NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE.

It has been reproduced from the best available copy to permit the broadest possible availability.

LBL-18367

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

**Materials & Molecular
Research Division**

ELECTRON OXIDATION OF GRAPHITE BY FLUOROSPECIES

G.L. Rosenthal
(Ph.D. Thesis)

September 1984

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LBL--18367

DE65 001196

ELECTRON OXIDATION OF GRAPHITE BY FLUOROSPECIES

Guy Leonard Rosenthal
Ph.D. Thesis

September 1984

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This work was supported by the U.S. Department of Energy
under Contract Number DE-AC03-76SF00098

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Dedication

This thesis is dedicated to my family. For all these years, I never really felt far away.

ELECTRON OXIDATION OF GRAPHITE BY FLUOROSPECIES

Table of Contents

List of Tables	v
List of Figures	vii
Acknowledgements	viii
Abstract	ix
Chapter 1- GENERAL INTRODUCTION	1
Chapter 2- GENERAL APPARATUS AND MATERIALS	3
Vacuum System	3
Reaction Vessels and Handling	4
General Instrumentation and Procedures	4
Debye-Scherrer X-ray powder photography	4
Infrared spectra	4
Raman spectra	4
Single-crystal X-ray diffraction	5
Vapor pressure vs. temperature measurements	5
Analyses	5
Materials	5
References	8
Figures	9
Chapter 3- THERMODYNAMICS OF INTERCALATION OF HEXAFLUOROPHOSPHATE ANION	10
Introduction	10
Experimental	10
SF ₃ PF ₆	10
ClO ₂ PF ₆	11
Van't Hoff plots for SF ₃ PF ₆ and ClO ₂ PF ₆	11
C ₁₁ PF ₆	12
C ₂₄ PF ₆	12
C ₂₄ PF ₆ .PF ₅	13
Higher-stage PF ₆ ⁻ salts	13
Results and Discussion	13
Summary	15
References	16
Tables	18
Figures	24

Chapter 4- STUDIES OF THE THERMODYNAMICS AND GRAPHITE CHEMISTRY OF THE TETRAFLUOROBORATE ANION	29
Introduction	29
Experimental	29
ClO_2BF_4	29
Dissociation pressure measurements	30
C_7BF_4	30
C_{16}BF_4	31
Higher-stage fluoroborates	31
Lattice enthalpy calculations	31
Results and Discussion	31
Summary	33
References	34
Tables	35
Figures	42
Chapter 5- SYNTHESIS AND REACTIONS OF A GRAPHITE FLUROSILICATE SALT	45
Introduction	45
Experimental	45
$\text{C}_{24}\text{SiF}_5$	45
Interaction of $\text{C}_{24}\text{SiF}_5$ with PF_5	46
Interaction of $\text{C}_{24}\text{SiF}_5$ with BF_3	46
Interaction of $\text{C}_{24}\text{SiF}_5$ with $\text{C}_6\text{F}_5\text{PF}_4$	47
Interaction of $\text{C}_{24}\text{SiF}_5$ with SF_6	47
Discussion	47
Summary	50
References	52
Tables	54
Chapter 6- A THERMODYNAMIC THRESHOLD FOR OXIDATIVE GRAPHITE INTERCALATION	56
Introduction	56
Experimental	57
Reaction of second-stage fluorophosphate with PF_3	57
Reaction of first-stage C_{12}PF_6 with PF_3	58
Reaction of C_{24}PF_6 with BF_3	58
Reaction of C_{28}PF_6 with BF_3 and F_2	58
Reaction of C_8BF_4 with PF_5	59
Infrared standards	59
Microdensitometer studies	59
Results and Discussion	59
1. PF_3 reductions	59

2. Displacement reactions	61
Summary	64
References	65
Tables	67
Figures	76
Chapter 7- BASAL-PLANE CONDUCTIVITIES OF C_xBF_{3+y} AND C_xPF_{5+y} COMPOUNDS	79
Introduction	79
Experimental	80
HOPG chips	80
C_xPF_6 ($x < 100$)	80
C_xPF_6 ($x > 100$)	81
C_xPF_{5+y}	81
C_xBF_4	82
C_xBF_{3+y}	82
Conductivity measurements	83
Results and Discussion	83
1. Synthesis, staging and stoichiometry	83
2. Conductivity	85
Summary	86
References	88
Tables	89
Figures	99

List of Tables

Table 3-1- Debye-Scherrer powder data for SF_3PF_6	18
Table 3-2- Debye-Scherrer powder data for ClO_2PF_6	19
Table 3-3- Vapor pressure vs. temperature measurements for SF_3PF_6 and ClO_2PF_6	20
Table 3-4- Debye-Scherrer data for graphite-phosphorus-fluorine intercalation compounds	21
Table 3-5- C-spacings of higher-stage fluorophosphates	22
Table 3-6- The fluoride-ion affinity of PF_5	23
Table 4-1- Crystal data for ClO_2BF_4	35
Table 4-2- Positional and thermal parameters for ClO_2BF_4	36
Table 4-3- Observed and calculated structure factors for ClO_2BF_4	37
Table 4-4- Bond distances and angles in ClO_2BF_4	38
Table 4-5- Dissociation pressure measurements for ClO_2BF_4	39
Table 4-6- Debye-Scherrer powder data for graphite tetrafluoroborate salts	40
Table-4-7- Gallery heights in BF_4^- salts	41
Table 5-1- Gravimetric and analytical data for $\text{C}_{24}\text{SiF}_5$ preparations	54
Table 5-2- X-ray powder data for $\text{C}_{24}\text{SiF}_5$ and derivatives	55
Table 6-1- Reaction conditions and results for second-stage fluorophosphate preparations	67
Table 6-2- Debye-Scherrer data for second-stage fluorophosphate preparations	68
Table 6-3- Reaction conditions and results for PF_3 reductions	69
Table 6-4- Debye-Scherrer results for PF_3 reductions	70
Table 6-5- Intensities of reflections in Debye-Scherrer patterns of pristine graphite and $\text{C}_x\text{PF}_6 + \text{PF}_3$	71
Table 6-6- Conditions and results for reactions of C_xPF_6 with BF_3	72
Table 6-7- Debye-Scherrer results for $\text{C}_x\text{PF}_6 + \text{BF}_3$ reaction	73
Table 6-8- Conditions and results for reactions of C_xBF_4 with PF_5	74

Table 6-9- Debye-Scherrer results for $C_xBF_4 + PF_5$ reaction	75
Table 7-1- Reaction times and resulting stoichiometries of C_xPF_6 compounds	89
Table 7-2- Conductivity vs. composition for C_xPF_6	90
Table 7-3- Conductivities of C_xPF_6 salts made with excess PF_5	91
Table 7-4- Reaction times and resulting stoichiometries of C_xPF_{5+y} compounds	92
Table 7-5- Conductivity vs. composition for C_xPF_{5+y}	93
Table 7-6- Reaction conditions and resulting stoichiometries of C_xBF_4 compounds	94
Table 7-7- Conductivity vs. composition for C_xBF_4	95
Table 7-8- Conductivities of C_xBF_4 salts made with excess BF_3	96
Table 7-9- Reaction times and resulting stoichiometries of C_xBF_{3+y} compounds	97
Table 7-10- Conductivity vs. composition for C_xBF_{3+y}	98

List of Figures

Figure 2-1- Pressure-equalizing gauge for vapor pressure measurements	9
Figure 3-1- Raman spectrum of SF_3PF_6	24
Figure 3-2- Raman spectrum of ClO_2PF_6	25
Figure 3-3- Van't Hoff plot for SF_3PF_6	26
Figure 3-4- Van't Hoff plot for ClO_2PF_6	27
Figure 3-5- Lattice energy vs. formula-unit volume relationship	28
Figure 4-1- Raman spectrum of ClO_2BF_4	42
Figure 4-2- Stereoview showing coordination in ClO_2BF_4	43
Figure 4-3- Stereo packing diagram of ClO_2BF_4	44
Figure 6-1- A thermodynamic cycle for oxidative graphite intercalation	76
Figure 6-2- Microdensitometer tracing of (a) pristine graphite and (b) reduction product of $\text{C}_x\text{PF}_6 + \text{PF}_3$	77
Figure 6-3- The $\text{B}_4\text{F}_{13}^-$ ion	78
Figure 7-1- Schematic diagram of contactless conductivity apparatus	99
Figure 7-2- The Daumas-Herold staging model	100

Acknowledgements

First, I would like to thank my research director, Prof. Neil Bartlett, for providing the means for this research, as well as many of the key insights which make this bewildering hodgepodge of data at least partially coherent.

I owe a great debt to my two mentors of my first three years, Tom Mallouk and Ray Brusasco. Tom's diverse body of knowledge, excellent chemical sense, quick wit, timely hitting and water-tight defense were inspirational and Ray's mechanical, electrical and oxidative expertise, as well as his dynamite Napoleons and sinful cream puffs kept me awake nights in awe and indigestion.

I would not have survived without the Bad Clams, DuxTM on the Pond, Grateful Dead and Yolo Drop Zone, four institutions which allowed me to relax and get my mind off of important things and on to more important things.

Many thanks to my roommates through the years, especially Steve Pacetti, Mark Young and the whole gang at R.F.I.

I have grown a lot in the past four years, and I am grateful to countless people for giving me the opportunity to grow. You all know who you are. Thanks.

This work was supported by the U.S. Department of Energy under contract no. DE-AC03-76 SF00098.

Blue Skies!

Electron Oxidation of Graphite by Fluorospecies

Guy L. Rosenthal

Abstract

The fluoride-ion affinity (A_{F^-}) of phosphorus pentafluoride was determined to be 100 kcal/mole from the heats of reaction of the Lewis bases SF_4 and ClO_2F with PF_5 near room temperature. The fluoride-ion affinity of boron trifluoride was determined to be 92 kcal/mole from the heat of reaction of ClO_2F with BF_3 . The crystal structure of ClO_2BF_4 was determined and a precise lattice energy was calculated from this structure and used to determine A_{F^-} . Both PF_5 and BF_3 were found to react with graphite in the presence of fluorine gas to yield a variety of non-stoichiometric compounds.

The fluoride-ion affinity of silicon tetrafluoride is not known, but it does not react with graphite and F_2 except at high pressures.

These and previous results suggested a threshold in oxidizing power of intercalating species below which the oxidative intercalation reaction would not occur. The reduction of C_xPF_6 by PF_3 proved that the reaction is thermodynamically controlled to some extent. The displacement of PF_5 in C_xPF_6 by BF_3 (with a smaller A_{F^-}) suggested that two BF_3 molecules may have a larger fluoride-ion affinity than one PF_5 and that $B_2F_7^-$ may be a stable anion in graphite.

Conductivity studies of PF_x and BF_y salts showed that a large drop in conductivity when the reaction reaches first stage is due in the most part to direct fluorination of carbon in graphite.

CHAPTER 1

GENERAL INTRODUCTION

In recent years, a boom has occurred in the study of oxidative graphite intercalation compounds, chiefly because of their two-dimensional metallic behavior. Unfortunately, the best conducting and most widely studied systems are among the most complex chemically and relatively little is known about the basic chemistry of these compounds. This work focuses on the simpler oxidative intercalation systems in an effort to understand the factors which influence the reaction itself, then continues on to attempt to place the conductivity properties of these simple systems into the scheme established through study of more complex systems.

The main body of the thesis is concerned with the thermodynamics of half-reactions which result in oxidative intercalation and with the corresponding intercalation reactions. Chapters 3-5 detail studies determining the fluoride-ion affinities of PF_5 and BF_3 and the syntheses and basic chemistry of compounds of composition $\text{C}_n\text{PF}_6 \cdot x\text{PF}_5$, $\text{C}_n\text{BF}_4 \cdot x\text{BF}_3$ and C_nSiF_5 . All of these simple systems obey what will be called the "thermodynamic threshold" rule, set out in Chapter 6.

Chapter 6 details the evolution of the threshold concept in earlier work and fits the systems studied in earlier chapters into the scheme. The validity of the thermodynamic threshold and the importance of thermodynamics in graphite intercalation are established with the experiments in reductive deintercalation of graphite with PF_3 . Results of displacement reactions of the Lewis acids used here are also discussed and the idea is put forth that graphite may act as a macrocation to stabilize unusual anions.

Finally, the conductivity behavior of the fluorophosphate and fluoroborate systems are studied in Chapter 7 in an effort to fit them into the patterns established in previous work studying the transition-metal hexafluoride intercalates and the more complex fluoroarsenate system. Questions are raised about the reasons for per-plane conductivity reaching a maximum before the limiting composition is reached, i.e., before the graphite is supposedly fully oxidized.

CHAPTER 2

GENERAL APPARATUS AND MATERIALS

Vacuum System

Nearly all of the compounds discussed in this thesis, both molecular and graphite-based, are extremely hydrolytically unstable to air and many of them also react with Pyrex or quartz glass. For these reasons, all reactions were carried out in a completely stainless-steel and Monel vacuum system. The main body of this system was made up of 3/8" o.d. stainless-steel tubing connected to ports through Swagelock fittings and stainless-steel ferrules. The line could be closed between any two ports by Monel Hoke M485 valves. The ports themselves were controlled through stainless steel Whitey 1KS6 valves, after which the tubing diameter was reduced to 1/4" o.d. to fit most gaseous reagent vessels and reaction vessels through Swagelock fittings and teflon ferrules. Pressures were monitored with an Acco Helicoid gauge (0-1500 torr) and a Hastings thermocouple gauge (0-1 torr).

A fluorine tank was connected to the line through a high-pressure manifold consisting of Autoclave Engineering 30VM6071 valves and thick-walled stainless-steel tubing. Fluorine pressure was monitored with a Crosby gauge (0-600 psia). Just before the liquid nitrogen trap, the system contained a bypass through a soda-lime tower to trap fluorine and chlorine trifluoride. The Welch 1400 mechanical pump routinely achieved pressures of 10 microns.

The total volume of the main body of the line was approximately 75 ml. Many reactions involved condensation of known pressures of gas from this volume into a small reaction vessel and warming to room temperature to achieve high gas pressures.

Reaction Vessels and Handling

Most of the graphite reactions were performed in small bombs made of three-inch sections of 3/8" Monel rod drilled out to 1/4" i.d. The volume of the vessels was approximately 3 ml. with fittings (stainless-steel ferrules) up to a 1/4" Whitey 1KS4 valve. A teflon filter was placed between the vessel and the valve to avoid loss of powdered graphite in pumping. Low pressure graphite and molecular reactions were performed in teflon FEP or quartz tubing, sealed at one end and connected to the line through Swagelock fittings (teflon ferrules) up to 1/4" Whitey valves. The quartz and teflon vessels withstood pressures up to 5 atm. and were used whenever possible to afford the opportunity for observation. Larger-scale gas preparations were performed in 100 ml. brass or Monel cans, in which the gases could be stored.

All air sensitive materials were handled and weighed in a Vacuum Atmosphere Corp. Dri-Lab.

General Instrumentation and Procedures

Debye-Scherrer X-ray powder photography: Debye-Scherrer patterns were obtained on a General Electric Precision camera of 45 cm. circumference using Ni-filtered CuK_α radiation. Samples were contained in sealed, thin-walled quartz capillaries of 0.5 or 0.7 mm. diameter (Charles Supper Co., Natick, Mass.). Compounds which were too volatile to be loaded in the glove box were made directly in capillaries which had been sealed to larger quartz tubing and fitted to the vacuum line.

Infrared spectra: Infrared (IR) spectra were recorded on a Perkin-Elmer 597 spectrophotometer. A Monel gas cell of 10 cm. path length with AgCl windows was filled to 25-100 torr for ordinary spectra.

Raman spectra: A J-Y Ramanor HG2S spectrometer with a double holographic

grating monochromator was used to obtain spectra, with krypton (647.1 nm.) or argon (514.5 or 488.0 nm.) laser radiation to excite. Samples were generally contained in quartz capillaries or in $1/4$ " sealed teflon FEP tubing. Samples particularly sensitive to the laser beam could be spread on a Kel-F disc and sealed with a sapphire cover held in place by a Kel-F collar. The disc was then rapidly rotated in the beam to spread the radiation over as large a sample as possible. Low temperature spectra were obtained by holding the sample in a stream of cold, dry nitrogen to reach temperatures as low as -140° .

Single-crystal X-ray diffraction: Precession photographs were taken on an Enraf-Nonius (Delft, Holland) camera, using Zr-filtered MoK_{α} radiation and a Polaroid XN-7 film cassette. Intensity data was gathered on an Enraf-Nonius four-circle diffractometer, using monochromatized MoK_{α} radiation. The diffractometer was interfaced through a PDP 8/a mini-computer to a DEC PDP 11/60. The structure was solved using the CHEXRAY facility and the (modified) Structure Determination Package of B.A. Frenz and Associates (College Station, Tex.) and Enraf-Nonius.

Vapor-pressure vs. temperature measurements: Dissociation pressures were measured by the method of Cromer,¹ equalizing pressure on a Monel diaphragm (Figure 2-1). The samples were prepared in the same quartz bulb used for the measurements (partially collapsed for better thermal contact) and purified first by sublimation. A water bath large enough to submerge the entire apparatus was used for temperature control.

Analyses: Routine carbon analyses were performed in the departmental microanalytical facility.

Materials

Graphite used was of two forms: SP-1 spectroscopic grade powder

from Union Carbide (Parma, Ohio) and HOPG chips and flakes, kindly provided by Dr. A.W. Moore of Union Carbide. The HOPG was occasionally filed into powder for comparison with SP-1 and found to produce identical products in all cases, although the larger particle-size HOPG was actually found to react more readily than SP-1. HOPG chips were used exclusively in the contactless conductivity studies, of course, and were subsequently filed into powder for characterization by Debye-Scherrer powder diffraction.

Gases: Fluorine (Matheson Gas Co., Inc., E. Rutherford, N.J.) was purified by photolysis of the liquid held at -196° to convert oxygen to oxygen fluorides, then distilled from -183° to -196° to separate from involatiles, including HF. Phosphorus pentafluoride (Matheson) was purified by trap-to-trap distillation. Phosphorus trifluoride was used as obtained from Peninsular Chemresearch, Inc., Gainesville, Fla. Silicon tetrafluoride was synthesized by reacting Si metal with F_2 in a Monel can at low pressures until the reaction became very slow. An excess of F_2 was then added and the reaction completed at 200° for 24 hours. Boron trifluoride was used as obtained from Matheson. Chloryl fluoride was prepared by the method of Smith, et. al.,² condensing ClF_3 onto excess $KClO_3$ in a Monel can and reacting at 150° for 72 hours. ClO_2F was collected by trap-to-trap distillation. Sulfur tetrafluoride (Matheson) was purified by trap-to-trap distillation. Traces of OSF_2 were assumed to be inert in the reactions studied. Chlorine trifluoride was used as obtained from Ozark-Mahoning (Tulsa, Okla.). All gases were checked for purity by IR.

Silicon metal was supplied by Matheson, Coleman and Bell (Norwood, Ohio) and potassium chlorate by J.T. Baker Chemical Co., Phillipsburg,

N.J.

Pentafluorophenyltetrafluorophosphorane ($C_6F_5PF_4$) was kindly provided by Prof. Reinhard Schmutzler of Braunschweig, West Germany.

References

- ¹ S. Cromer, U.S. At. En. Comm. MDDC-803, June 20, 1944.
- ² D.F. Smith, G.M. Begun and W.H. Fletcher, *Spectrochimica Acta*, 20, 1763 (1964).

Figure 2-1- Pressure-equalizing gauge for vapor pressure measurements

XBL 835-9967

CHAPTER 3

THERMODYNAMICS OF INTERCALATION OF HEXAFLUOROPHOSPHATE ANION

Introduction

It has been established¹ that transition-metal hexafluorides will not react with graphite to form oxidative intercalation compounds unless their electron affinities are greater than that of ReF_6 , around 110 kcal/mole.² Pentafluorides of the Group V elements P, As and Sb are also known to react with graphite in the presence of fluorine to form $\text{C}_x^+\text{MF}_6^-$ salts.^{4,5} The "electron affinity half-reactions"

of AsF_5 and SbF_5 are considerably more exothermic than that of PF_5 ,⁶ but this value had not been adequately evaluated for PF_5 . Since this half-reaction results in oxidative intercalation of all three hexafluoro-anions, it was important to establish the phosphorus value to discover if it defined a lower limit of exothermicity for reactions which result in intercalation.

The graphite-phosphorus-fluorine system had been investigated previously,^{4,7} and found to be quite tractable compared to the exceedingly complex arsenic system. PF_5 does not react with graphite by itself, as AsF_5 does, so the phosphorus analogy to the much-debated $\text{AsF}_5\text{-AsF}_6^-\text{-AsF}_3$ equilibrium⁸ was not a factor. These studies involve stoichiometries and structures of materials made with graphite, PF_5 and F_2 (neat), in an attempt to limit the variables and better understand the dynamics of these systems.

Experimental

SF_3PF_6 : SF_4 and PF_5 were combined in a 1:1 molar ratio to produce a colorless solid, purified by venting volatile impurities to a large

evacuated volume several times. The Raman spectrum, taken in a quartz capillary, is shown in Figure 3-1. The gases above the solid salt (vapor pressure = 650 torr at 23.5°) were confirmed by IR to be SF_4 and PF_5 . Debye-Scherrer powder data (Table 3-1) was indexed on the basis of a hexagonal cell, $a = 5.78\text{\AA}$; $c = 11.18\text{\AA}$; $V = 323.5\text{\AA}^3$; $Z = 2$. This data satisfies Zachariasen's criterion⁹ of ca. $17\text{\AA}^3$ per F or O atom in a formula unit. Single crystals of high enough quality for intensity data collection were not obtained, but the powder data showed clearly that SF_3PF_6 is not isostructural to SF_3AsF_6 .¹⁰

ClO_2PF_6 : The constituent gases were combined in a 1:1 molar ratio and yielded a pale yellow, highly volatile (vapor pressure >1400 torr at 25°) solid, purified in the same manner as SF_3PF_6 . The Raman spectrum (Fig. 3-2) was taken in a teflon FEP tube. The gases above the solid were again checked by IR and found to be ClO_2F and PF_5 . X-ray data were difficult to obtain at room temperature, since the salt tended to sublime out of the warm beam. Debye-Scherrer data (Table 3-2) was indexed on the basis of an orthorhombic cell, $a = 8.72\text{\AA}$; $b = 6.02\text{\AA}$; $c = 5.44\text{\AA}$; $V = 285.6\text{\AA}^3$; $Z = 2$. The cell dimensions were substantially confirmed by zero-layer precession photographs of a low-quality single crystal. ClO_2PF_6 also satisfies Zachariasen's criterion.

Van't Hoff plots for SF_3PF_6 and ClO_2PF_6 : Approximately one gram of sample was used in an experiment. Measurements were made at 3-4° intervals for each compound, both with ascending temperature and descending temperature. In cases where measurements differed (never by more than 5 torr) averages were used in the final least-squares plot. For SF_3PF_6 , measurements were taken from 0-23.5° (Table 3-3a) and for ClO_2PF_6 from -5° to 9° (Table 3-3b). From the van't Hoff relation, $\ln K =$

$-\Delta H/RT + \Delta S/R$, the resulting parameters are (σ in parentheses):

The data are plotted in Figures 3-3 and 3-4. Errors were 0-2 torr at low temperatures and 0-5 torr near room temperature.

C₁₁PF₆: A vacuum-stable first-stage hexafluorophosphate of composition C₁₁PF₆ (established by gravimetry) was prepared by passing F₂ (300 torr) and F₂ (300 torr) from the 75 ml. vacuum line into a 100 ml. reaction vessel (total pressure ca. 25 atm.) charged with graphite (typically 10 mmole) and agitating at 20° for 12 hours. Volatiles were removed in dynamic vacuum and the sample pumped on until further pumping produced no weight loss, typically 24 hours. Condensation of higher pressures of PF₅ and F₂ on the product and gentle heating (to 50°) produced no weight gain, so C₁₁PF₆ was taken as the limiting composition. Debye-Scherrer powder photographs were indexed on the basis of a hexagonal cell (Table 3-4), $a = 2.45(1)\text{\AA}$; $c = 7.79(5)\text{\AA}$. Carbon analysis showed %C = 47.3; required for C₁₁PF₆: 47.7%.

C₂₄PF₆: The second-stage fluorophosphate could be made in either of two ways. It was made directly by condensing PF₅ (200 torr) and F₂ (150 torr) into a Monel vessel (total pressure ca. 12 atm.) with graphite (ca. 10 mmole). The vessel was agitated for 45 minutes and the volatiles removed under dynamic vacuum. Sample weight typically stabilized after 20-40 hours of pumping time. Compositions (from gravimetry) of C₂₄₋₂₇PF₆ all seemed to show only a second-stage material in Debye-Scherrer photographs (Tables 3-4) with $a = 2.46(1)\text{\AA}$ and c ranging from 10.72Å to 10.92Å. Carbon analyses showed %C = 66-68; required for C₂₄PF₆: 66.5%.

Second-stage fluorophosphate could also be made simply by pumping on $C_{24}PF_6 \cdot PF_5$ for 72 hours.

$C_{24}PF_6 \cdot PF_5$: A large molar excess of PF_5 (600 torr) and just sufficient F_2 to meet the requirements of the $C_{24}PF_6 \cdot PF_5$ stoichiometry (60 torr) were condensed into a Monel vessel containing graphite (10 mmole), warmed to room temperature and agitated for 24 hours. Remaining gases were vented to the evacuated manifold (static vacuum) and then to the Dri-Lab atmosphere. If the product was not a homogeneous first-stage material, determined by Debye-Scherrer, it was again treated with PF_5 , containing a small concentration of F_2 (ca. 10 torr) for a further 8 hours at 20° . The final first-stage product was indexed to a hexagonal cell (Table 3-4), $a = 2.46(1)\text{\AA}$; $c = 7.62(1)\text{\AA}$. Both gravimetry and carbon analysis satisfied the stoichiometry $C_{24}PF_6 \cdot PF_5$. This material was converted to the second-stage $C_{24}PF_6$ by pumping off PF_5 (trapped and detected by IR), then could be reconverted to $C_{24}PF_6 \cdot PF_5$ by subjecting the second-stage salt to PF_5 pressure (500 torr condensed in a Monel vessel) for eight hours.

Higher-stage PF_6^- salts: Third and higher-stage salts could be seen in powder patterns of products of reactions using identical conditions to those of the $C_{24}PF_6$ synthesis, but shorter reaction times. These products were never found as single phases, but their c-spacings (generally from 001 reflections, see Table 3-5) obeyed the rule $c \approx 4.2 + 3.35n\text{\AA}$, where n is the stage (3.35Å is the van der Waals thickness of a carbon sheet in graphite) and 4.2Å is the height of a PF_6^- octahedron measured along a three-fold axis.

Results and Discussion

With the heats of reaction found in the dissociation pressure

measurements of SF_3PF_6 and ClO_2PF_6 , the fluoride-ion affinity of PF_5 could be evaluated from two mutually independent Born-Haber cycles. The enthalpies of ionization of SF_4 and ClO_2F were known and the lattice enthalpies could be estimated on the basis of the formula-unit volumes of SF_3PF_6 and ClO_2PF_6 . For a simple A^+B^- salt, the lattice enthalpy is dominated by the coulombic term and should depend on $M/r_{\text{A}^+\text{B}^-}$, where M is the Madelung constant and $r_{\text{A}^+\text{B}^-}$ the shortest anion-cation distance. If $M/r_{\text{A}^+\text{B}^-}$ is constant for various structure types,¹¹ then the lattice enthalpy should simply depend on the inverse cube root of the unit-cell volume, i.e. the average primitive cell length. Such a correlation was observed by Dr. T.E. Mallouk and is shown in Figure 3-5. The Born-Haber calculations are set out in Tables 3-6 and show a satisfying agreement between the two results. From these results, the fluoride-ion affinity of PF_5 [$\Delta H^\circ (\text{PF}_6^-(\text{g}) + \text{PF}_5(\text{g}) + \text{F}^-(\text{g}))$] is established as 100 kcal/mole and the enthalpy of the electron affinity half-reaction (1) for PF_5 is -162 kcal/mole.¹²

It is hardly surprising, then, that PF_5 intercalates graphite in the presence of fluorine so readily. This half-reaction is far more exothermic than the lowest electron affinity half-reaction of the transition-metal hexafluorides which intercalate graphite.² The fluoride-ion affinity, though, is not only useful in explaining why PF_5 reacts with graphite in the presence of fluorine but also in determining why PF_5 itself does not react with graphite. This will be discussed in Chapter 6.

The graphite-hexafluorophosphate system appears to be one of the simplest studied so far. It follows the staging-stoichiometry relationship $\text{C}_{(12-13)n}\text{PF}_6$, where n is the stage and where the galleries

in the first-stage compound can be crowded slightly more than in higher stages, resulting in the limiting composition $C_{11}PF_6$.

The hexafluorophosphate anion appears "short" compared to other hexafluoroanions, which ordinarily add 4.6Å or more to the carbon-layer spacing in an occupied gallery. The bonds in PF_6^- are indeed shorter than those in other MF_6^- ions,¹³ but some of this smaller c-spacing may be attributed to better "nestling" of the PF_6^- octahedra into the hexagonal rings of the graphite lattice.¹⁴

The reversible reaction of $C_{24}PF_6$ with neutral PF_5 was not unexpected. Many other graphite salts have been shown to take up neutral gaseous species or solvent molecules.^{4,15} The reaction with PF_5 may be more facile because of the possible role of $P_2F_{11}^-$ ions in helping PF_5 move into the galleries. Selig, et.al. have proposed the presence of such unusual species through nmr studies,¹⁶ and indeed graphite can be envisioned here as an extremely large cation, showing a remarkable tendency to stabilize unusual anions. This also will become evident in following chapters.

Summary

Determination of ΔH° for $SF_4(g) + PF_5(g) \rightarrow SF_3PF_6(s)$ and $ClO_2F(g) + PF_5(g) \rightarrow ClO_2PF_6(s)$ from van't Hoff measurements allowed the fluoride-ion affinity of PF_5 to be evaluated from Born-Haber cycles as 100 kcal/mole. The reaction of PF_5 with graphite and fluorine gas is understandably facile. Simple first and second-stage graphite hexafluorophosphates were synthesized in this manner and Debye-Scherrer powder diffraction yielded their unit-cell dimensions. The second-stage compound was found to reversibly take up PF_5 to form a first-stage salt.

References

- ¹ N. Bartlett, E.M. McCarron, B.W. McQuillan and T.E. Thompson, *Syn. Metals*, 1, 221 (1980).
- ² N. Bartlett, *Angew. Chem. Int. Ed.*, 7(6), 433 (1968). Bartlett concludes that the electron affinity of the third-row transition-metal hexafluorides increases smoothly from left to right across the periodic table at the rate of ca. 1 eV per step from WF_6 (81 kcal/mole³) to PtF_6 .
- ³ P.M. George and J.L. Beauchamp, *Chem. Phys.*, 36, 345 (1979).
- ⁴ E.M. McCarron, Ph.D. Thesis, University of California, Berkeley, 1980.
- ⁵ E. M. McCarron and N. Bartlett, unpublished results.
- ⁶ Both AsF_5 and SbF_5 will react with $A^+PF_6^-$ salts to prodⁿ $A^+AsF_6^-$ and $A^+SbF_6^-$ salts. This is true with graphite as well as with molecular cations.
- ⁷ J. Besenhard and H.P. Fritz, *Z. Naturforsch., Teil B*, 27, 1294 (1972).
- ⁸ N. Bartlett, R.N. Biagioni, B.W. McQuillan, A.S. Robertson and A.C. Thompson, *J. Chem. Soc. Chem. Comm.*, 200 (1978).
- ⁹ W.H. Zachariasen, *J. Am. Chem. Soc.*, 70, 2147 (1948).
- ¹⁰ D.D. Gibler, Ph.D. Thesis, Princeton Univ., 1973.
- ¹¹ A.F. Kapustinskii, *Zh. Fiz. Khim.*, 5, 59 (1934).
- ¹² $\Delta H^\circ_{f,298}(F^-(g)) = -62$ kcal/mole is taken from A.G. Sharpe, in "Halogen Chemistry" ed. V. Gutmann, Academic Press, 1980, p.5.
- ¹³ M. Webster, *Chem. Revs.*, 66, 1719 (1968).
- ¹⁴ F. Okino and N. Bartlett, to be published.
- ¹⁵ D. Billaud, A. Pron., F.L. Vogel and A. Herold, *Mat. Res. Bull.*, 15, 1627 (1980).
- ¹⁶ L.B. Ebert, D.R. Mills, J.C. Scanlon and H. Selig, *Mat. Res. Bull.*, 16, 831 (1981).

- ¹⁷ T.E. Mallouk, G.L. Rosenthal, R. Brusasco, G. Muller and N. Bartlett, **Inorg. Chem.**, submitted for publication.
- ¹⁸ P. Barberi, **Bull. Inform. Sci. Tech. Comiss. Energ. At.**, No. 180, 55, (1973).
- ¹⁹ M.A.A. Clyne, D.J. McKenney and R.T. Watson, **J. Chem. Soc., Faraday I**, 71, 322 (1975).
- ²⁰ I.P. Fisher, **Trans. Faraday Soc.**, 63, 684 (1967).

Table 3-1- Debye-Scherrer powder data for SF₃PF₆

<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
s	5.599	5.590	002
vs	5.016	5.006	100
vs	4.574	4.569	101
vs	3.730	3.729	102
s	2.988	2.989	103
s	2.891	2.890	110
s	2.798	2.798	111
m	2.569	2.567	112
m	2.502	2.503	200
s	2.440	2.440	104
m	2.284	2.285	202
mw	2.079	2.078	203
w	2.040	2.042	105
w	2.010	2.009	114
ms	1.863	1.863	006
ms	1.791	1.792	212
w	1.745	1.746	106
w	1.687	1.687	213
w	1.667	1.668	205
w	1.648	1.650	301
w	1.597	1.597	302
m	1.565	1.566	116
w	1.523	1.523	303
m	1.444	1.444	215
vw	1.375	1.377	311
m	1.347	1.347	223
w	1.327	1.328	216
w	1.284	1.283	224
mw	1.242	1.243	306
mw	1.220	1.221	217
w	1.142	1.142	404
w	1.125	1.125	322
vw	1.092	1.092	410

a= 5.78; c=11.18Å

Table 3-2- Debye-Scherrer powder data for ClO_2PF_6

<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
m	5.406	5.439	001
m	4.958	4.957	110
s	4.569	4.613	101
s	3.646	3.664	111
m	2.952	2.962	211
w	2.702	2.718	002
w	2.590	2.595	102
w	2.484	2.478	220
m	2.361	2.358	311
w	2.312	2.306	202
w	2.248	2.254	221
m	1.808	1.812	003
w	1.741	1.744	500
w	1.679	1.679	421
w	1.492	1.490	313

a= 8.72; b= 6.02; c= 5.44Å

Table 3-3a- Vapor pressure vs. temperature measurements for SF_3PF_6

<u>T</u>	<u>P_{obs}</u>	<u>P_{calc}</u>
0.0°	118	121
5.0°	178	178
9.0°	245	240
16.5°	424	411
20.0°	518	522
21.0°	547	556
23.5°	651	659

Table 3-3b- Vapor Pressure vs. Temperature Measurements for ClO_2PF_6

<u>T</u>	<u>P_{obs}</u>	<u>P_{calc}</u>
-5.0°	129	130
0.0°	192	191
2.0°	218	223
3.0°	243	240
6.0°	299	299
9.0°	371	371

Table 3-4- Debye-Scherrer data for graphite-phosphorus-fluorine intercalation compounds

<u>C₁₁PF₆</u>				<u>C₂₉PF₆</u>			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>	<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
m	7.639	7.789	001	mw	10.58	10.72	001
vs	3.867	3.894	002	vs	3.621	3.573	003
m	2.599	2.596	003	m	2.661	2.680	004
m	2.124	2.126	100	m	2.122	2.130	100
w	1.227	1.227	110	w	1.989	1.979	102
				m	1.228	1.229	110

a = 2.45(1); c = 7.79(5)Å

a = 2.46(2); c = 10.72(8)Å

<u>C₂₄PF₆</u>				<u>C₂₄PF₆·PF₅</u>			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>	<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
m	11.18	10.92	001	s	7.603	7.621	001
vs	3.632	3.642	003	vs	3.809	3.810	002
m	2.737	2.731	004	m	2.541	2.540	003
m	2.118	2.130	100	m	2.111	2.126	100
mw	1.993	1.984	102	m	1.227	1.227	110
w	1.815	1.820	006	w	1.212	1.212	111
mw	1.561	1.560	007	w	1.167	1.168	112
m	1.229	1.230	110				
w	1.165	1.165	113				

a = 2.46(1); c = 10.92(2)Å

a = 2.46(1); c = 7.62(1)Å

Table 3-5- C-spacings of higher-stage fluorophosphates

<u>Stage</u>	<u>c₀</u>	<u>Height of PF₆⁻</u>
1	7.79	4.44
2	10.87	4.17
3	14.27	4.22
4	17.62	4.22
5	20.87	4.12

Table 3-6- The fluoride-ion affinity of PF_5

	ΔH° (kcal/mole)
$\text{SF}_4(\text{g}) + \text{PF}_5(\text{g}) + \text{SF}_3\text{PF}_6(\text{g})$	-23(1)
$\text{SF}_3^+(\text{g}) + \text{F}^-(\text{g}) + \text{SF}_4(\text{g})$	-211(5) ^a
$\text{SF}_3\text{PF}_6(\text{s}) + \text{SF}_3^+(\text{g}) + \text{PF}_6^-(\text{g})$	+134(7) ^b
$\text{PF}_5(\text{g}) + \text{F}^-(\text{g}) + \text{PF}_6^-(\text{g})$	-100(9)
$\text{ClO}_2\text{F}(\text{g}) + \text{PF}_5(\text{g}) + \text{ClO}_2\text{PF}_6(\text{s})$	-23(1)
$\frac{1}{2}\text{Cl}_2(\text{g}) + \text{O}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) + \text{ClO}_2\text{F}(\text{g})$	-8(1) ^c
$\text{ClO}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) + \text{O}_2(\text{g})$	-24(1) ^d
$\text{ClO}_2^+(\text{g}) + \text{e}^- + \text{ClO}_2(\text{g})$	-247(2) ^e
$\text{F}^-(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) + \text{e}^-$	62(1) ^f
$\text{ClO}_2\text{PF}_6(\text{s}) + \text{ClO}_2^+(\text{g}) + \text{PF}_6^-(\text{g})$	139(7) ^b
$\text{PF}_5(\text{g}) + \text{F}^-(\text{g}) + \text{PF}_6^-(\text{g})$	-101(8)

^a Ref. 17^b From formula unit volumes of $143\text{\AA}^3$ for ClO_2PF_6 and $162\text{\AA}^3$ for SF_3PF_6 and 5 kcal/mole positive deviation from the empirical least-squares fit (Figure 5-5), as in the independently calculated ClO_2BF_4 and SF_3BF_4 .^c Ref. 18^d Ref. 19^e Ref. 20^f Ref. 12

Figure 3-1- Raman spectrum of SF_6

XBL 847-3055

Figure 3-2- Raman spectrum of ClO_2PF_6

Figure 3-3- Van't Hoff plot for SF₃PF₆

XBL 847-3051

Figure 3-4- Van't Hoff plot for ClO₂PF₆

XBL 847-3052

XBL 835-2968

Figure 3-5- Lattice energy vs. formula-unit volume relationship

CHAPTER 4

STUDIES OF THE THERMODYNAMICS AND GRAPHITE CHEMISTRY OF THE
TETRAFLUOROBORATE IONIntroduction

Like PF_6^- , BF_4^- is an extremely simple and common counterion for large complex cations. Its simplicity made it extremely attractive for these types of studies, as did the fact that the fluoride-ion affinity of BF_3 was a subject of controversy, the accepted values ranging from 62 kcal/mole¹ to 92 kcal/mole.²

BF_3 was also reported to react with graphite and fluorine,³ but the report was experimentally ill-documented. The BF_4^- ion had ordinarily been intercalated by reduction of NO_2BF_4 in nitromethane:⁴

In compounds such as this, however, with extensive intercalation of neutral species, the limits of graphite oxidation cannot be explored. The small size of the BF_4^- ion might allow more to be intercalated than the larger MF_6^- ions and, hence, test the extent to which the graphite can be oxidized without significantly disturbing the integrity of the planar carbon sheets.

The fluoride-ion affinity of BF_3 takes on further significance when one notes that much of the very sophisticated work in ion-cyclotron resonance^{5,6} in the past few years is based on comparisons of unknown thermodynamic quantities with $A(\text{F}^-)$ for BF_3 , assumed to be 71 kcal/mole. One particular quantity in this category is $A(\text{F}^-)$ of SiF_4 , whose intercalation compounds will be discussed in the next chapter.

Experimental

ClO_2BF_4 : ClO_2F and BF_3 were brought together in a 1:1 molar ratio. The

pale yellow solid was purified by venting to the open system, much like SF_3PF_6 and ClO_2PF_6 , for purposes of dissociation pressure measurements. The volatiles were checked by IR and found to be pure ClO_2F and BF_3 . The Raman spectrum is shown in Figure 4-1.

A single crystal was grown by sublimation in a quartz capillary at $25\text{--}30^\circ$. Precession photographs indicated space group C2/c (centric) or Cc (acentric). Data were gathered successfully at room temperature, although the crystal was observed to lose its well-defined shape, presumably because of sublimation in the X-ray beam (Table 4-1).

Refinement, in the acentric space group Cc (#9), with anisotropic thermal parameters, gave final convergence with weighted $R = .032$, unweighted $R = .023$, estimated standard deviation of an observation of unit weight = 1.828 for 72 variables and 577 independent observations. The largest parameter shift in the final refinement cycle was 0.1σ . The largest peak in the final difference Fourier was $0.274 \text{ e}^-/\text{\AA}^3$. Positional and thermal parameters are given in Table 4-2. Upon examination of the data it was found that three reflections gathered consecutively, the $-22-1$, -220 and -221 , showed the worst fit of F_{obs} to F_{calc} . Intensities of these reflections were apparently not fully measured due to misorientation and were omitted from the final refinement. Observed and calculated structure factors appear in Table 4-3.

Dissociation pressure measurements: Christie, et. al.⁷ reported vapor pressure vs. temperature measurements for ClO_2BF_4 . These measurements were rechecked and found to be accurate (Table 4-5).

$$\Delta H^\circ_{298} (\text{ClO}_2\text{F}(\text{g}) + \text{BF}_3(\text{g}) + \text{ClO}_2\text{BF}_4(\text{s})) = -24 \text{ kcal/mole.}$$

C_7BF_4 : Graphite (12 mmole) was treated with BF_3 (700 torr) and F_2 (600 torr) condensed from the vacuum line into a stainless steel vessel

(total pressure ca. 40 atm.), warmed to room temperature and agitated for 24 hours. Volatiles were removed in a dynamic vacuum at room temperature. Gravimetry indicated uptake of BF_4 commensurate with a limiting stoichiometry of $\text{C}_{7.2}\text{BF}_4$. Carbon analysis was in substantial agreement: %C required for $\text{C}_{7.2}\text{BF}_4$ = 49.9, C found = 49.8%. An X-ray powder photograph is shown in Table 4-5. The salt is deep blue in color.

C_{16}BF_4 : The second-stage fluoroborate was synthesized by treating ground graphite (6 mmole) with BF_3 (350 torr) and F_2 (250 torr) condensed from the vacuum line and agitated at room temperature for 3 hours. Volatiles were pumped off for 16 hours. The Debye-Scherrer powder photograph is indexed in Table 4-6.

Higher-stage fluoroborates: As in the fluorophosphate system, mixed phases became prevalent with lower gas pressures and shorter reaction times, probably due to lack of homogeneity in the solid-gas reaction. Some pure phases higher than three were synthesized, but purity proved difficult to reproduce. The stoichiometry-staging behavior followed a C_{8n}BF_4 rule and the c-spacings (Table 4-7) of higher-stage materials are somewhat larger than those of their PF_6^- counterparts.

Lattice Enthalpy Calculations- The Madelung term of the lattice enthalpy of ClO_2BF_4 was calculated by the method of Bertaut,⁸ modified by Templeton.⁹ A complete explanation is given by T.E. Mallouk of this laboratory.¹⁰

Results and Discussion

A stereoview (Figure 4-2) of the ClO_2BF_4 structure shows the coordination about the chlorine atom. Bond lengths and angles are given in Table 4-4. The closest Cl-F contacts (F_1 , 2.534(2) and F_3 , 2.580(1) Å) are those approximately normal to the plane defined by ClO_2^+ . The longer

Cl-F contacts (F_2 , 2.704(2) and F_4 , 2.731(2)Å) are in that plane. All four Cl-F contacts, together with the Cl-O bonds, complete a grossly distorted octahedral coordination about the chlorine atom. The closer contacts perpendicular to the ClO_2 plane are similar to those in the ClO_2GeF_5 structure,¹¹ where there are two crystallographically distinct ClO_2^+ . The in-plane Cl-F contacts are markedly different in ClO_2BF_4 from each of the arrangements in ClO_2GeF_5 . Evidently, the contacts perpendicular to the plane are more important than the others. The BF_4^- ions are almost tetrahedral. A packing diagram is shown in Figure 4-3.

The structure of ClO_2BF_4 , then, is quite unremarkable from a crystallographic standpoint, but its solution allowed a precise calculation of the lattice enthalpy and, therefore, a precise evaluation of the fluoride-ion affinity of BF_3 .

The fluoride-ion affinity of BF_3 was evaluated in a straightforward manner from the enthalpy of the reaction of ClO_2F and BF_3 , the data on the ionization of ClO_2F given in Table 3-6 and the lattice enthalpy (149(5) kcal/mole) calculated precisely based on the crystal structure.

Previous evaluations of this quantity^{1,2,5} have been extremely indirect, based on a tangled web of thermodynamic measurements and theories dating back to before the turn of the century.¹² The method used here provides a relatively direct and precise path to the desired number and avoids entanglement in the controversy about what exactly what was wrong in previous calculations.

$$\Delta H^\circ(\text{BF}_3(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{BF}_4^-(\text{g})) = -24(1) - 217(3) + 149(5) = -92(6) \text{ kcal/mole.}$$

This number can be used in the Born-Haber cycle of SF_3BF_4 to determine $\Delta H^\circ(\text{SF}_4(\text{g}) \rightarrow \text{SF}_3^+(\text{g}) + \text{F}^-(\text{g}))$,¹³ which was used in the SF_3PF_6 cycle. It can also be combined with data of Murphy and Beauchamp⁶ to

yield a first fluoride-ion affinity of 89 kcal/mole for $\text{SiF}_4(\text{g})$. This will be further discussed in the following chapter.

The intercalation compounds of BF_4^- appear to fit into a similar scheme to those of SO_3F^- .^{14,15} The vacuum-stability of the compound of limiting composition indicates no neutral species in the lattice and therefore a higher charge (C_7^+) than in the fluorophosphate (C_{11}^+). Biagioni¹⁶ reported a first-stage compound of composition $\text{C}_{4.9}\text{SO}_3\text{F}$, prepared directly from $\text{S}_2\text{O}_6\text{F}_2$, and Mallouk and Bartlett¹⁷ have reported a fluoride, C_2F , in which the graphite sheets may well be undisturbed, but Fischer¹⁸ maintains that in the graphite- AsF_5 system, where there is no elemental fluorine present, the limit of graphite oxidation is around C_{20}^+ , after which direct fluorination of the carbons takes place and neutral species and further complexed ions make up the gravimetric difference. Future structural studies may provide the positive solution to this controversy.

The gallery heights (Table 4-7) in the intercalation compounds are expected from BF_4^- tetrahedra with B-F bond lengths of $\sim 1.4\text{\AA}$.

Summary

The crystal structure of ClO_2BF_4 was solved in the acentric space group Cc. This structure was used in a precise calculation of the lattice enthalpy and a Born-Haber cycle was completed, yielding a fluoride-ion affinity of 92 kcal/mole for BF_3 . Graphite intercalation compounds of BF_3/F_2 were also studied. The limiting composition was $\text{C}_{7.2}\text{BF}_4$, suggesting an abnormally high charge on the carbon layers. BF_4^- was found to occupy a gallery height of $\sim 4.3\text{\AA}$.

References

- 1 A.P. Altshuller, *J. Amer. Chem. Soc.*, 77, 6187 (1955).
- 2 J.L. Bills and F.A. Cotton, *J. Phys. Chem.*, 64, 1477 (1966).
- 3 A.D. Cohen, *U.S. Pat. No.* 4,128,499 (1979).
- 4 D. Billaud, A. Pron, F.L. Vogel and A. Herold, *Mat. Res. Bull.*, 15, 1627 (1980).
- 5 J.C. Haartz and D.H. McDaniel, *J. Amer. Chem. Soc.*, 95, 8562 (1973).
- 6 M.K. Murphy and J.L. Beauchamp, *J. Amer. Chem. Soc.*, 99, 4562 (1977).
- 7 K.O. Christe, C.J. Schack, D. Pilopovich and W. Sawodny, *Inorg. Chem.*, 8, 2489 (1969).
- 8 E.F. Bertaut, *J. Phys. Radium*, 13, 499 (1952).
- 9 D.H. Tempieton, *J. Chem. Phys.*, 21, 1629 (1955).
- 10 T.E. Mallouk, Ph.D. Thesis, University of California, Berkeley, 1983.
- 11 T.E. Mallouk, B. Desbat and N. Bartlett, *Inorg. Chem.*, submitted for publication.
- 12 J. Thomsen, "Thermochemische Untersuchungen," Vol. 1, Verlag J.A. Barth, Leipzig, 1882, p. 231.
- 13 T.E. Mallouk, G.L. Rosenthal, R. Brusasco, G. Muller and N. Bartlett, *Inorg. Chem.*, submitted for publication.
- 14 N. Bartlett, R.N. Biagioni, B.W. McQuillan, A.S. Robertson and A.C. Thompson, *J. Chem. Soc. Chem. Commun.*, 200 (1978).
- 15 S. Karunanithy and F. Aubke, *Carbon*, 20(3), 237 (1982).
- 16 R.N. Biagioni, Ph.D. Thesis, University of California, Berkeley, 1980.
- 17 T.E. Mallouk and N. Bartlett, *J. Chem. Soc. Chem. Commun.*, 103 (1983).
- 18 J.W. Milliken and J.E. Fischer, *J. Chem. Phys.*, 78(9), 5800 (1983).

Table 4-1- Crystal data for ClO_2BF_4

crystal dimensions:	.04 x .02 x .02 cm
space group:	Cc (#9)
volume ($\text{\AA}^3$):	451.4(3)
ρ (calc'd):	2.269
cell dimensions:	$a = 5.522(1)$; $b = 8.646(1)$; $c = 9.549(2)\text{\AA}$; $\beta = 98.0(1)^\circ$
radiation:	MoK_α , graphite monochromator ($\lambda = .71073\text{\AA}$)
2θ range:	$3-45^\circ$
scan mode:	$\theta-2\theta$
scan rate:	variable, maximum 50 sec.
background:	$.25 \times \Delta\theta$, where $\Delta\theta = .50 + .347\tan\theta$
hkl range:	$\pm h$, $\pm k$, $\pm l$
reflections measured:	684
orientation standards:	$(-31-6)$, $(1-5-4)$, $(-11-6)$ every 50 reflections, frequent reorientation
intensity standards:	$(11-2)$, (060) , $(-13-5)$ every 100 reflections, non-linear decay correction applied
extinction coefficient:	8.3239×10^{-6}

Table 4-2- Positional and Thermal Parameters for ClO_2BF_4

Atom	X	Y	Z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cl	0.000	-0.7352(6)	0.250	0.0213(2)	0.0101(1)	0.0065(1)	-0.0005(2)	0.0020(2)	-0.0008(1)
O1	-0.0377(5)	0.0756(2)	0.2990(3)	0.0335(7)	0.0117(3)	0.0120(3)	0.0043(3)	-0.0020(0)	-0.0040(4)
O2	-0.0747(4)	-0.1995(2)	0.3237(2)	0.0347(7)	0.0132(3)	0.0110(3)	-0.0074(0)	0.0001(0)	0.0044(5)
B	0.4004(6)	0.0675(3)	0.0152(4)	0.0167(8)	0.0090(3)	0.0061(3)	0.001(1)	0.0003(1)	-0.0012(6)
F1	0.6340(4)	-0.0500(2)	0.0570(2)	0.0269(7)	0.0139(2)	0.0120(2)	0.0120(6)	-0.0113(0)	-0.0025(4)
F2	0.2652(4)	0.0549(2)	0.0626(2)	0.0273(6)	0.0200(3)	0.0114(2)	-0.0037(7)	0.0097(6)	0.0062(4)
F3	0.4492(3)	0.0723(2)	-0.1310(2)	0.0206(6)	0.0193(3)	0.0067(2)	-0.0020(6)	-0.0001(6)	-0.0001(3)
F4	0.6040(3)	0.2003(2)	0.0600(2)	0.0360(6)	0.0132(3)	0.0125(2)	-0.0075(6)	0.0037(7)	-0.0072(4)

The Form of the Anisotropic Thermal Parameter is:

$$\exp \{ -[B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl] \}$$

Table 4-3- Observed and Calculated Structure Factors for C10₂BP₄

Page 1									
Fobs	Fcalc	h	k	l	Fobs	Fcalc	h	k	l
389	330	9	4	1	1642	1638	18	3	5
372	374	7	4	2	264	269	18	3	6
1227	1217	12	4	2	1650	1651	11	3	6
67	98	4	4	4	249	253	9	3	6
916	916	18	4	4	474	474	6	3	6
316	328	7	4	4	1268	1268	11	3	6
1	1	1	4	6	1103	1103	12	3	6
1	1	2	4	6	939	925	19	2	4
1	1	3	4	6	941	937	18	2	4
1	1	4	4	6	1058	1057	18	2	4
1	1	5	4	6	1058	1057	18	2	4
1	1	6	4	6	1058	1057	18	2	4
1	1	7	4	6	1058	1057	18	2	4
1	1	8	4	6	1058	1057	18	2	4
1	1	9	4	6	1058	1057	18	2	4
1	1	10	4	6	1058	1057	18	2	4
1	1	11	4	6	1058	1057	18	2	4
1	1	12	4	6	1058	1057	18	2	4
1	1	13	4	6	1058	1057	18	2	4
1	1	14	4	6	1058	1057	18	2	4
1	1	15	4	6	1058	1057	18	2	4
1	1	16	4	6	1058	1057	18	2	4
1	1	17	4	6	1058	1057	18	2	4
1	1	18	4	6	1058	1057	18	2	4
1	1	19	4	6	1058	1057	18	2	4
1	1	20	4	6	1058	1057	18	2	4
1	1	21	4	6	1058	1057	18	2	4
1	1	22	4	6	1058	1057	18	2	4
1	1	23	4	6	1058	1057	18	2	4
1	1	24	4	6	1058	1057	18	2	4
1	1	25	4	6	1058	1057	18	2	4
1	1	26	4	6	1058	1057	18	2	4
1	1	27	4	6	1058	1057	18	2	4
1	1	28	4	6	1058	1057	18	2	4
1	1	29	4	6	1058	1057	18	2	4
1	1	30	4	6	1058	1057	18	2	4
1	1	31	4	6	1058	1057	18	2	4
1	1	32	4	6	1058	1057	18	2	4
1	1	33	4	6	1058	1057	18	2	4
1	1	34	4	6	1058	1057	18	2	4
1	1	35	4	6	1058	1057	18	2	4
1	1	36	4	6	1058	1057	18	2	4
1	1	37	4	6	1058	1057	18	2	4
1	1	38	4	6	1058	1057	18	2	4
1	1	39	4	6	1058	1057	18	2	4
1	1	40	4	6	1058	1057	18	2	4
1	1	41	4	6	1058	1057	18	2	4
1	1	42	4	6	1058	1057	18	2	4
1	1	43	4	6	1058	1057	18	2	4
1	1	44	4	6	1058	1057	18	2	4
1	1	45	4	6	1058	1057	18	2	4
1	1	46	4	6	1058	1057	18	2	4
1	1	47	4	6	1058	1057	18	2	4
1	1	48	4	6	1058	1057	18	2	4
1	1	49	4	6	1058	1057	18	2	4
1	1	50	4	6	1058	1057	18	2	4
1	1	51	4	6	1058	1057	18	2	4
1	1	52	4	6	1058	1057	18	2	4
1	1	53	4	6	1058	1057	18	2	4
1	1	54	4	6	1058	1057	18	2	4
1	1	55	4	6	1058	1057	18	2	4
1	1	56	4	6	1058	1057	18	2	4
1	1	57	4	6	1058	1057	18	2	4
1	1	58	4	6	1058	1057	18	2	4
1	1	59	4	6	1058	1057	18	2	4
1	1	60	4	6	1058	1057	18	2	4
1	1	61	4	6	1058	1057	18	2	4
1	1	62	4	6	1058	1057	18	2	4
1	1	63	4	6	1058	1057	18	2	4
1	1	64	4	6	1058	1057	18	2	4
1	1	65	4	6	1058	1057	18	2	4
1	1	66	4	6	1058	1057	18	2	4
1	1	67	4	6	1058	1057	18	2	4
1	1	68	4	6	1058	1057	18	2	4
1	1	69	4	6	1058	1057	18	2	4
1	1	70	4	6	1058	1057	18	2	4
1	1	71	4	6	1058	1057	18	2	4
1	1	72	4	6	1058	1057	18	2	4
1	1	73	4	6	1058	1057	18	2	4
1	1	74	4	6	1058	1057	18	2	4
1	1	75	4	6	1058	1057	18	2	4
1	1	76	4	6	1058	1057	18	2	4
1	1	77	4	6	1058	1057	18	2	4
1	1	78	4	6	1058	1057	18	2	4
1	1	79	4	6	1058	1057	18	2	4
1	1	80	4	6	1058	1057	18	2	4
1	1	81	4	6	1058	1057	18	2	4
1	1	82	4	6	1058	1057	18	2	4
1	1	83	4	6	1058	1057	18	2	4
1	1	84	4	6	1058	1057	18	2	4
1	1	85	4	6	1058	1057	18	2	4
1	1	86	4	6	1058	1057	18	2	4
1	1	87	4	6	1058	1057	18	2	4
1	1	88	4	6	1058	1057	18	2	4
1	1	89	4	6	1058	1057	18	2	4
1	1	90	4	6	1058	1057	18	2	4
1	1	91	4	6	1058	1057	18	2	4
1	1	92	4	6	1058	1057	18	2	4
1	1	93	4	6	1058	1057	18	2	4
1	1	94	4	6	1058	1057	18	2	4
1	1	95	4	6	1058	1057	18	2	4
1	1	96	4	6	1058	1057	18	2	4
1	1	97	4	6	1058	1057	18	2	4
1	1	98	4	6	1058	1057	18	2	4
1	1	99	4	6	1058	1057	18	2	4
1	1	100	4	6	1058	1057	18	2	4

Reflections flagged with an asterisk were considered unobserved.

Fobs end Fcfc (x 88.1) For C1025 BF4 - @ 25C

Page 2

H	K	L	Fobs	Fcfc	StgF	H	K	L	Fobs	Fcfc	StgF	H	K	L	Fobs	Fcfc	StgF
-1	1	6	1607	1639	9	-1	7	3	337	342	7	8	4	4	446	459	5
-1	1	7	346	362	6	-1	7	4	589	978	7	8	4	5	1646	1624	9
-1	1	8	436	436	6	-1	7	5	266	266	6	8	4	6	327	331	9
-1	1	9	369	367	6	-1	7	6	807	799	9	8	4	7	1791	1765	10
-1	1	10	1637	1676	11	-1	8	-1	588	994	1443	8	4	8	498	497	10
-1	1	11	167	189	11	-1	8	1	526	991	16	8	4	9	1838	991	10
-1	1	12	266	279	10	-1	8	2	462	499	7	8	4	10	285	286	9
-1	1	13	815	1893	18	-1	8	3	1817	962	17	8	4	11	766	773	13
-1	1	14	2632	2616	18	-1	8	4	1817	962	17	8	4	12	181	177	13
-1	1	15	466	462	8	-1	8	5	3365	5824	26	8	4	13	131	119	10
-1	1	16	2516	2636	7	-1	8	6	4912	939	26	8	4	14	97	97	8
-1	1	17	1118	1118	7	-1	8	7	851	939	26	8	4	15	2368	2366	9
-1	1	18	2768	2659	24	-1	8	8	874	948	26	8	4	16	1821	965	10
-1	1	19	1194	1124	4	-1	8	9	4991	5662	26	8	4	17	1821	965	10
-1	1	20	2821	2818	6	-1	8	10	3380	2289	6	8	4	18	786	789	10
-1	1	21	662	647	7	-1	8	11	381	285	6	8	4	19	1131	1131	11
-1	1	22	3817	3817	30	-1	8	12	1824	1888	11	8	4	20	779	764	7
-1	1	23	4176	4176	18	-1	8	13	886	1821	11	8	4	21	161	173	11
-1	1	24	1446	1446	9	-1	8	14	862	858	10	8	4	22	286	286	10
-1	1	25	671	661	9	-1	8	15	1245	1228	10	8	4	23	89*	89*	10
-1	1	26	1768	1751	10	-1	8	16	1276	1288	9	8	4	24	917	917	10
-1	1	27	216	201	9	-1	8	17	712	721	7	8	4	25	113	113	6
-1	1	28	733	779	8	-1	8	18	1488	1488	7	8	4	26	489	417	6
-1	1	29	369	361	7	-1	8	19	1512	1551	6	8	4	27	366	369	6
-1	1	30	483	509	6	-1	8	20	428	443	4	8	4	28	481	478	6
-1	1	31	1246	1258	11	-1	8	21	2817	2924	20	8	4	29	2817	2808	10
-1	1	32	1493	1494	11	-1	8	22	3672	3699	19	8	4	30	369	366	6
-1	1	33	1393	1422	9	-1	8	23	3868	2958	20	8	4	31	448	416	6
-1	1	34	1282	1266	9	-1	8	24	428	432	6	8	4	32	448	416	6
-1	1	35	1827	1819	9	-1	8	25	1559	1557	6	8	4	33	589	483	6
-1	1	36	1406	1451	9	-1	8	26	1401	1421	11	8	4	34	994	964	10
-1	1	37	1406	1449	9	-1	8	27	691	684	7	8	4	35	656	685	10
-1	1	38	1846	1809	9	-1	8	28	1286	1264	7	8	4	36	376	376	6
-1	1	39	1635	1635	9	-1	8	29	1248	1218	10	8	4	37	439	442	6
-1	1	40	1972	1899	9	-1	8	30	881	886	6	8	4	38	363	388	6
-1	1	41	1827	1827	10	-1	8	31	1818	1828	10	8	4	39	1542	1585	10
-1	1	42	1851	1851	10	-1	8	32	966	989	10	8	4	40	1838	1822	8
-1	1	43	781	851	8	-1	8	33	1761	1781	10	8	4	41	448	448	6
-1	1	44	389	395	8	-1	8	34	316	325	6	8	4	42	4237	4408	21
-1	1	45	748	788	8	-1	8	35	1426	1529	6	8	4	43	1887	1858	17
-1	1	46	117	106	16	-1	8	36	1838	1838	6	8	4	44	861	872	16
-1	1	47	1122	1147	18	-1	8	37	616	594	6	8	4	45	2888	2884	20
-1	1	48	255	262	9	-1	8	38	1861	1866	7	8	4	46	4381	4238	20
-1	1	49	1626	1702	11	-1	8	39	1465	1484	7	8	4	47	2611	2611	7
-1	1	50	117	136	19	-1	8	40	227	229	6	8	4	48	2618	1266	9
-1	1	51	626	638	7	-1	8	41	1527	1467	5	8	4	49	1298	1298	9
-1	1	52	331	329	7	-1	8	42	1141	1871	7	8	4	50	2815	1973	9
-1	1	53	1988	1878	10	-1	8	43	589	551	6	8	4	51	238	229	8

Reflections flagged with an asterisk were considered unobserved.

Fobs and Fcalc (x 50.3) for C102+ BF4- @ 28C

Page 3

M	K	L	Fobs	Fcalc	Sign	M	K	L	Fobs	Fcalc	Sign	M	K	L	Fobs	Fcalc	Sign
1	1	2	888	728	0	2	2	2	298	281	0	4	2	5	387	294	0
1	1	3	439	478	0	4	2	7	428	411	0	4	2	6	234	244	0
1	1	4	413	489	0	4	2	8	425	447	0	4	2	7	153	175	11
1	1	5	84	58	58	4	2	9	58	96	38	4	2	8	383	387	0
1	1	6	585	598	0	4	2	10	984	978	18	4	2	9	485	485	0
1	1	7	688	685	0	4	2	11	135	115	14	4	2	10	151	161	11
1	1	8	1633	1623	11	4	2	12	1841	1878	9	4	2	11	161	164	11
1	1	9	956	944	0	4	2	13	1577	1563	18	4	2	12	255	264	0
1	1	10	1023	1017	0	4	2	14	1726	1746	0	4	2	13	1886	1888	18
1	1	11	4258	4379	27	4	2	15	1299	1293	11	4	2	14	448	417	0
1	1	12	5685	5685	29	4	2	16	413	488	16	4	2	15	1375	1343	11
1	1	13	1257	1265	0	4	2	17	989	962	18	4	2	16	276	267	0
1	1	14	1486	1358	18	4	2	18	388	365	6	4	2	17	1565	1257	12
1	1	15	1233	1243	12	4	2	19	616	582	6	4	2	18	384	385	18
1	1	16	825	821	0	4	2	20	651	659	7	4	2	19	232	218	0
1	1	17	1149	1174	18	4	2	21	251	266	6	4	2	20	619	608	5
1	1	18	1455	1488	18	4	2	22	664	664	6	4	2	21	428	427	7
1	1	19	718	718	0	4	2	23	515	532	6	4	2	22	481	471	6
1	1	20	1135	1135	9	4	2	24	981	984	18	4	2	23	586	519	6
1	1	21	1303	1305	4	4	2	25	268	235	8	4	2	24	1878	1861	11
1	1	22	2155	2129	0	4	2	26	1124	1186	11	4	2	25	131	95	16
1	1	23	1418	1418	0	4	2	27	486	478	8	4	2	26	855	832	0
1	1	24	976	976	0	4	2	28	748	748	0	4	2	27	232	252	18
1	1	25	2494	2494	7	4	2	29	767	773	7	4	2	28	299	306	0
1	1	26	2812	2812	7	4	2	30	1566	1566	12	4	2	29	916	916	18
1	1	27	766	766	0	4	2	31	807	914	9	4	2	30	446	443	5
1	1	28	897	895	8	4	2	32	1196	1184	4	4	2	31	953	957	18
1	1	29	757	754	0	4	2	33	1851	1856	9	4	2	32	322	328	7
1	1	30	182	198	11	4	2	34	2726	2768	8	4	2	33	935	939	9
1	1	31	1877	1873	18	4	2	35	449	447	5	4	2	34	68	68	0
1	1	32	941	941	0	4	2	36	2437	2437	8	4	2	35	1248	1286	12
1	1	33	1327	1327	18	4	2	37	1718	1808	8	4	2	36	359	371	7
1	1	34	1266	1266	18	4	2	38	388	388	4	4	2	37	383	319	0
1	1	35	462	474	15	4	2	39	278	282	4	4	2	38	977	1082	18
1	1	36	2227	2264	16	4	2	40	285	282	2	4	2	39	317	317	7
1	1	37	388	388	0	4	2	41	1357	1372	11	4	2	40	753	757	7
1	1	38	1142	1142	9	4	2	42	589	597	4	4	2	41	662	559	6
1	1	39	457	457	4	4	2	43	148	149	14	4	2	42	1528	157	12
1	1	40	1258	1258	0	4	2	44	559	568	6	4	2	43	388	388	7
1	1	41	736	736	0	4	2	45	317	336	5	4	2	44	379	333	7
1	1	42	2711	2711	5	4	2	46	1758	1802	18	4	2	45	258	252	8
1	1	43	1123	1082	18	4	2	47	688	669	7	4	2	46	792	791	0
1	1	44	537	532	0	4	2	48	618	638	6	4	2	47	0	0	0
1	1	45	685	685	7	4	2	49	2433	2462	9	4	2	48	0	0	0
1	1	46	97	159	51	4	2	50	557	542	6	4	2	49	0	0	0
1	1	47	1763	1755	11	4	2	51	218	191	0	4	2	50	0	0	0

Reflections flagged with an asterisk were considered unobserved.

Table 4-4- Bond Distances and Angles in ClO_2BF_4 DISTANCES (Å)

Cl - O1	1.397(2)	B - F1	1.380(3)
Cl - O2	1.390(2)	B - F2	1.376(4)
Cl - F1	2.534(2)	B - F3	1.383(3)
Cl - F2	2.704(2)	B - F4	1.377(3)
Cl - F3	2.580(1)		
Cl - F4	2.731(2)		

ANGLES (deg.)

O1 - Cl - O2	119.0(1)	F1 - C - F2	87.07(6)
O1 - Cl - F1	93.0(1)	F1 - C - F3	159.69(6)
O1 - Cl - F2	87.9(1)	F1 - C - F4	78.18(5)
O1 - Cl - F3	91.6(1)	F2 - C - F3	73.34(5)
O1 - Cl - F4	158.2(1)	F2 - C - F4	71.97(5)
O2 - Cl - F1	98.4(1)	F3 - C - F4	90.40(5)
O2 - Cl - F2	152.01(8)	F1 - B - F2	110.8(2)
O2 - Cl - F3	96.62(9)	F1 - B - F3	108.9(2)
O2 - Cl - F4	82.25(8)	F1 - B - F4	108.9(2)
		F2 - B - F3	108.3(2)
		F2 - B - F4	109.9(2)
		F3 - B - F4	110.1(2)

Table 4-5- Dissociation pressure measurements for ClO_2BF_4

<u>T</u>	<u>P_{obs}</u>	<u>P_{calc}</u> ^a
10.8°	80	81
13.6°	101	100
17.5°	137	133
23.0°	195	195

^a From Christe, et. al.⁷, $\log P_{\text{mm}} = 11.1482 - 2623.1/T$.

Table 4-6- Debye-Scherrer powder data for graphite tetrafluoroborate salts

<u>C_{7.2}BF₄</u>			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
m	7.684	7.725	001
m	6.500	6.389	(1/3 00) broad
s	3.854	3.863	002
m	2.575	2.575	003
ms	2.120	2.127	100
mw	1.228	1.228	110

$$a = 2.46(2); c = 7.73(2) \text{ \AA}$$

<u>C₁₆BF₄</u>			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
m	11.02	10.93	001
vs	3.665	3.644	003
ms	2.742	2.733	004
m	2.120	2.128	100
mw	1.830	1.838	103
m	1.567	1.562	007
mw	1.363	1.367	008
m	1.229	1.228	110

$$a = 2.46(2); c = 10.93(6) \text{ \AA}$$

Table 4-7- Gallery heights in BF_4^- salts

<u>Stage</u>	<u>c_0</u>	<u>Height of BF_4^-</u>
1	7.73	4.38
2	10.93	4.23
3	14.18	4.13
4	17.55	4.15
7	27.76	4.31

Figure 4-1- Raman spectrum of ClO_2BF_4

104 847-3056

NBL 835-9963

Figure 4-2- Stereoview showing coordination in ClO_2BF_4

Figure 4-3- Stereo packing diagram of C₁₀BF₂₄

IN 807-2053

CHAPTER 5

SYNTHESIS AND REACTIONS OF A GRAPHITE FLUOROSILICATE SALT

Introduction

The reaction of graphite with SiF_4 and fluorine gas was attempted under ordinary pressures¹ and found to be unsuccessful. This result was disquieting in that the fluoride-ion affinity of SiF_4 , and therefore its "electron-affinity half-reaction" to form SiF_5^- , were thought to be exothermic enough to oxidize graphite under these conditions. The value of $A(\text{F}^-)$ for BF_3 , determined in the previous chapter, coupled with the data of Murphy and Beauchamp,² yield an estimate for the "electron-affinity" value of 150 kcal/mole, more favorable than that of OsF_6 . Since the pentafluorosilicate ion should have a similar space requirement to a hexafluoroanion, its lattice energy should be nearly the same and the thermodynamics of its interaction with graphite should be similar to those of the fluorospecies.³

T.E. Mallouk⁴ finally obtained a third-stage product of the reaction of graphite, SiF_4 and F_2 , under extreme conditions, but the stoichiometry of this compound was left undetermined, as was the limiting composition of the intercalation salt product of this reaction.

The study of the interaction of SiF_4 and fluorine with graphite will complete the study of the simplest MF_5 , MF_4 and MF_3/F_2 intercalation compounds and sets the stage for study of the chemical and physical properties of the compounds themselves.

Experimental

$\text{C}_{24}\text{SiF}_5$ - Silicon tetrafluoride (500 torr) and fluorine (500 torr) were each condensed from the vacuum line on graphite contained in the reaction vessel which was warmed to room temperature and agitated for

eight hours. Remaining gases were vented and SiF_4 (1000 torr) and F_2 (1000 torr) were again added from the line and the vessel warmed to 40° in a water bath for 12 hours. Volatiles were then vented and sampled for IR, then removed under dynamic vacuum. Results for four preparations are listed in Table 5-1. They indicate an approximate composition $\text{C}_{24}\text{SiF}_5$. Infrared spectra of volatiles showed (besides SiF_4) a small peak at 1283 cm^{-1} , indicating formation of CF_4 . This peak becomes extremely large if the reaction temperature is raised to 75° . X-ray powder data (Table 5-2) established $\text{C}_{24}\text{SiF}_5$ to be a second-stage compound with $a = 2.46(1)\text{\AA}$; $c = 11.30(2)\text{\AA}$.

Interaction of $\text{C}_{24}\text{SiF}_5$ with PF_5 - A large molar excess of PF_5 was condensed on $\text{C}_{24}\text{SiF}_5$ in the small-volume reaction vessel and the reactants were left at room temperature for 20 hours. The gases were vented to a closed volume of the vacuum line which incorporated the infrared cell. IR of the volatiles showed that they were rich in SiF_4 , as well as the excess PF_5 . The solid product was a first-stage compound, identical in its X-ray powder pattern to $\text{C}_{24}\text{PF}_6 \cdot \text{PF}_5$ and which gravimetrically fits this formula. When this product was subjected to a dynamic vacuum it lost PF_5 , as expected and yielded the second-stage material C_{24}PF_6 .

Interaction of $\text{C}_{24}\text{SiF}_5$ with BF_3 - $\text{C}_{24}\text{SiF}_5$ (typically .1-.2 mmole) was placed in the reaction vessel and a large excess (600 torr) of BF_3 condensed in from the line. The vessel was warmed to room temperature and agitated for 16-20 hours. Volatiles were vented to the open system and infrared cell, and the reaction vessel transferred to the dry box. The IR spectrum showed considerable SiF_4 , in addition to the excess BF_3 . Gravimetry indicated that, assuming quantitative displacement of SiF_4 ,

3.6 moles of BF_3 were taken up per mole of SiF_4 displaced. X-ray powder diffraction showed (Table 5-2) a first-stage compound which, when subjected to dynamic vacuum for 24 hours, lost almost exactly $1/2$ of the original BF_3 , leaving 1.8 moles per mole of SiF_4 in the starting material. This was a very poorly crystalline second-stage compound (Table 5-2) with a c-spacing of 11.1 Å.

Interaction of $\text{C}_{24}\text{SiF}_5$ with $\text{C}_6\text{F}_5\text{PF}_4$ - Equimolar amounts of $\text{C}_{24}\text{SiF}_5$ and $\text{C}_6\text{F}_5\text{PF}_4$ (.15 mmole) were placed in a teflon FEP reaction vessel in the dry box. This reaction vessel was agitated at room temperature for 24 hours. The originally two-phase mixture ($\text{C}_6\text{F}_5\text{PF}_4$ is a dense, clear liquid) was dry and the product was observed to behave like a small-particle-size powder. Volatiles were checked by IR and found to be predominantly SiF_4 . Debye-Scherrer photography (Table 5-2) showed a hexagonal graphite-like pattern with $c = 11.25 \text{ Å}$.

Interaction of $\text{C}_{24}\text{SiF}_5$ with SF_6 - $\text{C}_{24}\text{SiF}_5$ (.1 mmole) was placed in a Monel reaction vessel and SF_6 (300 torr) condensed in. After six hours at room temperature, no change in weight was observed.

Discussion

Although the fluorosilicate salt was satisfying to synthesize, its difficulty to synthesize raises pressing questions about either the validity of the thermodynamic threshold in this case, or the estimated fluoride-ion affinity of SiF_4 . It is hardly conceivable that a pentafluoroanion could occupy significantly more space than a hexafluoroanion and thus afford a much poorer lattice enthalpy for the graphite salt, and the X-ray data supports this. Although SiF_5^- is somewhat "taller" than PF_6^- , it is close to the gallery height requirement of many other MF_6^- ions, including OsF_6^- with its relatively

small electron affinity.

Beauchamp's claim² that SiF_4 lies within 3 kcal/mole in fluoride-ion affinity to BF_3 might well be in error. Beauchamp concedes that free energy changes larger than 3 kcal/mole are beyond the accurate range of the trapped-ion ICR technique. Rhynes and Dillard⁵ note that the ion-molecule studies do not account for internal energy or kinetic energy of the reactant and product species and use this fact to explain the fact that, in an experiment similar to Beauchamp's, they actually determined fluoride-ion affinities near zero for both SiF_4 and BF_3 . An ion-molecule study by Thynne and McNeil⁶ found that $A(\text{F}^-)$ for SiF_4 was in excess of 148 kcal/mole. Clearly, the quantitative value of such studies is subject to question in this range.

Indeed, from the difficulty of oxidizing graphite to form the SiF_5^- salt, and from the fact that the small amount of energy afforded by the raised pressure⁷ appears to push the reaction "over-the edge," it is reasonable to conclude that the free energy obtained in forming the SiF_5^- ion is very near to the threshold needed to oxidize graphite. Assuming that this threshold is the same for SiF_5^- as for a hexafluoroanion³, the "electron-affinity half-reaction" must be less favorable for $\text{SiF}_4/\text{SiF}_5^-$ than for $\text{OsF}_6/\text{OsF}_6^-$ and the fluoride-ion affinity of SiF_4 should be less than 70 kcal/mole.

Once the fluorosilicate was synthesized and an apparent limiting composition reached, the identity of the intercalating anion was still an unsettled question. The difficulty in making SiF_5^- salts of "ordinary" cations suggested that the intercalating species could be SiF_6^{2-} . Lacking reliable microanalytical data,⁸ the problem was addressed chemically. Since PF_5 does not add more than one F^- , it

appeared that the displacement of SiF_4 ⁹ would provide for counting the number of F^- coordinated to SiF_4 in this manner:

Actually, the formation of the first-stage $\text{C}_{24}\text{PF}_6\cdot\text{PF}_5$ was not anticipated at the time of the experiment, although from Ebert's work,¹¹ it might have been. It was quickly noted, however, that this product was not vacuum-stable and lost PF_5 reversibly to form the second-stage compound C_{24}PF_6 . This displacement establishes the stoichiometry $\text{C}_{24}\text{SiF}_5$.

The products of the displacement reaction with BF_3 are intriguing for several reasons. The initial displacement product, presumably $\text{C}_{24}\text{SiF}_5\cdot 2.6\text{BF}_3$, has a C:B ratio of 6.7, not far from that of the first-stage fluoroborate, which is satisfying, but interesting in that the galleries are so crowded with neutral species. The observation that not all of the "extra" BF_3 can be removed under vacuum, though, suggests that these species may not be behaving as dielectric spacers, as solvent molecules¹² are assumed to behave, but as in the $\text{PF}_6^-/\text{PF}_5$ ¹¹ and $\text{AsF}_6^-/\text{AsF}_3$ ¹³ cases, are involved in dynamic equilibria with charged species, in effect spreading the charge out in large, complex, even polymeric anions. The failure to achieve the stoichiometry C_{24}BF_4 under dynamic vacuum even suggests that relatively stable B_2F_7^- species¹⁴ may be present in the graphite galleries.

This easy complexation of $\text{PF}_6^-/\text{PF}_5$ and $\text{BF}_4^-/\text{BF}_3$, however, makes the unattainability of a first-stage fluorosilicate even more curious. Not only is SiF_5^- the only fluoroanion to intercalate graphite and stop before reaching the first stage, but it also appears to be an exception in that it does not complex with neutral species to help "carry" them

into the graphite galleries. Even dielectrics such as SF_6 ¹ are known to add to galleries of other second-stage compounds. This is a knotty problem, presumably involving the complexation abilities of SiF_5^- . It even suggests that in no case are so-called "neutral spacer" molecules not in equilibrium with ions in the graphite galleries.

Finally, the displacement of SiF_4 by $\text{C}_6\text{F}_5\text{PF}_4$ suggests a novel use of the second-stage fluorosilicate as a step in the synthesis of potentially more interesting and useful compounds. $\text{C}_6\text{F}_5\text{PF}_4$, which appears to decompose upon interaction with fluorine before it can intercalate graphite as $\text{C}_6\text{F}_5\text{PF}_5^-$, does replace SiF_4 when placed on $\text{C}_{24}\text{SiF}_5$. If it does exist in the graphite lattice as $\text{C}_6\text{F}_5\text{PF}_5^-$ (not yet established), it should orient itself in such a way that the phenyl ring is parallel to the graphite sheets. The π -systems of the graphite and C_6F_5 units, then, would be in position to interact, possibly resulting in interesting electronic properties, both within the ab plane, due to further charge delocalization, and in the c direction also, due to possible creation of a band perpendicular to the carbon layers. Unfortunately, the inability to synthesize SiF_5^- salts with large oriented graphite chips precludes the accurate conductivity measurement of this compound.

Summary

The second-stage fluorosilicate salt $\text{C}_{24}\text{SiF}_5$ was synthesized. Its difficulty in synthesis suggested that previous estimates of the fluoride-ion affinity of SiF_4 might be erroneous. The Si:F ratio was established by displacement of SiF_4 by PF_5 to form, eventually, the vacuum-stable salt C_{24}PF_6 . SiF_4 was also displaced by BF_3 , forming the vacuum-stable $\text{C}_{24}\text{BF}_4 \cdot 0.8\text{BF}_3$. Reaction of $\text{C}_{24}\text{SiF}_5$ with $\text{C}_6\text{F}_5\text{PF}_4$ resulted

in loss of SiF_4 and possible formation of $\text{C}_x^+\text{C}_6\text{F}_5\text{PF}_5^-$.

References

- ¹ E.M. McCarron, Ph.D. Thesis, University of California, Berkeley, 1980.
- ² M.K. Murphy and J.L. Beauchamp, *J. Am. Chem. Soc.*, 99, 4562 (1977).
- ³ See Chapter 6 or B.W. McQuillan, Ph.D. Thesis, University of California, Berkeley, 1980.
- ⁴ T.E. Mallouk, Ph.D. Thesis, University of California, Berkeley, 1983.
- ⁵ T.C. Rhyne and J.G. Dillard, *Inorg. Chem.*, 10, 730 (1971).
- ⁶ J.C.J. Thynne and K.A.G. McNeil, *Inorg. Chem.*, 9, 1946 (1970).
- ⁷ Assuming 25 atm of pressure of SiF_4 and F_2 , for $\text{SiF}_4(\text{g}) + \frac{1}{2} \text{F}_2(\text{g}) \rightarrow \text{SiF}_5^-(\text{g})$, $\text{RTlnQ} = 3 \text{ kcal/mole}$ at 298° .
- ⁸ The extreme air-sensitivity of this compound resulted in analyses which included large amounts of oxygen and which never added to within 1% of 100%.
- ⁹ S.H. Anderson and D.J.L.Chung, *Synth. Met.*, 7, 107 (1983).
- ¹⁰ Even though PF_6^- is larger in volume than SiF_5^- and the lattice energies of salts of the former are smaller than those of the latter, silicon tetrafluoride is conspicuously less able to form stable salts with fluoride-ion donors than is PF_5 . Thus SF_3PF_6 and ClO_2PF_6 are in equilibrium with their constituent gases at room temperature and ordinary pressures, whereas there is no evidence for the existence of the corresponding SiF_5^- salts even at low temperatures. From these observations, it was confidently predicted that PF_5 would displace SiF_4 .
- ¹¹ L.B. Ebert, D.R. Mills, J.C. Scanlon and H.Selig, *Mat. Res. Bull.*, 16(7), 831 (1981).
- ¹² G.R. Miller, H.A. Resing, M.J. Moran, L. Banks, F.L. Vogel, A. Pron and D. Billaud, *Synth. Met.*, 8, 77 (1983).
- ¹³ L. Facchini, J. Bouat, H.Sfihi, A.P. Legrand, G. Furdin, J. Meliu and

R. Vangelisti, *Synth. Mats.*, 5, 11 (1982).

¹⁴ T. Cyr and S. Brownstein, *J. Inorg. Nucl. Chem.*, 39, 2143 (1977).

Table 5-1 Gravimetric and analytical data for $C_{24}SiF_5$ preparations

<u>mmoles of carbon</u>	<u>mmoles of SiF_5^-</u>	<u>C:SiF_5^- ratio</u>	<u>%C found</u>
17.0	0.71	24	69.6
18.8	0.86	22	70.5
17.0	0.71	24	-
18.4	0.79	23	-

Table 5-2- X-Ray powder data for $C_{24}SiF_5$ and derivatives

<u>$C_{24}SiF_5$</u>				<u>$C_{24}BF_4 \cdot 2.6BF_3$</u>			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>	<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
vs	3.760	3.768	003	s	7.607	7.641	001
m	2.833	2.826	004	vs	3.813	3.820	002
s	2.125	2.128	100	s	2.546	2.547	003
w	1.614	1.615	007	s	2.116	2.129	100
s	1.228	1.228	110	mw	1.528	1.528	005
				m	1.228	1.229	110
				ms	1.214	1.213	111

a = 2.46(1); c = 11.30(3)Å

a = 2.46(2); c = 7.64(1)Å

<u>$C_{24}BF_4 \cdot 0.8BF_3$</u>				<u>$C_{24}SiF_5 + C_6F_5PF_4$</u>			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>	<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
m	11.24	11.06	001	vs	3.704	3.751	003
m	5.721	5.529	002	s	2.838	2.813	004
vs	3.653	3.686	003	ms	2.128	2.131	100
w	2.765	2.764	004	w	1.864	1.875	006
m	2.121	2.128	100	mw	1.611	1.607	007
m	1.228	1.228	110	m	1.229	1.230	110
				w	1.202	1.202	112

a = 2.46(2); c = 11.1(2)Å

a = 2.46(1); c = 11.25(7)Å

CHAPTER 6

A THERMODYNAMIC THRESHOLD FOR OXIDATIVE GRAPHITE INTERCALATION

Introduction

Although AsF_5 and PF_5 are physically similar, graphite is spontaneously intercalated by the former and not the latter.¹ Earlier work in this laboratory established that AsF_5 oxidized the graphite according to the half-reaction:²

There has been much discussion concerning the extent of the intercalated AsF_5 conversion to AsF_6^- and AsF_3 ,^{3,4} but it is now clear, based on the recent work of Fujio Okino in this laboratory,⁵ that there is some AsF_5 in equilibrium with these species, although the extent of oxidation is high.

Oxidation of graphite by transition metal hexafluorides in forming graphite intercalation compounds has also been clearly established.⁶ Previous findings indicated that the intercalation of hexafluorides to form $\text{C}_x^+ \text{MF}_6^-$ salts required an oxidizing potential greater than that afforded by ReF_6 or WF_6 , but that the oxidizing potentials of UF_6 , OsF_6 and IrF_6 were sufficiently high. Based on the values of ReF_6 ,^{6,7} and UF_6 ,⁸ the threshold of electron affinity above which a hexafluoride will react spontaneously with graphite was established between 108 and 133 kcal/mole.⁹

A thermodynamic cycle for salts of the formula $\text{C}_x^+ \text{MF}_6^-$ (Fig. 6-1) shows, since all MF_6^- ions are approximately of the same size, and since the ionization, layer separation and lattice terms are independent of M, that the only term significantly affecting the enthalpy of the reaction is the half-reaction which forms the intercalating monocation.

It was not surprising, then, to discover a threshold⁹ in the electron affinities of the transition metal hexafluorides below which the oxidative intercalation reaction should not occur. This same threshold, in fact, should hold for other half-reactions which are known to result in intercalation of MF_6^- (Fig. 6-1). Indeed, from the experimental evidence of Chapters 4 and 5, MF_4^- and MF_5^- anions occupy similar gallery heights to MF_6^- ions, so assuming their lattice energy terms are comparable, C_xMF_4 and C_xMF_5 compounds will obey similar thresholds. The results of the previous chapters indicate that BF_4^- , SiF_5^- and PF_6^- fit well into this scheme.

The role of thermodynamics in the oxidative intercalation reaction remained in question, even with the electron affinity threshold firmly established. It could be asserted that this threshold merely represented the oxidizing power necessary to overcome a large activation barrier to intercalation and that the reaction is not thermodynamically controlled. In order to establish that a true thermodynamic threshold exists, the ions must be removed from the graphite in a reductive deintercalation reaction of a system whose thermodynamics are well-known.

Experimental

Reaction of second-stage fluorophosphate with PF_3 : C_xPF_6 ($23 < x < 33$) was prepared essentially as described in Chapter 3. Exact reaction conditions and resulting stoichiometries are summarized in Table 6-1.

The second-stage fluorophosphate (established by Debye-Scherrer, results in Table 6-2) was placed in a stainless steel reaction vessel and PF_3 (large excess, usually, ~400 torr) was condensed from the vacuum line into the vessel, which was warmed to room temperature and agitated for 20-48 hours. Reaction conditions and results of several reactions

are summarized in Table 6-3. The volatiles were vented to vacuum and sampled for IR and the sample was placed in dynamic vacuum for 20-48 hours, until no further weight loss was observed. The resulting compounds were weighed, analyzed for carbon content and examined by the Debye-Scherrer technique. Results of X-ray studies are summarized in Table 6-4.

Reaction of first-stage $C_{12}PF_6$ with PF_3 : $C_{12}PF_6$ (~.4 mmoles), prepared as described in Chapter 3, was placed in a stainless steel vessel and the same procedure followed as in the reduction of second-stage fluorophosphate. Several attempts to reduce first-stage $C_{12}PF_6$ were made. In no case was reaction observed (from gravimetry, IR and X-ray evidence) at room temperature or at 200°.

Reaction of $C_{24}PF_6$ with BF_3 : $C_{24}PF_6$ (~.3 mmoles), prepared as described in Chapter 3 and established as pure second-stage by Debye-Scherrer, was placed in a stainless steel reaction vessel and BF_3 (400 torr) condensed in from the line. The system was warmed to room temperature and agitated for 18 hours. The volatiles were vented to a large volume and sampled for IR and the product was transferred to the dry box, without pumping, to be weighed and sampled for Debye-Scherrer. This initial product was then placed under dynamic vacuum for 30 hours, after which no further weight loss was observed, and transferred to the dry box for gravimetric and X-ray analysis. Results are summarized in Table 6-6. Debye-Scherrer patterns of resulting compounds are indexed in Table 6-7.

Reaction of $C_{24}PF_6$ with BF_3 and F_2 : The same procedure was followed as for the reaction with BF_3 alone, but F_2 (250 torr, 0.9 mmoles) was condensed into the vessel along with BF_3 . The Debye-Scherrer powder data are indexed in Table 6-7.

Reaction of C_xBF_4 with PF_5 : C_xPF_6 ($19 < x < 23$) was prepared by condensing BF_3 (200 torr) and F_2 (100 torr) into a stainless steel reaction vessel charged with graphite (~10 mmoles), warming to room temperature and agitating for 25 min. The volatiles were vented to vacuum and the sample pumped until vacuum-stable (24-36 hours). From this point, exactly the same procedure was used as in the converse reaction, substituting PF_5 for BF_3 . Results are summarized in Table 6-8. Debye-Scherrer patterns of resulting compounds are indexed in Table 6-9.

Infrared standards: IR spectra were compared to several standard spectra of PF_5 and BF_3 of known pressures. The strength of the ν_5 absorption of PF_5 (1026 cm^{-1}) and the ν_3 absorption of BF_3 (1505 cm^{-1}) were compared to the strengths of these absorptions in standards to determine the composition of the volatile products of the reactions.

Microdensitometer studies: Intensities were measured on a Joyce-Loebl MK IIIIC recording microdensitometer using a scan rate of 0.66 deg./sec. for purposes of intensity measurement. A faster scan rate (1.32 deg./sec.) yielded the trace in Figure 6-2.

Results and Discussion

1. PF_3 reductions

Knowing the fluoride-ion affinity of PF_5 from Chapter 3 and the standard heats of formation^{10,11} at 298K of PF_5 , PF_3 and F_2 , $\Delta G^\circ(3/2\text{ }PF_5(g) + e^- \rightarrow PF_6^-(g) + 1/2\text{ }PF_3(g))$ ¹² was determined as -86(9) kcal/mole. This half-reaction is far less exothermic than even the electron affinity half-reaction of WF_6 , which explains the fact that PF_5 does not oxidize graphite as WF_5 does.

This reaction, though, afforded an opportunity to test the importance of thermodynamics in the graphite intercalation reaction, as

well as the reversibility of these reactions. The reduction of a graphite hexafluorophosphate salt with PF_3 by the reaction:

should be possible if the thermodynamic factor is comparable to the kinetic barriers in opening the graphite lattice and ordering the intercalating species inside the lattice.

The reaction of the second-stage fluorophosphate salt with PF_3 at room temperature results in substantial weight loss of the sample and a crystalline product whose Debye-Scherrer powder pattern (Tables 6-4,5) can be indexed to a graphite unit cell. The infrared spectrum of the volatile products shows a substantial absorption at 1026 cm^{-1} , indicating PF_5 release. The analytical data, however, require that there be residual compounds, which we must assume to be amorphous. The presence of low angle halos from poorly crystalline material can account for the high observed intensity of the broad 002 reflection in the reduced product in Table 6-5. Attempts to obtain analytically better carbon in this reduction by carrying the reaction out at 200° gave no better results.

A possible explanation for the incomplete reduction of the fluorophosphate (from gravimetry) and the difference in powder data could lie in the direct fluorination of some carbons in the graphite lattice when exposed to elemental fluorine in the synthesis of C_xPF_6 . This fluorine would not be as easy to remove as the PF_6^- ions, being a direct, very low-energy C-F bond. If small islands of fluorination existed in the graphite, possibly trapping some PF_6^- in a completely disordered manner, they would not show up in the diffraction pattern themselves, but would produce long-range disorder in the predominant

graphite lattice, as is indicated by the intensities of the reflections. Even a large excess of PF_5 in the synthesis of C_xPF_5 , however, does not seem to prevent this fluorination, which may occur simply through local microscopic excesses of F_2 on graphite. In addition, a small amount of PF_6^- may exist simply due to a small kinetic barrier to completing deintercalation (and starting intercalation). A very high-stage residual product would appear similar to graphite and may be the reason that the c_0 values are consistently slightly higher than that of SP-1 (Table 6-4).

The unsuccessful reduction of first-stage C_{12}PF_6 with PF_3 (no reaction) indicates that a kinetic barrier does exist in forcing the interaction of the reagent and the species in fully occupied galleries. Perhaps this reduction requires a sequence of reactions, some of which may be concerted, and the PF_3 needs to have ready entry into the gallery. Reactions of PF_3 with predominantly first-stage C_xPF_6 containing some second stage show the first-stage material to be unreacted.

2. Displacement reactions

Another test of the significance of thermodynamics in the graphite intercalation reaction is the expected displacement of weaker Lewis acids by stronger ones. Chapter 5 described the displacement of SiF_4 by PF_5 and BF_3 , both much stronger fluoroacids. Knowing the fluoride-ion affinities of BF_3 (92 kcal/mole) and PF_5 (100 kcal/mole), one would predict that PF_5 would at least partially displace BF_3 from higher-stage (>1) C_xBF_4 compounds and that BF_3 would be incorporated in the lattice of, but not displace PF_5 from, C_xPF_6 compounds.

The surprising result is nearly the opposite. The volatile products

of the reaction of BF_3 with C_xPF_6 show a strong absorption at 1026 cm^{-1} , indicating PF_5 displacement. From the strength of this absorption, at least half of the PF_5 in the starting material has been displaced. Gravimetry suggests that nearly all of the PF_5 has been replaced by BF_3 and that the same product is obtained as in the $\text{BF}_3/\text{C}_x\text{SiF}_5$ reaction; approximately four moles of BF_3 are taken up per mole of PF_5 displaced. In a dynamic vacuum, this product loses half of its BF_3 and IR shows PF_5 to be absent. From gravimetry (Table 6-6), it is clear that the residual solid contains two BF_3 molecules per fluoride ion. Carbon elemental analyses confirm the gravimetric results.

In the converse reaction of PF_5 with C_xBF_4 , the IR spectrum indicates only a trace of boron trifluoride, less than 10% of the BF_3 in the starting material, but the solid product shows a substantial weight gain and the Debye-Scherrer pattern indicates a significant expansion of the c axis in the second-stage material, all suggesting that the material takes up neutral PF_5 . Upon pumping, this material loses essentially all of the PF_5 it absorbed (from gravimetry and analysis) and returns to a material with the same c-spacing as the original C_xBF_4 .

With cations such as SF_3^+ and ClO_2^+ , the greater lattice energy of the tetrafluoroborate compounds essentially cancels the larger fluoride-ion affinity of PF_5 , resulting in enthalpies of gaseous acid-base reactions being essentially equal. (See Chapters 3 and 4 and reference 14.) However, from the lattice energy-formula-unit volume relationship set out in Chapter 3, the lattice energy advantage of BF_4^- is expected to be smaller with larger cations. Graphite, commonly pictured as a macrocation, has a very small effective radius in the c direction, though, so the true lattice energy of the PF_6^- compound may be

substantially smaller than that of the BF_4^- material.

The gravimetric results suggest another explanation for this anomaly. The vacuum-stable product of the displacement of PF_5 by BF_3 contains two BF_3 molecules per PF_5 displaced, suggesting formation of a B_2F_7^- ion.¹⁵ If $\Delta G^\circ(2 \text{BF}_3(\text{g}) + \text{F}^-(\text{g}) + \text{B}_2\text{F}_7^-(\text{g}))$ is less than $\Delta G^\circ(\text{PF}_5(\text{g}) + \text{F}^-(\text{g}) + \text{PF}_6^-(\text{g}))$, then the result can be thermodynamically rationalized. In order for the free energy of the B_2F_7^- half-reaction to be less than that of the PF_6^- half-reaction, the enthalpy must be at least 12 kcal/mole less, reflecting the entropy of condensing one more mole of gas at room temperature. But this reaction cannot be so exothermic that B_2F_7^- salts of small cations are predicted to be stable at room temperature, since such salts are not known. In this sense, then, due to its extensive charge delocalization, graphite does act as a macrocation.

As a test of the exothermicity of the B_2F_7^- half-reaction, the displacement reaction was repeated, but in the presence of fluorine gas, on the assumption that B_2F_7^- would not be favored over BF_4^- in the presence of excess fluorine [$\text{A}_\text{F}-(2\text{BF}_3) < 2\text{A}_\text{F}-(\text{BF}_3)$] and that under these conditions PF_5 would not be displaced, but BF_4^- would simply enter unoccupied galleries. This appears to be the case, since the IR spectrum of the volatile products shows only a very small PF_5 absorption (less than 10% of original PF_5) and the first-stage product is vacuum-stable.

The identity of the intercalating species in the non-vacuum-stable displacement product of $\text{BF}_3 + \text{C}_x\text{PF}_6$ is of some interest. One may postulate a $\text{B}_4\text{F}_{13}^-$ species in which three of the fluorines of one BF_4^- ion bridge to BF_3 fragments with one fluorine remaining terminal (Figure 6-3). This would, of course, be an extremely fluxional species and would

probably take up little more space (in the c direction) than a BF_4^- ion. Of course, adding a fourth BF_3 species at the apical fluorine would require a large expansion along c. More spectroscopic evidence is required to confirm the existence of both $\text{B}_4\text{F}_{13}^-$ and B_2F_7^- .

Summary

Phosphorus trifluoride was found to react with second-stage graphite fluorophosphate, resulting in reduction of the carbon to graphite, liberating PF_5 . The crystallinity of the product was poor, and the reaction did not proceed to completion, possibly due to direct fluorination of the graphite. BF_3 was found to displace PF_5 from C_xPF_6 , yielding a compound with four moles of BF_3 per mole of PF_5 displaced. This compound lost half of its BF_3 in a dynamic vacuum, yielding the postulated $\text{C}_x^+\text{B}_2\text{F}_7^-$. Apparently, the fluoride-ion affinity of 2 BF_3 to yield B_2F_7^- is well in excess of the fluoride-ion affinity of PF_5 . PF_5 did not displace BF_3 from C_xBF_4 , even though $A_{\text{F}}-(\text{PF}_5) > A_{\text{F}}-(\text{BF}_3)$.

References

- ¹ F.R. Falardeau, *J. Chem. Soc. Chem. Commun.*, 389 (1977).
- ² N. Bartlett, R.N. Biagioni, B.W. McQuillan, A.S. Robertson and A.C. Thompson, *J. Chem. Soc. Chem. Commun.*, 200 (1978).
- ³ H. Selig, M.J. Vasile, F.A. Stevie and W.H. Sunder, *J. Fluorine Chem.*, 10, 299 (1977).
- ⁴ M.J. Moran, J.E. Fischer and W.R. Salanck, *J. Chem. Phys.*, 73, 629 (1980).
- ⁵ F. Okino and N. Bartlett, to be published.
- ⁶ N. Bartlett, E.M. McCarron, B.W. McQuillan and T.E. Thompson, *Synth. Met.*, 1, 221 (1980).
- ⁷ P.M. George and J.L. Beauchamp, *Chem. Phys.*, 36, 345 (1979).
- ⁸ Third-row transition metals are expected to show a smooth increase in electron affinity of ~1 eV per step across the periodic table. See N. Bartlett, *Angew. Chem. Int. Ed.*, 7(6), 433 (1968).
- ⁹ T.E. Mallouk, G.L. Rosenthal, G. Muller, R. Brusasco and N. Bartlett, *Inorg. Chem.*, accepted for publication.
- ¹⁰ N. Bartlett and B. W. McQuillan, from "Intercalation Chemistry," ed. Whittingham and Jacobson, Academic Press, 1981.
- ¹¹ E. Rudzitis, E.H. VanDeventer and W.H. Hubbard, *J. Chem. Thermodynamics*, 2, 221 (1970).
- ¹² A.G. Sharpe, in "Halogen Chemistry," ed. V. Gutmann, Academic Press, 1980.
- ¹³ For half-reactions which involve equal numbers of moles of gas in reactants and products, ΔS° is assumed to be zero and $\Delta G^\circ = \Delta H^\circ$.
- ¹⁴ N. Bartlett and P.L. Robinson, *J. Chem. Soc.* 3417 (1961).
- ¹⁵ L.B. Ebert, D.R. Mills, J.C. Scanlon and H. Selig, *Mat. Res. Bull.*

16(7), 831 (1981).

Table 6-1 Reaction conditions and results for second-stage fluorophosphate preparations

No.	Graphite	mg PF ₅ (mmoles)	mg F ₂ (mmoles)	mg C (mmoles)	Time (min.)	Pumping Time (hours)	Solid Product Wt. (mg.)	x ^a
1	SP-1	210 (1.7)	15 (0.4)	121.1 (10.1)	110	28	182.8	23.7
2	HOPG	280 (2.2)	35 (0.9)	146.9 (12.2)	60	24	219.9	24.3
3	SP-1	100 (0.8)	20 (0.5)	145.6 (12.1)	45	36	217.6	24.4
4	SP-1	70 (0.6)	15 (0.4)	144.1 (12.0)	30	24	196.5	33.0
5	HOPG	100 (0.8)	20 (0.5)	160.4 (13.4)	45	24	242.3	23.7
6	SP-1	100 (0.8)	20 (0.5)	142.0 (11.8)	45	30	210.7	25.0
7	Coke ^b	100 (0.8)	20 (0.5)	135.4 (11.3)	45	24	192.4	28.7
8	SP-1	200 (1.5)	8 (0.2)	169.1 (14.1)	120	28	233.2	31.9

^a from gravimetry

^b Heated to >3000°, provided by Union Carbide.

Table 6-2- Debye-Scherrer data for second-stage fluorophosphate preparations (d spacings in Å)

No. ^a	<u>d₀₀₁</u>	<u>d₀₀₃</u>	<u>d₀₀₄</u>	<u>d₁₀₀</u>	<u>d₁₀₂</u>	<u>d₀₀₆</u>
1	10.74	3.612	2.686	2.113		1.807
2		3.621	2.673	2.108	1.994	
3		3.616	2.721	2.121		1.810
4	10.83	3.591	2.675	2.110	1.979	1.797
5	10.22	3.657	2.675	2.108	1.973	1.820
6	11.18	3.632	2.737	2.118	1.993	1.815
7		3.621	2.661	2.122	1.989	
8	11.14	3.598	2.720	2.122	2.004	1.797

No.	<u>d₀₀₇</u>	<u>d₁₁₀</u>	<u>d₁₁₃</u>	<u>c₀^b</u>	<u>c₀(1st stage)-Int.^c</u>
1	1.537	1.230	1.164	10.79	7.83, >102
2		1.228	1.164	10.78	
3	1.552	1.229		10.86	7.91, <102
4	1.534	1.226	1.162	10.75	
5	1.516	1.228	1.163	10.87	7.48, <102
6	1.561	1.229	1.165	10.92	
7		1.228		10.72	
8	1.551	1.229	1.163	10.84	7.96, >102

^a Identifies preparation in Table 6-1.

^b $a_0 = 2.46\text{Å}$ in all cases.

^c Intensity of first-stage 002 compared to second-stage 102.

Table 6-3- Reaction conditions and results for PF_3 reductions

No.	mg C_xPF_6 (mmoles)	ΣC^a	mg PF_3 (mmoles)	Time (hr.)	Pumping Time (hr.)	Solid Product Wt.(mg)	$\Sigma\text{C}(\text{grav.})$	$\Sigma\text{C}(\text{anal.})$
1	177.4 (.413)	66.2	130 (1.5)	20	30	154.0	76.2	
2	187.9 (.430)	66.8	175 (2.0)	24	28	146.6	85.6	84.8
3	96.8 (.221)	67.0	150 (1.7)	24	48	89.5	73.3	
4	179.7 (.332)	73.4	150 (1.7)	24	24	130.8	100.8	84.5
5	160.2 (.373)	66.2	130 (1.5)	20	24	138.2	76.7	
6	122.8 (.276)	67.4	130 (1.5)	48	30	102.5	80.8	79.8
7	127.8 (.261)	70.4	130 (1.5)	40	32	105.4	84.9	
8	161.3 (.305)	72.5	130 (1.5)	24	20	133.9	81.4	81.2

^a Percentage of carbon in C_xPF_6 , from gravimetry. Carbon analyses agreed, in all cases within 1%.

Table 6-4- Debye-Scherrer results for PF_3 reductions

<u>No.</u>	<u>d_7</u>	<u>d_{002}</u>	<u>d_{100}</u>	<u>d_{101}</u>	<u>d_{102}</u>	<u>d_{004}</u>	<u>d_{103}</u>	<u>d_{110}</u>	<u>d_{112}</u>
1	3.917	3.363	2.134	2.034	1.780	1.676	1.542	1.231	1.157
2		3.367	2.132	2.034	1.802	1.680	1.545	1.231	1.156
3		3.360	2.127	2.031		1.678		1.229	1.155
4		3.379	2.128	2.032		1.676	1.545	1.229	1.155
5		3.332	2.130	2.034	1.817	1.676	1.547	1.231	1.156
6		3.365	2.131	2.032	1.802	1.680	1.545	1.232	1.156
7		3.430	2.080	2.027		1.671		1.231	1.154
8		3.367	2.131	2.034	1.802	1.669	1.546	1.230	1.156
SP-1		3.354	2.132	2.032	1.799	1.677	1.543	1.231	1.155

<u>No.</u>	<u>d_{006}</u>	<u>d_{201}</u>	<u>d_{114}</u>	<u>d_{116}</u>	<u>d_{211}</u>	<u>a_0</u>	<u>c_0</u>
1	1.117					2.452	6.720
2		1.053	0.993	0.828	0.800	2.463	6.717
3			0.992			2.460	6.718
4			0.992			2.461	6.716
5	1.120	1.053	0.992			2.464	6.722
6	1.119	1.053	0.993	0.828	0.800	2.458	6.722
7	1.120	1.053	0.991		0.799	2.461	6.720
8	1.119	1.053	0.992			2.463	6.714
SP-1	1.118	1.053	0.992	0.827	0.800	2.461	6.706

Table 6-5- Intensities of reflections in Debye-Scherrer patterns of pristine graphite and $C_xPF_6 + PF_3$

<u>hkl</u>	SP-1 <u>I</u> *	Reduced C_xPF_6 <u>I</u> *
002	1000	1000
100	121	65
101	437	256
102	36	14
004	87	66
103	59	31
104	<5	--
110	133	68
112	150	76
105	4	<2
006	7	1.5
200	<5	--
201	13	5
202	<5	--
114	90	49
203	5	<2
115	<	--
107	<5	--
008	<5	<2
116	69	28
210	18	6
211	94	29
212	89	<2

* Intensities of <5 or <2 were observed on the film, but could not be accurately integrated. Intensities of -- were not observed on the film.

Table 6-6- Conditions and results for reactions of C_xPF_6 with BF_3

No.	x	mmoles C_xPF_6	mmoles BF_3	Time (hr.)	mmoles BF_3 uptake ^a
1	23.5	.412	1.5	18	1.48
2	25.7	.404	1.5	20	1.43
3	28.7	.438	1.5	20	.947

No.	mole ratio BF_3/PF_5	Pumping Time(hr.)	ratio after pumping
1	3.6	30	1.8
2	3.5	36	1.7
3	4.0	48	2.1

^a Assuming all PF_5 displaced

Table 6-7~ Debye-Scherrer data for $C_xPF_6 + BF_3$ reaction

$C_{25.7}PF_6$				$C_{25.7}PF_6 + BF_3$ (pumped 18 hours)			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>	<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
a	3.650	3.599	003	m	11.216	10.928	001
w	2.671	2.698	004	s	3.627	3.643	003
m	2.122	2.133	100	m	2.737	2.732	004
n	2.103	2.092	101	mw	2.125	2.130	100
mw	1.982	1.983	102	mw	2.099	2.090	101
n	1.228	1.231	110	w	1.986	1.984	102
mw	1.166	1.165	113	vw	1.561	1.561	007
				mw	1.229	1.229	110
				w	1.163	1.165	113

$$a = 2.46(1); c = 10.79(7) \text{ \AA}$$

$$a = 2.46(1); c = 10.93(9) \text{ \AA}$$

$C_{25.7}PF_6 + BF_3$ (no pumping)				$C_{28.7}PF_6 \cdot 2.7BF_4$			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>	<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
m	7.670	7.687	001 ^a	m	7.654	7.729	001
vs	3.826	3.844	002 ^a	m	6.540	6.380	(1/3 00?)
mw	3.687	3.649	003 ^b	vs	3.864	3.864	002
w	2.728	2.737	004 ^b	m	2.575	2.576	003
m	2.558	2.562	003 ^a	ms	2.119	2.127	100
m	2.114	2.126	100 ^{a,b}	w	1.545	1.546	005
mw	1.978	1.981	102 ^b	mw	1.228	1.228	110
w	1.537	1.537	005 ^a				
mw	1.227	1.227	110 ^{a,b}				

$$a = 2.45(1); c = 7.69(2) \text{ \AA}^a \\ 10.95(6) \text{ \AA}^b$$

$$a = 2.46(1); c = 7.73(1) \text{ \AA}$$

^a first-stage phase

^b second-stage phase

Table 6-8- Conditions and results for reactions of C_xBF_4 with PF_5

No.	x	mmoles C_xBF_4	mmoles PF_5	Time (hr.)	mmoles PF_5 uptake ^a
1	22.8	.500	1.5	18	.473
2	19.2	.515	1.5	12	.263
3	20.5	.494	1.5	20	.283

No.	mole ratio PF_5/BF_4	Pumping Time(hr.)	ratio after pumping
1	.95	24	.07
2	.51	18	.00
3	.57	24	.02

^a Assuming no BF_3 is displaced

Table 6-9- Debye-Scherrer results for $C_{20.5}BF_4 + PF_5$ reaction

$C_{20.5}BF_4$				$C_{20.5}BF_4 + PF_5$ (pumped 20 hrs.)			
<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>	<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
ms	11.455	10.848	001	m	11.821	10.855	001
vs	3.594	3.616	003	vs	3.582	3.618	003
s	2.740	2.712	004	m	2.819	2.714	004
m	2.125	2.128	100	ms	2.126	2.129	100
ms	2.086	2.088	101	ms	2.082	2.089	101
m	1.985	1.981	102	m	1.998	1.982	102
m	1.794	1.808	006	w	1.795	1.809	006
m	1.554	1.549	007	w	1.360	1.357	008
ms	1.228	1.228	110	ms	1.229	1.229	110
m	1.162	1.163	113	m	1.162	1.163	113

$$a = 2.46(1); c = 10.85(6) \text{ \AA}$$

$$a = 2.46(1); c = 10.85(10) \text{ \AA}$$

$C_{20.5}BF_4 + PF_5$ (no pumping)

<u>I</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>hkl</u>
w	11.135	11.012	001
vs	3.679	3.671	003
m	2.759	2.753	004
m	2.127	2.130	100
m	2.101	2.091	101
mw	1.985	1.986	102
mw	1.821	1.835	006
m	1.574	1.573	007
m	1.229	1.229	110
mw	1.164	1.166	113

$$a = 2.46(1); c = 11.01(3) \text{ \AA}$$

Figure 6-1- A thermodynamic cycle for oxidative graphite intercalation

XBL 847-3243

Figure 6-2- Microdensitometer tracing of (a) pristine graphite and
(b) reduction product of $C_xPF_6 + PF_3$

XBL 847-3245

Figure 6-3- The $B_4F_{13}^-$ ion

XBL 848-3600

CHAPTER 7

BASAL-PLANE CONDUCTIVITIES OF C_xBF_{3+y} AND C_xPF_{5+y} ($y \leq 1$) COMPOUNDSIntroduction

The electronic properties of graphite-donor compounds (reductive intercalate salts) are both theoretically^{1,2} and experimentally^{3,4} well-studied. At least for some simple binary systems, the band structures are well-enough known to provide convincing explanations for observed electronic conductivity both in the ab plane and along the c-axis. This is not the case for the graphite-acceptor compounds studied here. These systems are more complex structurally than the binary or ternary donor systems making them far more difficult to model theoretically with precision.⁵ To a very rough approximation the salts may be viewed as a two-dimensional graphite π -system, perturbed by charges above and below the carbon layers.⁶ Experimentally, the extraordinary anisotropy of the acceptor compounds and their chemical reactivity, render many of the usual techniques applied to donor compounds⁷ difficult to use. Construction of band structures is therefore much more difficult.⁸

Perhaps the greatest problem, though, in developing a coherent picture of the electronic properties of these ternary systems, in contrast to the simple alkali-metal intercalates, is the purely chemical problem of identifying the species present in the graphite galleries and their bonding relationships within themselves and to the carbon layers. This has been a particular problem with the most eagerly-studied graphite-acceptor system, that of AsF_5 , in which there is still much debate not only over the identity of the intercalated species,^{9,10} but also over the actual basal-plane conductivity behavior.^{11,12}

With this problem in mind, this study concentrates on the simpler

systems described earlier, whose thermodynamics and basic chemistry are, at least, better-understood than those of the arsenic salts. While the intercalating species are not unambiguously defined, synthetic procedures are well-established for compounds rich in Lewis acid or fluorine and clear comparisons can be made. From these studies, various hypotheses can be considered on a chemical level and, with a new body of data, a working predictive model can hopefully be offered for relative conductivities in oxidative graphite intercalation compounds.

Experimental

Experimental conditions involved in making fluorophosphate and fluoroborate salts with HOPG chips were always more forcing than those involved with SP-1 or HOPG powders.

HOPG chips: All chips were cut to approximate dimensions 5mm. x 5mm. x .3mm. and prepared for these studies by treating them with fluorine (500 torr) for three hours. They were then transferred to the dry box and their initial dimensions measured by micrometer ($\pm 10^{-5}$ m).

C₆PF₆(x<100): Three or four chips of HOPG (~4 mmole) were placed in a Monel reaction vessel. PF₅ (300 torr) and F₂ (200 torr) were condensed from the fixed volume of the vacuum line into the vessel. The sample was warmed to room temperature and agitated for a time which varied with the desired stoichiometry as shown in Table 7-1. Reaction times greater than three hours usually resulted in exfoliation of the chips. The sample was then subjected to a dynamic vacuum until further vacuum produced no weight change (5-48 hours, depending on stoichiometry). The sample was transferred to the dry box, where the thicknesses of all of the chips were measured and their conductivities determined individually. A representative chip was then filed into powder for a Debye-Hcherrer

pattern to determine the stoichiometry-staging relationship. The conductivity results are summarized in Table 7-2.

In order to determine the effect of elemental fluorine on conductivity in vacuum-stable compounds, a series of fluorophosphates was synthesized with a large excess of PF_5 over F_2 . PF_5 (700 torr) and F_2 (70 torr) were condensed into a Monel reaction vessel charged with HOPG chips (4-5 mmole). The vessel was warmed to room temperature and agitated for 2-24 hours, depending on final composition desired. The sample was then placed into a dynamic vacuum for 24 hours before conductivity was measured. These results are summarized in Table 7-3.

$\text{C}_x\text{PF}_6(x>100)$: As with the lower-stage compounds, 3-4 chips of HOPG (~4 mmole) were placed in a Monel reaction vessel. PF_5 (400 torr) and F_2 (250 torr) were then introduced from the line to the vessel and the system was left at 650 torr total pressure with the vessel open to the line. After a time which varies as shown in Table 7-1, the residual gases were removed and the system left under dynamic vacuum for 6 hours. The sample was transferred to the dry box and the standard procedure followed to determine conductivity. These high-stage compounds were nearly indistinguishable from graphite in their powder patterns except for weaker and slightly shifted high-angle reflections. Conductivity results are summarized in Table 7-2.

C_xPF_5+y : Three or four HOPG chips (~4 mmole) were placed in a Monel reaction vessel. PF_5 (900 torr) and F_2 (15 torr) were condensed in and the vessel agitated for 16-24 hours at room temperature. The sample was then transferred to the dry box and the conductivities of the chips determined. The chips were returned to the vessel and the reaction and measurement processes repeated until the chips finally exfoliated.

Reaction time and conductivity results are summarized in Tables 7-4 and 7-5.

C_xBF₄: The procedure was entirely analogous to that of the C_xPF₆ syntheses, with 350 torr and 200 torr of BF₃ and F₂, respectively, used for stoichiometries where x<10 and with 250 torr and 150 torr used for stoichiometries between C₁₀BF₄ and C₁₀₀BF₄. A summary of reaction conditions and resulting stoichiometries appears in Table 7-6. Unlike the PF₆⁻ salts, the BF₄⁻ salts were not found to exfoliate under these conditions. Salts with C:B ratios in excess of 100 were also prepared in an analogous manner to those of PF₆⁻, with 350 torr of BF₃ and 200 torr of F₂ in an open system. These results are also in Table 7-6. Conductivity data appears in Table 7-7.

As with the fluorophosphates, a series of vacuum-stable compounds of graphite, BF₃ and fluorine was prepared using a large excess of BF₃ over F₂. BF₃ (400 torr) and F₂ (40 torr) were condensed into a reaction vessel charged with HOPG chips (~5 mmole), warmed to room temperature and agitated for a time which varied with desired stoichiometry (15-180 minutes). Residual gases were vented and the resulting compound left in a dynamic vacuum for 20 hours, before transfer to the dry box. Conductivity results are summarized in Table 7-8.

Except in rare cases, HOPG chips were found to exfoliate when left in BF₃ longer than three hours, in contrast to the results observed with excess F₂.

C_xBF_{3+y}: Samples were prepared in an analogous manner to those of C_xPF_{5+y}. BF₃ (450 torr) and F₂ (15 torr) were condensed into a Monel vessel with four HOPG chips (~4 mmole). The samples were warmed to room temperature and agitated for 30-180 minutes, depending on desired

composition. Longer exposures resulted in exfoliation of the chips, as did repeated exposures to excess BF_3 . Samples were also observed to lose weight in the inert atmosphere of the dry box, so all conductivities were measured within one hour of venting the vessel. Reaction times and compositions are shown in Table 7-9. Conductivity data appear in Table 7-10.

Conductivity measurements: Basal-plane conductivity measurements were made by the contactless inductive technique,¹³ on an apparatus kindly provided by Dr. T.E. Thompson (Figure 7-1). Samples were measured in closed rectangular quartz tubing sealed to round tubing and fitted to $1/4''$ Whitey valves through Swagelock fittings and teflon ferrules. The rectangular tubing allowed the samples to fit into the slot in the ferrite core. The conductive chips induced a voltage change according to the empirically derived equation of Zeller, Denenstein and Foley $\Delta V = ks^2t\sigma$, where k is an instrumental constant, s is the surface area of the sample and t is the thickness of the sample.

Results and Discussion

1. Synthesis, staging and stoichiometry

The chief problem in developing at least an empirical predictive model for conductivity in acceptor compounds is their chemical complexity. With this in mind, the systems studied here were prepared in the simplest and most direct manner possible. Even if the exact identities of the intercalating species are not known, they are all fluorospecies, the central atoms, boron and phosphorus, are fully oxidized and the syntheses can easily be reproduced for further spectroscopic or diffraction studies.

The first striking result of these studies is the markedly

different behavior of HOPG chips compared to the SP-1 or even ground HOPG chips utilized in the previous studies. Not only are the reactions significantly slower due to smaller surface area exposed to attack by the intercalants, but the resulting compounds, in some cases, also appear to be fundamentally different from compounds of the same apparent stoichiometry synthesized with small particle-size graphite as a starting material.

It appears that in the fluorophosphate salts, the transition from second to first stage does not occur until the stoichiometry $C_{16}PF_6$ is reached, although some space may still be occupied by "neutral" PF_5 in the form of $P_2F_{11}^-$. This explains the unusually small values of t/t_0 (values larger than 1.7 are probably due to partial exfoliation) for compounds of $x < 20$ (Tables 7-2,3,5), the exfoliation of fluorophosphates after reaching $C_{16}PF_6$, and the lack of evidence of a first-stage compound in any of the X-ray powder patterns of the chips ground after intercalation. In transition-metal fluorides, the second-first stage transition is very exothermic and often results in exfoliation.¹³ It was long assumed^{14,15} that the limiting compositions of PF_6^- and AsF_6^- compounds was C_8MF_6 , representing the closest possible packing of hexafluoro-species in the graphite gallery. In the Daumas-Herold domain model¹⁶ for staging in these systems (Figure 7-2), the second stage ($C_{16}PF_6$) involves maximum strain in the carbon sheets. In this system, the large graphite particle size forces the intercalating species to crowd into their most closely-packed configuration (the thermodynamic requirements for transition to first stage are more than satisfied), so when further intercalation finally forces elimination of the strain on the layers and proceeds to first stage, it releases enough energy to

exfoliate the chip. This result also illustrates that the true limiting composition of PF_6^- and AsF_6^- salts, namely $\text{C}_{-11}\text{MF}_6$, may involve a charge limit of the graphite sheets for the oxidizer involved.

These studies also point out the enormous complexation abilities of BF_4^- . The exfoliations of chips under excess BF_3 and not under excess F_2 is probably related to the PF_6^- exfoliation. The BF_3 , being a flat species, intercalates easily to form large complex $\text{B}_n\text{F}_{3n+1}^-$ species, which limit the mobility of actual charged species needed to open the new galleries until the occupied galleries are extremely crowded. The result is exfoliation when the transition to first stage does occur.

2. Conductivity

While the conductivity studies leave some fundamental questions unanswered, they provide data which will be coupled with structural information to elucidate the nature of conductivity in acceptor compounds as well as the limits of that conductivity.

The compounds, both in the phosphorus and boron systems, which were prepared with a stoichiometric excess of fluorine show conductivity behavior similar to that of the transition-metal hexafluorides and hexafluoroarsenates observed by McCarron.¹⁴ The per-plane conductivity increases smoothly until the C/anion ratio reaches about 25, then shows a precipitous decrease as more species are intercalated. It is notable that although the PF_6^- system did not reach first stage under these conditions, a decrease in per-plane conductivity was still observed. This result does not support the contention¹⁷ that the decrease in conductivity is due simply to the localization of charge in the graphite π -system by negative charges above and below each sheet, as in a first-stage material.

The preparation of vacuum-stable C_xPF_6 and C_xBF_4 compounds using an excess of Lewis acid was intended to address the question of whether direct fluorination is a factor in limiting the conductivities of low-stage acceptor compounds. In the fluorophosphate case, the compounds prepared in this manner achieve significantly higher conductivities at C/PF_6^- ratios less than 20, suggesting that excess fluorine in the reaction mixture does result in lower conductivity, presumably due to direct C-F interactions. This agrees with recent work by Fujio Okino¹⁸ which suggests that only a small amount of excess fluorine can destroy metallic conductivity in the AsF_5 system. Due to the extraordinary abilities of C_xBF_4 compounds to take up BF_3 , low-stage vacuum-stable compounds were not prepared with excess BF_3 .

In light of these results, then, the behavior of the non-vacuum-stable fluorophosphate and fluoroborate systems was predictable. Their conductivity behavior is similar to that of the AsF_5 system^{11,18} which involves an equilibrium between charged and neutral species. Even in these systems, though, conductivity is not observed to increase smoothly as more species intercalate, indicating that mobility of holes in the graphite π -system is at least partially limited by charge concentrations near the carbon layers as the lattice becomes more crowded with intercalants.

Summary

Various graphite-phosphorus-fluorine and graphite-boron-fluorine compounds were prepared using HOPG chips for conductivity studies. The chips were found to react significantly more slowly than powdered graphite and also to transition to first stage (in the fluorophosphate system) at a different stoichiometry than powdered samples.

Conductivity results suggested that compounds prepared with stoichiometric excesses of fluorine had far lower per-plane conductivities at low stages than those prepared with excess fluoroacid due to direct carbon-fluorine interactions. Compounds prepared with excess PF_5 and BF_3 had higher conductivities, but their conductivities did not increase smoothly up to the limiting compositions.

References

- ¹ D.P. Divincenzo, N.A.W. Holzwarth and S. Rabi, *Physica*, 99B, 406 (1980).
- ² I.P. Batra and L. Samuelson, *Synth. Mets.*, 1, 233 (1979).
- ³ M. Zanini and J.E. Fischer, *Mat. Sci. Eng.*, 31, 169 (1977).
- ⁴ J.J. Ritsko and E.J. Mele, *Physica*, 99B, 425 (1980).
- ⁵ F. Batallan, I. Rosenman, C. Simon, G.Furdin and H. Fuzellier, *Physica*, 99B, 411 (1980).
- ⁶ M.S. Dresselhaus, G. Dresselhaus and J.E. Fischer, *Phys. Rev. B*, 15, 3180 (1977).
- ⁷ A.W. Moore, *Chem. Phys. Carbon*, 17, 234 (1981).
- ⁸ J.E. Fischer, *Phys. Chem. Mat. Layered Strucs.*, 6, 481 (1979).
- ⁹ R. Pentenrieder and H.P. Boehm, *Rev. Chim. Miner.*, 19, 371 (1982).
- ¹⁰ N. Bartlett, B.W. McQuillan and A.S. Robertson, *Mat. Res. Bull.*, 13, 1259 (1978).
- ¹¹ L.V. Interrante, R.S. Markiewicz and D.W. McKee, *Synth. Mets.*, 1, 287 (1979).
- ¹² H.A. Resing and M.J. Moran, *J. Chem. Phys.*, 76, 1706 (1982).
- ¹³ C. Zeller, A. Denenstein and G.M.T. Poley, *Rev. Sci. Instrum.*, 50, 602 (1979).
- ¹⁴ E.M. McCarron, Ph.D.Thesis, University of California, Berkeley, 1980.
- ¹⁵ N. Bartlett, R.N. Biagioni, B.W. McQuillan and T.E. Thompson, *Synth. Mets.*, 1, 221 (1979).
- ¹⁶ N. Dumas and A. Herold, *Comptes Rend. Acad. Sci.*, C268, 373 (1969).
- ¹⁷ T.E. Thompson, E.M. McCarron and N. Bartlett, *Synth. Mets.*, 3, 255 (1981).
- ¹⁸ F. Okino and N. Bartlett, unpublished results.

Table 7-1- Reaction times and resulting stoichiometries of C_xPF_6 compounds

<u>Time (min.)</u>	<u>x^a</u>	<u>Stage, $c_0(A)^c$</u>
360	16.2	2 nd , 10.89
100	22.6	2 nd , 10.77
60	24.0	2 nd , 10.79
60	27.7	
30	40.0	4 th , 17.6
30	42.6	
20	67.4	5 th , 20.9
15	77.	
120 ^b	107.	HOPG
60 ^b	257.	
40 ^b	>500.	HOPG

^a Based on gravimetry. Confirmed to within 2% by carbon analysis. All weight uptake assumed to be PF_6^- ion.

^b Open system conditions. See p. 81.

^c Debye-Scherrer data for ground samples.

Table 7-2- Conductivity vs. composition for C_xPF_6

x	t/t_0^a	σ ($\times 10^5 \Omega^{-1} \text{cm}^{-1}$)	σ/σ_G	k/k_G^b
16.2	2.01	0.77	3.1	6.2
22.6	1.63	1.8	7.2	11.5
24.0	1.81	1.5	6.0	11.4
27.7	1.60	2.2	8.8	14.1
40.0	1.35	1.9	7.6	10.3
42.6	1.35	2.2	8.8	11.9
67.4	1.21	2.0	8.0	9.6
77.	1.19	1.3	5.2	6.2
107.	1.20	1.1	4.4	5.3
257.	1.0	0.89	3.6	3.6
>500.	1.0	0.68	2.7	2.7

^a t = thickness of graphite chip. Ideal t/t_0 values may be calculated from c-axis dimensions of intercalated compounds compared to pristine graphite. First stage (7.8Å) t/t_0 = 2.3; 2nd stage (10.9Å) = 1.6; 3rd stage (14.3Å) = 1.4; 4th stage (17.6Å) = 1.3.

^b $k = \sigma \times t/t_0$

Table 7-3- Conductivities of C_xPF_6 salts made with excess PF_5

<u>x</u>	<u>τ/τ_0</u>	<u>$\sigma (\times 10^5 \Omega^{-1} \text{cm}^{-1})$</u>	<u>σ/σ_G</u>	<u>k/k_G</u>
15.8	1.81	2.0	8.0	14.5
18.0	1.78	2.4	9.6	17.1
19.4	1.83	2.0	8.0	14.6
22.6	1.65	2.5	10.0	16.5
32.1	1.50	2.2	8.8	13.2
44.3	1.33	2.0	8.0	10.6

Table 7-4- Reaction times and resulting stoichiometries of C_xPF_{5+y} compounds

<u>Time (hr.)</u>	<u>x^a</u>	<u>Stage, c₀(Å)</u>
5	120.	
29	34.4	
45	23.6	
63	21.9	2 nd , 10.80
79	19.8	
95	16.4	2 nd , 11.01
28	24.1	
58	21.0	
84	16.0	2 nd , 11.05
18	40.1	4 th , 17.7
42	29.8	
62	21.2	
80	16.4	2 nd , 10.87
104	15.4	

^a For purposes of computation, all weight uptake was assumed to be in the form of PF_6^- ion.

Table 7-5- Conductivity vs. composition for C_xPF_{5+y}

x	t/t_0	$\sigma (\times 10^5 \Omega^{-1} \text{cm}^{-1})$	σ/σ_G	k/k_G
120.	1.24	1.1	4.4	5.5
34.4	1.37	1.8	7.2	9.9
23.6	1.54	1.9	7.6	11.7
21.9	1.62	2.0	8.0	13.0
19.8	1.70	2.0	8.0	13.6
16.4	1.86	1.6	6.4	11.9
24.1	1.27	2.5	10.0	12.7
21.0	1.38	2.4	9.6	13.2
16.0	1.50	2.1	8.4	12.6
40.1	1.31	2.3	9.2	12.0
29.8	1.41	2.5	10.0	14.1
21.2	1.52	2.6	10.4	15.8
16.5	1.65	2.4	9.6	15.8
15.4	1.72	2.0	8.0	13.8

Table 7-6- Reaction conditions and resulting stoichiometries of C_xBF_4 compounds

P_{BF_3} (torr)	P_{F_2} (torr)	Time (min.)	x^a	Stage, $c_0(\lambda)$
400	300	300	7.6	1 st , 7.73
400	300	270	9.7	2 nd , 10.92
350	250	150	11.6	2 nd , 10.93
350	250	180	16.7	2 nd , 10.97
350	250	180	17.6	2 nd , 10.91
350	250	120	20.5	2 nd , 10.94; 3 rd , 14.4
300	200	50	21.5	3 rd , 14.1
300	200	50	22.7	3 rd , 14.2
250	150	35	23.6	
250	150	10	26.6	
250	150	25	27.1	
250	150	15	31.2	4 th , 17.5
250	150	7	60.7	7 th , 27.8
350	200	90 ^b	176.	
350	200	60 ^b	220.	

^a All weight uptake assumed to be BF_4^- ion. Confirmed by analysis.

^b Open system conditions. See p. 82.

Table 7-7- Conductivity vs. composition for C_xBF_4

x	t/t_0	$\sigma (\times 10^5 \Omega^{-1} \text{cm}^{-1})$	σ/σ_G	k/k_G
7.6	2.3	0.095	0.38	0.87
9.7	2.1	0.30	1.2	2.5
11.6	2.0	0.43	1.7	3.4
16.7	1.6	0.65	2.6	4.2
17.6	1.6	0.87	3.5	5.6
20.5	1.5	1.0	4.0	6.0
21.5	1.4	1.8	7.2	10.1
22.7	1.4	2.1	8.4	11.8
23.6	1.4	2.7	10.8	15.1
26.6	1.4	2.4	9.6	13.4
27.1	1.3	2.1	8.4	11.3
31.2	1.3	1.9	7.6	9.9
60.7	1.2	1.7	6.8	8.2
176.	1.0	0.74	3.0	3.0
220.	1.0	0.47	1.9	1.9

Table 7-8- Conductivities of C_xBF_4 salts made with excess BF_3

x	t/t_0	σ ($\times 10^5 \Omega^{-1} \text{cm}^{-1}$)	σ/σ_G	k/k_G
25.8	-	2.0	8.0	-
26.1	1.41	2.6	10.4	14.7
31.1	1.37	2.1	8.4	11.5
31.7	1.24	1.9	7.6	9.4
41.3	1.20	1.7	6.8	8.2

Table 7-9- Reaction times and resulting stoichiometries for C_xBF_{3+y} compounds

<u>Time (min.)</u>	<u>x^a</u>
240	15.5
180	12.2
180	20.4
150	17.6
120	15.3
120	24.6
90	17.9
30	22.8

^a For purposes of computation, all weight uptake was assumed to be in the form of BF_4^- ion.

Table 7-10- Conductivity vs. composition for C_xBF_{3+y}

x	t/t_0	σ ($\times 10^5 \Omega^{-1} \text{cm}^{-1}$)	σ/σ_G	k/k_G
12.2	1.37	2.9	11.6	15.9
15.3	1.36	2.4	9.6	13.1
15.5	1.40	3.0	12.0	16.8
17.6	1.30	2.6	10.4	13.5
17.9	1.38	2.4	9.6	13.2
20.4	1.33	2.7	10.8	14.4
22.8	1.28	2.2	8.8	11.3
24.6	1.33	2.5	10.0	13.3

Figure 7-1- Schematic diagram of contactless conductivity apparatus

XBL 847-3244

Figure 7-2- The Daumas-Herold staging model

XBL 848-3601

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.