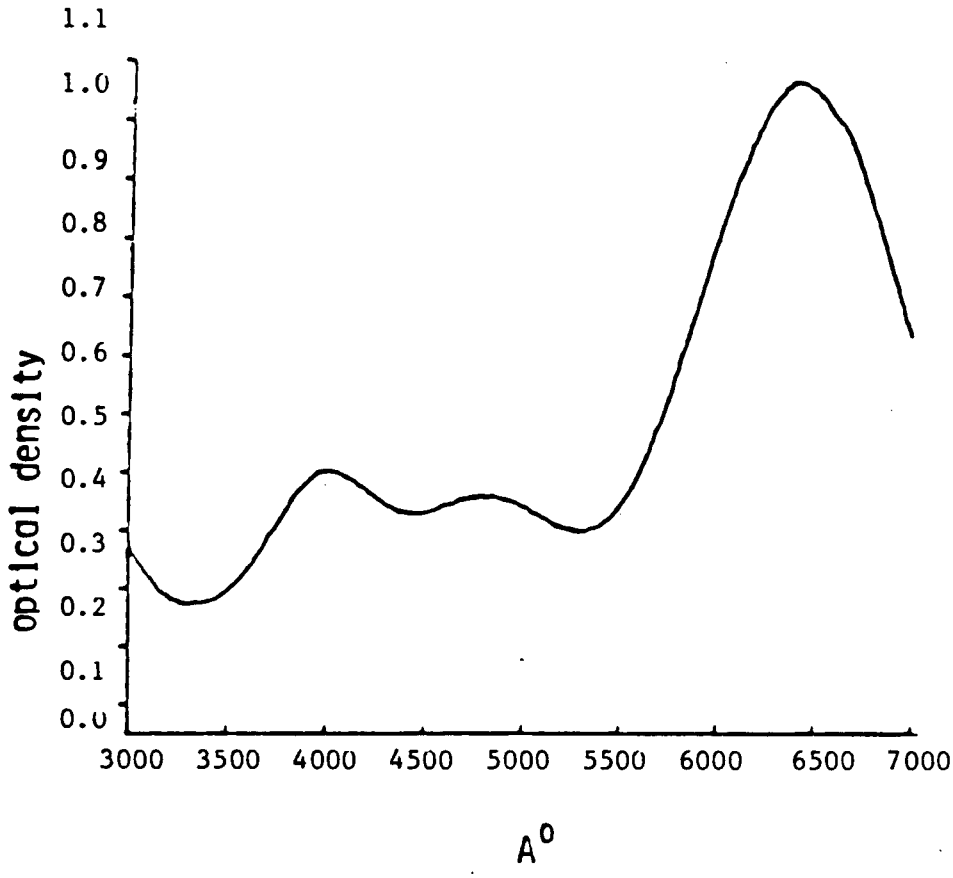


Figure 4.2: Absorption Spectrum of $IOSO_2F$ Dissolved in Fluorosulfuric Acid.
from reference 74.

4.1.3 $I(SO_3F)_3$

Iodine(III) fluorosulfate can be synthesized by reacting I_2 with an excess of $S_2O_6F_2$.[73] The reaction is mildly exothermic, and the product is a highly viscous liquid or a low melting solid (Table 4.1) of light yellow color. When heated to 50°C in vacuo, $I(SO_3F)_3$ disproportionates approximately:[93]

$$2I(SO_3F)_3 \longrightarrow ISO_3F + IF_3(SO_3F)_2 + 3SO_3$$

The Raman spectrum of liquid $I(SO_3F)_3$ has been reported and interpreted as indicating the presence of both bidentate bridging and monodentate SO_3F groups in a polymeric structure.[95]

The compound shows amphoteric behavior in HSO_3F, capable of reacting as an acid or as a base. Only a single resonance is observed in the ^{19}F-NMR spectrum of $I(SO_3F)_3$ in HSO_3F.[94] The basic and acidic ionizations in fluorosulfuric acid can be represented as follows:

Basic behavior: $I(SO_3F)_3 \rightleftharpoons I(SO_3F)_2^+ + SO_3F^-$

Acidic behavior: $I(SO_3F)_3 + SO_3F^- \rightleftharpoons I(SO_3F)_4^-$

Solutions of $I(SO_3F)_3$ in HSO_3F are pale yellow in color and no absorption maximum is observed in the optical spectrum above 300 nm. However, at shorter wavelengths, there is a strong absorption, the maximum of which has not been reported.

Table 4.1: **Selected Physical Properties of Some Halogen Fluorosulfates***

Property	$BrSO_3F$	$ClSO_3F$	ISO_3F	$Br(SO_3F)_3$	$I(SO_3F)_3$
melting point (°C)	+31.5	-84.3	+50.2	+59.0	+32.2
boiling point (°C)	+117.3	+45.1	-	-	+114 @ 30 Torr under decomp.
density (g/ml)	2.238 @ 25°C	1.711 @ 20°C	-	-	2.40 @ 25°C
vapour pressure at 25°C (Torr)	16.98	363.1	-	-	-
stability and color	red liquid stable up to 150°C	yellow liquid	black-brown solid, stable upto 150°C	pale yellow solid, slowly decomposes at room temp.	pale yellow solid, or a high viscous liquid slowly decompose at room temp
^{19}F NMR chemical shift rel. to $CFCl_3$ (ppm)	34.6	33.9	44.0	39.0	47.0

* from reference 93.

4.1.4 $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$

The preparative method for both compounds reported by Lustig and Cady[76] is the oxidation of KI or KBr by an excess amount of $S_2O_6F_2$. This synthetic route is rather impractical since the reactions proceed in a heterogeneous phase and usually require at least a few weeks before pure products are obtained. In order to accelerate the reaction, the original synthesis is modified by adding a small amount of HSO_3F as the solvent together with excess $S_2O_6F_2$, as described in Section 2.6.7(b). The acid acts as the solvent for the two products $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$.

The oxidation process reaches completion within a few hours, and fine crystalline products can be isolated by removing the excess HSO_3F and $S_2O_6F_2$ in a dynamic vacuum.

$K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$ dissolve readily in HSO_3F, giving pale yellow solutions due to the anions $I(SO_3F)_4^-$ and $Br(SO_3F)_4^-$ respectively. For the synthetic reactions with graphite, these solutions were used immediately.

So far, no solution studies of these compounds in HSO_3F has been reported. Raman spectra of $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$ are known, and are very similar.[96] Three S-O stretching vibrations in the region of 1500 cm^{-1} - 900 cm^{-1} suggest that all four SO_3F groups are identical and best described as monodentate in bonding. Also, a single band attributed to the S-F stretching vibration found at ~835 cm^{-1} is consistent with this conclusion. A square planar environment for I and Br respectively is suggested in both $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$.[96]

Section B

As in the synthesis of binary iodine fluorosulfates, similar compounds of bromine such as $BrSO_3F$ and $Br(SO_3F)_3$ can be made by the system Br_2-$S_2O_6F_2$ in the absence of fluorosulfuric acid. The ternary compound $K[Br(SO_3F)_4]$ and the interhalogen fluorosulfate IBr_2SO_3F are included as intercalants in this section as well, since both these species contain bromine in their compositions.

4.1.5 $Br(SO_3F)_3$

Bromine(III) fluorosulfate can be synthesized using Br_2 and an excess amount of $S_2O_6F_2$ according to[73]

$$Br_2 + \text{excess } S_2O_6F_2 \longrightarrow 2Br(SO_3F)_3$$

$Br(SO_3F)_3$ is a pale yellow, very moisture sensitive solid compound and has to be used immediately since it tends to decompose slowly at room temperature, resulting in the formation of a red colored product, presumed to be $BrSO_3F$.

The Raman spectrum of the compound shows structural similarity with $I(SO_3F)_3$ in the solid state, and suggests a SO_3F bridged associated structure for both $Br(SO_3F)_3$ and $I(SO_3F)_3$.[96]

$Br(SO_3F)_3$ dissolves readily in HSO_3F, and the resulting solution is light yellow in color. The UV-visible spectra of Br_2:$S_2O_6F_2$ at various

ratios in HSO_3F is shown in Fig. 4.3 On oxidation of Br_2, the intensity of the band at 375 nm, assigned to the Br_3^+ cation, increases until at the 0.33 ratio, corresponding to Br_3^+ formation, the curve B is observed. Above this ratio, the shoulder at 375 nm decreases in intensity, but a shoulder at 310 nm increases until at $S_2O_6F_2$:Br_2 ratio of 3, which relates to the formation of $Br(SO_3F)_3$, no further change is noted.[92] It appears that $Br(SO_3F)_3$ is quite stable in fluorosulfuric acid, and no appreciable disproportionation is observed. UV-visible spectra however, are not sufficiently differentiated to allow quantitative conclusions during intercalation.

In a super-acid system like SbF_5-$3SO_3$-HSO_3F, $Br(SO_3F)_3$ does not act as a nonelectrolyte, but functions as a base:[97]

$$Br(SO_3F)_3 + H_2SO_3F^+ \longrightarrow Br(SO_3F)_2^+ + 2HSO_3F$$

4.1.6 $BrSO_3F$

An exactly equimolar mixture of Br_2 and $S_2O_6F_2$ is required to synthesize pure $BrSO_3F$,[77] a red brown liquid, thermally stable in a sealed pyrex tube up to 150°. It is extremely sensitive to moisture, reducing agents and fluorocarbon grease, which cause it to darken to a deep red brown color. Pure $BrSO_3F$ melts ~31.5°C and the ^{19}F-NMR spectrum of the compound shows a single peak at 35 ppm relative to $CFCl_3$. The vapor pressure of the liquid (~17 Torr at 25°C) is sufficient for transfer in vacuo in a grease free line to avoid

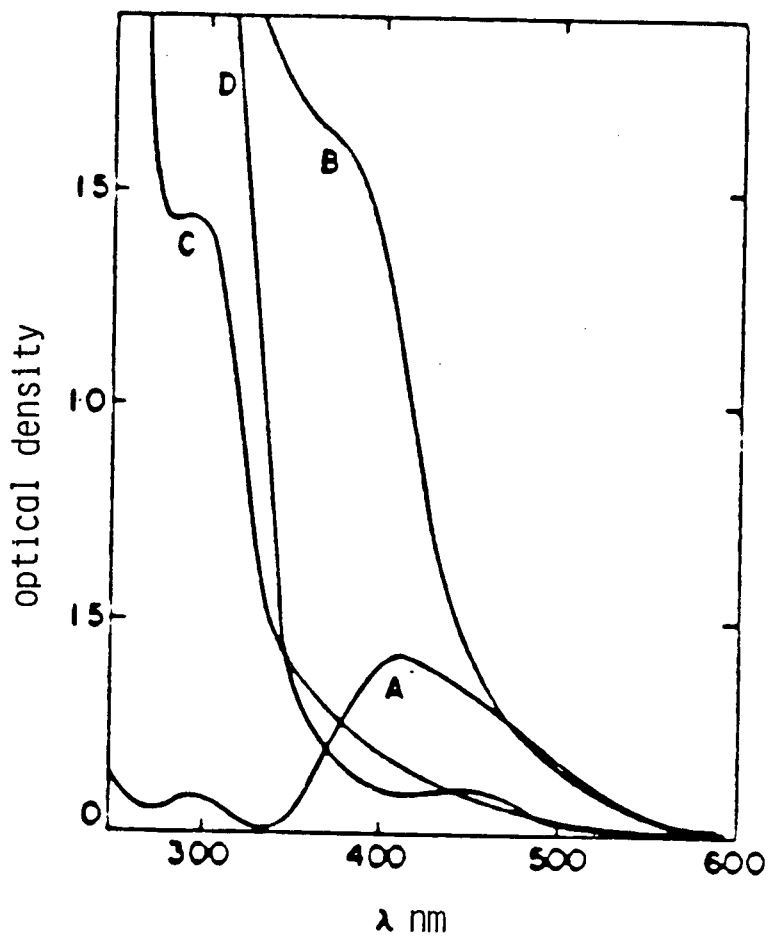


Figure 4.3: UV and Visible Spectra in HSO_3F. Br_2:$S_2O_6F_2$ ratio: A, 1:0; B, 1:0.33; C, 1:1; D, 1:3 and 1:5.

from reference 97.

contamination.

$BrSO_3F$ dissolves well in fluorosulfuric acid to give stable brown solutions, and in conductometric studies, a slight increase in the conductivity is observed, showing that $BrSO_3F$ behaves as a very weak electrolyte. As could be seen from Fig. 4.3, when the ratio of Br_2: $S_2O_6F_2$ in HSO_3F approaches unity, the shoulder at 310 nm increases in intensity, but the 375 nm peak of Br_3^+ decreases. Therefore, it could be assumed that $BrSO_3F$ is disproportionated to some extent into Br_3^+ and $Br(SO_3F)_3$ in fluorosulfuric acid.[97]

Raman spectra and conductometric data of $BrSO_3F$ in the super acid system HSO_3F-$3SO_3$-SbF_5 indicate the presence of both Br_3^+ and Br_2^+ cations:[97]

$$5BrSO_3F + 2H_2SO_3F^+ \rightleftharpoons 2Br_2^+ + Br(SO_3F)_3 + 4HSO_3F$$

$$4BrSO_3F + H_2SO_3F^+ \rightleftharpoons Br_3^+ + Br(SO_3F)_3 + 2HSO_3F$$

4.1.7 $NOSO_3F$

Nitrosonium fluorosulfate, $NOSO_3F$, is best prepared by the reaction between $NO_{(g)}$ and $S_2O_6F_2$ to give a white solid with a melting point of 230°C.[79] The compound is rather hygroscopic and appears isostructural with KSO_3F in having an orthorhombic unit cell.

The white crystalline material is very soluble in fluorosulfuric acid and behaves as a strong, extensively dissociated base according to:

$$NOSO_3F \xrightarrow{HSO_3F} NO^+_{(solv)} + SO_3F^-_{(solv)}$$

The Raman spectrum of $NOSO_3F$ in HSO_3F shows a strong absorption at 2320 cm^{-1}, attributed to the N-O stretching vibration in NO^+ ion.[98]

The complete dissociation of $NOSO_3F$ in HSO_3F is useful in regard to the synthetic reactions with graphite. In solution, NO^+ ions could be expected to oxidize the graphite lattice, thereby facilitating the insertion of other ions and neutral molecules.

4.1.8. IBr_2SO_3F

When a large excess of Br_2 is reacted with freshly prepared ISO_3F, a rust brown solid product of composition IBr_2SO_3F is formed.[75,99] Like most of the interhalogen fluorosulfates, IBr_2SO_3F is extremely moisture sensitive and best stored under atmospheric pressure. The synthesis follows the general addition reaction according to:

$$ISO_3F + X_2 \longrightarrow IX_2SO_3F \qquad X = Cl, Br \text{ or } I.$$

IBr_2SO_3F is thermally stable upto 90°C and Raman and IR spectra indicate a complex structure with a SO_3F^- ion where C_{3v} symmetry is strongly perturbed. IBr_2SO_3F dissolves in HSO_3F readily to give stable solutions, and like other interhalogen fluorosulfates, behaves as a strong base. According to conductometric measurements, IBr_2SO_3F is

completely dissociated to:[75]

$$IBr_2SO_3F \xrightarrow{HSO_3F} IBr_2^+(solv) + SO_3F^-(solv)$$

The ^{19}F-NMR spectra of IBr_2SO_3F in fluorosulfuric acid give only a single resonance, indicating dissociation and SO_3F^- formation. Solutions of IBr_2SO_3F in strong protonic acids show distinct absorption bands, and in HSO_3F, λ_{max} values of 560 (shoulder), 455 (shoulder), 361 and 232 nm are observed in the electronic spectrum, corresponding to $IBr_2^+(solv)$ ions. Hence, it was anticipated that IBr_2SO_3F in HSO_3F should function as an oxidative intercalant in the reaction with graphite.

4.1.9 Attempted Oxidation of $K[I(SO_3F)_4]$

The reaction between excess $S_2O_6F_2$ and $K[I(SO_3F)_4]$ in fluorosulfuric acid was carried out (at 75°C for 18 h and at 90°C for one day) in order to oxidize the latter compound according to:

$$K[I(SO_3F)_4] + \text{excess } S_2O_6F_2 \xrightarrow{HSO_3F} K[I(SO_3F)_6]$$

It has been reported that solid $K[I(SO_3F)_4]$ is stable towards further oxidation, and when exposed to a stream of F_2 at 100°C, no reaction was observed.[76] The ease with which iodine is oxidized in HSO_3F from -1 to

+3 suggests further oxidation to +5 may be possible at elevated temperature and prolonged reaction time to obtain either $[I(SO_3F)_6]^-_{(solv)}$ or species of the type $[IF_n(SO_3F)_{6-n}]^-$ should SO_3 be eliminated. It should be recalled that I_2 is oxidized by $S_2O_6F_2$ in order to give the compound $IF_3(SO_3F)_2$[93] (see Section 4.1.3).

The removal of all the excess acid and $S_2O_6F_2$ yielded a highly viscous red liquid. However, an overall weight decrease was observed during the synthesis. From these observations, it has to be concluded that the presumed reaction $K[I(SO_3F)]_4 \xrightarrow{oxid.} K[I(SO_3F)_6]$ did not take place as anticipated.

4.1.10 Reaction of $K[I(SO_3F)_4]$ with excess Br_2

This reaction is unprecedented. It is performed in order to understand the reaction between intercalated $[I(SO_3F)_4]^-$ and Br_2, which may give some indication regarding the nature of the intercalants present in the graphite lattice.

The reaction was expected to proceed as follows:

$$K[I(SO_3F)_4] + \text{excess } Br_2 \xrightarrow{R.T.} 2\ BrSO_3F + K[IBr_2(SO_3F)_2]$$

The reaction was monitored by gravimetry and the difference observed in weight suggests $K[IBr_2(SO_3F)_2]$ as a possible product in the synthesis. However, infrared spectra obtained on the solid product(s) show S-O stretching frequencies at 1225 cm^{-1} and 1060 cm^{-1} respectively, suggest-

ing a nearly ionic SO_3F group which is consistent with the presence of interhalogen fluorosulfate IBr_2SO_3F.[75] The red brown color of the solid product may also be due to this compound. ^{19}F-NMR values of the volatiles showed two weak peaks at 45 and 62 ppm, which were significantly different from the expected value for $BrSO_3F$[93] (34.6 ppm), but since $BrSO_3F$ is extremely sensitive to fluorocarbon grease, this observed deviation in NMR data could be due to grease contamination as well.

4.1.11 Reaction of $I(SO_3F)_3$ with excess Br_2

$$I(SO_3F)_3 + \text{excess } Br_2 \longrightarrow IBr_2SO_3F + 2BrSO_3F$$

The above products were anticipated for the reaction between $I(SO_3F)_3$ and excess Br_2 (at room temperature for 2 days and at 65°C for 5 h). Based on observations made during the preceding reaction, the above synthetic reaction was attempted in order to prepare the interhalogen fluorosulfate IBr_2SO_3F in a different manner from the original addition reaction of Br_2 to ISO_3F, to yield IBr_2SO_3F,[75] as part of a general reaction:

$$ISO_3F + X_2 \longrightarrow IX_2SO_3F \quad X = Cl, Br \text{ or } I$$

The dark red viscous liquid was initially assumed to be IBr_2SO_3F, but no solid product could be isolated even by supercooling the liquid at liquid N_2 temperature.

UV-visible spectra of the product were obtained for concentrations ~ 4.19 x 10^{-3} moles/kg in fluorosulfuric acid and typically, pale blue solutions were observed, which indicated the presence of I_2BrSO_3F.[75]

The color is characteristic of the I_2^+ cation in HSO_3F, and is assumed to be formed by solvent oxidation. Typical data from optical spectra were as follows:

λ_{max} (nm)	Absorbance	ϵ_{max} (cm^{-1} $mole^{-1}$ L)	
635	0.923	1273	
490	0.311	429	ratio ~1:3
395	0.420	579	

The ϵ_{max} ratio of the 635 and 490 nm peaks is ~1:3, which is the value obtained for I_2^+ species in HSO_3F by Gillespie and Milne.[72] Hence, the product obtained seems to be I_2BrSO_3F for the reaction between $I(SO_3F)_3$ and excess Br_2. The ^{19}F-NMR of the volatiles showed two resonances at 44.16 and 49.72 ppm, which rules out $BrSO_3F$ as a potential product.

4.2 Intercalation of Iodine Containing Species

4.2.1 Intercalation of $I_2^+{}_{(solv)}$

It is generally acknowledged that I_2 itself will not intercalate into graphite (see Sec. 1.8.1). If this is due to the relatively low oxidizing ability, then the strongly oxidizing I_2^+ would offer a better

chance of iodine being intercalated.

At low concentrations, a solution of molar ratio 2:1 in I_2 to $S_2O_6F_2$ in HSO_3F contains predominantly I_2^+ ions,[72] and very little disproportionation is observed. Therefore, the oxidizing species in the reaction with graphite is most likely the $I_2^+{}_{(solv)}$. The reaction takes place in a relatively short time (18 h), indicating a fast oxidation of the graphite lattice by I_2^+ solution. Intercalation was also confirmed visually by the metallic blue tint observed on the dried graphite product surface and by the swelling of the grains to a factor of about two.

Interestingly, the suspension of graphite and $I_2^+{}_{(solv)}$ in HSO_3F at the end of 18 h showed a reddish brown color. This suggests that $I_2^+{}_{(solv)}$ has been reduced by graphite to $I_3^+{}_{(solv)}$, which is brown in color. This can be shown as:

$$3I_2^+{}_{(solv)} + e^- \longrightarrow 2I_3^+{}_{(solv)}$$

However, when excess I_2^+ solution was added, the reddish brown color could not be detected, and the suspension remained blue in color. This observation gives additional evidence that confirms the role of $I_2^+{}_{(solv)}$ as the oxidizing agent during the synthesis.

The elemental analysis data of the product indicate a compound with formula $C_{32}SO_3F.3HSO_3F.0{\cdot}2I$. The carbon percentage value of 47.2 points to an intercalation compound with a low stage index. The data, in particular the low iodine content, also suggest preferential intercalation of SO_3F^- groups and neutral HSO_3F molecules. It appears that this

synthesis follows precedents where protonic acids such as H_2SO_4 or HSO_3F intercalate only in the presence of an external oxidizing agent.[35,36]

In these systems, the external oxidizer (e.g. CrO_3) usually does not intercalate together with the other intercalant species. The very small amount of intercalated iodine suggests some of the oxidizing agent is retained in the graphite lattice, but little can be deduced from this information regarding the oxidation state of iodine in the intercalant layers.

The low stage index (stage one) of this compound can be inferred from the X-ray powder diffraction data. The I_c value of 7.99 Å agrees well with the value reported by Yaddaden et al. for the intercalation of HSO_3F-20% SO_3 with graphite.[60] This I_c value is typical for graphite acid fluorosulfates when both SO_3F groups and neutral acid molecules are present as intercalates in the GIC.[43,58]

The ^{19}F-NMR spectra are useful in determining the chemical environment of the intercalant species. Surface adsorbed or condensed graphite products show chemical shifts which are closer to those formed for the free intercalant(s), whereas intercalated compounds give typical resonances shifted to higher fields (lower frequencies).

The solid state ^{19}F-NMR spectrum of $C_{32}SO_3F.3HSO_3F.0{\cdot}2I$ exhibits only a single resonance at 20.2 ppm (Fig. 4.4). This value is significantly shifted to a higher field as compared with the liquid HSO_3F resonance which appears at 40.6 ppm relative to $CFCl_3$.[43] ^{19}F-NMR may however not be a suitable technique to differentiate between intercalated SO_3F^- and HSO_3F, since resonances due to these species are closely spaced and have been observed at 37.4 and 40.6 ppm in high resolution

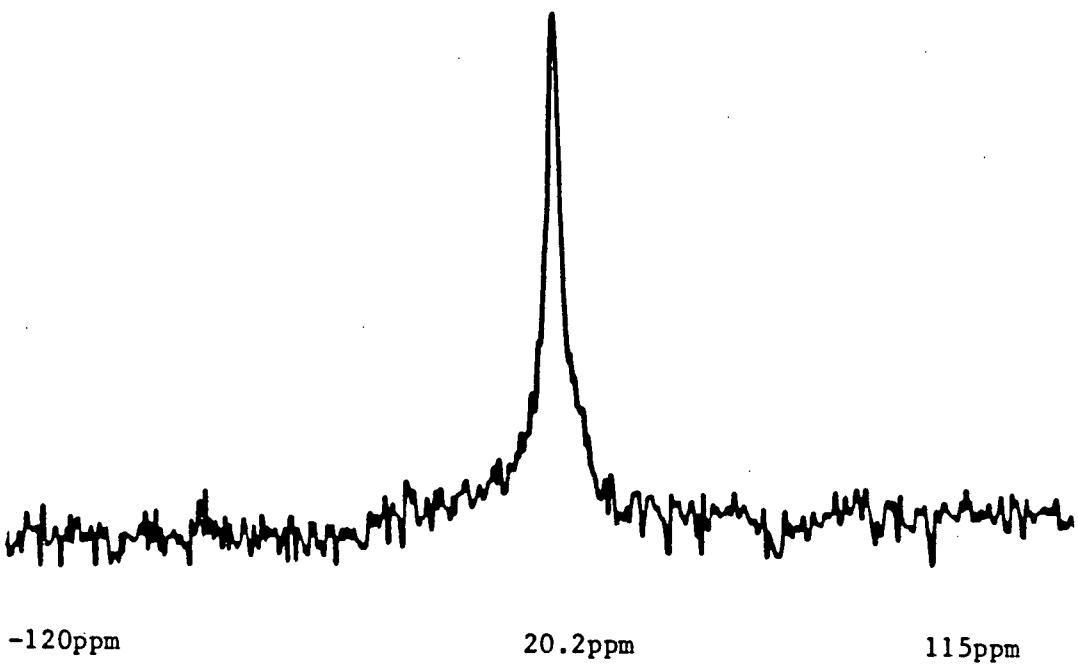


Figure 4.4: ^{19}F-NMR Spectrum of $C_{32}SO_3F.3HSO_3F.0{\cdot}2I$

spectra.[78] Iodine, I_2 was found as a deintercalated sublimed product when the GIC was heated to 200°C for 4 h. The high temperature and relatively long heating time confirm the existence of iodine as an intercalant rather than a surface adsorbed species in the graphite lattice.

The electrical conductivity of intercalated HOPG samples show enhanced conductance in the basal planes. Typical data obtained were as follows:

Table 4.2: Typical Conductivity Measurements for Graphite-$I_2^+{}_{(solv)}$ Compound

Compound: $C_{32}SO_3F.3HSO_3F.0{\cdot}2I$

Dimensions: $S^2 = 9.59 \times 10^{-2}$ cm^2, $t = 5.70 \times 10^{-2}$ cm

$\sigma \times 10^{-4}$ (ohm^{-1} cm^{-1})	$\sigma/\sigma g^*$	k/kg	t/to
23.5	10.13	12.56	1.24

* $\sigma_g = 2.32 \times 10^4$ ohm^{-1} cm^{-1}
(see Sec. 2.4 for the definitions of terms used)

Interestingly, the conductivity observed in this compound show a much larger value than for graphite acid fluorosulfates where the only intercalants are SO_3F^- and HSO_3F.[43] These high conductivity values are almost comparable to values obtained for graphite-AsF_5 intercalation compounds.[100,101]

4.2.2 Intercalation of $I(SO_3F)_3$

The synthetic reactions carried out using $I(SO_3F)_3$ as the intercalant showed a clear dependence of the reactions on the concentration of $I(SO_3F)_3$. This factor will be discussed in more detail later. The high concentration (~1.20 M) synthesis is to be examined here first. As shown earlier in Sec. 4.1.3, $I(SO_3F)_3$ could behave either as a base or an acid in fluorosulfuric acid.[94] In both cases, ions such as $I(SO_3F)_4^-$, $I(SO_3F)_2^+$ or $I(SO_3F)_3$ itself may function as the oxidizing agent, where iodine exists in a +3 oxidation state. This gives the typical pale yellow color to $I(SO_3F)_3/HSO_3F$ solutions. The graphite lattice was oxidized in a rather short period (18 h) by the iodine species and the dark black blue color of the product surface indicated intercalation. The green blue color of the filtrate points to the fact that iodine(III) has been reduced by graphite according to:

$$2I^{+3} + 5e^- \longrightarrow 2I^{+1/2} \text{ or } I_2^+$$

and/or,

$$3I^{+3} + 8e^- \longrightarrow 3I^{+1/3} \text{ or } I_3^+$$

A mixture of I^{+3} (yellow) and $I^{+1/2}$ (blue) can produce the blue green color observed. Also, $I^{+1/2}$ and $I^{+1/3}$ (brown) can give identical results. The microanalysis results, with C:I:S:F ratio of 21.5:1:2.99:2.93, points to a compound with composition $C_{22}I(SO_3F)_3$. Interestingly, hydrogen was found to be absent, which led to the conclusion that no appreciable amount of HSO_3F intercalation had taken place

in the sample. Therefore, it can be assumed that $I(SO_3F)_3$ acts as a strong oxidative intercalant, functioning both as the oxidant and intercalant during the synthesis. An alternative formula may also be considered for the product, i.e. $C_{22}I.3SO_3F$. In this case, the mechanism of intercalation could be significantly different as compared to $C_{22}I(SO_3F)_3$ formation.

That the product is of stage one can be clearly seen from the interlayer separation value of 7.94 ± 0.03 Å. It has been noted before that all interlayer separations for the fluorosulfates fall well below 8.0 Å, suggesting closely packed structures with electron transfer from graphite to intercalant causing Coulombic attraction between the carbon and intercalant layer.[43,102] The small I_c value observed is justified (even though $I(SO_3F)_3$ is quite a large molecule) if one assumes square planar configuration for iodine, as shown earlier in Sec. 4.1.3 and 4.1.5. The frequency shift of the E_{2g_2} vibrational mode to 1640-1642 cm^{-1} in the Raman spectra also agrees with published data reported from other first stage compounds.[103,104]

The ^{19}F-NMR spectrum of $C_{22}I(SO_3F)_3$ (Fig. 4.5) indicates a single resonance at 23.6 ppm, which is about a 23.4 ppm shift to higher field compared to free $I(SO_3F)_3$ (47.0 ppm). This value is in good agreement with other reported values for intercalated halogen fluorosulfates.[43] No surface adsorbed or condensed $I(SO_3F)_3$ is observed in these spectra.

The intercalated sample was heated at 100°C for seven days, and the volatile products were analyzed by I.R. spectroscopy. The spectra showed peaks corresponding to CO_2, SO_2 and possibly SO_2F_2. The ^{19}F-NMR of the remaining solid sample gave a resonance at 21 ppm. It was noted

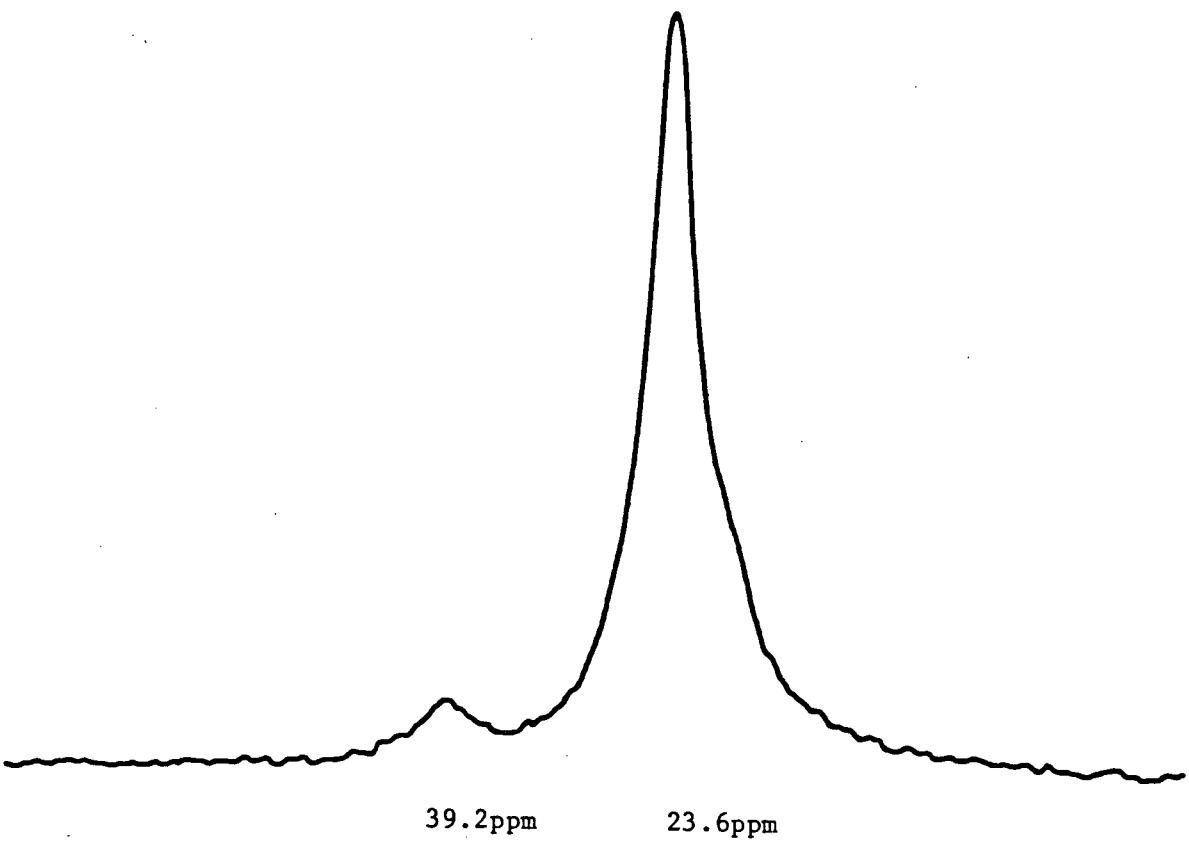


Figure 4.5: ^{19}F-NMR Spectrum of $C_{22}I(SO_3F)_3$

earlier in Sec. 4.1.3 that at 50°C in vacuo, $I(SO_3F)_3$ disproportionates to ISO_3F, $IF_3(SO_3F)_2$ and SO_3 respectively. Therefore, it is possible that the remaining solid product may be composed of graphite-ISO_3F or $IF_3(SO_3F)_2$. Alternatively, a mixture of both these intercalants could be present in the lattice as well. However, the latter possibility is unlikely since only a single resonance was observed for the product in the ^{19}F-NMR spectra.

Interestingly, for the case of graphite-$BrSO_3F$ intercalation, the ideal composition $C_{12}BrSO_3F$ has been calculated earlier using the interlayer separation and density of $BrSO_3F$.[102] In a similar manner, the ideal packing for graphite-$I(SO_3F)_3$ is deduced as follows: the interlayer separation of 7.94 Å gives a gallery volume of 11.99 $Å^3$/C atom, and using the reported density of $I(SO_3F)_3$ at 25°C which is 2.40 g/cm^3,[93] the molecular volume is calculated as 293 $Å^3$. This suggests the ideal composition as $C_{24.44}$ $I(SO_3F)_3$. The discrepancy between the ideal composition and the value obtained by microanalysis may be due to a more tightly packed structure than that assumed in the above calculations. This situation can arise when an appreciable amount of charge transfer takes place between the graphite and the intercalants, causing a closer packing due to an increase in electrostatic attraction.

In order to study the function of $I(SO_3F)_3$ concentration in the final product formation, various stoichiometric amounts of $I(SO_3F)_3$ and graphite were reacted in HSO_3F, based on the composition of $C_{22}I(SO_3F)_3$. The filtrate as before gave a blue green color, indicating the oxidation of graphite by the iodine species. However, the microanalysis data on

the products showed the absence of iodine as an intercalant. The carbon percentage remained almost constant in all the products, and no significant variations were seen in hydrogen compositions, which showed only small values relative to carbon. These results indicate that at lower $I(SO_3F)_3$ concentrations, only neutral acid molecules and possibly SO_3F groups intercalate into graphite to form first stage intercalation compounds. In the high concentration synthesis, about a five fold excess $I(SO_3F)_3$ was used as the intercalant. It seems clear from these observations that an excess of $I(SO_3F)_3$ is necessary to obtain GIC's which function both as the oxidizer and intercalant. This can be rationalized as follows: Initially, $I(SO_3F)_3$ acts as the oxidizing species, and if only small amounts of it are present in the solution, $I(SO_3F)_3$ intercalation could not take place. Instead, preferential intercalation of HSO_3F and SO_3F^- is observed. At high concentrations, sufficient amounts of $I(SO_3F)_3$ are available to function simultaneously as the oxidizing agent and intercalant, which leads to the product $C_{22}I(SO_3F)_3$.

The intercalated HOPG samples were used to obtain electrical conductivity values and typical results were as follows:

Table 4.3: Electrical Conductivity Values of $C_{22}I(SO_3F)_3$

Compound: $C_{22}I(SO_3F)_3$

Dimensions: $s^2 = 9.51 \times 10^{-2}$ cm^2, $t = 3.50 \times 10^{-2}$ cm

$\sigma \times 10^{-4}$ (ohm^{-1} cm^{-1})	σ/σ_g*	k/kg	t/to
15.2	6.55	11.7	1.78

* $\sigma_g = 2.32 \times 10^4$ ohm^{-1} cm^{-1}

The data indicate a considerable enhancement in the conductivity along the basal plane, and the σ/σ_g value of 6.55 points to extensive electron transfer from graphite to the intercalant. Although it is evident from all the information presented so far that $I(SO_3F)_3$ acts as an acceptor in the above synthesis, the exact extent of charge transfer and the anions formed in the intercalant layer on charge transfer are major questions which still need to be resolved.

4.2.3 Intercalation of $K[I(SO_3F)_4]$

The rationale for attempting the intercalation of the solvated $[I(SO_3F)_4]^-$ ion comes from the inability to clearly intercalate $I_2^+{}_{(solv)}$, which was discussed in Sec. 4.2.1. It was assumed that the initial oxidation of the graphite lattice according to $C_n \longrightarrow C_n^+ + e^-$ would impart positive charges on the graphite layers, which in turn would lead to electrostatic repulsion between the graphite lattice and the intercalant.

It must also be recalled that cation intercalation is indeed rare and that such simple cations like NO^+ or NO_2^+ oxidize graphite, but do not intercalate themselves. However, in the case of neutral intercalants such as $I(SO_3F)_3$ and $Br(SO_3F)_3$ (to be discussed in Sec. 4.3.2), relatively high percentages of iodine and bromine, i.e. 18.60 and 10.56 respectively, were found in the intercalated products. Interestingly, the first stage compounds thus obtained did not show solvent intercalation at high intercalant concentrations. This then suggests that $[Hal(SO_3F)_4]^-$ will intercalate well again, provided that the anion is a sufficiently strong oxidizing agent. In order to verify this hypothesis, the negatively charged $[I(SO_3F)_4]^-$ was used as the reacting species in fluorosulfuric acid. As explained in Sec. 4.1.4, solution studies of $K[I(SO_3F)_4]$ in HSO_3F have not been reported up to now, although the salt dissolves quite easily in the acid, giving $I(SO_3F)_4^-$ ions. Furthermore, the following equilibrium is also possible in solution,

$$I(SO_3F)_4^- + HSO_3F \rightleftharpoons H[I(SO_3F)_4] + SO_3F^-$$

Hence the exact nature of the oxidizing agent(s) cannot be deduced clearly in this synthesis. However, the green color observed for the filtrate indicates that I^{+3} (from $I(SO_3F)_4^-$ or from neutral $H[I(SO_3F)_4]$) has been reduced by graphite to $I^{+1/2}$ (blue) and/or $I^{+1/3}$ (brown) during the initial intercalation process. A similar observation was made during the graphite-$I(SO_3F)_3$ synthesis, as discussed in Sec. 4.2.2. The elemental analysis values indicate a compound with composition $C_{86}I.10.51\ SO_3F$. An alternative formula such as $C_{86}I(SO_3F)_4.6.51SO_3F$ can also be written for the final product. Two important features can be observed in the composition of the product:

a) significant amount of iodine intercalation (5.55%), and

b) the absence of solvent (HSO_3F) in the intercalated product.

These two factors suggest that in addition to neutral intercalants such as $I(SO_3F)_3$ and $Br(SO_3F)_3$, anions like $I(SO_3F)_4^-$ in HSO_3F may also function as oxidative intercalants when reacted with graphite. The presence of neutral or negatively charged intercalants seems to lead toward preferential solute intercalation, whereas intercalant species carrying a positive charge such as $I_2^+{}_{(solv)}$ give predominantly solvent intercalated products.

The low carbon content found for the compound $C_{86}I.10.51SO_3F$ makes it reasonable to assume that the product is of low stage (most probably stage one). Also, taking into consideration that there are 10.51 SO_3F^- groups per unit formula, the composition seems to indicate the limiting value for this synthesis.

The ^{19}F-NMR spectrum of the solid product showed only a single

broad resonance at 18 ppm, which excludes the presence of any chemiadsorbed or condensed intercalants in the final compound (Fig. 4.6).

The results obtained in the above synthesis indicate the feasibility of only solute intercalation in a protonic solvent medium like HSO_3F. It is also clear from this study, as in $I(SO_3F)_3$ and $Br(SO_3F)_3$ intercalation, that oxidative intercalation does occur during the synthesis. The absence of acid in the product is possibly due to the greater ability of the iodine species to undergo oxidative intercalation with graphite. In summary, it appears that $K[I(SO_3F)_4]$ in HSO_3F, which may be defined as a base in the acid, is a sufficiently good oxidizing agent to effect intercalation. However, the $SO_3F^-_{(solv)}$ ions present, provide a competition for $[I(SO_3F)_4]^-$ as intercalants during the reaction. While a higher iodine concentration is achieved in the GIC when $[I(SO_3F)_4]^-$ acts as the intercalant than for $I_2^+{}_{(solv)}$, an approximately neutral medium is found in $I(SO_3F)_3$ (and $Br(SO_3F)_3$) intercalation, which seems to provide a better opportunity for the intercalation of iodine fluorosulfates into graphite.

4.2.4 Attempted Intercalation of ISO_3F

Solutions of ISO_3F were reacted with graphite in a manner similar to other iodine fluorosulfates discussed so far. When mixed with graphite, inhomogeneous suspension mixtures were observed. The products were vacuum dried for 3 h, and when totally dry the samples indicated possible intercalation since the product surfaces appeared to be black

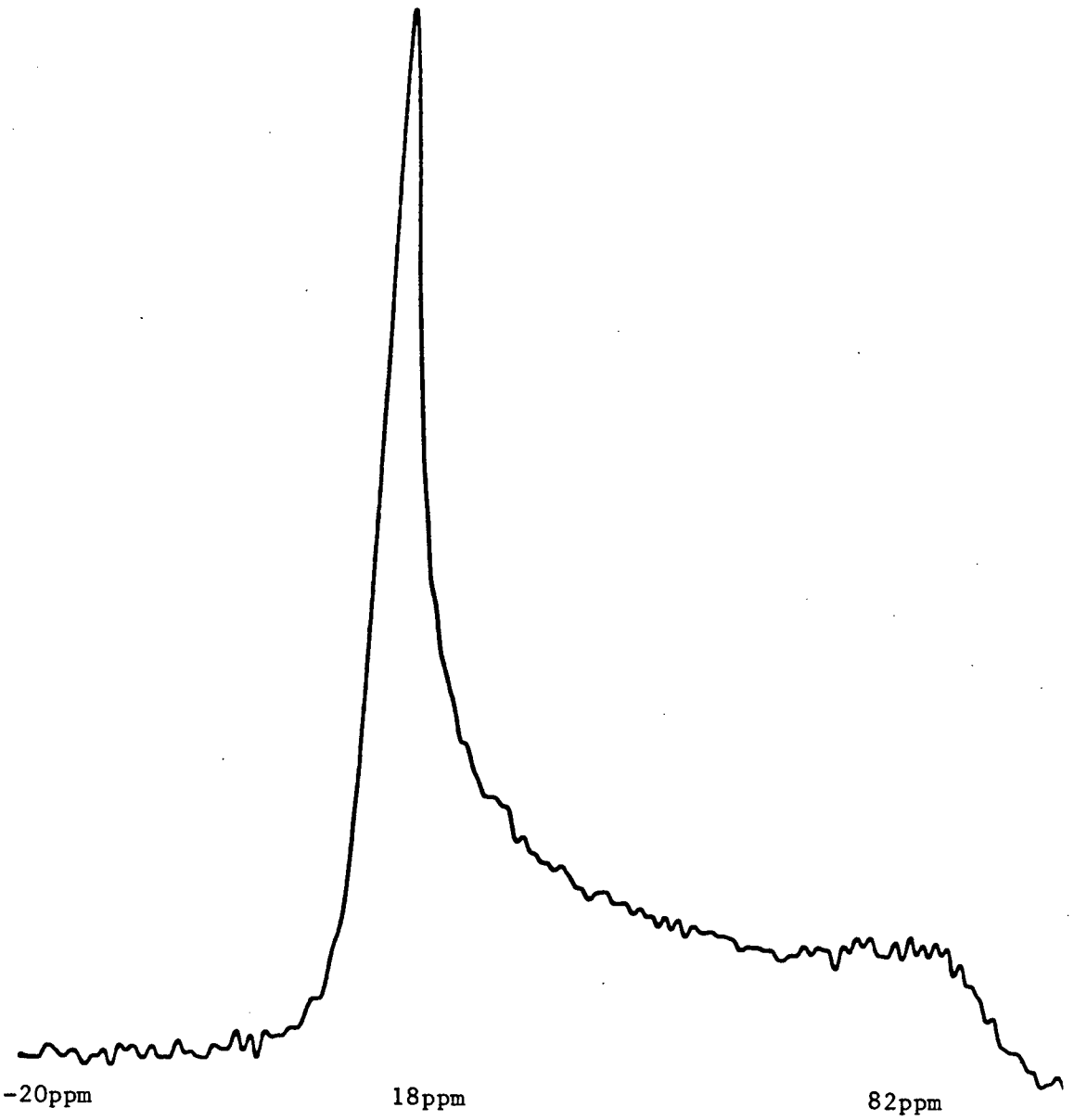


Figure 4.6: ^{19}F-NMR Spectrum of $C_{86}I.10 \cdot 51SO_3F$

blue in color.

However, the ^{19}F-NMR spectra of the compounds gave resonances in the region of ~44 ppm, indicating only surface adsorbed fluorosulfate species. Hence it was concluded that no oxidative intercalation has occurred in the synthesis between ISO_3F and graphite. The absence of any oxidizing species in the solutions of ISO_3F may be responsible for the lack of intercalation. A comparable observation has been reported earlier for pure ISO_3F intercalation.[43] The solutions could behave in a manner similar to iodine itself, which does not intercalate into graphite, since it does not meet the energy requirements to open the galleries in the graphite lattice to initiate the intercalation process.

4.3 Intercalation of Bromine Containing Compounds

4.3.1 Intercalation of $BrSO_3F$

The reaction between liquid bromine(I) fluorosulfate and graphite has been carried out earlier and a first stage compound with a composition of $C_{12}BrSO_3F$ was reported.[43,102] However, the synthetic reaction between these compounds in fluorosulfuric acid proceeds in a significantly different manner.

The relatively short intercalation time (18 h) indicates a fast oxidation of the graphite lattice. The microanalysis data with F:S ratio of 1:1.02 indicate a compound of formula $C_{11}HSO_3F.0{\cdot}5SO_3F.xBrSO_3F$ ($x \leq 0.025$). As shown by these results, only a small fraction of

bromine, assumed to be in the form of $BrSO_3F$, was found as an intercalate. An alternative composition is also possible for the product, i.e. $C_{11}HSO_3F.(0.5 + x)SO_3F.xBr$. The existence of $BrSO_3F$ as such in the graphite lattice cannot be confirmed by microanalysis (or ^{19}F-NMR) values. It may exist as an anionic species among the intercalant layers on charge transfer.[101]

The c-axis layer repeat distance I_c and the low carbon content found by microanalysis points to a first stage intercalation compound. The I_c value of 8.22 Å is close to the value obtained for the intercalation product with $I_2^+{}_{(solv)}$ as the oxidizing agent, discussed in Sec. 4.2.1 (~7.99 Å). This is expected since both products contain predominantly the same intercalants, i.e. neutral HSO_3F molecules and SO_3F^- groups. As shown before, this is a typical interlayer separation distance observed for first stage graphite acid fluorosulfates.[43,58] The ^{19}F-NMR spectrum of the compound does not differentiate between the HSO_3F and SO_3F (or $BrSO_3F$) resonances, and consequently only a single signal at 14.92 ppm is observed (Fig. 4.7). This chemical shift value agrees more with GIC's having general composition $C_n.XHSO_3F.YSO_3F$, than with halogen fluorosulfate intercalated compounds.[43]

In summary, it is clear from the above discussion that the intercalation of pure $BrSO_3F$ and as a HSO_3F solution results in the formation of quite different products. Direct intercalation employs $BrSO_3F$ as the only oxidizing agent and as a result, it is found as the sole intercalate. Solutions of $BrSO_3F$ in fluorosulfuric acid lead to a stage one GIC, but now SO_3F^- and HSO_3F are the predominant intercalates with $BrSO_3F$ or a similar bromine-SO_3F species present as a minor intercalate.

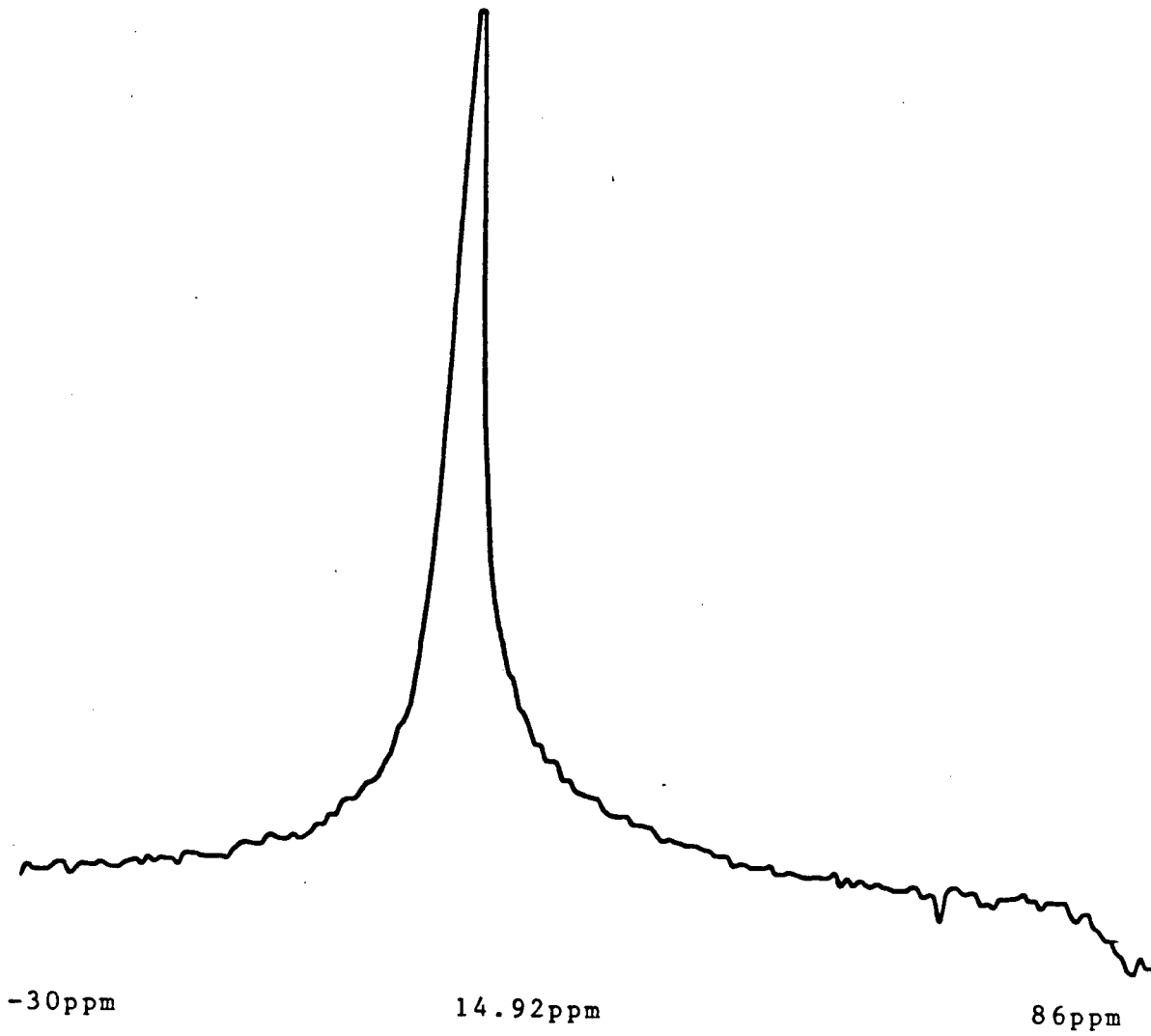


Figure 4.7: ^{19}F-NMR Spectrum of $C_{11}HSO_3F \cdot 5SO_3F.xBrSO_3F$ ($x \leq 0.025$)

However, neither microanalysis, interlayer separation values from X-ray data or ^{19}F-NMR spectra allow a clear identification of all the intercalates in the above compound.

4.3.2 Intercalation of $Br(SO_3F)_3$

The chemical and physical properties of $Br(SO_3F)_3$, a solid at room temperature with a tendency towards decomposition at this temperature, makes this material unsuitable for direct intercalation. A previously reported route, the oxidation of intercalated $BrSO_3F$,[43,102] in the form of $C_{12}BrSO_3F$ yields a compound of general composition $C_{16}Br(SO_3F)_3$. It does, however appear from both the high intercalate to carbon ratio and the ^{19}F-NMR spectrum that some $Br(SO_3F)_3$ is not intercalated and possibly only surface adsorbed. Therefore, intercalation of $Br(SO_3F)_3$ from solutions in HSO_3F is attempted. As seen in Sec. 4.1.5, $Br(SO_3F)_3$ is quite stable in fluorosulfuric acid, and little dissociation and virtually no disproportionation are observed.[97]

Hence, it seems almost certain that $Br(SO_3F)_3$ functions as the oxidizing species in the reaction with graphite. The bluish tint observed on the graphite surface at the end of the reaction period (24 h) confirms intercalation of the lattice by $Br(SO_3F)_3$. The intercalated product indicates a composition of $C_{26.8}Br.4SO_3F$, derived from microanalysis results. The composition of the GIC can also be formulated as $C_{26.8}Br(SO_3F)_3.SO_3F$ or $C_{26.8}BrSO_3F.3SO_3F$. As compared to $C_{16}Br(SO_3F)_3$, which shows a carbon percentage of only 33.8, $C_{26.8}Br.4SO_3F$ suggests a

product closer to the limiting composition, considering the intercalate size. This can be seen clearly from X-ray and ^{19}F-NMR data obtained for the product. The X-ray powder value for the layer repeat distance I_c = 7.88 Å points to a stage one compound. In addition, the small I_c value also suggests extensive charge transfer between the graphite lattice and the intercalate(s). The ^{19}F-NMR spectrum of the compound consists of only a single broad resonance at 12 ppm, which is compatible with chemical shifts observed for other SO_3F^- intercalated graphite compounds.[43]

It is interesting to note that for the $C_{16}Br(SO_3F)_3$ compound, as discussed earlier, a broad peak is seen at 10 ppm, in addition to a second resonance at 38.3 ppm (relative to $CFCl_3$) in the ^{19}F-NMR spectrum. The ^{19}F-NMR spectra of $C_{26.8}Br.4SO_3F$ show the absence of any surface adsorbed or condensed intercalants in the final product. The UV-visible spectra of the filtrates were taken in the range of λ = 360-750 nm, in order to detect any reduced bromine species such as Br_3^+ or Br_2^+. However, these attempts did not prove to be successful. The spectra obtained were similar to the ones observed for $Br(SO_3F)_3$ in HSO_3F (Fig. 4.3, curve D). Even if Br_3^+ cations had been present in the filtrate, they may have existed in very low concentrations below the detection limit, as only small amounts of graphite (~12.5 mmol) were used as the reducing agent in the reactions. As an example, for 12.5 mmol graphite and 2.02 mmol $Br(SO_3F)_3$ (typical amounts, see Sec 3.4) only 0.16 mmol Br_3^+ would be produced, and in the same filtrate 1.86 mmol unreacted $Br(SO_3F)_3$ would be present as well.

In summary, it appears that neither microanalysis nor any of the

physical techniques used are able to differentiate between two possible intercalate formulations as either $Br(SO_3F)_4^-$ or $Br(SO_3F)_3 + SO_3F^-$. Also, it is not exactly clear why the products derived from the intercalation of $I(SO_3F)_3$ and $Br(SO_3F)_3$, both from solutions in HSO_3F, differ in their compositions with a possible neutral intercalate present in one case and a negatively charged species in the other.

4.3.3 Intercalation of $K[Br(SO_3F)_4]$

As in the case of $K[I(SO_3F)_4]$-graphite synthesis, the intercalation reaction of $K[Br(SO_3F)_4]$ was carried out in order to study the oxidative intercalant behavior of $[Br(SO_3F)_4]^-$ with graphite (see Sec. 4.2.3). Since both $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$ exhibit very similar chemical behaviour in fluorosulfuric acid, the reaction of these compounds with graphite lead, not surprisingly, to GIC's having closely related chemical and physical properties. Hence, the intercalation of $K[Br(SO_3F)_4]$ will be explained only briefly in the following discussion.

In HSO_3F-$K[Br(SO_3F)_4]$ solutions, both $[Br(SO_3F)_4]^-$ and $H[Br(SO_3F)_4]$ can exist as potential oxidizing agents. In analogy with the $K[I(SO_3F)_4]$-graphite reaction, it could be assumed that during the synthesis, Br^{+3} is reduced by graphite to $Br^{+1/2}$ and/or $Br^{+1/3}$ in the acid medium. However, $Br^{+1/2}$ may not be present as a stable species in fluorosulfuric acid.[97]

The microanalysis results, which indicate a composition of $C_{84}Br.11.22SO_3F$, show a substantial amount of bromine in the product

(cf. $C_{86}I.10.51SO_3F$). The formula of the compound can also be expressed as $C_{84}Br(SO_3F)_4 7.22SO_3F$. The absence of hydrogen in the intercalated compound suggests a solvent-free GIC. Again, as in the $K[I(SO_3F)_4]$ reaction, the relatively small carbon percentage seen for the product points to a low stage compound.

It is clear from the observations made so far for both $K[I(SO_3F)_4]$ and $K[Br(SO_3F)_4]$ insertion reactions that oxidative intercalation does take place during the syntheses. Therefore, the conclusions drawn for the $K[I(SO_3F)_4]$-graphite synthesis apply equally well for the present reaction too. In summary, although $K[Br(SO_3F)_4]$ in fluorosulfuric acid functions as a relatively good oxidizing agent, the intercalation of high concentrations of bromine-fluorosulfates can be achieved more effectively by utilizing an apparently neutral intercalant such as $Br(SO_3F)_3$.

4.3.4 Intercalation of IBr_2SO_3F

It was seen earlier in Sec. 4.2.1 that $I_2^+{}_{(solv)}$ promoted intercalation produced GIC's with predominantly SO_3F^- and neutral HSO_3F molecules as intercalates. Therefore, it seems interesting to carry out a similar cation-promoted synthetic reaction in HSO_3F using IBr_2SO_3F as the intercalant. As observed in Sec. 4.1.8, IBr_2SO_3F behaves as a strong base in fluorosulfuric acid, undergoing complete dissociation to give $IBr_2^+{}_{(solv)}$ and $SO_3F^-{}_{(solv)}$ ions. Hence, during the reaction with graphite, it is possible that IBr_2^+ may function as the oxidizing agent.

A relatively long reaction time (2 days) was required for this synthesis, suggesting weaker oxidizing ability of IBr_2^+ ions. The metallic blue color observed on the graphite powder surface confirmed initial intercalation of the lattice. The compositional analysis of the intercalated product is not complete and does not include the halogens and sulfur. Due to this reason, a general formula cannot be formulated for the final product. However, the low carbon content and the absence of hydrogen in the GIC are significant with regard to the stage and composition. The carbon percentage obtained by microanalysis falls within the range of first stage intercalation compounds (see Sec. 3.1, 3.3, 3.5 and 3.6). In order to confirm this observation, X-ray diffraction values of the sample have to be taken into account.

In contrast to other cation promoted intercalation reactions discussed in this thesis (i.e. $I_2^+{}_{(solv)}$ and $NO^+{}_{(solv)}$, to be discussed in Sec. 4.4), the present synthesis does not indicate appreciable hydrogen insertion. This observation leads to the conclusion that neutral acid molecules are absent in the GIC. Therefore, it is very likely that the final product will contain SO_3F^- groups, and possibly halogen species as intercalates. However, the presence of halogen in the graphite lattice has to be verified by elemental analysis.

In summary, it can be assumed that the reaction between IBr_2SO_3F and graphite in HSO_3F proceeds in a different manner when compared to $I_2^+{}_{(solv)}$ or $NO^+{}_{(solv)}$ induced reactions, the most important difference being the absence of acid molecules as intercalates. To understand this system in greater detail, additional data such as elemental halogen compositions, X-ray diffraction and ^{19}F-NMR have to be obtained for the

intercalated compound.

4.4 Nitrosonium Ion (NO^+) Promoted Intercalation

The synthesis of intercalation compounds using NO^+ (and NO_2^+) as the oxidizing agent in non-protonic solvents such as nitromethane, which is a moderately polar, coordinating and weakly ionizing solvent, was discussed in Sec. 1.8.3. For example, it was found that the compounds thus made have the ideal composition $C_{23n}^{+}MF_6^{-}(solvent)_y$, where n is the stage, M = P or Sb, and y usually ~1.7 to 2.5.[36]

Therefore, it seems interesting to carry out a similar study in a protonic solvent like HSO_3F, which is strongly ionizing. $NOSO_3F$ was used as the intercalant dissolved in fluorosulfuric acid. As shown before in Sec. 4.1.7, solid $NOSO_3F$ is extensively dissociated into NO^+ and SO_3F^- according to:

$$NOSO_3F_{(solv)} \overset{HSO_3F}{\rightleftharpoons} NO^+_{(solv)} + SO_3F^-_{(solv)}$$

In analogy to non-protonic solvent synthesis, it was expected that $NO^+_{(solv)}$ would function as the oxidant in the reaction with graphite, as had been the case in nitromethane.

The reactant concentrations and reaction times were varied in order to observe any effect on the composition of the final product. When the GIC's from these syntheses were analyzed for carbon, hydrogen and

nitrogen, varying compositions were obtained and even the same preparation gave inconsistent elemental analysis values (detailed values of CHN compositions are given in Table 3.2). An explanation for the above observations may be found in the inhomogeneous nature of the sample compositions. The microanalytical data did not indicate the presence of nitrogen in the final products. This suggests that no neutral $NOSO_3F$, NO or any other nitrogen containing species has been cointercalated. Hence, the role of $NO^+_{(solv)}$ as the oxidizing agent seems clear from the results obtained for product compositions.

Assuming that the remaining intercalants in the GIC are SO_3F^- groups, a general formula such as $C_nxSO_3F.yHSO_3F$ can be derived from microanalysis for these compounds. Similar compositions have been proposed by Herold et al. for the GIC's synthesized in a non-protonic solvent like nitromethane[36] (e.g. $C_{23n}MF_6(solvent)_y$). However, the compositions of the compounds formed in the protonic solvent HSO_3F do not suggest a significant dependence on reactant concentrations or reaction times (see Table 3.2 for numerical data). One general observation can be made safely: The high carbon percentages obtained indicate that the products are of a higher stage index. The X-ray diffraction value measured, with $I_c = 10.59 \pm 0.03$ Å, also confirms a second stage compound. For average carbon and hydrogen compositions 72% and 0.20%, with SO_3F^- ~27.8%, the formula of the product can be written as $C_{74}SO_3F.2\cdot 4HSO_3F$, which shows a substantial amount of solvent intercalation in the final product.

The ^{19}F-NMR of the sample gave two broad resonances at 25 and 36 ppm respectively (Fig. 4.8). This observation differs from the earlier

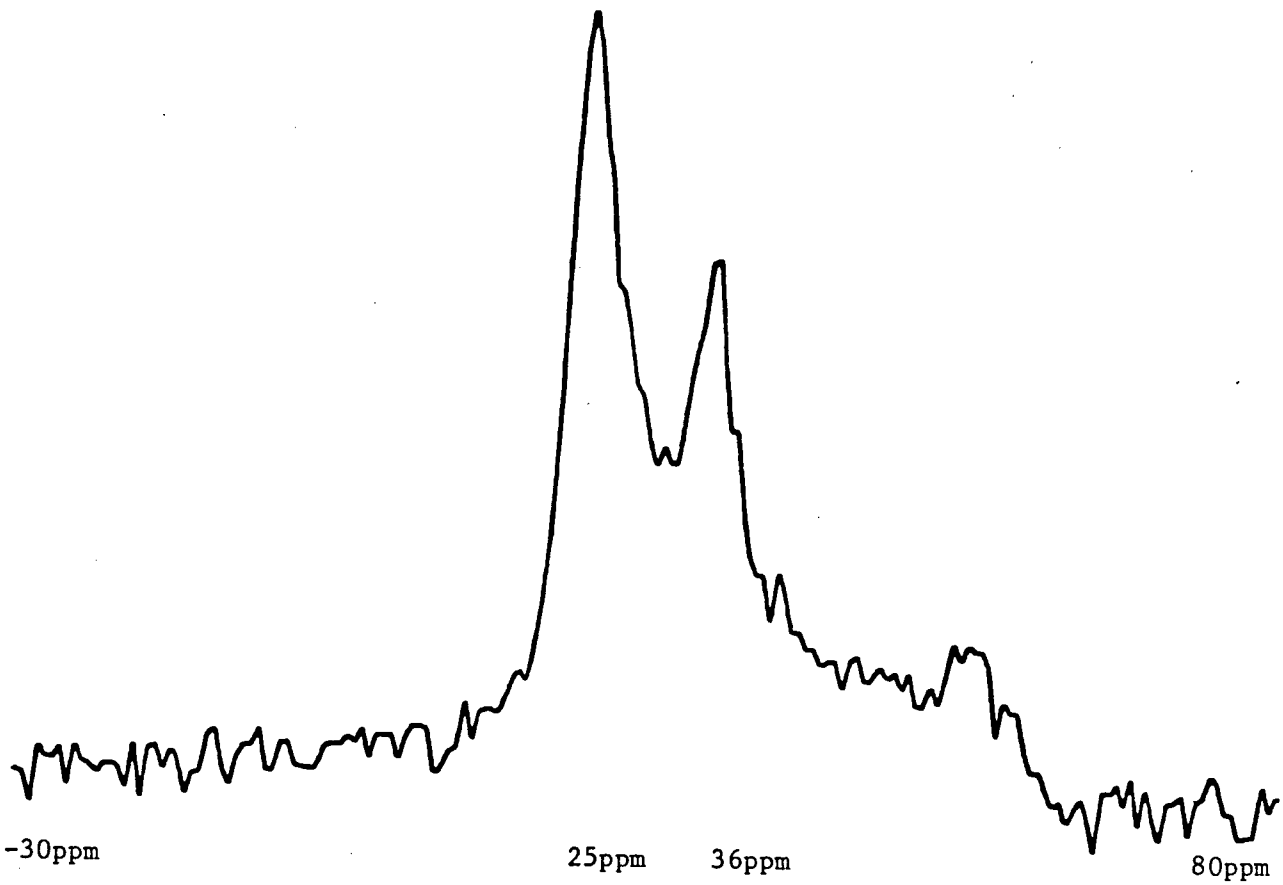


Figure 4.8: ^{19}F-NMR Spectrum of Graphite + $NOSO_3F$ Compound

^{19}F-NMR values given for compositionally homogeneous graphite acid fluorosulfates, where only a single broad resonance was seen for both SO_3F and HSO_3F intercalates.[43] (see also Fig. 4.4 and 4.7).

Of the two values, the signal at 25 ppm is assigned to the SO_3F^- ions intercalated into graphite. The assignment of the second value at 36 ppm to intercalated HSO_3F is based on an earlier reported observation in which a sample of C_7SO_3F with some residual surface adsorbed HSO_3F showed a ^{19}F resonance at 39 ppm.[43] In addition, a compound of formula $C_{14}SO_3F.1{\cdot}05HSO_3F$ was reported as showing two ^{19}F-NMR resonances at 14.1 and 35.9 ppm respectively.[43] As in this GIC, the present product may have SO_3F and acid molecules intercalated in different alternate layers in the graphite lattice, which will lead to a non-homogemeous packing arrangement along the c-axis direction. The small upfield shift observed in regard to HSO_3F in the ^{19}F-NMR spectrum (~4.6 ppm) could be due to a limited charge transfer from graphite to molecular HSO_3F. In contrast, the large upfield shift of the SO_3F^- groups (~12.4 ppm) suggests extensive charge transfer between the graphite lattice and SO_3F in the GIC. Attempts to detect NO in the gas phase by mass spectroscopy after intercalation proved to be unsuccessful. This is not totally unexpected, since, for example, for a general formula of $C_{74}SO_3F.2{\cdot}4HSO_3F$ and ~12.0 mmol of graphite, only 0.162 mmol of NO could be formed during the reaction. This small fraction of NO may dissolve quite easily in the excess HSO_3F, hence never appearing as a volatile product in the vapor phase. In addition oxidation of NO in HSO_3F and subsequent further reactions of NO_2 in HSO_3F are possible. Finally, small amounts of SO_3 in HSO_3F may act as an oxidizing agent, resulting

in the formation of NO_2 initially, which could subsequently interact further. The overall reaction, based on the results discussed above, can be written as follows:

$$C_n + NOSO_3F \xrightarrow{HSO_3F} C_nSO_3F.y.HSO_3F + NO_{(g)}$$

where y ~2.4 and n ~74, which are average values of several sample compositions.

In summary, intercalation of SO_3F^- by NO^+ oxidation in HSO_3F does not lead to first stage compounds, as had been the case in nitromethane, albeit using different anions.[36] There is obviously no advantage in using this route over oxidative intercalation by $S_2O_6F_2$ in the presence or absence of HSO_3F, taking into account that $NOSO_3F$ is initially synthesized from $S_2O_6F_2$.

The large amount of solvent intercalated is rather surprising. However, the observation of ^{19}F-NMR resonances is not unexpected. H-bridged ions like $[H(SO_3F)_2]^-$ [107] are only realistic as long as the acid content is below one mole per mole SO_3F.

4.5 General Comments and Conclusion

This thesis has described the synthesis of bromine- and iodine fluorosulfate intercalation compounds in fluorosulfuric acid, and some general conclusions based on this study are summarized below. In all

the synthetic reactions, HSO_3F functions as an excellent oxidation resistant solvent for the highly viscous and solid intercalants like $I(SO_3F)_3$ and $Br(SO_3F)_3$, which due to their physical properties and limited thermal stability cannot be intercalated directly into graphite. The broad liquid range of the acid allows wide temperature variations and its ability to form solutions without extensive solute disproportionation make the syntheses relatively uncomplicated since both $Br(SO_3F)_3$ and $I(SO_3F)_3$ act as weak electrolytes in HSO_3F.

The oxidation of the graphite lattice by iodine species in HSO_3F is confirmed by the observed color changes in the intercalant solutions. Whenever $I(SO_3F)_3$, $Br(SO_3F)_3$ and $K[Hal(SO_3F)_4]$ are used in high concentrations, no appreciable solvent intercalation is noted. Cationic intercalant species such as $I_2^+{}_{(solv)}$ and $NO^+{}_{(solv)}$ give GIC's with substantial amounts of acid present in the final products even at high concentrations, with no NO species and only very little iodine intercalated in the respective compounds. This leads to the conclusion that fluorosulfuric acid and SO_3F^- intercalate preferentially into the host material when cations solvated in HSO_3F are used as oxidizers.

Neutral intercalants such as $I(SO_3F)_3$ and $Br(SO_3F)_3$ or anionic solutes like $K[Hal(SO_3F)_4]$ give rise to the formation of iodine and bromine containing intercalation compounds.

The $NO^+{}_{(solv)}$ promoted intercalation reaction, where HSO_3F and SO_3F^- are the most possible intercalates, does not offer any distinct synthetic advantage over the graphite-$S_2O_6F_2$ intercalation reaction because only high stage materials are obtained, and furthermore, $NOSO_3F$ is initially prepared from $S_2O_6F_2$.

Finally, although in addition to microanalysis, physical methods such as X-ray powder diffraction, Raman spectroscopy, Solid state ^{19}F-NMR and UV-visible spectroscopic techniques were used, the identification and characterization of the species present in the intercalant layers still remain, to a large extent, the most difficult challenge in graphite intercalation chemistry. The use of high resolution Electron microscopy and extended X-ray absorption fine structure (EXAFS) measurements, together with the above cited physical techniques may in future research facilitate the complete characterization of guest molecules/ions present in the graphite lattice.

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