RESEARCH IN INORGANIC FLUORINE CHEMISTRY

FINAL REPORT

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RESEARCH TRIANGLE PARK, NC 27709

A basic research program was carried out in the area of inorganic fluorine chemistry. Major achievements accomplished during this program include: The first purely chemical synthesis of elemental fluorine was realized. Solid propellant based pure fluorine gas generators were developed. The first examples of $\text{NF}_4^-$ salts containing halogen fluoride counterions were prepared and characterized. Also $\text{NF}_3 \text{CF}_2^-$ was synthesized and characterized. The bond length in $\text{NF}_3^-$ was estimated from its general Valence Force Field and was verified by a crystal structure determination of $\text{NF}_3 \text{CF}_2\. Difluoramidine and $\text{NHF}_2$ were prepared, characterized, and their alkali metal fluoride adducts were studied. These adducts were shown to contain $[\text{F}^- \text{HNF}_3^-]$ anions. The nature of the association in solid $\text{HNF}_3^- \text{CF}_2$ was explored. The interaction of difluoramino compounds with Lewis acids was studied. The reaction chemistry of $\text{CF}_2^-$ and $\text{NHF}_2$ was studied and several new compounds were prepared and characterized. The nitrate anion was found to be an excellent and readily available reagent for accomplishing fluorine-oxygen exchange in certain halogen fluorides.
19. Key Words (Continued)

Chromium Fluorides, Bromine Trifluoride Oxide, Tetrafluorobromine Oxide Anion, Krypton Fluorides, Platinum Hexafluoride Oxonium Salts, Chlorine Oxyfluorides, Trifluoromethyl Azide, Nickel (II) Hexafluoroantimonate.

20. Abstract (Continued)

This work resulted in new, simplified syntheses for compounds such as \( \text{BrF}_3\text{O} \), \( \text{BrF}_4\text{O}^- \) salts, \( \text{BrNO}_3 \) and \( \text{N}_2\text{O}_5 \). Based on its Raman spectra, solid \( \text{N}_2\text{O}_5 \) was shown to contain nonlinear \( \text{NO}_2^+ \) cations. The salts Cs[\( \text{Br(NO}_3\text{)}_2 \)] and NO\(_2\)[\( \text{Br(NO}_3\text{)}_2 \)] were prepared and characterized. It was shown that the previously reported \( \text{Br(NO}_3\text{)}_3 \) actually is \( \text{NO}_2\)[\( \text{Br(NO}_3\text{)}_2 \)]. A total of 33 papers, manuscripts and patents are included in the Appendix.
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PREFACE

The research reported herein was supported by the U.S. Army Research Office with Dr. B. Spielvogel as Scientific Officer. Other support of this work was provided by the Office of Naval Research with Dr. H. Guard as Scientific Officer. This report covers the period 1 March 1984 through 28 February 1987. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out mainly by Drs. K. O. Christe, W. W. Wilson and C. J. Schack and Mr. R. D. Wilson. Other contributors to these research efforts, at no cost to the contract, were Drs. R. Bougon, P. Charpin and E. Soulie (French Atomic Energy Commission), Prof. J. Fawcett (University of Leicester, U.K.), Profs. H. Oberhammer and D. Christen (Universitat Tubingen, W-Germany), Profs. G. Olah and R. Bau (University of Southern California), Dr. M. D. Lind (Science Center of Rockwell International) and Prof. N. Thorup (University of Lingby, Denmark). The program was administered by Dr. L. Grant and after his resignation by Dr. J. Flanagan.
INTRODUCTION

This is the final report of a research program carried out at Rocketdyne between 1 March 1984 and 28 February 1987. The purpose of this program was to explore the synthesis and properties of energetic inorganic halogen oxidizers. Although the program was directed toward basic research, applications of the results were continuously considered.

Only completed items of research, which have been summarized in manuscript form, are included in this report. A total of 18 technical papers were published and 8 papers are in press in major scientific journals. In addition, 10 papers were presented at international and national conferences, and 14 invited lectures were given in the US and abroad. A further testimony to the creativity of this program is the fact that it resulted in 7 US patents and 3 patent disclosures. The technical papers and issued patents are given as Appendices A through Y and AA through GG, respectively.

During 1985, the author served as a member on the Committee on Energetic Materials Science and Technology appointed by the Board on Army Science and Technology. Rocketdyne's outstanding contributions to fluorine chemistry were also recognized by the American Chemical Society with its 1986 Award for Creative Work in Fluorine Chemistry.
PUBLICATIONS AND PATENTS GENERATED UNDER THIS PROGRAM

PUBLICATIONS


17. "Chemical Synthesis of Elemental Fluorine," by K. O. Christe, 

18. "Preparation and Characterization of Ni(SbF₆)₂," by K. O. 
   Christe, W. W. Wilson, R. A. Bougon and P. Charpin, 

PAPERS IN PRESS

   Metal Fluoride Adducts," by K. O. Christe and R. D. Wilson, 
   Inorg. Chem.

20. "New, One Step Syntheses of BrF₃O and BrF₄O⁻ Salts and the 
   Preparation and Characterization of RbBrF₄O and NaBrF₄O," 


   Chem.

23. "Solid Propellant Based Pure Fluorine Gas Generators," by 

24. "Preparation of Halogen Oxyfluorides," by K. O. Christe, 
   contributed chapter to Volume 3 of Inorganic Reactions and 
   Methods.


26. "Self-Association in HOF and HNF₂. Which Atoms are the 
   Better Proton Acceptors, Fluorine, Oxygen or Nitrogen?" 
PAPERS PRESENTED AT MEETINGS


29. "\( \text{CrF}_5 \) Chemistry and Synthesis of \( \text{NF}_4\text{CrF}_6 \)," by R. A. Bougon, W. W. Wilson, and K. O. Christe, presented at the Seventh Winter Fluorine Conference, Orlando, Florida.


31. "Synthesis and Characterization of \( \text{CrF}_4\text{O}, \text{Krf}_2\cdot\text{CrF}_4\text{O} \) and \( \text{NO}\cdot\text{CrF}_5\text{O}^{-} \)," by W. W. Wilson, R. A. Bougon and K. O. Christe paper presented at 191st National ACS Meeting, April 13-18, 1986, New York City.


INVITED LECTURES

Invited lectures on work done under this contract were given at:

37. University of Utah, Salt Lake City
38. University of British Columbia, Canada
39. University of California, Santa Barbara
40. Universitat Dortmund, W-Germany
41. Ruhr-Universitat Bochum, W-Germany
42. Freie Universitat Berlin, W-Germany
43. Technische Universitat Stuttgart, W-Germany
44. Universitat Ulm, W-Germany
45. Phillips Universitat Marburg, W-Germany
46. Universitat Hannover, W-Germany
47. Universitat Gottingen, W-Germany
48. University of Alabama, Tuscaloosa
49. Clemson University, South Carolina
50. Stanford University, Stanford, CA
PATENTS ISSUED


PATENT DISCLOSURES


AWARDS

RESULTS AND DISCUSSION

In view of the vast amount of data generated under this program, this discussion will be limited to a highlight of some of the major achievements. For more detail, the interested reader is referred to the manuscripts given in the Appendices.

CHEMICAL SYNTHESIS OF ELEMENTAL FLUORINE

The chemical synthesis of elemental fluorine had been pursued for at least 173 years by many notable chemists, including Davy, Fremy, Moissan, and Ruff. All their attempts had failed, and the only known practical synthesis of F₂ was Moissan’s electrochemical process, which had been discovered 100 years ago.

Although in principle the thermal decomposition of any fluoride is bound to yield fluorine, the required reaction temperatures and conditions are so extreme that rapid reaction of the evolved fluorine with the hot reactor walls preempts the isolation of significant amounts of fluorine. Thus, even in the well-publicized case of K₃PbF₇, only trace amounts of fluorine were isolated.

These failures, combined with the fact that fluorine is the most electronegative element and generally exhibits the highest single bond energies in its combinations with other elements, had led to the widely accepted belief that it was impossible to generate fluorine by purely chemical means.

The Centenary of the Discovery of Fluorine by Moissan which was held in August 1986 in Paris prompted us to study the possibility of a purely chemical synthesis of fluorine. This goal was achieved within two weeks, just in time for presentation at the Moissan Centenary. Our chemical synthesis of F₂ was based on
the fact that thermodynamically unstable high-oxidation-state transition-metal fluorides can be stabilized by anion formation. Thus, unstable NiF$_4$, CuF$_4$, or MnF$_4$ can be stabilized in the form of their corresponding MF$_6^{2-}$ anions. Furthermore, it was well-known that a weaker Lewis acid, such as MF$_4$, can be displaced from its salts by a stronger Lewis acid, such as SbF$_5$.

$$K_2MF_6 + 2SbF_5 \rightarrow 2KSbF_6 + [MF_4]$$  \hspace{1cm} (1)

If the liberated MF$_4$ is thermodynamically unstable, it will spontaneously decompose to a lower fluoride, such as MF$_3$ or MF$_2$, with simultaneous evolution of elemental fluorine.

$$[MF_4] \rightarrow MF_3 + 1/2F$$  \hspace{1cm} (2)

Since a reversal of (2) is thermodynamically not favored, fluorine can be generated even at relatively high pressures.

Consequently, the chemical generation of elemental fluorine was accomplished by a very simple displacement reaction and by selecting a suitable complex fluoro anion which can be prepared without the use of elemental fluorine and is derived from a thermodynamically unstable parent molecule. The salt selected for this study was K$_2$MnF$_6$. It had been known since 1899 and is best prepared from aqueous HF solution.

$$2KMnO_4 + 2KF + 10HF + 3H_2O_2 \ stackedunder{50\% \text{aq HF}} \rightarrow 2K_2MnF_6 + 8H_2O + 3O_2$$  \hspace{1cm} (3)

The other starting material, SbF$_5$, was prepared in high yield from SbCl$_5$ and HF.

$$SbCl_5 + 5HF \rightarrow SbF_5 + 5HCl$$  \hspace{1cm} (4)
Since both starting materials, $K_2MnF_6$ and $SbF_5$, can be readily prepared without the use of $F_2$ from HF solutions, the reaction

$$K_2MnF_6 + 2SbF_5 \rightarrow 2KSF_6 + MnF_3 + 1/2F_2 \quad (5)$$

represents a truly chemical synthesis of elemental fluorine.

The displacement reaction between $K_2MnF_6$ and $SbF_5$ was carried out in a passivated Teflon-stainless-steel reactor at 150°C for 1 h. The gas, volatile at -196°C, was measured by PVT and shown by its reaction with mercury and its characteristic odor to be fluorine. The yield of fluorine based on (5) was found to be reproducible and in excess of 40%. Fluorine pressures of more than 1 atm were generated in this manner.

Our successful chemical synthesis of fluorine received much attention and was published within one month in Inorganic Chemistry (Appendix Q). It was also highlighted in journals such as Chemical and Engineering News, Chem Matters, and the Yearbook of Science and the Future for Encyclopaedia Britannica.

**Solid Propellant Pure Fluorine Gas Generators**

The principle outlined above for the chemical synthesis of elemental fluorine can also be applied to solid propellant pure fluorine gas generators by a simple replacement of the volatile Lewis acid $SbF_5$ by a nonvolatile solid Lewis acid such as $BiF_5$ or $TiF_4$. This concept was successfully demonstrated (Appendix W) for the $K_2NiF_6$-$BiF_5$, $Cs_2CuF_6$-$BiF_5$, $Cs_2MnF_6$-$BiF_5$, $K_2NiF_6$-$TiF_4$, and $K_2NiF_6$-$TiF_4$-$BiF_5$ systems. This type of generator holds great potential for applications such as pulsed DF chemical lasers using a gas recirculating system.
**NF$_4^+$ Chemistry**

In view of the fact that the NF$_4^+$ cation is the most useful and most stable highly energetic cationic oxidizer presently known, the chemistry of NF$_4^+$ was further explored.

The first examples of NF$_4^+$ salts with halogen fluoride anions were synthesized and characterized. These salts are NF$_4$BrF$_4$ and NF$_4$BrF$_4$O and are described in Appendix J. Similarly, the synthesis and characterization of NF$_4$CrF$_6$ is described in Appendix H.

The bond length in NF$_4^+$ has been estimated from its General Valence Force Field as 1.31Å (see Appendix P). Experimental verification of this value has finally been achieved by an x-ray single crystal structure determination of NF$_4$BF$_4$ which resulted in a value of 1.30Å. These results will be reported on in a future publication. A review of synthetic procedures for the preparation of NF$_4^+$ salts was published in Inorganic Syntheses (see Appendix M).

**NF$_2$ Chemistry**

Since difluoramine is an important intermediate in the preparation of other oxidizers such as N$_2$F$_4$, a better knowledge of this poorly characterized material was desired. This work was complicated by the fact that HNF$_2$ is a vicious explosive. Samples of HNF$_2$ and pure DNF$_2$ were prepared and studied in both the liquid and the solid phase (Appendix S). It was shown that, surprisingly, association in the condensed phases occurs through N-H--bridges and not through N-H--F bridges (Appendix Y). The structures of the alkali metal fluoride ·HNF$_2$ adducts were studied and it was shown that the different alkali metal adducts all contain the [F···HNF$_2$]"
anion (Appendix S). Evidence was obtained for two different adducts which do not differ by nature but only by the relative strength of their F⁻-H-N bridge. The more strongly bridged adducts might account for the explosive nature of some of the adducts.

It was also found that certain difluoramino compounds are unstable towards Lewis acids and readily undergo intramolecular redox reactions (see Appendix G).

CHROMIUM FLUORIDE CHEMISTRY

Since CrF₆ is expected to be a very powerful oxidizer (CrF₅ can already oxidize O₂ to O₂⁺), we became interested in chromium fluoride chemistry. Although the synthesis of CrF₆ in bulk quantities has so far proven elusive, the reaction chemistry of CrF₅ (Appendix H) and CrF₄O (Appendices O and X) was studied and several new adducts such as KrF₂·CrF₄O, NO⁺CrF₅O⁻ and CrF₄O·SbF₅ were synthesized and characterized. It was shown that some of these adducts are extremely powerful oxidizers.

OXYGEN-FLUORINE EXCHANGE REACTIONS

The nitrate anion was found to be a very versatile, cheap and readily available reagent for achieving fluorine-oxygen exchange in many cases. For example, the previously rather unaccessible BrF₃O molecule and its BrF₄O⁻ salts can now be prepared with great ease in quantitative yields (see Appendix T):

\[
\text{LiNO}_3 + \text{BrF}_5 \rightarrow \text{LiF} + \text{FNO}_2 + \text{BrF}_3\text{O} \quad (6)
\]

\[
\text{KNO}_3 + \text{BrF}_5 \rightarrow \text{KBrF}_4\text{O} + \text{FNO}_2 \quad (7)
\]
The latter type reaction was used to synthesize and characterize the novel salts NaBrF$_4$O and RbBrF$_4$O. By using an excess of MNO$_3$ in these reactions, it was found that BrONO$_2$ and N$_2$O$_5$ became the major products. Since BrONO$_2$ had previously been only poorly characterized, this compound and its reaction chemistry were studied in more detail (Appendix V). It was found that N$_2$O$_5$ forms with BrONO$_2$ the ionic adduct NO$_2$$^+$(Br(ONO$_2$)$_3$)$^-$. Furthermore, it was shown that the previously reported compound Br(ONO$_2$)$_3$ is identical to NO$_2$$^+$(Br(ONO$_2$)$_2$)$^-$ and had been incorrectly identified.

In connection with this study we have also discovered a new synthesis of N$_2$O$_5$ according to

$$\text{LiNO}_3 + \text{FNO}_2 \rightarrow \text{LiF} + \text{N}_2\text{O}_5$$

This synthesis offers the advantage of eliminating the need for an ozone generator required for the previously used methods. The laser Raman spectrum of N$_2$O$_5$ was also recorded and it was shown that solid N$_2$O$_5$ which has the ionic structure NO$_2$$^+$$\text{NO}_3^-$ cannot contain completely linear NO$_2$$^+$ cations. The latter result is in contrast to previous, low-precision x-ray diffraction data (Appendix U).

Extension of this work to other fluorides and oxoanions is under progress.

CONCLUSION

The work during this contract period has again been extremely fruitful. The first chemical synthesis of elemental fluorine not only represented a major breakthrough in basic chemistry, but also resulted in useful applications such as a solid propellant pure fluorine gas generator for high-power, pulsed DF lasers. Another example is the class of oxygen-fluorine exchange reactions using nitrates which resulted in an improved synthesis of pure N$_2$O$_5$. These and the other examples highlighted above demonstrate again the benefits which can be expected from well-planned, goal-oriented basic research and program continuity.
APPENDIX A

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Contribution from Rockwell International, A Division of
Rockwell International, Canoga Park, California 91304

Coordinately Saturated Fluoro Cations. Oxidative Fluorination Reactions with KrF+ Salts and PtF6

KARL O. CHRISTE,* WILLIAM W. WILSON, and RICHARD D. WILSON

Received August 24, 1983

The usefulness of KrF+ salts and PtF6 as oxidative fluorinators for the syntheses of the coordinately saturated complex fluorocations NF+, CIF+, and BrF+, was studied. The syntheses of NF3SbF6, NF3AsF6, NF3BF6, and NF3TiF6-2rTiF6 from KrF+—Lewis acid adducts and NF3 were investigated under different reaction conditions. The fluorination of NF3 by KrF+—SbF6 in HF solution was found to proceed quantitatively at temperatures as low as -31 °C, indicating an ionic two-electron oxidation mechanism. An improved synthesis of KrF+—MF6 (M = As, Sb) was studied. The fluorination of KrF+—MF6 in HF at -40 °C are reported. Attempts to fluorinate OF6, CIF6, and CIF6+ with KrF+ salts were unsuccessful. Whereas KrF+ is capable of oxidizing NF3, CIF3, and BrF3 to the corresponding complex fluorocations, PtF6 was shown to be capable of oxidizing only NF3 and CIF3. Since the yield and purity of the NF3+ fluoroplatinate salts obtained in this manner were low, NF3PtF6 was also prepared from NF3, F2, and PtF6 at elevated temperature and pressure. General aspects of the formation mechanisms of coordinately saturated complex fluorocations are discussed briefly.

Introduction

The preparation of coordinately saturated complex fluorocations presents a great challenge to the synthetic chemist. The nonexistence of the corresponding parent molecules precludes the normally facile cation formation by a simple F- abstraction from a parent molecule, and an F+ addition to a lower fluoride is ruled out by the fact that fluorine is the most electronegative element and therefore F+ cannot be generated by chemical means.1 In view of these difficulties it is not surprising that at the present time only three coordinately saturated fluorocations, NF3+,2 CIF3+,3 and BrF3+,4 are known to exist. In addition to their challenge to the synthetic chemist, the formation mechanism of these cations represents an intriguing and as yet unsolved puzzle.5

These problems were complicated by the facts that each of the three known coordinately saturated fluorocations had been prepared by a different method2-4 and that these methods could not readily be transferred from one cation to another. The purpose of this study was to examine whether the synthesis of each coordinately saturated fluorocation is indeed limited to a specific method and whether these methods possess any commonalities.

Experimental Section

Apparatus. Volatile materials used in this work were handled in a stainless-steel-Teflon FEP vacuum line. The line and other hardware used were well passivated with CIF3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry-nitrogen atmosphere of a glovebox. Metastable reactions and solubility measurements were carried out in HF solution with use of an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.5

Infrared spectra were recorded in the range 4000-200 cm⁻¹ on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an

References

Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-A exciting line of an Ar ion laser and Claessen filter for the elimination of plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing-transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

Materials. Literature methods were used for the preparation of PrF$_3$, KrF$_2$, F$_2$, CIF, $\text{F}_4$, ONF$_2$, and CIF$_2$, and for the drying of HF. Nitrogen trifluoride (Rochester), F$_3$ (Air Products), OF$_3$, (Allied Chemical), BrF$_3$, and BF$_3$ (Matheson), and AsF$_5$, SbF$_5$, and TiF$_5$ (Ozark Mahoning) were commercially available. Their purity was checked by vibrational spectroscopy prior to use and, where necessary, improved by fractional condensation or distillation.

Preparation of KrF$_3$BrF. Antimony pentfluoride (21.7 mmol) was syringed in the drybox into a preassembled Teflon FEP U-tube equipped with two stainless steel valves. The tube was connected to the vacuum line, and dry HF (5 ml of liquid) was distilled into the tube. The HF and SbF$_5$ were allowed to homogenize at ambient temperature. A wet sample of KrF$_2$ (22.9 mmol) was transferred under a dynamic vacuum into the U-tube at $-196^\circ$C. The mixture was warmed toward room temperature until a slight effervescence was noted. At this point the tube was cooled again, and the warmup procedure was repeated. After a total of three warm-up cycles, a second sample of KrF$_2$ was added to the tube and the reaction was allowed to proceed. After a period of 2 days at ambient temperature, the sample was transferred to a prepessivated quartz tube, and the HF was distilled off. The material contained a small amount of solid KrF$_3$BrF$_2$ (6.15 mmol), KrF$_3$ (2.9 mmol), and the sample was allowed to homogenize at $-196^\circ$C.

Reactions of HF with KrF$_3$ and SbF$_5$. A preassembled (with CIF$_2$) 10-ml stainless steel Hoke cylinder equipped with a $\frac{1}{4}$-in. valve and stainless steel valve was loaded on the vacuum line at $-196^\circ$C with KrF$_2$ (6.15 mmol), SbF$_5$ (3.07 mmol), and HF (21.9 mmol). The cylinder was placed in a liquid-N$_2$-dry-ice slush bath and allowed to warm slowly to room temperature over a 30-hour period and then was kept in an oven at 35 $^\circ$C for 4 days. The cylinder was cooled to $-210^\circ$C (N$_2$ slush bath, prepared by pumping on liquid N$_2$), and the volatile products were separated during warmup of the cylinder by fractional condensation through traps kept at $-156^\circ$C (nothing) and $-210^\circ$C (24.9 mmol of NF$_2$ and KrF$_3$). The white solid residue (827.6 mg = 2.97 mmol) was identified by infrared and Raman spectroscopy as pure NF$_2$,SbF$_5$ (19.7% yield based on SbF$_5$).

Reactions of NF$_2$ with KrF$_3$ and SbF$_5$. The reaction was carried out as described above for the corresponding AsF$_5$ system, except for a 40% reduction in the amount of starting materials used. The yield of solid NF$_2$,SbF$_5$ was 30.6% based on SbF$_5$.

Characterization of the solid KrF$_3$BrF$_2$. The solid KrF$_3$BrF$_2$ (2.42 mmol) was added in the drybox to a preassembled Teflon PFA U-tube (59 ml volume) equipped with Teflon FPA valves. The tube was connected to the vacuum line, and the NF$_2$ (2.43 mmol) was added at $-196^\circ$C. After 3 h at 22 $^\circ$C, the volatile products were analyzed. Analyses of the volatile material and of the solid residue showed that 12.7% of the KrF$_3$BrF$_2$ was recovered to an NF$_2$ salt.

When the reaction was repeated with 2.32 mmol of KrF$_3$BrF$_2$ and 6.84 mmol of NF$_2$ at 30 $^\circ$C for 3.5 h, the conversion of KrF$_3$BrF$_2$ to NF$_2$,SbF$_5$ was 43.8%. An additional treatment of the solid mixture of NF$_2$,SbF$_5$ and more NF$_2$ for 4 h at 30 $^\circ$C resulted in little further conversion to NF$_2$,SbF$_5$ salts. Vibrational spectra of the white solid product showed the presence of the NF$_2$, KrF$_{18}$ SbF$_{18}$, and SbF$_{18}$ ions.

<table>
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<th>Temperature $^\circ$C</th>
<th>Reaction time, h</th>
<th>Conversion of KrF$_3$BrF$_2$, %</th>
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<td>100</td>
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<td>-31</td>
<td>1:1</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>1:1</td>
<td>100</td>
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(20) Toberg, W. E., et al., unpublished results.
removed in vacuo at room temperature and separated by fractional condensation. It consists of the HF solvent and CIF₄ (2.1 M). The orange-yellow solid residue (0.91 g) was found by infrared and Raman spectroscopy to be an approximatively mixed CIF₄PtF₆ and CIF₄PtF₄⁵ (weight calculated for a mixture of 1.05 mmol of CIF₄PtF₆ and 1.05 mmol of CIF₄PtF₄ is 0.923 g).

When the reaction was repeated under the same conditions, except for replacing of BF₃ in place of CIF₄, no evidence for the formation of a stable BrF₅ salt was obtained.

Results

Syntheses and Some Properties of KrF₆-Lewis Acid Adducts. Although the synthesis of KrF₆-MF₆ (M = A₁, Sb) salts is well-known,⁴,¹⁰,¹¹,¹²,²² the reported direct combination of KrF₂ with the Lewis acids can result in a spontaneous exothermic decomposition of KrF₂ accompanied by a bright flash and gas evolution.¹³ In this study this problem was avoided by dissolving the Lewis acid in a large excess of anhydrous HF before adding a stoichiometric amount of KrF₂. This procedure resulted in an easily controllable, scalable, and quantitatively synthesis of the desired KrF₂-Lewis acid adducts.

Since the Raman spectra of solid KrF₆-MF₆ salts show many bands than expected for an isolated diatomic cation and an octahedral anion,¹⁸ we have recorded the Raman spectrum of KrF₆-SBF₆ in HF solution at −5 °C. The total number of bands was reduced to four, as expected for a diatomic KrF₂⁺ (610 cm⁻¹) and octahedral SBF₆⁻ (ν1(A1g) = 567, ν2(E₂g) = 278 cm⁻¹) characteristic for KrF₂⁺-xSBF₆ and a weak band at 779 cm⁻¹ due to ν2(A1g) of BF₄⁻.¹⁴ The bands expected for BF₄⁻ were difficult to observe under the given conditions due to their low relative intensity and the low signal to noise ratio. Removal of volatile material under a dynamic vacuum at −78 °C resulted in a white solid residue which, on the basis of its Raman spectrum (461 cm⁻¹) at −110 °C, consisted of KrF₂⁺.¹⁵ These results clearly show that KrF₂ does not form a stable solid adduct with BF₄⁻ at temperatures as low as −78 °C but that in HF solution, even at temperatures as high as −40 °C, ionization to [KrF₂⁺-xBF₄⁻][BF₄⁻] occurs. The observation of free BF₄⁻ is readily accounted for by the formation of krypton fluoride polycations, which leaves most of the BF₄⁻ uncomplexed. Whether any free KrF₂ is also present in the HF solution is difficult to say because the KrF₂ band coincides with the 462-cm⁻¹ band of KrF₂⁺-xBF₄⁻.¹⁶

Fluorination Reactions with KrF₂ Salts. The oxidative fluorination of NF₃ to NF₆⁺ by KrF₂ salts was first discovered by Art'yukhov and Khorochev and independently rediscovered in our laboratory. In our study, mixtures of NF₃, KrF₂, and either AsF₃ or BF₃ in molar ratios of 7:2:1 were allowed to warm in stainless steel cylinders from −196 to +50 °C under autogenous pressures of about 75 atm. In 2-day F₂, AsF₃, and NF₃, BF₃ had formed in 97 and 30% yield, respectively, based on the limiting reagents AsF₃ and BF₃, agreement with the equations

\[ \text{NF}_3 + \text{KrF}_2 + \text{AsF}_3 \rightarrow \text{NF}_6 \text{AsF}_3 + \text{Kr} \]

\[ \text{NF}_3 + \text{KrF}_2 + \text{BF}_3 \rightarrow \text{NF}_6 \text{BF}_3 + \text{Kr} \]

In the Russian study the reactions were carried out at room temperature either with solid KrF₂SBF₆ and 1 atm of NF₃, or in HF solution with stoichiometric amounts of KrF₂, NF₃, and one of the Lewis acids SBF₆, NbF₆, PF₃, TiF₆, and BF₃ at total pressures of 3–4 atm with reaction times of 1–3 h. On the basis of elemental analyses and vibrational spectra their products were assigned to NF₆⁺ salts of SBF₆⁺, NbF₆⁺, TiF₆⁺, and BF₆⁺, respectively.³³ We have repeated some of these reactions in our laboratory because for (NF₆)₂TiF₆ and NF₆SbF₆ the reported vibrational spectra were those of polyanions.¹⁷,²⁰ and no yields and concentration or temperature dependences were given that would help to shed some light on the possible mechanism of these reactions.

Our results for the reaction of solid KrFSbF₆ with NF₃, showed that indeed the NF₆⁺ cation is formed but that under the reported conditions the reaction is incomplete and that the NF₆⁺ salt is mainly NF₆SbF₆⁺ and not NF₆SbF₆. When the reaction of KrFSbF₆ mixtures or of preformed KrFSbF₆ with stoichiometric amounts of NF₃ was carried out, as previously reported, in HF solution at ambient temperature, the reaction was complete in less than 3 h. However, contrary to the previously reported elemental analysis but in agreement with the listed vibrational spectra,²³ the solid product consisted mainly of NF₆SbF₆⁺ (~90%) and not NF₆SbF₆. The formation of mainly NF₆SbF₆⁺ suggests that under these conditions the oxidation of NF₃ by KrFSbF₆ is not quantitative and that some KrFSbF₆ decomposes to Kr₃ and SbF₆ with the latter combining with NF₆SbF₆ to form NF₆SbF₆⁺. By lowering the reaction temperature, we succeeded in completely suppressing the formation of NF₆SbF₆⁺ and NF₆SbF₆ was obtained as the only product, contaminated by large amounts of unreacted KrFSbF₆. However, a quantitative oxidation of NF₃ by KrFSbF₆ according to

\[ \text{NF}_3 + \text{KrFSbF}_6 \rightarrow \text{NF}_6 \text{SbF}_6 + \text{Kr} \]

was accomplished by the use of a sufficient excess of NF₃. Since the concentration of NF₃ in the HF solution is proportional to the NF₃ pressure above the solution,²³ the excess of NF₃, required for a complete reaction can be minimized by using a small vial in the reactor. This results in a high NF₃ pressure and consequently in a high concentration of NF₃ in the HF solution. The results of a series of runs are summarized in Table I and demonstrate that, for example at −31 °C in HF solution at an NF₃ pressure of 1000 mm, NF₃ can quantitatively be oxidized by KrFSbF₆ to NF₆SbF₆ in less than 1 h.

In the absence of yield data in the previous report,²³ it was of interest to examine whether NF₆BF₃ can also be formed quantitatively under similar conditions. We found that an equimolar mixture of KrF₂, NF₃, and BF₃ in anhydrous HF, when allowed to warm slowly from −196 to +25 °C and kept at 25 °C for 3 h, resulted in only a 28.1% yield of pure NF₆BF₄. When the reaction was carried out at −78 °C for 3 h, the yield of NF₆BF₄ (7.1%) was, contrary to the NF₆BF₃ system, still appreciable. Without the use of HF as a solvent and at ambient pressure, no detectable amounts of NF₆BF₃ were obtained after 3 h at 25 °C. However, as stated above, the use of a sevenfold excess of NF₃ at 45 atm pressure and gentle heating to 53 °C for 4 days resulted in a 31% yield of NF₆BF₄.

In view of the known tendency of TiF₃ to form polyanions salts with (NF₆)₂TiF₆²⁸ and the fact that the vibrational bands


A-3
The NF₆PF₆ salt is a stable solid that shows spectra characteristic for tetrahedral NF₆⁺ and octahedral PF₆⁻.

It was shown that the known oxidative fluorination of CIF₄ to CIF₄⁺ with PtF₆⁺ can also be carried out at room temperature in HF solution without requiring UV irradiation:

\[ 2\text{CIF}_4 + 2\text{PtF}_6^- \xrightarrow{23^\circ \text{C}} \text{CIF}_4^+\text{PtF}_6^- + \text{CIF}_4\text{PtF}_6^- \]

However, attempts to prepare BrF₅⁺PtF₆⁻ in an analogous manner from BrF₅ and PtF₆ were unsuccessful.

Discussion

Syntheses of Coordinatively Saturated Fluoro Cations. At present, only three coordinatively saturated fluoro cations, i.e. NF₆⁺, CIF₄⁺, and BrF₅⁺, are known to exist. They can be prepared from the corresponding lower fluorides by one of the following three methods: (1) oxidation of KrF⁺ salts; (2) oxidation by PtF₆; (3) oxidation by F₂ in the presence of a strong Lewis acid and an activation energy source.

One of the goals of this study was to examine the scope of these methods. A priori one would expect that the ease of preparing a given coordinatively saturated fluoro cation should increase with increasing oxidizing power of the fluorinating agent and with decreasing oxidation potential of the desired coordinatively saturated fluoro cation. Although the oxidation potentials of the three coordinatively saturated fluoro cations are unknown, a comparison with those of either the isoelectronic fluorides CF₄, SF₆, and SeF₆, or the corresponding oxo anions in the same oxidation states, i.e. NO₃⁻, ClO₄⁻, and BrO₃⁻, suggest that the oxidation potentials should increase in the order NF₆⁺ < CIF₄⁺ < BrF₅⁺. As far as the order of oxidizing power of KrF⁺, PtF₆, and F₂ is concerned, Sokolov et al. have shown that KrF⁺ can oxidize PtF₆ to PtF₆⁺ and both KrF⁺ and PtF₆ are expected to be stronger oxidizers than mixtures of F₂ with Lewis acids. Therefore, the oxidizer strength should increase in the order F₂-Lewis acid < PtF₆ < KrF⁺.

The results of this study are in accord with these predictions. Thus, KrF⁺, the most powerful oxidizer, is capable of oxidizing all three substrates, NF₆, CIF₄, and BrF₅. The second strongest oxidizer, PtF₆, can still fluorinate NF₆ and CIF₄, whereas the weakest oxidizer, the Lewis acid-F₂ mixtures, can oxidize only NF₆. These results show that the preparative methods are transferable from one coordinatively saturated fluoro cation to another, provided that the oxidant is powerful enough to oxidize the substrate. Obviously, secondary effects such as the possibility of high activation energy barriers and competitive side reactions might also be important. For example, the activation energy sources used in the F₂-Lewis acid method can cause breakdown of CIF₄ and BrF₅ to F₂ and lower fluorides with the latter being continuously removed from the equilibrium by rapid complexing with the Lewis acid. For NF₆, such a side reaction is not effective, and the F₂-Lewis acid method is therefore well suited for the preparation of NF₆⁺ salts.

Formation Mechanisms of Coordinatively Saturated Fluoro Cations. Previous reports have concerned almost exclusively with the formation and decomposition mechanisms of NF₆⁺ salts, and several different mechanisms have been proposed. These include the heterolytic fission of fluorine (mechanism 1), the dissociation of NF₆AsF₆ to yield unstable mechanism 1.

\[ \text{NF}_6^+ + \text{F}^+ - \text{F}^- + \text{AsF}_6^+ \xrightarrow{\Delta} \text{NF}_6^+\text{AsF}_6 \]

\[ 2\text{NF}_6 + \text{F}^+ - \text{F}^- + \text{AsF}_6^+ \xrightarrow{\Delta} \text{NF}_6^+\text{AsF}_6 \]


NF₃ (mechanism II), the formation of an intermediate

\[ \text{NF₃} \rightarrow \text{[NF₃]} \]

mechanism II

strongly oxidizing Lewis acid–F radical (mechanism III),

\[
\begin{align*}
\text{F} + \text{NF₃} & \rightarrow \text{[NF₃]} + \text{AsF₆}^- \\
\text{[NF₃]} & \rightarrow \text{NF₃} + \text{F} \\
\end{align*}
\]

the formation of an intermediate NF₃ radical (mechanism IV), and the absorption and ionization of NF₃ on a KrF⁺MF₆⁻ mechanism

\[
\begin{align*}
\text{F} + \text{NF₃} & \rightarrow \text{[NF₃]} \\
\text{[NF₃]} + \text{AsF₆}^- & \rightarrow \text{NF₃} + \text{AsF₆}^- \\
\text{NF₃} + \text{AsF₆}^- & \rightarrow \text{NF₃} + \text{AsF₆}^- \\
\text{[NF₃]} & \rightarrow \text{NF₃} + \text{F} \\
\end{align*}
\]

from NF₃, F₂, and Lewis acids, the importance of the F₂ dissociation step and of NF₃ formation has previously been experimentally confirmed,[13] thus rendering mechanisms III and IV most likely. Of these two mechanisms, mechanism IV has previously been preferred by us because the formation and decomposition of NF₃⁺ salts were assumed to follow the same mechanism, and the decomposition of NF₃⁺AsF₆⁻ was suppressed more strongly by AsF₆⁻ than by NF₃⁺. However, recent ab initio molecular orbital calculations[14] have provided evidence for NF₃⁺ being energetically unfavorable, and the formation and decomposition of NF₃⁺ salts do not necessarily proceed by the same mechanism. These considerations prompted us to reconsider our previous preference.

The results of the present study confirm that NF₃⁺ salts can be formed from NF₃ and F₂–Lewis acid mixtures, KrF⁺ salts, or PtF₆. Furthermore, the fact that the reaction of KrF⁺ with NF₃ not only proceeds quantitatively but also proceeds at temperatures (31 to 45 °C) at which KrF⁺/AsF₆⁻ is completely sealed rules out a free-radical mechanism based on the decomposition of KrF₂ to Kr and F atoms and supports a radical mechanism for the KrF⁺–NF₃ reaction. In such an ionic mechanism, NF₃ is oxidized either to an intermediate NF₃⁺ radical cation or directly to NF₃⁺. In view of the quantitative yields of NF₃⁺ salts and our failure to obtain evidence for an intermediate NF₃⁺ radical cation in these KrF⁺ reactions by ESR spectroscopy, the direct fluorination to NF₃⁺ is preferred. One can easily envision an intermediate activated complex between the electrophilic KrF⁺ cation and the, albeit weak, electron donor NF₃, which could readily decompose to NF₃⁺ with Kr elimination.

For the reactions of NF₃ with F₂–Lewis acid mixtures the requirement for an activation energy source capable of dissociating F₂, the ESR evidence for the intermediate formation of the NF₃⁺ radical cation, and the unlikely formation of an NF₃⁺ radical favor free-radical mechanism III. For the thermal decomposition of NF₃⁺ salts which are derived from stable Lewis acids, mechanism H is preferred because it best explains the observed strong rate suppression by the Lewis acids. Even in the absence of experimental data it appears rather safe to propose for the PtF₆ oxidation reactions a one-electron transfer leading to NF₃⁺PtF₆⁻ as an intermediate, which is then further fluorinated by a second PtF₆ molecule to NF₃⁺. Such a mechanism is in accord with the rather low yields of NF₃⁺ salts obtained for the NF₃–PtF₆ system and has previously also been proposed for the CIF₃–PtF₆ system.[15]

Considering all the experimental evidence presently available for the formation mechanisms of coordinatively saturated complex fluoro cations, it appears that all reactions exhibit a certain commonality. The crucial step in all systems appears to be the reaction of a powerful one-electron (PtF₆ or Lewis acid–F) or two-electron (KrF⁺) oxidizer with the substrate (NF₃, CIF₃, or BrF₅) resulting in an electron transfer from the substrate to the oxidant, with a simultaneous (in the case of KrF⁺) or subsequent (in the case of PtF₆ and Lewis acid–F) fluorination of the intermediate radical cation (NF₃⁺, CIF₃⁺, BrF₅⁺) to give the final product (NF₃⁺, CIF₃⁺, BrF₅⁺). Thus, the mechanisms of the three presently known methods for the syntheses of NF₃⁺ salts might be written

Lewis acid–F₂ system

\[
\begin{align*}
\text{F}_2 & \rightarrow 2\text{F} \\
\text{F} + \text{NF₃} & \rightarrow \text{[NF₃]} \\
\text{AsF₆}⁻ + \text{NF₃} & \rightarrow \text{NF₃} + \text{AsF₆}⁻ \\
\text{NF₃} + \text{AsF₆}⁻ & \rightarrow \text{NF₃} + \text{AsF₆}⁻ \\
\text{[NF₃]} & \rightarrow \text{NF₃} + \text{F} \\
\end{align*}
\]

PtF₆ system

\[
\begin{align*}
\text{NF₃} + \text{PtF₆} & \rightarrow \text{NF₃} + \text{[PtF₆]} \\
\text{[NF₃]} + \text{PtF₆} & \rightarrow \text{NF₃} + \text{[PtF₆]} \\
\text{[PtF₆]} + \text{NF₃} & \rightarrow \text{NF₃} + \text{[PtF₆]} \\
\text{[PtF₆]} + \text{NF₃} & \rightarrow \text{NF₃} + \text{[PtF₆]} \\
\end{align*}
\]

KrF⁺ system

\[
\begin{align*}
\text{NF₃} + \text{[KrF⁺]} & \rightarrow \text{[KrF⁺–NF₃]} + \text{[KrF⁺–NF₃]} \\
\text{[KrF⁺–NF₃]} + \text{[KrF⁺–NF₃]} & \rightarrow \text{[KrF⁺–NF₃]} + \text{[KrF⁺–NF₃]} \\
\end{align*}
\]

As can be seen from these equations, an ionic oxidant (KrF⁺) results in an ionic mechanism and a radical oxidant (LAF or BrF₅) in a radical mechanism.

If in the Lewis acid–F₂ reactions the hard base NF₃ is replaced by a soft base, such as Xe, the reaction can proceed even in the absence of an activation energy source, as was demonstrated by Stein for the Xe–F₂–SbF₆ system.[17] Although XeF⁺ is not a coordinatively saturated cation, this reaction is most interesting. Contrary to the NF₃–F₂–Lewis acid reactions, it probably proceeds as a two-electron oxidation reaction by F₂ and therefore might be considered as the only presently known example of an actual heterolytic fission of fluorine by a Lewis acid and a Lewis base.[19]

The lower activation energy required for fluorinating Xe, compared to that for NF₃, is attributed mainly to its increased polarizability (i.e., it is a softer base) and to a lesser degree to the difference in their ionization potentials (IPF₂ = 13.0 eV, IPF₆ = 12.13 eV), because the hard base O₂ has an even lower IP of 12.06 eV but does not react with fluorine and a


\[\text{(36) Peppens, N. J. S., Allen, L. C., De Fries, D. J., Popple, J. A. to be submitted for publication}\]

\[\text{(37) Stein, L. J. Fluorine Chem. 1982, 20, 65}\]
Lewis acid in the absence of an activation energy source.

Conclusion. Although the present study has provided us with more insight into the formation reactions of coordinatively saturated complex fluoro cations, and particularly into those involving the use of KrF* salts as an oxidant, there is a definite need for more experimental and theoretical work in this field to further establish the mechanisms of these interesting reactions.

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Registry No. KrFSbF, 52708-44-8; SbF, 7783-70-2; NF, 7783-54-2; NF,AsF, 16871-75-3; BF, 7637-07-2; NF,BF, 15640-92-4; NF,SbF, 58702-89-9; PtF, 13693-05-3; NF,PtF, 90025-87-9; CIF, 13637-63-3; F, 7782-41-4; CIF,PtF, 38123-69-2; CIF,PtF, 36609-91-3; BrF, 7789-30-2; AsF, 7784-36-3.
SOME INTERESTING OBSERVATIONS IN CHLORINE OXYFLUORIDE CHEMISTRY

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SUMMARY

A new synthesis of $\text{FOC}_3$ was discovered involving the fluorination of $\text{ClO}_4^-$ with $\text{ClF}_6^+$. An unexpected oxygen abstraction from $\text{ClF}_4\text{O}^-$ was observed when $\text{CsClF}_4\text{O}$ was reacted with $\text{FOSO}_2\text{F}$.

INTRODUCTION

We would like to report two interesting reactions observed during our studies in the area of chlorine oxyfluorides. The first reaction involved the low-temperature metathesis of $\text{ClF}_6\text{AsF}_6$ with $\text{CsClO}_4$ in anhydrous HF solution. In view of the known $\text{NF}_4^+$ reaction (1)

$$\text{NF}_4\text{SbF}_6 + \text{CsClO}_4 \xrightarrow{\text{HF, } -45^\circ\text{C}} \text{CsSbF}_6 + \text{NF}_4\text{ClO}_4$$

$$\text{NF}_4\text{ClO}_4 \xrightarrow{25^\circ\text{C}} \text{NF}_3 + \text{FOC}_3$$

it was interesting to study whether $\text{ClF}_6^+$ is also capable of oxidizing $\text{ClO}_4^-$ to $\text{FOC}_3$. The thermal stability of $\text{ClF}_6\text{ClO}_4$ was found to be lower than that of $\text{NF}_4\text{ClO}_4$ (1) and did not permit the isolation of solid $\text{ClF}_6\text{ClO}_4$ even at temperatures as low as $-45^\circ\text{C}$. However, the corresponding decomposition products, $\text{FOC}_3$ and $\text{ClF}_5$, were observed in good yield.
Although this presents an alternative synthetic path to FOC1O₃, the NF₄⁺ reaction is preferred from a synthetic point of view since the NF₄SbF₆ starting material is more readily accessible [2].

The second reaction involved CsClF₄O and FOSO₂F. Fluorine fluorosulfate is known to be a useful reagent for the synthesis of hypofluorites [3], such as

$$\text{CsTeF}_5\text{O} + \text{FOSO}_2\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{TeF}_5\text{OF}$$

For CsClF₄O, however, the major reaction was not the formation of either the unknown ClF₄OF or its expected decomposition products, but oxygen abstraction accompanied by SO₂F₂ elimination according to the following reaction.

$$\text{CsClF}_4\text{O} + \text{FOSO}_2\text{F} \rightarrow \text{CsClF}_4 + \text{SO}_2\text{F}_2 + \text{O}_2$$

This unexpected reaction path might be rationalized in terms of an addition of FOSO₂F to the Cl=O bond in one of the favored resonance structures of ClF₄O⁻[4], followed by an intramolecular nucleophilic substitution (S_N¹) reaction accompanied by O₂ and SO₂F₂ elimination:

![Chemical Reaction Diagram]

To our knowledge, this is the first example of a reaction in which FOSO₂F acts as a deoxygenating agent.
EXPERIMENTAL

**Apparatus** Volatile materials were handled in a stainless steel-Teflon FEP vacuum line [5]. The line and other hardware used were well passivated with ClF₃ and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution using a previously described apparatus [6].

Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer. Spectra of solids were obtained using dry powders pressed between AgCl windows. Spectra of gases were obtained by using a Teflon cell of 5 cm path length equipped with AgCl windows. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar-ion laser.

**Materials** Literature methods were used for the syntheses of ClF₆AsF₆[7], CsClF₄O[8] and FOSO₂F[9] and for the drying of the HF solvent [10]. The CsClO₄ (ROC/RIC) was used as received.

**Reaction of ClF₆AsF₆ with CsClO₄** In the drybox ClF₆AsF₆ (0.318 mmol) and CsClO₄ (0.304 mmol) were placed into the bottom U-tube of the metathesis apparatus [6]. On the vacuum line, dry HF (1.1 ml of liquid) was added at -78°C. The resulting mixture was agitated at -45°C for 1.5 hr and then filtered at -78°C through a porous Teflon filter while the filtrate was collected at -45°C. All material volatile at -45°C was pumped off for 2.5 hr and separated by fractional condensation through a series of traps kept at -126, -142 and -196°C. The -126°C trap contained the HF solvent and a small amount of FClO₂, the -142°C trap contained a mixture of FClO₃ and ClF₅ (0.445 mmol), and the -196°C trap contained FClO₃ (0.128 mmol). Essentially no filtrate residue was left behind. The white solid filter cake (106 mg, weight calcd for 0.304 mmol of CsAsF₆ 98 mg) was identified by infrared and Raman spectroscopy as CsAsF₆. The FClO₃ formed in the above reaction is attributed to decomposition of a small amount of FClO₃. For a larger scale reaction, the percentage of FClO₃ in the product is expected to decrease significantly.
Caution! Fluorine perchlorate is highly shock sensitive [11] and proper safety precautions must be taken when working with this material.

Reaction of CsClF₄O with FOSO₂F In the dry box CsClF₄O (2.24 mmol) was placed into a 10 ml stainless steel cylinder. On the vacuum line FOSO₂F (4.97 mmol) was added to the cylinder at -196°C. The cylinder was kept at 0°C for 3 days, then cooled to -196°C. Oxygen (2.23 mmol) was pumped off at -196°C, and all material volatile at ambient temperature was separated by fractional condensation through traps kept at -112, -142, and -196°C. The -112°C trap contained small amounts of ClF₃O, FCIO₂, and ClF₃. The -142°C trap contained FOSO₂F (2.6 mmol) and SO₂F₂ (1.7 mmol), and the -196°C trap showed SO₂F₂ (0.52 mmol). The white solid residue showed a weight loss of 39 mg (calcd weight loss for 1.12 mmol of O₂ 36 mg) and was identified by infrared and Raman spectroscopy as CsClF₄ [12] containing a small amount of CsSO₃F.

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Structure and Vibrational Spectra of Oxonium Hexafluoroarsenates(V) and Antimonates(V)

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The salts OD$_4$AsF$_6$, OD$_3$SbF$_6$, and partially deuterated OH$_3$SbF$_6$ were prepared and characterized by X-ray and neutron diffraction techniques, DSC measurements, and vibrational spectroscopy. At room temperature, OH$_3$SbF$_6$ exists in a plastic phase where ions, centered on the atomic positions of the NaCl structure, are in motion or oscillation. No valuable information on atomic distances or angles in OH$_3$SbF$_6$ could be obtained due to these dynamic structural disorder problems. For OH$_3$SbF$_6$ the phase transition from an ordered to a disordered phase was shown to occur above room temperature. The room-temperature phase can be described by an ordered hydrogen-bonded model based on a CsCl type structure. Vibrational spectra were recorded for these oxonium salts and confirm the presence of the different phases and phase transitions. Improved assignments are given for the OH$_3$ and OD$_3$ cations, and the OH–FM bridge stretching mode and some of the bands characteristic for OD$_3$ and ODH$_2$ were identified. A modified valence force field was calculated for OH$_3$*, which is in good agreement with the known general valence force field of inorganic NH$_3$ and values obtained by ab initio calculations. From the OH–FM stretching mode, the hydrogen-bond bridge strength was found to be 1.77 kcal mol$^{-1}$.

Introduction

Although the existence of oxonium salts at low temperature had been well known for many years, the synthesis of surprisingly stable OH$_3$* salts containing the AsF$_6$ and SbF$_6$- anions has been reported only in 1975. Since then, numerous papers have been published on other OH$_3$* salts containing complex fluoro anions such as UF$_6$*, BiF$_6$*, IrF$_6$*, PF$_6$*, RuF$_6$*, TiF$_6$*, or BF$_6$*. In these oxonium salts the cations and anions are strongly hydrogen bonded, as shown by the short O–F distances of 2.51–2.61 Å found by X-ray diffraction studies. Since the nature of these hydrogen bridges is strongly temperature dependent, these oxonium salts show phase transitions and present interesting structural problems. In this paper we report unpublished results accumulated during the past 8 years in our laboratories for these oxonium salts.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF and HF or DF) Monel Teflon SEP vacuum system. Nonvolatile materials were handled separated in a well-passivated (with Teflon FEP vacuum system.) Nonvolatile materials were handled separated in a glovebox. Hydrogen fluoride (99.6%, Matheson Co.) was dried in the dry-nitrogen atmosphere of a glovebox. Hydrogen fluoride (Matheson Co.) was dried by storage over BiF$_3$. SbF$_6$ and AsF$_6$ (Ozark Mahoning Co.) were purified by distillation and fractional condensation, respectively, and DF (Ozark Mahoning Co.) and D$_2$O (99.6%, Volk) were used as received. Literature methods were used for the preparation of OD$_4$AsF$_6$, OD$_3$SbF$_6$, and OD$_2$HAsF$_6$. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). For low-temperature spectra, the pressed silver halide disks were placed in a copper block cooled to −196 °C with liquid N$_2$ and mounted in an evacuated 10-cm path length cell equipped with Cu1 windows.

Raman spectra were recorded on a Cary Model 83 spectrophoto-}
Oxonium Hexafluorarsenates(V) and -antimonates(V)

with a syringe. The mixture was agitated for several hours at 25 °C, and all material volatile at 45 °C was pumped off for 1 h. The white solid residue (21.987 g; weight calculated for 84.63 mmol of OD·SbF₃·21.813 g) was identified by spectroscopic methods as mainly OD·SbF₃ containing a small amount (less than 1%) of OD₂H·SbF₄.

Preparation of Partially Deuterated OH·SbF₄. A sample of OH·SbF₄ (2.0016 g; 7.857 mmol) was dissolved in liquid DF (2.012 g; 95.81 mmol) in a Teflon sample for 1 h. All volatile material was pumped off at 45 °C for 3 h, leaving behind a white solid residue (2.020 g; weight calculated for 7.857 mmol of OD₂·SbF₄·20.2522 g) that on the basis of its vibrational spectra showed about equimolar amounts of OD₂ and OD·SbF₄ and smaller amounts of OD·SbF₄·(calculation: statistical product distribution for 19.76% H and 80.24% D (mol%): OD₂·51.68; OD·H*·38.16; OD·H+·9.33; OH·H+·0.77).

Results and Discussion

Synthesis and Properties of Deuterated Oxonium Salts. The OD₂ salts were prepared by the same method as previously reported for the corresponding OH·H+ salts, except for replacing H₂O and HF by D₂O and DF, respectively.

\[ \text{D}_2\text{O} + \text{DF} + \text{MF}_3 \xrightarrow{\text{DF}} \text{OD}_2\text{MF}_6 \quad \text{M} = \text{As}, \text{Sb} \]

The yields are quantitative, and the samples were almost completely deuterated. The small amounts of OD·H+ observed in the infrared spectra and to a lesser degree in the Raman spectra of the products (see below) are attributed to small amounts (0.6%) of H₂O in the D₂O starting material and to exchange with traces of moisture during the preparation of the IR samples. A partially deuterated sample of OH·SbF₄ was prepared by treating solid OH·SbF₄ with an excess of DF.

\[ \text{OH}_2\text{SbF}_6 + n\text{DF} \rightarrow \text{OH}_2\text{D}_2\text{SbF}_6 + n\text{HF} \]

The exchange appeared to be fast, and the product exhibited the correct statistical OD₂, OD·H+, OD·H+, and OH+ distribution based on the H/D ratio of the starting materials. As expected, the physical properties of the deuterated oxonium salts were practically identical with those of the corresponding OH·H+ salts.

DSC Data. Since the neutron and X-ray diffraction data suggested (see below) that at room temperature OH·SbF₄ is ordered whereas OH·AsF₄ exists in a plastic phase, low-temperature DSC data were recorded to locate the corresponding phase change points.

The OD·AsF₄ salt exhibited on warm-up from −90 °C a large endothermic phase change at 2.5 °C that was shown to be reversible, occurring at −7.5 °C on cooling. For OH·AsF₄ this phase change was observed only at very low temperatures. No other endotherms or exotherms were observed between −90 °C and the onset of irreversible decomposition. The observed phase-change temperatures are in excellent agreement with those found by low-temperature Raman spectroscopy (see below).

For OH·SbF₄ three small endotherms at 20, 49, and 81 °C and a large endothermic phase change at 100 °C were observed on warming. All of these were reversible, occurring at 19, 42, 77, and 96 °C, respectively, on cooling. For OD·SbF₄ the corresponding changes were observed at 20, 48, 82, and 100 °C on warming and 20, 43, 74, and 75 °C on cooling. Again no other heat effects were observed in the temperature range. The temperature differences observed for phase changes between the heating and cooling data are attributed to hysteresis, which normally is a problem in salts of this type. The smaller heat effects observed for OH·SbF₄ below the major order–disorder phase transition may be attributed to damping of rotational motions of the ions, similar to those found for O₂AsF₄.

For OH·BiF₄ no phase transitions were observed between −90 °C and the onset of decomposition.

Structural Studies

OH·AsF₄. As previously reported, this compound is cubic at room temperature, and a cell parameter of 8.043 (8) Å was found in this study from X-ray powder data. It exhibits only one phase transition at −2 ± 5 °C (based on DSC and Raman data) in the temperature range from −90 °C to its decomposition point. The X-ray powder pattern at −153 °C is given in Table I and indicates a lowering of the symmetry in agreement with the low-temperature vibrational spectra (see below). Attempts to index the pattern were unsuccessful. It is interesting to compare X-ray powder diffraction patterns of OH·AsF₄ and O₂AsF₄. Whereas their room-temperature patterns and cell parameters are for practical purposes identical, their low-temperature patterns (Table I and ref 19) are very distinct due to different ion motion freezing. Since OH·H+, OD·H+, and O₂+ are weak X-ray scatterers, but contribute strongly to the neutron scattering, neutron diffraction powder patterns were also recorded at room temperature for their AsF₄ salts (see Table II). As expected, the cell dimensions were for practical purposes identical, but the observed relative intensities were very different.

Attempts were made to obtain structural information from the room-temperature neutron diffraction powder patterns of OH·AsF₄.

Table I. X-ray Diffraction Powder Pattern of OH·AsF₄ at −153 °C

<table>
<thead>
<tr>
<th>hkl</th>
<th>d_{obsd} Å</th>
<th>Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>obsd</td>
<td>Intensities</td>
</tr>
<tr>
<td></td>
<td>6.35</td>
<td>2.024</td>
</tr>
<tr>
<td></td>
<td>4.95</td>
<td>2.010</td>
</tr>
<tr>
<td></td>
<td>4.72</td>
<td>1.942</td>
</tr>
<tr>
<td></td>
<td>4.12</td>
<td>1.913</td>
</tr>
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<td></td>
<td>3.87</td>
<td>1.877</td>
</tr>
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<td></td>
<td>3.749</td>
<td>1.871</td>
</tr>
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<td>3.730</td>
<td>1.802</td>
</tr>
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<td>3.473</td>
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<td></td>
</tr>
<tr>
<td>3.225</td>
<td>1.769</td>
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</tr>
<tr>
<td>3.163</td>
<td>1.739</td>
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</tr>
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<td>3.029</td>
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</tr>
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<td>2.845</td>
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<td>2.837</td>
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</tr>
<tr>
<td>2.596</td>
<td>1.648</td>
<td></td>
</tr>
<tr>
<td>2.530</td>
<td>1.612</td>
<td></td>
</tr>
<tr>
<td>2.362</td>
<td>1.585</td>
<td></td>
</tr>
<tr>
<td>2.139</td>
<td>1.581</td>
<td></td>
</tr>
<tr>
<td>2.061</td>
<td>1.545</td>
<td></td>
</tr>
<tr>
<td>2.035</td>
<td>1.515</td>
<td></td>
</tr>
</tbody>
</table>

* Cu Kα radiation and Ni filter.

Table II. Neutron Diffraction Powder Patterns of the Face-Centered Cubic, Room-Temperature Phases of OH·AsF₄, OD·AsF₄, and O₂AsF₄

<table>
<thead>
<tr>
<th>hkl</th>
<th>d_{obsd} Å</th>
<th>Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td>311</td>
<td>137</td>
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<td></td>
<td>422</td>
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<td></td>
<td>222</td>
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<td></td>
<td>331</td>
<td>5</td>
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<tr>
<td>420</td>
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<td></td>
</tr>
<tr>
<td>422</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>511</td>
<td>333</td>
<td></td>
</tr>
</tbody>
</table>

* Intensities in arbitrary units.


(19) Naulin, C.; Bougon, R. J. Chem. Phys. 1976, 64, 4155
OH₃AsF₆ and OD₂AsF₆. It was shown that the unit cell is indeed face-centered cubic and that an alternate solution, a primitive cubic CaF₂ structure, can be ruled out for both compounds. The number of observed peaks is rather small, but the respective intensities due to the substitution of hydrogen by deuterium (scattering lengths b₀ = -0.374 and b₁ = 0.667) are very different (Table II). The rapid vanishing of intensities at large diffraction angles and the presence of a bump in the background level implying a short distance order are characteristic of plastic phases with ions in motion. The only models that could be tested to describe such a motion have been tried successively. The first one is a disordered model with statistical occupancy factors for fluorine atoms and hydrogen atoms in the Fm3 symmetry group. This corresponds to four equivalent positions of the octahedra around the fourfold axes, and to eight positions for the OH⁺ ion. With use of the intensities observed for OH₃AsF₆, the solution refines to R = 0.047 but is not considered acceptable because the resulting distances As-F = 1.58 Å and O-H = 0.82 Å are too short when compared to As-F = 1.719 (3) Å in KAsF₆²⁰ and O-H = 1.011 (8) Å in OH⁺p-CH₃C₆H₄SO₃.²¹

The second one is a rotating model that places As at the 0, 0, 0 position connected to fluorines by a complex term

\[ b₀ + b₁ \sin(\theta) / \lambda \]

and O at the 1/2, 1/2, 1/2 position connected to H atoms by

\[ b₀ + 3b₁ \sin(\theta) / \lambda \]

where b₀, b₁, b₂, and b₃ are the scattering lengths of As, F, O, and H, respectively. The As-F distance, r₃, and the O-H distance, r₄, are the only unknowns with the scale factor of the structure.²² The best results (R = 0.059) are obtained with the combination As-F = 1.59 Å and O-H = 0.81 Å, not so different indeed from the first model.

For OD₂AsF₆, the second model gives more plausible distances, As-F = 1.65 Å and O-D = 1.01 Å with R = 0.054, if the intensity of the 200 reflections is arbitrarily lowered by 20%, with the excessive intensity being assumed to be due to preferential orientation.

On the basis of the short distances found for OH₃AsF₆, we can consider that the real structure is probably not properly accounted for by either one of the models, due to the motion of the ions, which is not correctly simulated as for other plastic phases.

OH₃SbF₆. On the basis of the DSC data (see above), the transition from an ordered to a disordered phase occurs at 88 ± 12 °C. The existence of an ordered phase at room temperature for OH₃SbF₆ and its deuterated analogues was confirmed by the diffractometric studies. The X-ray powder diffraction pattern, which originally had been read backwards due to very intense back-reflections and indexed incorrectly as tetragonal, is listed in Table III. By analogy with a large class of other MFe₆ compounds such as O₃PbF₆,²³ and O₅SbF₆,²⁴ the OH₃SbF₆ pattern can be indexed for a cubic unit cell with a = 10.143 (3) Å (CEN) data or 10.090 Å (Rockefeller data). The cell dimensions were confirmed by the neutron diffraction data (see below) that resulted in a = 10.090 Å. Although all of the observed X-ray reflections obey the conditions (h + k + l = 2n and k+l = 2n) for space group Pm3, the neutron diffraction data (see below) suggest a lower symmetry subgroup such as I2/3. In the following paragraphs the results obtained for the ordered cubic, room-temperature phase of OH₃SbF₆ are discussed in more detail.

Single-Crystal X-ray Study. The OH₃SbF₆ single crystal had the approximate dimensions 0.46 x 0.35 x 0.22 mm and was sealed in a Pyrex capillary. Preliminary cell dimensions were obtained from Weissenberg and precession photographs. The final value for the unit cell parameter was determined from the optimized counterangles for zero-layer reflections on a Stoe Weissenberg diffractometer. The data were collected for layers 0kl to 6kl of the aligned pseudotetragonal cell, using the Stoe Stadi-2 diffractometer, in the four quadrants h, k, ±l, and an ω-scan technique with graphite-monochromated Mo Kα radiation. The intensities of reflections with 0.086 < (sin θ)/λ < 0.702 Å⁻¹ were collected and a total of 719 reflections obtained with I/σ(I) > 3. Check reflections were monitored during the data collection of each layer, and no deterioration of the crystal was indicated. Lorentz and polarization corrections were made to the data set.

The program system SHELX²⁵ was used to solve the structure. Neutral scattering factors were used with anomalous dispersion corrections. Three cycles of least-squares refinement with anisotropy at (1/2, 1/2, 1/2) in the space group Pm3 gave an R factor of 0.27. The Fourier difference map located a 9 e Å⁻³ peak, assumed to be oxygen, on the position (1/8, 1/8, 1/8), with two sets of possible fluorine octahedra each at 1.90 Å from Sb. Three cycles of refinement with the oxygen atom included reduced the R factor to 0.22. The inclusion of either of the sets of F atoms about Sb, with all atoms refining isotropically, resulted in a reduced R factor of 0.13, however, the refinement cycles moved the F atoms to 2.0 Å from Sb. The inclusion of fluorine atoms also resulted in a more complex difference Fourier map, with several peaks at 3 Å⁻¹ remaining. The alternate fluorine atom positions indicated were refined in partially occupied sites, initially adjusting the site occupation factors and then their temperature factors. The resultant R factor of 0.12 was not significantly less than with either ordered structure; one of the partial fluorine atoms refined to a position

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(22) a,b, program written by G. Langlet.


Oxonium Hexafluorarsenates(V) and -antimonates(V)

Table IV. Final Atomic Positional and Thermal Parameters (with ESD's in Parentheses) for OH\(_2\)Sb\(_F_6\) from X-ray Data

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(_{11})</th>
<th>U(_{22})</th>
<th>U(_{33})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0205 (18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.043 (17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.4334</td>
<td>0.6444</td>
<td>0.6021</td>
<td>0.059 (13)</td>
<td>0.158 (12)</td>
<td>0.003 (12)</td>
</tr>
<tr>
<td>H</td>
<td>not located</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table V. X-ray and Neutron Powder Patterns of OD\(_2\)Sb\(_F_6\) at Room Temperature

<table>
<thead>
<tr>
<th>hkl</th>
<th>X-ray</th>
<th>neutron</th>
<th>hkl</th>
<th>X-ray</th>
<th>neutron</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>100</td>
<td>6</td>
<td>450</td>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>211</td>
<td>2</td>
<td>640</td>
<td>440</td>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>222</td>
<td>3</td>
<td>642</td>
<td>440</td>
<td>21</td>
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<td>13</td>
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<tr>
<td>422</td>
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<td>440</td>
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<td>13</td>
</tr>
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<td>822</td>
<td>440</td>
<td>21</td>
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<tr>
<td>470</td>
<td>3</td>
<td>900</td>
<td>440</td>
<td>21</td>
<td>13</td>
</tr>
</tbody>
</table>

2.2 Å from Sb, and further possible fluorine sites appeared in the Fourier map. Refinement of various models with either ordered fluorine atoms or disordered atoms constrained to be 1.86 (3) Å from antimony did not improve the R factor or the residual Fourier map. Accordingly, the F atom parameters given in Table IV represent an ordered solution in 1a3; the actual F atom chosen was that which remained at the expected distance from antimony during the various trial refinements. This represents an incomplete solution, as there are residual peaks at Sb-F distances in the final Fourier difference map. This is reflected in the structure factors, where agreement between |F1| and |F2| is good for even, even reflections with dominant contributions by the antimony and oxygen atoms but poor for odd, odd, even reflections, which are dependent only upon the fluorine (and hydrogen) atom parameters. Final residual indices for 155 unique reflections are |R| = 0.119 and |R\(_e\)| = 0.131.

Neutron Powder Diffraction Study. For OD\(_2\)Sb\(_F_6\), 46 reflections were observed (see Figure 1) out of which 4 could not be indexed on the basis of the cubic cell and are attributed to an unidentified impurity (mainly lines at 3.26, 2.235, and 2.225 Å). The list of observed reflections is given in Table V in comparison with X-ray data. The cell parameter is 10.116 (6) Å.

The Rietveld program for profile refinement\(^{24}\) was used to solve the structure. The first refinement was attempted in the 1a3 space group starting from the X-ray values for Sb, O, and F and adding approximate values for D, with the OD\(_3^+\) ion being disordered on two equivalent positions (occupancy factor 1/2 of general positions x, y, z). The system refined to |R| = 0.135 with the following parameters:

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B, Å(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.94 (25)</td>
</tr>
<tr>
<td>O</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.35 (12)</td>
</tr>
<tr>
<td>F</td>
<td>0.441 (6)</td>
<td>0.604 (6)</td>
<td>0.641 (7)</td>
<td>2.88 (13)</td>
</tr>
<tr>
<td>D</td>
<td>0.300 (1)</td>
<td>0.317 (1)</td>
<td>0.204 (1)</td>
<td>2.98 (27)</td>
</tr>
</tbody>
</table>

The y and z coordinates of the fluorine atom have been permuted, probably due to the choice of the coordinates of deuterium. The atomic distances and angles are then

<table>
<thead>
<tr>
<th>dist, Å</th>
<th>angle, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb-F</td>
<td>1.87</td>
</tr>
<tr>
<td>O-F</td>
<td>2.67</td>
</tr>
</tbody>
</table>

which compare relatively well with the X-ray values of Table IV. At this stage, our attention was drawn to the presence of a weak but well-isolated line at an angle \(\theta\) high enough not to be attributed to the impurity. This line corresponded to a 730 reflection, a forbidden reflection in the space group 1a3 (hk0; h, k = 2n). In view of a similar observation for the cubic phase of K\(_2\)Sb\(_F_6\) (II) (in this case the 310 reflection),\(^{27}\) the trouble with locating the fluorine atoms by difference X-ray syntheses, and mainly the incompatibility of the group 1a3 with the observed Raman and IR spectra (see below), we considered the possibility of an ordered structure in a subgroup of the 1a3 space group, first the noncentrosymmetric f2,3 space group (No. 199).

Since the symmetry center does not exist anymore, the local symmetry of the Sb and O atoms is then only a threelfold axis. The structure has to be described with two sets of fluorine atoms F1 and F2, and the oxonium ion is ordered with a full

---


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The neutron model was tested against the X-ray data for the ODCHrCH 3 compound. The geometry of the ODCHrCH 3 cation is conﬁrmed with the Raman and IR spectra. Although many papers have been presented are approximately located at 0, 0, 0 and 1/2, 1/2, 1/2 along the [1, 1, 1] direction and bring the environment to an plastic phase. Such a phase may however exist at higher temperatures and explains the phase changes observed before the decomposition point. To obtain more information on the motions of the ions in the different phases, additional experimental data such as second moment and relaxation time NMR measurements are required.

As far as the exact geometry of the ODCHrCH 3 cation is concerned, it must be pointed out that the precision of the results obtained from the powder diffraction data is not very high and that the final values depend on the starting points used for the different refinements. Thus, the O–H distance was found to vary from 0.91 to 1.05 Å, with the ODO angle varying from 116° to 92°. The correct values certainly lie between these extreme values. This is also reﬂected by the higher thermal parameters found for the deuterium and oxygen positions (see above), indicating high thermal motion of the ODCHrCH 3 cation itself. For the O–H bond length in ODCHrCH 3, a lower limit of 0.97 Å appears more realistic for the following reasons: The bond length in free OH 2 is already 0.96 Å, and both the hydrogen–ﬂuorine bridging and the increased O–H=O 2+ polarity of the O–H bond in OH 2 SbF 6 are expected to increase the O–H bond length. This bond weakening in OH 2 is when compared to free OH 2 is also supported by the force constant calculations given below. The most likely range of the O–H bond length in these OH 2 SbF 6 salts is therefore 0.98–1.05 Å, which is in excellent agreement with the values of 1.013 (8), 1.020 (3), and 0.994 (5) Å previously found for OH 2 CH 2 HOCH 2 , 21 ODCH 2 CH 3 CH 2 OH, 25 and ODCH 2 CH 3 CH 2 OH, 25 respectively, by neutron diffraction and values of 1.01–1.04 Å for OH 2 NO 2 and OH 2 CI 2 O 2 , derived from wide-line NMR measurements. 26

The value of 1.19 Å, previously reported 4 for the O–H bond length in OH 2 SbF 6 , is based on X-ray data and therefore is deemed unreliable. It should be pointed out that the OH–F distances in OH 2 SbF 6 and ODCH 2 AsF 6 are practically identical (2.60 Å). This suggests that r0–H and r0–D in these two compounds should also be similar.

The neutron model was tested against the X-ray data for OH 2 SbF 6 , but there was no improvement in the reﬁnement or the appearance of the Fourier difference map. Vibrational Spectra. Although many papers have been published on the vibrational spectra and force ﬁeld of the

The interesting point of this structure is the existence of an ordered solution for all atoms with a scheme of hydrogen bonding that prevents at room temperature the existence of

occupation of deuterium atoms on the general positions. The Sb and O atoms are also allowed to move along the threefold axes from their ideal positions (0, 0, 0; 1/3, 1/3, 1/3). This hypothesis was tested and led to a better R factor (0.106) with the following parameters:

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B. Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>-0.012(1)</td>
<td>-0.012(1)</td>
<td>-0.012(1)</td>
<td>0.13(0.38)</td>
</tr>
<tr>
<td>O</td>
<td>0.238(3)</td>
<td>0.238(3)</td>
<td>0.238(3)</td>
<td>3.50(0.75)</td>
</tr>
<tr>
<td>F</td>
<td>0.044(1)</td>
<td>-0.118(1)</td>
<td>-0.143(2)</td>
<td>1.26(0.42)</td>
</tr>
<tr>
<td>F'</td>
<td>-0.75(2)</td>
<td>0.091(1)</td>
<td>0.137(2)</td>
<td>1.89(0.45)</td>
</tr>
<tr>
<td>D</td>
<td>0.199(2)</td>
<td>0.184(1)</td>
<td>0.299(1)</td>
<td>3.40(0.30)</td>
</tr>
</tbody>
</table>

Figure 1 gives the resulting proﬁle of observed and calculated neutron diffraction diagrams and shows satisfactory agreement.

The Sb and O atoms are displaced from their ideal positions by 0.21 Å and the environment of the Sb atom has 3 F atoms at 1.80 Å and 3 F atoms at 1.94 Å, which seems to be compatible with the Raman and IR spectra.

The F 2 atoms are closer to the oxygen atom of the oxonium group than the F 3 atoms with F 2–O = 2.60 Å and F 3–O = 2.79 Å. The F 2–O distance is within the correct range for a strong OD–F hydrogen bridge bond (2.51–2.56 Å in OH 2 TiF 4 and 2.58–2.61 Å in OH 2 BF 4). 25

The deuterium atoms are located at 0.91 Å from the oxygen atom (with a D–D distance of 1.54 Å and a DOD angle of 116°) on the line O–F 2 (OD + DF = 0.91 + 1.69 = 2.60 Å). This conﬁrms, in the precision of our results, the quasi-linearity of the O–D–F bond in this compound. The geometry of the ODCHrCH 3 cation itself is a ﬂat pyramid with C 3 symmetry. The oxygen atom lies 0.18 Å out of the plane of the three deuterium atoms.

Figure 2 illustrates the environment around the oxonium ion, with the F 2 atoms being differentiated from the F 3 atoms by traces of the ellipses. The two SbF 6 octahedra fully represented are approximately located at 0, 0, 0 and 1/2, 1/2, 1/2 along the [1, 1, 1] direction and bring the environment to an icosahedron. The distinction between F 1 and F 2 implies a small displacement of the ﬂuorine atoms from their average positions obtained in the Ia3 space group (F–F or F–F distances are about 0.20 Å), but the angular distorsion of the octahedron is small, one side being ﬂattened and the other one being elongated. To obtain a reﬁnement in the F 2,3 symmetry group, we had to allow the existence of antiphase domains without local symmetry centers, but which are images of each other.
Oxonium Hexafluoroarsenates(V) and -antimonates(V)

Figure 3. Vibrational spectra of solid OD$_2$AsF$_6$ at room temperature: trace A, infrared spectrum of the solid pressed between AgCl disks (broken line indicates absorption due to the window material; bands marked by an asterisk are due to OD$_2$H$^+$ mainly formed during sample handling); traces B and C, Raman spectra recorded at two different sensitivities with a spectral slit width of 3 and 8 cm$^{-1}$, respectively.

Figure 4. Vibrational spectra of solid OD$_2$AsF$_6$ at low temperature: trace A, infrared spectrum of the solid pressed between AgCl disks and recorded at -196 °C; traces B and C, Raman spectra recorded at -100 °C at two different sensitivities.

oxonium ion,\textsuperscript{42,43,45} many discrepancies exist among these data. Frequently, the infrared bands observed for the stretching modes are very broad and overlap and are complicated by Fermi resonance with combination bands. Also, the smooth transition from highly ionic OH$_2^+$ salts to proton-transfer complexes and the interpretation of some of the

Figure 5. Raman spectra of OD$_2$SbF$_6$ and OD$_2$AsF$_6$ at different temperatures contrasting the slow gradual temperature induced line broadening for the ordered OD$_2$SbF$_6$ phase against the abrupt change within a narrow temperature range for OD$_2$AsF$_6$ caused by the transition from an ordered to a plastic phase.

Figure 6. Vibrational spectra of solid OD$_2$SbF$_6$, OH$_2$SbF$_6$, and partially deuterated OH$_2$SbF$_6$ at room temperature: trace A, IR spectrum of OH$_2$SbF$_6$; trace B, IR spectrum of partially deuterated OH$_2$SbF$_6$ containing about equimolar amounts of OD$_2$SbF$_6$ and OD$_2$HsBF$_6$ and smaller amounts of OD$_2$SbF$_6$; trace C, IR spectrum of OD$_2$SbF$_6$ containing a significant amount of OD$_2$HsBF$_6$ formed during sample handling; trace D, IR spectrum of OD$_2$SbF$_6$ containing only a small amount of OD$_2$HsBF$_6$; traces E and F, Raman spectra of OD$_2$SbF$_6$ recorded at two different sensitivities.

more weakly ionized proton-transfer complexes in terms of discrete OH$_2^+$ salts may have significantly contributed to the

\textsuperscript{35} Millen, D. J.; Vasil, E. G. J. Chem. Soc. 1954, 2913.
\textsuperscript{39} Ferraro, J. R.; Williams, J. M.; La Bonville, P. Appl. Spectrosc. 1974, 28, 379.
\textsuperscript{40} Huong, P. V.; Desbat, B. J. Raman Spectrosc. 1974, 2, 373.
\textsuperscript{44} Desbat, B.; Huong, P. V. Spectrochim. Acta, Part A 1975, 31, 1109.
The observed infrared and Raman spectra and the more important frequencies are given in Figures 3-7 and Table VI.

**Room-Temperature Spectra of OD₃AsF₆**

Figure 3 shows the room-temperature spectra of solid OD₃AsF₆. As can be seen, the bands are broad and show no splittings or asymmetry as expected for ions undergoing rapid motion in a plastic phase.³⁸ On the basis of their relative infrared and Raman intensities, the band at about 2450 cm⁻¹ can be assigned with confidence to the antisymmetric OD₃* stretching mode ν₁(OD₃*), the band at about 2300 cm⁻¹ to the symmetric OD₃* stretching mode ν₁(A₃*). This assignment of ν₁ > ν₂ is further supported by all the other spectra recorded in this study (see below). Also, their frequency separation of about 150 cm⁻¹ is very similar to that of 144 cm⁻¹ found for isoelectronic ND₃.⁵⁰

Furthermore, a recent ab initio calculation for OD₃* also arrived (after applying the suggested −12.3% correction to all frequencies) at ν₁ being 165 cm⁻¹ higher than ν₂, (see Table VII).⁴⁹ This finding that in a strongly hydrogen-bridged oxonium salt ν₁ is higher than ν₂ disagrees with the previous suggestion that the order of the OH₃* stretching frequencies should invert when ν₁ in X−H−Y becomes shorter than the van der Waals radius sum.³⁴

The assignment of the 1192-cm⁻¹ infrared and the 1178-cm⁻¹ Raman band to the antisymmetric OD₃* deformation ν₂(A₂) is straightforward and again is in excellent agreement with the frequency values of 1191 and 1161 cm⁻¹, found for iso-electronic ND₃.⁵₀ and calculated for OD₃* by ab initio methods.⁴⁹ respectively (see Table VII).

The assignment of the last yet unassigned fundamental of OD₃*, the symmetric deformation mode ν₂(A₁), is more difficult. On the basis of an analogy with ND₃, this mode should occur at about 750 cm⁻¹, and indeed the Raman spectrum of OD₃AsF₆ exhibits a band at 770 cm⁻¹ of about the right intensity. The failure to observe a well-defined infrared counterpart could possibly be due to its great line width. The ab initio calculations for ν₂(A₁) of OD₃* predict an intense infrared band at 549 cm⁻¹. Indeed the infrared spectrum of OD₃AsF₆ (trace A, Figure 3) shows a medium-strong band at 580 cm⁻¹. However, we prefer to assign this band to ν₊(E) of AsF₆³⁻ for the following reasons: This mode frequently becomes infrared active in many AsF₆³⁻ salts. Furthermore, it has also been observed in OH₃AsF₄⁺ if it were due to OD₃*, it would have been shifted in OH₃AsF₄⁺ to a significantly higher frequency. This assignment to ν₊(E) of AsF₆³⁻ is also supported by the low-temperature infrared spectra of OH₃AsF₄⁺ and OD₃AsAsF₆ (Figure 4), both of which show two sharp bands of almost identical intensities and frequencies at about 580 and 560 cm⁻¹.

The remaining bands due to AsF₆³⁻ in OD₃AsF₆⁺ are in excellent agreement with those previously observed for OH₃AsF₄⁺ and can be assigned accordingly.⁴ IR: ν₁(AsF₆³⁻), 389 cm⁻¹; ν₂(AsF₆³⁻), 390 cm⁻¹. Raman: ν₁(AsF₆³⁻), 560; ν₂(AsF₆³⁻), 363 cm⁻¹. Several weak bands in the spectrum of OD₃AsAsF₆ are marked by an asterisk. These are due to a small amount of OD₃H⁺ and will be discussed below.

**Low-Temperature Spectra of OD₃AsF₆⁺**

Figure 4 shows the low-temperature spectra of OD₃AsF₆⁺. The most prominent changes from the room-temperature spectra are the pronounced sharpening of all bands accompanied by splittings. As discussed above, these changes are caused by freezing of librational motions. The change from the plastic phase to an ordered one, occurring on the basis of DSC measurements in the −7 to +2 °C temperature range, was confirmed by Raman spectroscopy. As can be seen from Figure 5, the freezing out of the ion motion occurs indeed within the very narrow temperature range.

Compared to the room-temperature spectra, the low-temperature spectra do not provide much additional information on the fundamental vibrations of OD₃*. The ν₁(A₁) fundamental is shown to occur at a lower frequency than ν₁(E), and ν₂(E) shows a splitting into two components in the infrared spectrum. The ν₂(A₁) deformation mode is again difficult to locate but clearly cannot be attributed to the 582-cm⁻¹ infrared band for the above given reasons.

From the AsF₆³⁻ part of the spectra some conclusions concerning the possible site symmetry of AsF₆³⁻ might be reached. All degeneracies appear to be lifted for the fundamentals, and the bands are not mutually exclusive. This eliminates all centrosymmetric space groups and site symmetries such as O₃, T₃, or C₃. The highest possible site symmetry appears to be...
Table VI. Vibrational Spectra of OD₃AsF₆, OD,SeF₆, and Their Partially Deuterated Analogues

<table>
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<tr>
<th>Mode</th>
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<th>RA</th>
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<th>OD₅As₃₃</th>
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<td>νₕ(AsO₂⁻)</td>
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<td>m</td>
</tr>
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</table>

a Uncorrected Raman intensities  
Idealized point groups were assumed for the ions; this approximation is reasonable for the disordered phases but is not valid for the ordered phases in which the site symmetry of the ions is C₃ or lower.  
The spectra of these compounds contain bands due to some OD₅H⁺ resulting from a small amount of H₂O in the D₂O starting material (~0.6%) and from handling of the IR samples.
Table VII. Frequencies (cm⁻¹), Frequency Shifts on Deuteration, and Relative Infrared Intensities of OD₃⁺ and OH₃⁺ Compared to Those of Gaseous ND₃ and NH₃, and to the Results from ab Initio Calculations

| assign for | approx | of mode | OD₃⁺,s | OH₃⁺ | v(OD₃⁺) | ND₃ | NH₃ | OD₃⁺,s | OH₃⁺ | v(OD₃⁺) | ND₃ | NH₃ | OD₃⁺,s | OH₃⁺ | v(OD₃⁺) |
| point group | descrpn | | obsd | calc | obsd | | | obsd | calc | obsd | | obsd | calc | obsd |
| C₂ | X₂ (A) | 2300 | 3150 | 2420 | 3336 | 1.37 | 1.38 | 2424 (6.4) | 3411 (1.0) | 1.41 |
| | | 715 | 748 | 950 | 2.27 | 549 (6.4) | 725 (13.9) | 1.32 |
| | | 2450 | 3300 | 250 | 1.34 | 2589 (7.0) | 3516 (13.5) | 1.36 |
| | | 1182 | 1620 | 1.37 | 1191 | 1.37 | 1161 (1.3) | 1598 (3.8) | 1.38 |

* Data from ref 50. b Data from ref 49 after application of the suggested -12.3% frequency correction.

Table VIII. Frequencies (cm⁻¹) and Relative Infrared Intensities of OD₄⁺ and OH₄⁺ Compared to Those of Solid ND₄⁺H and NH₃, and to the Results of ab Initio Calculations

| assign for | approx | of mode | OD₄⁺,s | OH₄⁺ | v(OD₄⁺) | ND₄⁺ | NH₄⁺ | OD₄⁺,s | OH₄⁺ | v(OD₄⁺) | ND₄⁺ | NH₄⁺ | OD₄⁺,s | OH₄⁺ | v(OD₄⁺) |
| point group | descrpn | | obsd | calc | obsd | | | obsd | calc | obsd | | obsd | calc | obsd |
| C₃ | X₂ (A) | 3484 | 3150 | 2420 | 3336 | 1.37 | 1.38 | 2532 (4.4) | 2447 | 3 |
| | | 2476 | 3 | | | | | | | |
| | | 1847 | 1481 | 1.77 | | | | | | |
| | | 611 | 905 | 671 | 1.51 | | | | | |
| | | 2589 | 250 | 1.34 | 3516 (13.5) | 3359 vs | 1.32 |
| | | 1186 | 1229 | 1.37 | 1580 (3.4) | 1613 mw | 1602 mw |

* Data from ref 52. b Data from ref 49 after application of the suggested -12.3% frequency correction. c Frequency values taken from the low-temperature IR spectra of the SBF₆⁻ salts.

C₃, in agreement with our triply hydrogen-bonded model possessing AsF₆⁻ ions with three shorter and three longer As-F bonds. Since that unit cell contains more than one molecule, additional splittings are possible due to in-phase out-of-phase coupling effects within the unit cell.

The low-temperature spectra of OD₃⁺AsF₆ show a medium-strong IR band at 341 cm⁻¹ and a Raman band at 329 cm⁻¹. These bands cannot be assigned to AsF₆⁻ because their frequencies are too low for νₐ and also they were not observed in the low-temperature spectra of OH₃⁺AsF₆. In OH₃⁺AsF₆, however, two corresponding bands were observed at 467 cm⁻¹ (IR) and 480 cm⁻¹ (Raman). Since their average frequency values, 335 and 474 cm⁻¹, respectively, are exactly in a ratio of 1:2:1, these bands must involve the hydrogen atoms and therefore are assigned to the D-F and H-F stretching modes, respectively. As expected, these bands due to H-F stretching are not observed in the plastic-phase, room-temperature spectra due to rapid motion of the ions.

From a simple diatomic model and the average observed frequencies (νₓₓ = 2474 and νₓᵧ = 335 cm⁻¹), the corresponding force constants are fₓₓ = 0.1258 mdyn/Å and fₓᵧ = 0.1204 mdyn/Å, respectively. Their averaged value (0.1231 mdyn/Å) corresponds to a hydrogen bridge bond energy of 1.77 kcal mol⁻¹, indicative of a weak hydrogen bond.

Spectra of OD₅OH₃⁺, OD₄SbF₆⁺, and Partially Deuterated OH₃SbF₆. Figure 5 shows the low-temperature vibrational spectra of OD₅OH₃⁺, OD₄SbF₆⁺, and partially deuterated OH₃SbF₆. Although the Raman lines due to SBF₆⁻ (670, 590, 555, and 282 cm⁻¹ in trace E) are broadened, the 670-cm⁻¹ line had a pronounced shoulder at 644 cm⁻¹, the ν₁(A₁) mode is split into its two degenerate components (see Figure 5), and the D-F stretching mode at 355 cm⁻¹ (trace E of Figure 6) and H-F stretching mode at 487 cm⁻¹ (trace A of Figure 6) are observed. All these features are indicative of OD₅OH₃⁺ and OD₄SbF₆⁺ are ordered at room temperature, thus confirming the above given DSC and neutron diffraction data.

The assignments for OD₅⁺ in its SBF₆⁻ salt can be made by complete analogy to those given above for OD₃⁺AsF₆. The increased splitting of the 2430- and 2330-cm⁻¹ bands and their relative infrared intensities (trace D of Figure 6) lend further support to the νₓ > νᵧ assignment for the oxonium salts. On cooling (see Figure 7), all the important spectral features are retained, but become more evident due to better resolution caused by the narrow line widths. Thus, the D-F stretching vibrations at 380 cm⁻¹ become very prominent in the infrared spectra.

An infrared spectra of OD₅⁺ salt shows bands at about 3160, 2920, and 1470 cm⁻¹, marked by an asterisk in Figure 3, which could not readily be attributed to combinations: bands of OD₅⁺. Assignment of the 1470 cm⁻¹ infrared band to the antisymmetric stretching mode of H₂F⁺ is also unsatisfactory, because the band was also observed in the Raman spectrum, which in turn did not show the expected symmetric HF₂⁺ stretching mode at 600 cm⁻¹. Furthermore, OD₅⁺SBF₆⁺ should result in the formation of DF₂⁻ and not of HF₂⁻. Consequently, we have examined the possibility of these bands being due to small amounts of incompletely deuterated oxonium ions by recording the spectra of partially deuterated OH₃SbF₆. As can be seen from trace B of Figure 6, the intensity of the band at about 3160, 2920, and 1470 cm⁻¹ has increased strongly for the partially deuterated sample, and therefore these bands are assigned to the OD₅⁺ cation. The observed frequencies closely correspond to those of isoelectronic ND₅⁺H⁺ and the ab initio calculated OD₅⁺ values (see Table VIII). Consequently the 3160- and 1470-cm⁻¹ bands are assigned to the OH stretching mode and the antisymmetric (A') OD₅⁺ deformation mode, respectively, of OD₅⁺. The 2920-cm⁻¹ band can readily be assigned to the first overtone of the 1470-cm⁻¹ band being in Fermi resonance with the OH stretching mode. The antisymmetric (A') OD₅⁺ stretching modes of OD₅⁺ are expected to have frequencies of about 2400 and 2300 cm⁻¹, respectively, and therefore are hidden underneath the intense OD₅⁺ stretching modes. The antisymmetric (A') OD₅⁺ deformation mode is expected to have a frequency between 1190 and 1250 cm⁻¹ and therefore can be assigned to the infrared band at 1220 cm⁻¹ observed in trace B of Figure 6.

In addition to the bands attributed to OD₅⁺ and OD₅⁺, the infrared spectra of the partially deuterated OH₃SbF₆ sample (calculated product distribution (mol %): OD₅⁺: 51.88, OD₅⁺: 31.43, OD₅⁺: 17.06, OD₅⁺: 0.70, OD₅⁺: 0.16, OD₅⁺: 0.05).
that for a vibrationally weakly coupled system such as different force fields were computed for valence force and observed frequencies. The results of these computations described method to obtain an exact fit between calculated bridging.

In summary, most of the features observed for the vibrational spectra of the oxonium salts can satisfactorily be attributed to the D-F and H-F stretching modes of the hydrogen bridges. is slightly higher and the deformation constant \( f_{OH} \) in OD\(_3\)SbF\(_6\) is mainly due to the broadness of the OH\(^+\) vibrational bands and the associated uncertainties in their frequencies. Since the stretching frequencies of OD\(^+\) are more precisely known than those of OH\(^+\), the OD\(^+\) force field should be the more reliable one. The fact that \( F_{15} \) in NH\(_3\) and ND\(_3\) is somewhat larger than the value obtained for \( F_{15} \) in our F\(_3\) = minimum force field is insignificant because in the published\(^5\) NH\(_3\) force field \( F_{15} \) was not well determined and was consequently assumed to equal \(-2F_{34}\). The fact that the stretching force constant \( f_{OH} \) in OD\(^+\) is slightly lower and the deformation constant \( f_{OH} \) in OD\(^+\) is slightly higher than those in ND\(_3\) is not unexpected. The ND\(_3\) frequencies were those of the free molecule, whereas the OD\(^+\) values are taken from the ionic solid OD\(_3\)AsF\(_6\). In this solid, D-F bridging occurs (see above), thereby lowering the OD stretching and increasing the deformation frequencies. As secondary effects, the higher electronegativity of oxygen and the positive charge in OD\(^+\) are expected to increase the polarity of the O-D bonds, thereby somewhat decreasing all the frequencies. These explanations will well account for the observed differences.

For the bending force constant \( f_{OD} \), values of 0.563 and 0.542 mdy/d\(^2\) were obtained for OD\(_3\) and OH\(^+\), respectively. These values are in excellent agreement with the value of 0.55 mdy/d\(^2\) obtained for OH\(^+\) by an ab initio calculation.\(^4\)

In summary, the results from our normal-coordinate analysis lend strong support to our analysis of the vibrational spectra. They clearly demonstrate the existence of discrete OH\(^+\) ions that in character closely resemble the free NH\(_3\) molecule, except for some secondary effects caused by hydrogen-fluorine bridging.

**Conclusion.** The results of this study show that OD\(_3\)AsF\(_6\) exists at room temperature in a plastic phase, whereas OD\(_3\)SbF\(_6\) has an ordered structure. Based on diffraction data and vibrational spectra, a structural model is proposed for the ordered phase of OD\(_3\)SbF\(_6\). More experimental data are needed to define the exact nature of the ion motions and the associated phase changes in these salts. Many of the obser-

Table IX. Symmetry and Internal Force Constants\(^a\) of OD\(^+\) Compared to Those of OH\(^+\), NH\(_3\), and ND\(_3\),\(^b\)

<table>
<thead>
<tr>
<th>Force field (^c)</th>
<th>DFF</th>
<th>OD(^+)</th>
<th>F(<em>{14}) &amp; F(</em>{15})</th>
<th>NH(_3)</th>
<th>NH(_3)-ND(_3) GVF</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 ( F_{14} = 2f_{OD} )</td>
<td>0.94</td>
<td>0.61</td>
<td>0.58</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>B ( F_{14} = 2f_{OD} )</td>
<td>0.94</td>
<td>0.61</td>
<td>0.58</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

\(^a\) Stretching constants in mdy/\(\AA\), deformation constants in mdy/\(\AA\)/rad, and stretch-bend interaction constants in mdy/\(\AA\)/rad. The following bond angles and lengths were used: \( OD_{AsF_6} \) and \( ODH_{2} \). NH\(_3\), 101° and 101° A. The bending coordinates were weighted by unit (A) distance. Frequency values: \( OD_{AsF_6} \), \( \nu_{s} = 2300, \nu_{s} = 715, \nu_{b} = 2450, \nu_{b} = 1182, OH_{2} \), \( \nu_{s} = 3150, \nu_{s} = 900, \nu_{b} = 3300. \nu_{b} = 1620 \text{ cm}^{-1} \) \( \nu_{b} \) Values from ref \( 57 \) with the assumption \( F_{14} = -2F_{34} \) \( \nu_{b} \) The potential energy distribution for OD\(^+\) showed all fundamentals to be close to or 100% characteristic, with the largest amount of mixing being observed for \( \nu_{b} \) in the NH\(_3\) transfer force field of OH\(^+\).

Our preferred force field is that assuming \( F_{15} \) and \( F_{34} \) being a minimum. This type of force field has previously been shown\(^6\) to be a good approximation to a general valence force field for vibrationally weakly coupled systems. As can be seen from Figures 4 and 7, with the decreased line widths allowing a more precise location of the individual frequencies. Most of the infrared bands observed in the 320-510 cm\(^{-1}\) range (trace B of Figure 6) but cannot be located precisely due to their broadness.

The above assignments for OD\(_3\)H\(^+\) and OD\(_3\) are further substantiated by the low-temperature spectra shown in Figures 4 and 7, with the decreased line widths allowing a more precise location of the individual frequencies. Most of the infrared bands observed in the 320-510 cm\(^{-1}\) region for the low-temperature spectra of the different oxonium SbF\(_6\) salts are attributed to the D-F and H-F stretching modes of the hydrogen bridges.

In summary, most of the features observed for the vibrational spectra of the oxonium salts can satisfactorily be accounted for by the assumption of disordered higher temperature and ordered, hydrogen-bridged, lower temperature phases. Reasonable assignments can be made for the series OH\(_3\), ODH\(_3\), OD\(_3\)H\(^+\), and OD\(_3\)\(^+\) (see Table VI) that are in excellent agreement with those of the corresponding iso-electronic ammonia molecules\(^5\) \& \(^6\) and the results of recent ab initio calculations\(^5\) (see Tables VII and VIII). The only discrepancy between the ab initio calculations and the experimental data exists in the area of the symmetric deformation modes. This could be caused by the low barrier to inversion in OH\(_3\)\(^+\).

**Force Constants.** In view of our improved assignments for the oxonium cation, it was interesting to re-determine its force field. The frequencies and assignments given in Table VIII, a bond length of 1.01 Å, and a bond angle of 110° were used to calculate a valence force field of OD\(_3\)\(^+\) by using a previously described method\(^4\) to obtain an exact fit between calculated and observed frequencies. The results of these computations are summarized in Table IX.

Since isotopic shifts obtained by light-atom substitution such as H-D are virtually useless for the determination of a general valence force field,\(^5\) approximating methods were used. Three different force fields were computed for OD\(_3\)\(^+\) to demonstrate that for a vibrationally weakly coupled system such as OD\(_3\)\(^+\) the choice of the force field has little influence on its values.


\(^6\) Sawodny, W. J. Mol. Spectrosc. 1969, 30, 56.

\(^7\) Shimanouchi, T.; Nakagawa, I., Hirano, J., Ithu, M. J. Mol. Spectrosc. 1966, 19, 78.
vations made in this study are in poor agreement with previous reports for other oxonium salts and cast some doubt on the general validity of some of the previous conclusions. Due to their good thermal stability, oxonium salts of complex fluorocations are well suited for further experimental studies.

Acknowledgment. The authors are indebted to Drs. C. Schack, R. Wilson, and W. Wilson of Rocketdyne, Dr. P. Meriel of CEN Saclay, and Dr. P. Aldebert of ILL Grenoble for their help with experiments. K.O.C. thanks the U.S. Army Research Office and the Office of Naval Research for financial support.

Registry No. \( \text{OH} \cdot \text{AsF}_6^+ \cdot 21501-81-5; \text{OD} \cdot \text{AsF}_6^+ \cdot 92186-28-2; \text{O}_2 \cdot \text{AsF}_6^+ \cdot 12370-43-3; \text{OD} \cdot \text{SbF}_6^+ \cdot 92186-29-3; \text{OH} \cdot \text{SbF}_6^+ \cdot 55649-03-1; \text{D-O} \cdot 7789-20-0; \text{DF} \cdot 14333-26-7; \text{AsF}_6 \cdot 7784-36-3; \text{SbF}_6 \cdot 7783-70-2; \text{OD}_2 \cdot \text{H} \cdot \text{SbF}_6^+ \cdot 92186-30-6; \text{ODH} \cdot \text{SbF}_6^+ \cdot 92186-31-7; \text{OD}_2 \cdot 24847-51-6; \text{MoF}_6 \cdot 14459-59-7; D_2 \cdot 7782-39-0. \)
APPENDIX D

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Contribution from the Institut für Physikalische und Theoretische Chemie der Universität Tübingen, 7400 Tübingen, West Germany, and Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91304

Gas-Phase Structure of Azidotrifluoromethane. An Electron Diffraction, Microwave Spectroscopy, and Normal-Coordinate Analysis

KARL O. CHRISTE,* DINES CHRISTEN,† HEINZ OBERHAMMER,* and CARL J. SCHACK*+}

Received February 28, 1984

The geometric structure of azidotrifluoromethane has been obtained by a combined analysis of electron diffraction intensities and ground-state rotational constants derived from the microwave spectrum. The following parameters were obtained (errors in Å and deg with 2σ uncertainties in units of the last decimal): C-F = 1.328 (2), C-N = 1.425 (5), N-N = 1.252 (5), N-F-N = 1.118 (3), zCN,N = 112.4 (2), zCF = 108.7 (2). The CF3 group is in the staggered position with respect to the N3 group and tilted away from it by 51.3 (4)°.

Introduction

Structural data on covalent azides are rare due to the explosive nature and handling difficulties encountered with these compounds. One of the more stable covalent azides is CF3N3, a compound originally prepared by Makarov and co-workers and recently studied in more detail by two of us. Although the closely related CH3N, molecule has previously been studied by both electron diffraction and microwave spectroscopy, the available data were insufficient to determine whether the N3 group is linear and to obtain a reliable value for the tilt angle of the methyl group. Furthermore, comparison of the structures of CH3N3 and CF3N3 was expected to contribute to our knowledge of how the substitution of a CH3 group by a CF3 group influences the structure of the rest of the molecule.

Experimental Section

Synthesis and Handling of CF3N3. The sample of CF3N3 was prepared as previously described. Prior to the electron diffraction experiments, a small amount of N2, formed by decomposition of some CF3N3, was pumped off at -196 °C. The only other decomposition was:

(3) Oberhammer, H. J. Fluorine Chem. 1983, 24, 14

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and at data values for the total 0, the nozzle voltage was about cm) on Kodak electron products curve between experus al 25-cm Background for each Figure

**Table I.** Interatomic Distances, Vibrational Amplitudes from Spectroscopic and Electron Diffraction Data, and Vibrational Corrections $\Delta$ (Å)

<table>
<thead>
<tr>
<th>Atom pair $r_{ij}$</th>
<th>Vibrational amplitudes $a^a$</th>
<th>$\Delta = r_a - r_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2-N_4$</td>
<td>1.12</td>
<td>0.034</td>
</tr>
<tr>
<td>$N_2-N_3$</td>
<td>1.25</td>
<td>0.042</td>
</tr>
<tr>
<td>$C-F$</td>
<td>1.33</td>
<td>0.045</td>
</tr>
<tr>
<td>$C-N_2$</td>
<td>1.43</td>
<td>0.053</td>
</tr>
<tr>
<td>$C-N_3$</td>
<td>2.16</td>
<td>0.054</td>
</tr>
<tr>
<td>$C-N_4$</td>
<td>2.18</td>
<td>0.061</td>
</tr>
<tr>
<td>$C-F$</td>
<td>2.30</td>
<td>0.063</td>
</tr>
<tr>
<td>$C-N_2$</td>
<td>2.33</td>
<td>0.067</td>
</tr>
<tr>
<td>$C-N_3$</td>
<td>2.36</td>
<td>0.046</td>
</tr>
<tr>
<td>$C-N_4$</td>
<td>2.71</td>
<td>0.169</td>
</tr>
<tr>
<td>$C-F$</td>
<td>3.27</td>
<td>0.085</td>
</tr>
<tr>
<td>$C-N_2$</td>
<td>3.31</td>
<td>0.092</td>
</tr>
<tr>
<td>$C-N_3$</td>
<td>3.56</td>
<td>0.229</td>
</tr>
<tr>
<td>$C-F$</td>
<td>4.42</td>
<td>0.141</td>
</tr>
</tbody>
</table>

**Table II.** Geometric Parameters (Å and deg) for $CF_3N_2$ from Electron Diffraction and Combined Electron Diffraction-Microwave Analysis

<table>
<thead>
<tr>
<th>$r_a^a$</th>
<th>$r_{av}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C-F$</td>
<td>1.229 (3)</td>
</tr>
<tr>
<td>$C-N_2$</td>
<td>1.427 (5)</td>
</tr>
<tr>
<td>$N_2-N_3$</td>
<td>1.259 (7)</td>
</tr>
<tr>
<td>$N_3-N_4$</td>
<td>1.117 (4)</td>
</tr>
<tr>
<td>$C-N_4$</td>
<td>1.118 (1.1)</td>
</tr>
<tr>
<td>$N_2-N_4$</td>
<td>175.3 (4.3)</td>
</tr>
<tr>
<td>$FCF^c$</td>
<td>108.4 (0.6)</td>
</tr>
<tr>
<td>$C-N_2$</td>
<td>1.222 (5)</td>
</tr>
<tr>
<td>$C-N_3$</td>
<td>1.118 (3)</td>
</tr>
<tr>
<td>$N_3-N_4$</td>
<td>112.4 (0.2)</td>
</tr>
<tr>
<td>$N_2-N_4$</td>
<td>169.6 (3.4)</td>
</tr>
<tr>
<td>$FCF^c$</td>
<td>108.7 (0.2)</td>
</tr>
<tr>
<td>$C-N_2$</td>
<td>4.4 (1.2)</td>
</tr>
<tr>
<td>$C-N_3$</td>
<td>5.8 (0.4)</td>
</tr>
</tbody>
</table>

**Structure Analysis**

A preliminary analysis of the radial distribution function (Figure 2) clearly demonstrates that the $CF_3$ group is staggered with respect to the $N_2$ chain. Model calculations for the eclipsed configuration result in very bad agreement with the experimental data in the range $r > 2.5$ Å (see Figure 2). The radial distribution function for the eclipsed configuration was calculated with the final geometric parameters derived for the staggered conformation. Increase of the $C-F_3$ angle to about 130° improved the fit for the peaks at 3.3 Å, but the disagreement for the peaks around 2.7 and 4.5 Å remained. Therefore, in the following analysis the $CF_3$ group was constrained to the staggered position. However, small torsional deviations (<10°) from this position cannot definitely be excluded.

In the least-squares analysis a diagonal-weight matrix was applied to the intensities and scattering amplitudes, and the phases of Haase\(^{11}\) were used. The spectroscopic corrections, $\Delta r$ (Table I), were incorporated into the refinement. For torsional vibrations, the concept of perpendicular (rectilinear)
amplitudes results in unrealistically large contributions to these.

The corrected force field. This is justified, since the experiment, were constrained to the spectroscopic values, structure of CF$_3$ corrections for torsion-independent distances, results in unrealistically not definitively been assigned. higher

Figure 3. The $J = 4 \rightarrow 5$ rotational transitions at a Stark field of 200 V/cm. Arrows indicate frequencies at which $K_1 = 0$ lines appear at higher Stark fields. $\nu_1 = \nu_{v1}$. $\nu_1 = 4$ indicates the center of the A components of the torsionally split $\nu_1 = 4$ state. The $K_1 = 1$ lines have not definitively been assigned.

Table III. Force Field$^a$ for CF$_3$N$_2$

|        | CF/CF | CF/CN | CN/NCF | CN/NCF (opp) | NCF  | FCF  | CN/NNN | FCF/FCF | FCF/NNN | NNN/tors | NNN/tors 
|--------|-------|-------|--------|--------------|------|------|--------|--------|---------|----------|----------
| CF     | 6.69  |       |        |              |      |      |        |        |         |          |
| CN     | 4.84  |       |        |              |      |      |        |        |         |          |
| Mg     | 7.75  |       |        |              |      |      |        |        |         |          |
| MgN$_2$ | 16.88 |       |        |              |      |      |        |        |         |          |
| FCF    | 1.82  |       |        |              |      |      |        |        |         |          |
| NCF    | 1.20  |       |        |              |      |      |        |        |         |          |
| CNN    | 1.49  |       |        |              |      |      |        |        |         |          |
| NNN    | 0.67  |       |        |              |      |      |        |        |         |          |
| tors   | 0.03  |       |        |              |      |      |        |        |         |          |

$^a$ Stretch in mdyn/A, stretch/bend in mdyn/rad, and bend in mdyn/Å/rad$^2$.

Figure 4. The $J = 5_{19} \rightarrow 6_{19}$ transitions showing several vibrationally excited states at a Stark field of 800 V/cm. $\nu_1 = \nu_{v1}$.

The modified harmonic force field (Table III) looks reasonable, but is, of course, underdetermined.

The mean deviation between measured and calculated frequencies is $\Delta \nu = 4$ cm$^{-1}$.

Rotational Spectrum

The assignment of the band heads in the K-band region to the $J = 4 \rightarrow 5$ (19.62 GHz) and $J = 5 \rightarrow 6$ (23.54 GHz) transitions was straightforward since these band heads appeared very close to the frequencies predicted by the preliminary electron diffraction model ($B + C = 3.94$ GHz), but the high-resolution recordings did not openly display the characteristic pattern of a nearly prolate ($K = -0.989$) rotor (see Figure 3). The deviations arise from excited vibrational states—especially the low-lying torsional states—as will be discussed below. The frequencies of all measured transitions and the ensuing rotational constants have been collected in Table IV. The $K_1 = 1$ lines stand out quite clearly, though, and recording at different Stark fields permitted the identification of $K_1 = 0$ lines that appear only at high fields. Subsequently higher $K_1$ lines were identified, but because many of them are subject to heavy overlapping, some of them could only be measured using a radio-frequency/microwave double-resonance technique (RFMWDR) as described below.

The lowest $J$ lines show signs of quadrupole hyperfine structure, but no attempt was made to resolve and analyze these splittings. Stark measurements on different M compo-

of serious overlapping of lines and Stark components. (RFMWDR) could circumvent this problem. RFMWDR for transitions falling between the two increasing frequency (decreasing intensity), and the method fails higher excited states.

Table IV. Measured Rotational Transitions and Derived Rotational Constants (MHz)

<table>
<thead>
<tr>
<th>u = 0</th>
<th>u₁ = 1</th>
<th>u₂ = 2</th>
<th>u₃ = 3</th>
<th>u₄ = 4*</th>
<th>v₁₄ = 1</th>
<th>v₁₄ = 2</th>
<th>v₁₄ = 3</th>
<th>v₁₄ = 1, v₁₄ = 1</th>
<th>v₁₄ = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>I₁₂ = ₁₄₂₃</td>
<td>7845.90</td>
<td>7845.36</td>
<td>7831.39</td>
<td>7854.87</td>
<td>7853.13</td>
<td>7851.84</td>
<td>7857.67</td>
<td>7853.68</td>
<td></td>
</tr>
<tr>
<td>I₁₂ = ₁₄₂₄</td>
<td>11738.22</td>
<td>11750.70</td>
<td>11764.79</td>
<td>11778.62</td>
<td>11877.38</td>
<td>11777.53</td>
<td>11777.72</td>
<td>11780.40</td>
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</tr>
<tr>
<td>I₁₂ = ₁₄₂₅</td>
<td>11768.73</td>
<td>11772.52</td>
<td>11777.05</td>
<td>11782.32</td>
<td>11787.35</td>
<td>11777.53</td>
<td>11777.72</td>
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<td>I₁₂ = ₁₄₂₆</td>
<td>11768.73</td>
<td>11772.33</td>
<td>11776.69</td>
<td>11781.82</td>
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<td>11777.53</td>
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<td>I₁₂ = ₁₄₂₇</td>
<td>11799.67</td>
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<td>19584.34</td>
<td>19606.66</td>
<td>19620.92</td>
<td>19572.60</td>
<td>19581.52</td>
<td>19592.76</td>
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</tr>
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<td>I₁₂ = ₁₄₂₉</td>
<td>19612.98</td>
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<td>19625.77</td>
<td>19636.63</td>
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<td>I₁₂ = ₁₄₃₀</td>
<td>19613.36</td>
<td>19620.17</td>
<td>19629.70</td>
<td>19637.11</td>
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<td>19627.90</td>
<td>19641.95</td>
<td>19633.17</td>
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<td>I₁₂ = ₁₄₃₁</td>
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<tr>
<td>I₁₂ = ₁₄₃₃</td>
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<td>19621.02</td>
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<td>I₁₂ = ₁₄₃₄</td>
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<td>19657.02</td>
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<td>19640.92</td>
<td>19686.00</td>
<td>19706.00</td>
<td>19675.23</td>
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</tr>
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<td>I₁₂ = ₁₄₃₅</td>
<td>23475.89</td>
<td>23503.96</td>
<td>23527.92</td>
<td>23557.02</td>
<td>23486.88</td>
<td>23497.42</td>
<td>23510.98</td>
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<td></td>
</tr>
<tr>
<td>I₁₂ = ₁₄₃₆</td>
<td>23534.01</td>
<td>23540.81</td>
<td>23549.30</td>
<td>23551.87</td>
<td>23552.18</td>
<td>23568.80</td>
<td>23569.08</td>
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<td>I₁₂ = ₁₄₃₇</td>
<td>23534.97</td>
<td>23543.71</td>
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<td>23564.72</td>
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<td>I₁₂ = ₁₄₃₈</td>
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<td>23542.48</td>
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<td>23560.39</td>
<td>23553.51</td>
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<td>23609.94</td>
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</tr>
</tbody>
</table>

A* A species. b Fixed to value determined from structural model and harmonic effects. c B + C. d kHz. * Assumed.

NOTES:


D = 4
values; ref 20. 

It seems, although the evidence is sparse, that the weakenes of the third excited torsional state transitions and thus provide a somewhat r

transitions around 4.35 kcal/mol on excitation of the groups are bonded to electronegative atoms. Hence the CH3N3 potential would somewhat 

Hence the CH3N3 potential would somewhat 

The most significant features of the bond lengths of the nonlinearity of the N2 group, and the torsion and tilt angle of the CF3 group with respect to the N1 group. These features are discussed in the following paragraphs.

Discussion

The most significant features of the CF3N3 structure are the bond lengths, the nonlinearity of the N2 group, and the torsion and tilt angle of the CF3 group with respect to the N1 group. These features are discussed in the following paragraphs.

Bond Lengths. The above results clearly demonstrate that in CF3N2, the N2-CF3 bond is significantly shorter than the N2-N4 bond. This can be attributed to the electron-withdrawing effect of the CF3 group. A comparison of the MN2, series (M = alkali metal, (CH3)2Si, H, Cl, CF3) shows that if M is of very low electronegativity, as for example in the alkali metals, we have an ion\s~N2~ structure (I) with two degenerate N-N bonds of 1.16 Å each. With increasing electronegativity of M, the M-N bond becomes more covalent and the contribution from resonance structure III increases, due to the electron-withdrawing effect of M. This causes an increase in the bond length difference between N2-N4 and N2-N3 (see Table V). A comparison of the C-N bond lengths in CH3N3 and CF3N2 also shows the expected effect. Replacement of the CH3 by the CF3 group results in bond shortening if the groups are bonded to electronegative atoms or groups. Hence the C-N bond in CF3N2 (1.425 Å) is significantly shorter than that in CH3N2 (1.468 Å).

Torsional Angle of the CH3 Group. In general, methyl or trifluoromethyl groups prefer the staggered position with respect to single bonds but prefer an eclipsed position with respect to double bonds. Representative examples in the case of C=C double bonds are CH2=CHCH2 and trans-CX2CH=CHCX2. Only strong steric repulsions can force CF3 groups to abandon the eclipsed position, such as in cis-CF3CH=CHCF3. Only one example is known for N-N double bonds: trans-CX2N=N=NCX2, where the CX2 groups again eclipse the N-N double bond and stagger the N lone pair. In CF3N2, the CF3 group occupies a staggered position with respect to the N2 group as shown by IV, and this indicates a significant contribution from resonance structure III. For this structure, configuration IV minimizes the re

pulsion between the fluorine free valence electrons and the two sterically active free electron pairs on the \( N_7 \) atom (indicated by broken lines in IV). In contrast to \( \text{CF}_2\text{N}_3 \), the \( \text{CH}_3 \) group in \( \text{CH}_3\text{N}_3 \) appears to be in an intermediate position between eclipsed and staggered,\(^7\) (25 ± 7° from the eclipsed position), which may be explained in the following manner: resonance structure II should result in a staggered configuration (V) and resonance structure III in an eclipsed (VI) configuration. Since, as discussed above, the bond lengths indicate that structure II contributes more strongly to the structure of \( \text{CH}_3\text{N}_3 \) than to that of \( \text{CF}_2\text{N}_3 \), the observation of an intermediate torsional angle is not surprising.

**Linearity of the \( N_7 \) Group and \( \text{CF}_3 \) Tilt Angle.** In \( \text{CF}_2\text{N}_3 \) the \( N_7 \) group is slightly (10°) bent away from the \( \text{CF}_3 \) group, and the \( \text{CF}_3 \) group is tilted away from the \( N_7 \) group by 5.8°. This is readily explained by the repulsion between the fluorine free valence electron pairs and the \( \pi \)-bond electron system of the \( N_7 \) group. A comparison of these values with those in \( \text{CH}_3\text{N}_3 \) would be most interesting, but unfortunately no experimental values are presently available for \( \text{CH}_3\text{N}_3 \). It is interesting to note that the angles of the \( N_7 \) group found for \( \text{HN}_3, \text{CIN}_3, \text{NCN}_3, \) and \( \text{CF}_2\text{N}_3 \) are all very similar. However, it should be kept in mind that most of these values carry rather large uncertainties.

**Torsional Effects on the Structure.** The present data for the excited torsional states do not allow a determination of the structural changes upon excitation of \( \nu_4 \). It is clear from model calculations, however, that several parameters must change their value in order to reproduce the rotational constants of the excited states. Thus heavy relaxation, not only in the trifluoromethyl group but also in the tilt and the \( \text{CN}_3\text{N}_3 \) angle, is assumed to take place.

**Acknowledgment.** We are grateful to Dr. G. Pawelke for providing a sample of \( \text{CF}_2\text{N}_3 \) for the RFMWDR measurements. D.C. and H.O. acknowledge financial support by the Fonds der Chemie. K.O.C. and C.J.S. thank the Office of Naval Research and the U.S. Army Research Office for financial support.

*Registry No.* \( \text{CF}_2\text{N}_3, 3802-95-7. \)

**Supplementary Material Available:** Listings of total electron diffraction intensities for two camera distances (50 and 25 cm) for two sets of plates (2 pages). Ordering information is given on any current masthead page.
POSITIVE FLUORINE - REALITY OR MISCONCEPTION?

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SUMMARY

Polar covalence theory arguments are presented against the existence of a permanent positive polarization of fluorine in heteronuclear X-F molecules and against the existence of X groups having a higher electronegativity than fluorine itself. The heterolytic fission of fluorine and the possibility of inducing a positive fluorine dipole in X-F molecules with highly electronegative X groups are briefly discussed.

INTRODUCTION

Fluorination reactions with highly electronegative compounds are frequently explained by invoking a positive fluorine. In a recent note [1], this author took exception to the postulate of positive fluorine by criticizing a recent paper of Cartwright and Woolf on this subject [2]. In the preceding paper [3], the same authors (C+W) summarized some arguments in favor of positive fluorine. Since the issue of a positive fluorine is largely a conceptual problem and is not readily accessible to direct experimental measurements, a speculative interpretation of the mechanism of poorly studied complex organic reactions has little merit. A systematic analysis of this problem therefore appeared more rewarding and is given below.
DISCUSSION

Definition of a Positive Fluorine

A positive fluorine is the direct result of a transfer of electron density in a covalent X-F bond from F to X resulting in the following polar covalence X-F, where XF can be either heteronuclear (X is different from F) or homonuclear (X equals F). If XF is homonuclear, i.e. F₂, one cannot have a permanent but only an induced dipole. If XF is heteronuclear, one can have both a permanent and an induced dipole. It should be noted that this dipole is not identical with the experimentally measurable overall dipole moment of the XF molecule due to other factors such as lone valence electron pair effects.

Definition of the Problem

The issue raised by us in our previous critique [1] was that there is no experimental and theoretical justification for the assumption of a permanent X-F polarity in a heteronuclear XF molecule. Therefore, unless stated otherwise, the following arguments will be referring to this issue.

Theoretical Arguments

The assumption of a permanent positive fluorine dipole in a heteronuclear XF atom violates the principle of electronegativity equalization which was first published in 1951 by Sanderson [4] and proven correct by quantum mechanics in 1978 by Parr and coworkers [5] and in 1979 by Politzer and Weinstein [6]. This principle states that when two or more atoms unite to form a compound, their electronegativities become adjusted to the same intermediate value within the compound. In other words, the different kinds of atoms become equal in electronegativity by unequal sharing of the bonding electrons. This means that the more electronegative atom must acquire a negative charge and the less electronegative atom a positive charge. Since fluorine is without doubt the most electronegative element, a heteratomic X-F bond can be permanently polarized in only one direction, i.e. X-F. This principle also rules out the possibility that X groups, such as CF₃O-, SeF₅O-, or TeF₅O-, which consist of fluorine substituted heteroatoms of lower electronegativity can become more electronegative than fluorine itself [1,7-10].
Experimental Arguments

Electrophilic substitution reactions are not a convincing argument in favor of a positive fluorine. First of all, the mechanisms of most of these complex reactions have not been established. Secondly, in these reactions a strong electrophile attacks an electron rich center, and the polarity of the bonds within the electrophile is of lesser importance than other factors. In $\text{NF}_4^+$, for example, the nitrogen atom is coordinatively saturated. Consequently, $\text{NF}_4^+$ can attack an electron rich center only through one of its fluorine ligands but not through its nitrogen atom. The fact that $\text{NF}_4^+$ can undergo electrophilic substitution reactions is therefore no indication for a positively polarized fluorine.

On the other hand, addition reactions in which a polar X-F molecule is added across a polar double bond, are capable of yielding information about the polarity of the X-F bond. Several such studies have recently been carried out using $\text{ClO}_3\text{OF}[11], \text{TeF}_5\text{OF}$, and $\text{CF}_3\text{OF}[12]$ and did not provide any evidence for a positive fluorine in these hypofluorites.

One piece of experimental evidence for positive fluorine, cited by (C+W) is the selective substitution at acidic hydrogens,

\[
\text{Na}^+\text{CH(NO}_2)_2^- + \text{F}_2 \xrightarrow{H_2O} \text{Na}^+\text{F}^- + \text{FCH(NO}_2)_2\quad \text{e.g.}
\]

(C+W) concluded that, if half the fluorine becomes fluoride, by a simple charge-balance the other half must be positive fluorine. The shallowness of this conclusion can easily be demonstrated by the following analogous equation which would prove that the fluorine in HF must be positive.

\[
\text{Li}^+\text{H}^- + \text{F}_2 \rightarrow \text{Li}^+\text{F}^- + \text{HF}
\]
**Induced Polarization and Heterolytic Fission of Fluorine**

Although our original critique of the paper by (C+W) was only concerned with the permanent dipole of a heteronuclear XF molecule, the preceding paper [3] requires some comment on the heterolytic fission of fluorine. If in XF molecules X becomes more and more electronegative and eventually becomes F, the energy required to induce a dipole moment decreases and the possibility of forming an induced positive fluorine dipole increases. Although the formation of NF$_4$AsF$_6$ was originally postulated [13] to involve the heterolytic fission of F$_2$,

\[
\begin{array}{c}
\text{F}_3\text{N}l & \rightarrow & \text{F} \quad \text{AsF}_5 \quad \text{NF}_4^+\text{AsF}_6^-
\end{array}
\]

subsequent studies [14-16] have shown that the mechanism of this reaction is more complicated, requires predissociation of F$_2$, and involves the formation of the NF$_3^+$ radical cation as an intermediate. However, if the hard Lewis base NF$_3$ is replaced by the soft base Xe, the following reaction proceeds spontaneously even in the dark [17].

\[
\text{Xe} + \text{F} + \text{SbF}_5 \rightarrow \text{XeF}^+\text{SbF}_6^-
\]

It is likely that this reaction is a rare example of an actual heterolytic fission of fluorine and therefore involves a Lewis acid - Lewis base induced polarization of fluorine. However, the possible existence of such a reaction for homonuclear difluorine has no bearing on the formation of a permanent positive fluorine in the heteronuclear XF molecules discussed above.

**ACKNOWLEDGEMENT**

The author wishes to thank Drs. C. J. Schack and W. W. Wilson for helpful discussions and the Army Research Office and the Office of Naval Research for financial support.
REFERENCES

APPENDIX F

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Synthesis and Characterization of Bis(difluorooxycarboline(V)) Hexafluoronicelate(IV), (CIF₉O)₀NiF₆

William W. Wilson and Karl O. Christe

Received January 10, 1984

It is well-known that CIF₉O can form with strong Lewis acids, such as BiF₃, SbF₅, AsF₃, PF₃, TaF₅, NbF₅, VF₅, SnF₅, UF₃, SF₆, BF₃, HF, and MoF₅, adducts containing the CIF₉O⁺ cation. All these adducts have been prepared by the direct combination of CIF₉O with the corresponding Lewis acids. The purpose of this study was to examine whether CIF₉O⁺-containing salts derived from unstable Lewis acids, such as NiF₆, can be prepared by the indirect metathetical methods developed for NF₆⁺ salt chemistry.

Experimental Section

Materials and Apparatus. Literature methods were used for the syntheses of Cs₂NiF₆ and CIF₉O₂SbF₆ and the drying of the HF solvent. Volatile materials were manipulated in a well-passivated atmosphere. Solvents were handled in the drybox intosa previously described. Infrared spectra were recorded on a Cary Model Ecoino spectrophotometer using the 6471-A exciting line of an Ar ion laser. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and a Spex Model 1403 spectrophotometer using the 6471-Å exciting line of a Kr ion laser and premonochromators for the elimination of plasma lines. Sealed quartz tubes were used as sample containers. The low-temperature spectra were recorded by using a previously described device.

Synthesis of (CIF₉O)₀NiF₆. A mixture of CIF₉O₂SbF₆ (7.008 mmol) and Cs₂NiF₆ (3.505 mmol) was loaded in the drybox into a previously described double-U-tube filter apparatus. Dry HF (185 mmol) was condensed at −196 °C into the apparatus on the vacuum line, and the mixture was warmed for 30 min to 25 °C with agitation. The apparatus was cooled to −78 °C and inverted, and the solid and liquid phases were separated by filtration assisted by 2 atm of dry N₂ gas. The material volatile at 25 °C was pumped off for 12 h and consisted mainly of HF. The filter cake (2.768 g; weight calculated for 7.01 mmol of CsSbF₆, 2.584 g) was shown by vibrational spectroscopy to consist of mainly CsSbF₆ containing small amounts of CIF₉O⁺⁺ and NiF₆²⁻. The filtrate residue (965 mg; weight calculated for 3.505 mmol of (CIF₉O)₀NiF₆, 1.232 g, corresponding to a 78% yield) was shown by elemental analysis and vibrational spectroscopy to have the following composition (wt %): (CIF₉O)₀NiF₆, 93.06; CIF₉O₂SbF₆, 4.49, CsSbF₆, 2.47. Anal. Calcd: Ni, 15.54; Cl, 18.93; Cs, 1.97; Sb, 2.36. Found: Ni, 15.6; Cl, 18.7; Cs, 2.07; Sb, 2.48. The losses of (CIF₉O)₀NiF₆ can be attributed mainly to hang-up of some (CIF₉O)₀NiF₆ on the filter cake.

Results and Discussion

Synthesis and Properties of (CIF₉O)₀NiF₆. The metathetical process previously developed for (NF₆)₀NiF₆ has successfully been transferred to the synthesis of (CIF₉O)₀NiF₆ according to

\[ 2\text{CIF}_9\text{O}_2\text{SbF}_6 + \text{Cs}_2\text{NiF}_6 \xrightarrow{\text{HF solution}} \text{2CsSbF}_6 + (\text{CIF}_9\text{O})_0\text{NiF}_6 \]

The new compound (CIF₉O)₀NiF₆ is a deep purple crystalline solid that is stable at 60 °C under a dynamic vacuum. At 110 °C the observed decomposition rate was about 25%/h. The main decomposition products, volatile at ambient temperature but condensable at −196 °C, were CIF₉O and a small amount of FClO₂ (arising from handling of the CIF₉O) as shown by their ¹⁹F NMR and infrared spectra. An exhaustive pyrolysis of a sample in a sapphire reactor at 110 °C under a dynamic vacuum resulted in quantitative CIF₉O evolution and the

formation of a previously described nonstoichiometric brown nickel fluoride NiF$_2$ residue. Contrary to the pyrolysis of (NO)$_2$NiF$_6$, which results in the formation of NF$_3$O,$^{13}$ no evidence for the formation of the unknown compound CIF$_5$O was observed.

The presence of CIF$_2$O$^+$ and NiF$_6^{2-}$ ions in (CIF$_2$O)$_2$NiF$_6$ was established by vibrational spectroscopy. The spectra of the solid showed bands characteristic for CIF$_2$O$^+$ (IR, 1324 vs ($v_1$), 700 vs, br ($v_2$, $v_3$), 502 s ($v_4$), 406 m ($v_5$), 376 m ($v_6$))$^{11}$ and NiF$_6^{2-}$ (IR, 625 vs ($v_1$), 330 m ($v_2$); Raman, 565 vs ($v_1$), 525 s, 512 ms ($v_2$), 308 m, 290 w ($v_3$))$^7$ with $v_2$ and $v_4$ of NiF$_6^{2-}$ showing splittings due to lifting of the degeneracies of these modes. Due to the intense color of the sample, it was difficult to obtain Raman spectra and only the bands due to NiF$_6^{2-}$ could be observed even at $-100$ °C.

Conclusion. The above results show that CIF$_2$O$^+$ salts derived from unstable Lewis acids, such as NiF$_6$, can be prepared by metathetical methods. Furthermore, (CIF$_2$O)$_2$NiF$_6$ is the first example of CIF$_2$O$^+$ having been coupled successfully to a highly energetic anion in the form of a stable salt.

Acknowledgment. The authors are grateful to Drs. C. J. Schack and L. R. Grant and R. D. Wilson for their help. This work was supported in part by the Office of Naval Research.

Registry No. (CIF$_2$O)$_2$NiF$_6$, 91443-95-7; CIF$_2$O$_2$F$_2$, 38199-85-8; Cs$_2$NiF$_6$, 17218-49-4.

APPENDIX G

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Contribution from Rocketdyne, A Division of
Rockwell International, Canoga Park, California 91304

Lewis Acid Induced Intramolecular Redox Reactions of Difluoramino Compounds

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Received March 30, 1984

It is shown that strong Lewis acids, such as AsF₅ or SbF₅, which are good fluoride ion acceptors, strongly catalyze an intramolecular redox reaction of difluoramino compounds, such as CF₃NF₂, SF₂NF₂, CINF₃, CF₃ONF₂, and SF₂ONF₂. In the CINF₂-AsF₅ system a thermally unstable intermediate is formed at -78 °C, which on the basis of its Raman spectra is the fluorne-bridged donor-acceptor adduct CINF₂AsF₅. The nature of the final decomposition products can be rationalized in terms of their stability. In connection with the low-temperature Raman studies, an unidentified, unstable, blue-green species was observed that gives rise to a resonance Raman spectrum with ν = 177 cm⁻¹ and that is also formed from CINF₂AsF₅ and excess CINF₂. For NF₂Cl,¹⁻¹N⁻¹⁹F spin–spin coupling was observed in its ¹⁹F NMR spectrum.

Introduction

During experiments aimed at the oxidative fluorination of CF₃NF₂ to CF₃NF₂⁺AsF₅⁻ by KrF⁺AsF₅⁻, an unusual observation was made. Besides the NF₂ and CF₃ products expected for an oxidative fission of the C-N bond, significant amounts of gaseous trans-N₂F₂ and solid N₂F₂⁺AsF₅⁻ were obtained. Since KrF⁺ is the strongest oxidative fluorinating agent presently known¹ and N₂F₂ is a reduction product of CF₃NF₂, KrF⁺ was unlikely to cause the observed N₂F₂ formation. Since KrF⁺AsF₅⁻ is thermally unstable and decomposes to Kr, F₂, and AsF₅⁻ we have considered

The possibility that the strong Lewis acid AsF₅ might induce this decomposition of CF₃NF₂ was of interest. Many difluoramino compounds are thermodynamically unstable toward decomposition reactions involving the formation of multiply bonded nitrogen species, such as N₂F₂ or N₃, and more highly fluorinated byproducts. Therefore, these difluoramino compounds are only kinetically but not thermodynamically stable, and their kinetic stability is determined by the activation energy barrier toward decomposition. Hence, it would not be surprising that complexing with a strong Lewis acid could lower this activation energy barrier. It was found that, with Lewis acids or acid could lower this activation energy barrier.

Preparation of difluoramino compounds with Lewis acids or bases are scarce. Although the instability of HNF₃ in the presence of alkali-metal fluorides, for example, is well documented, only one detailed study on the interaction of difluoramino compounds with Lewis acids has been published. It was found that, with HNF₃ and alkyldifluoramines, BF₃ forms unstable, N-B bridged, donor-accepted complexes, which on warming reversibly decompose to the starting materials. With CINF₂BF₃ was found to be only weakly associated below --78°C, and with NBF₃, a large positive deviation from Raoult's law was observed, indicating no association. For BF₃, a positive interaction was reported only with HNF₃ and CH₃NF₂, and the resulting adducts underwent irreversible decomposition on warming. Although low-temperature infrared spectra of the HNF₃:BF₃ adduct were recorded, they were very complex and did not permit any conclusions concerning the nature of the adduct.

In view of the paucity of the available information and our above mentioned observations, a more systematic study of the interaction of difluoramino compounds with strong Lewis acids was of interest.

Experimental Section

Cautions! Some difluoramino compounds are known to be sensitive, and appropriate safety precautions should be used when working with larger amounts of these materials.

Materials and Apparatus. Literature methods were used for the syntheses of CF₃NF₂, CF₃,NF, SF₅NF, SF₅NF₂, CINF₄, CINF₃BF₄, CINF₂BF₃, SF₅NF, SF₅NF₂, SF₅NF₃, SF₅NF₄, CINF₃, CINF₂BF₄, SF₆Br, SF₆ONF, and SF₆FONF. For some of the compounds the previously reported product yields were significantly improved: for CF₃NF₂ from 70 to 99% by carrying out the fluorination of CF₃N with a fourfold excess of F₂ in a Monel cylinder at 70°C for 24 h; for SF₅ONF from 60 to 84% by carrying out the UV photolysis of equimolar amounts of SF₅OF and CF₃N in a flasked-out quartz bulb at 1.5-atm pressure for 16 h with water-filtered radiation from a 140-W medium-pressure mercury arc lamp; for SF₅NF₂ from 30 to 78% by UV photolysis of equimolar amounts of SF₅N and SF₅F in a stainless-steel cell equipped with a sapphire window, using the water-filtered radiation from a 1-kW Oriel Model 6141 HgXe lamp and an irradiation time of 2 h. The vapor pressure was measured by fractional condensation prior to use. SF₅F (Ozark-Mahoning Co.) was purified by distillation, and SF₅ONF (Matheon Co.) was used as received.

Volatilé materials were manipulated in a well-passivated with CIF₃ stainless-steel Teflon-FEP vacuum system. Solids were handled in the dry N₂ atmosphere of a glovebox.

The ²⁹F NMR spectra were recorded on a Varian Model EM390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (Wilmad Glass Co.) with positive shifts being downfield from the external standard, CFCI. Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded either on a Cary Model 83 spectrophotometer using the 488.0-nm exciting line of an Ar ion laser, or a Classen filter for the elimination of plasma lines, and sealed melting point capillaries as sample containers or on a Spex Model 1403 spectrophotometer using the 6471-A exciting line of a Kr ion laser. The low-temperature spectra were recorded by using a previously described device.

SF₆NF₃-KrF₅SF₆BF₄ System. KrF₅-SF₆BF₄ (2.14 mmol) was placed in the drybox into a prepasivated (with CIF₃ and HF) Teflon-FEP ampule clipped by a stainless-steel valve. The ampule was connected to the vacuum line, and HF (1 mL, liquid) and SF₆NF (4.63 mmol) were added at --196°C. The mixture was warmed to ambient temperature for 18 h, and the volatile products were separated by fractional condensation. They consisted of SF₆F₄ (4.4 mmol), Kr, and a mixture (4.1 mmol) of NF₃ and trans-NF₃F. The residue in the ampule consisted of SF₆F₄, and polyanion salts of NF₃F₁⁹ and small amounts of NF₃F₂. Previous reports on the interaction of difluoramino compounds with strong Lewis acids have been cited.

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Redox Reactions of Difluoramino Compounds

The volatile materials consisted of SF₃ (3.13 mmol) and AsF₅ (0.14 mmol). The white solid consisted of NO₂AsF₆ (2.44 mmol). Some NO₂AsF₆ had deposited in the vacuum-line section and therefore could not be recovered.

CF₃ONF₂ - AsF₅ System. CF₃ONF₂ (0.49 mmol) and AsF₅ (0.49 mmol) were condensed in a sealed-off 3-mm-d. quartz tube. The mixture was held at -78 °C for 13.5 h. Separation of the products resulted in CF₃ONF₂ (0.46 mmol), NO₂AsF₆ (0.03 mmol), and solid NO₂AsF₆ (0.42 mmol).

SF₂Br - AsF₅ System. SF₂Br (2.28 mmol) was condensed into a passivated sample tube at -196 °C, and its vapor pressure at -78 °C was measured to be 111 torr. The vapor pressure of liquid AsF₅ under the same conditions was found to be 182 torr. The tube was cooled back to -196 °C and AsF₅ (2.36 mmol) was added. The mixture was warmed to -78 °C and the vapor pressure above the resulting clear liquid was determined as 75 ± 1 torr (calculated vapor pressure for an ideal mixture based on Raoult's law = 100 torr). All material could be removed from the sample tube by pumping at -78 °C.

CF₃F - AsF₅ System. The vapor pressures of pure CF₃F, and pure AsF₅ were measured at -79 °C and found to be 405 and 182 torr, respectively. Then equimolar amounts (5.65 mmol each) of CF₃F and AsF₅ were condensed at -196 °C in a passivated Teflon-TEP U-trap. The trap was allowed to slowly warm from -196 to -79 °C by means of a liquid N₂ dry-ice bath. At -79 °C, the tube contained a white solid with a pressure of about 220 torr above it. The tube was cooled back to -196 °C, and AsF₅ (2.36 mmol) was added. The tube was warmed again to -79 °C, and the vapor pressure above the solid was 610 torr. In addition to a white solid, some yellow solid was also formed, particularly at temperatures slightly higher than -79 °C. Most of these solids were unstable at ambient temperature, and fractional condensation of the volatile decomposition products to a series of traps kept at -78, -126, -156, and -196 °C showed N,F, N₂F, N₃F, N₄F, AsF₆, and ClF. Smaller amounts of a stable white solid residue, left behind at room temperature, were shown by vibrational spectroscopy to be a mixture of N₂F,AsF₆ and N₄F,AsF₆.

More accurate molar balances for these systems were obtained using different ratios of starting materials and other apparatus or passivated quartz reactors and by recording low-temperature Raman spectra of the intermediate unstable products formed in this system. With a 1:1 mole ratio of CF₃F and AsF₅, a typical molar balance was as follows: starting materials, CF₃F and AsF₅ (2.59 mmol each), products, NO₂AsF₆ (0.16 mmol), AsF₅ (1.23 mmol), ClF (0.15 mmol), trans-N₂F₂ (0.10 mmol), and N₃FAsF₆ + N₄F,AsF₆ (0.10 mmol). For CF₃F (3.60 mmol) and AsF₅ (1.25 mmol), the products consisted of NO₂AsF₆ (2.28 mmol), NO₂AsF₆ (0.40 mmol), ClF (1.78 mmol), and AsF₅ (1.07 mmol). Then, NO₂AsF₆ (trace), and N₃FAsF₆ + N₄F,AsF₆ (0.17 mmol). For CF₃F (3.67 mmol) and AsF₅ (0.07 mmol), the products were CF₃F (2.40 mmol), N₄F,AsF₆ (0.26 mmol), NO₂AsF₆ (0.06 mmol), ClF (0.62 mmol), and N₃FAsF₆ + N₄F,AsF₆ (0.03 mmol).

Cl₂ - AsF₅ System. An equimolar mixture of Cl₂ and AsF₅, when kept at -79 °C in a sample tube, resulted in a clear yellow liquid exhibiting a vapor pressure of 115 torr (calculated vapor pressure for an ideal mixture based on Raoult's law = 121 torr). All material could be removed from the sample tube by pumping at -78 °C.

Results and Discussion

A study of the CF₃NFAsF₅ system showed that in the presence of AsF₅, the normally stable CF₃NF undergoes even at -78 °C a slow decomposition according to (1): Since N,F, exerts

2CF₃NF => 2CF₃ + N₂F, (1)

as two isomers, cis and trans, and since only the cis isomer forms an adduct with AsF₅. (2)

cis-N₂F₂ + AsF₅ → N₄F²AsF₆ (2)

the observation of both, gaseous trans-N₂F₂ and solid N₄F²AsF₆, can readily be rationalized by the formation of both cis-N₂F₂ isomers in reaction (1). Therefore, the surprising observation of trans-N₂F₂ and N₄F²AsF₆ in the KrF²AsF₆-CF₃NF reaction system can be attributed to a Lewis acid promoted intramolecular redox reaction of CF₃NF, in which the CF₃ group is oxidized to CF₃ and the NF₂ groups are reduced to N₂F₂.

To test the generality of this Lewis acid promoted intramolecular redox reaction, we have also studied the effect of AsF₅ on CINF₃, SF₃NF, CF₃ONF₂, and SF₂ONF₂, which, in the absence of typical Lewis acids, are all thermally stable compounds.

Thus, SF₃NF undergoes an analogous, albeit faster and quantitative, decomposition according to (3) and (2). It should be pointed out that the SF₃ and N₂F₂ products formed in (3) are different from those (SF₃F₁₀ and N₂F₄) formed in the uncatalyzed thermal decomposition of SF₃NF. (23)

For CF₃ONF₂ and SF₂ONF₂, the addition of AsF₅ also promotes an intramolecular redox reaction at low temperature. After several hours at -78 °C, the mixture is completely colorless, and the resulting clear liquid was moted an intramolecular redox reaction at low temperature. After several hours at -78 °C, the mixture is completely colorless, and the resulting clear liquid was moted an intramolecular redox reaction at low temperature. After several hours at -78 °C, the mixture is completely colorless, and the resulting clear liquid was moted an intramolecular redox reaction at low temperature. After several hours at -78 °C, the mixture is completely colorless, and the resulting clear liquid was moted an intramolecular redox reaction at low temperature. After several hours at -78 °C, the mixture is completely colorless, and the resulting clear liquid was moted an intramolecular redox reaction at low temperature. After several hours at -78 °C, the mixture is completely colorless, and the resulting clear liquid was moted an intramolecular redox reaction at low temperature.
The coupling has previously been reported for $-60^\circ\text{C}$ showed SFNF decomposition reactions. Since even at other hand, it is well-known that action. Thus, $\text{excitation}$, and spectral slit width of $11\text{wv I.}$

The spectrum of the known N-donor adduct CHCN-$\text{AsF}_3$. The two possible vibrations.' an ionic CINFI$^-$ structure can be ruled out. In the position. In the $\text{Raman spectra of the solid}$ were recorded at $-60^\circ\text{C}$ and of $\text{CINF}$, and $\text{SbF}_3$ in $\text{SO}_2$ at $-60^\circ\text{C}$ showed that in both cases CINF$_2$ had undergone decomposition. In the absence of $\text{AsF}_3$ or $\text{SbF}_3$, CINF$_2$ was stable in both solvents. Its NMR spectra showed signals at $\phi 141$ in $\text{SO}_2$ at $-60^\circ\text{C}$ and at $\phi 137$ in HF at $-80^\circ\text{C}$. In both cases, a partially resolved triplet was observed due to nitrogen-fluorine spin-spin coupling $J_{\text{N-F}} = 120 \text{ Hz.}$ To our knowledge, no N-F spin-spin coupling has previously been reported for CINF$_2$.

In view of the instability of CINF$_2$ in solutions containing $\text{AsF}_3$ or $\text{SbF}_3$, Raman spectra of the solid 1:1 adduct formed between CINF$_2$ and $\text{AsF}_3$ at $-78^\circ\text{C}$ were recorded at $-130^\circ\text{C}$. A typical spectrum is shown in Figure 1. On the basis of the large number of observed bands and the absence of the characteristic $\text{AsF}_3^-$ vibrations,$^{11}$ an ionic CINF$_2^-$ structure can be ruled out. Of the two possible covalent, donor-acceptor complexes, structure II is preferred, on the basis of a comparison with the Raman spectrum of the known N-donor adduct CH$_3$CN-$\text{AsF}_3$. The intense Raman bands at 492, 439, and 277 cm$^{-1}$ can only be reconciled satisfactorily with structure II. The observed frequencies and their tentative assignments for II are given in Figure 1. In the spectra a weak band of variable intensity was also observed at about 1060 cm$^{-1}$, which could be due to small amounts of N$_2$F$^2$.$^{19}$ However, the possibility cannot be ruled out that this band represents the NF stretching mode. Then, the 947 cm$^{-1}$ band must be assigned to the NCI stretching mode and the 710- and 688-cm$^{-1}$ bands to the doubly degenerate antisymmetric AsF$_3^-$ stretching mode.

Several interesting observations were made in connection with these Raman studies. When the sample was warmed to above $-78^\circ\text{C}$, the white solid decomposed and an unstable yellow solid formed, which was shown to be As$_2$F$_6$.

During its decomposition in a closed system, a blue-green unstable material also formed, which with 6471-Å excitation gave a resonance Raman spectrum with its fundamental at 177 cm$^{-1}$. After pumping off all material volatile at room temperature, a small amount of a white solid was left behind, which on the basis of its Raman and infrared spectra was a mixture of N$_2$F$^-$AsF$_3^-$ and N$_2$F$_3^-$AsF$_4^-$.

The origin of the unstable blue-green species was shown to be due to CINF$_2^+$ and an excess of CINF$_2$. A sample of CINF$_2^+$AsF$_3^-$, when warmed in the presence of an excess of CINF$_2$ to temperatures slightly above $-78^\circ\text{C}$, produced the same blue-green species. Possible candidates for this species could be the unknown Cl$_2^+$ cation or Cl$_2$, radical, but the frequency of 177 cm$^{-1}$ appears rather low for either one of these, and attempts were unsuccessful to isolate a Cl$_2^+$Cl$_2$AsF$_6^-$ species from Cl$_2^+$AsF$_3^-$ and an excess of CINF$_2$ at temperatures as low as $-95^\circ\text{C}$. It should be noted that the 177-cm$^{-1}$ band, which previously has also been reported for Cl$_2$AsF$_3^-$ as an unassigned band of 20% intensity at 170 cm$^{-1}$, most likely does not belong to Cl$_2^+$AsF$_3^-$.

In our study, this band was completely absent in some of the CINF$_2^+$AsF$_3^-$ spectra and was observed with variable intensity in others.

The possibility of attributing the complexity of the Raman spectrum of Figure 1 to a polyanion, such as As$_2$F$_6^2$,$^{17}$ was also investigated but rejected. When As$_2$F$_6$ was reacted with a large excess of CINF$_2$, the solid residue at $-78^\circ\text{C}$ exhibited a spectrum identical with that in Figure 1.

Another interesting question was whether catalytic amounts of As$_2$F$_6$ suffice to decompose these RNF$_2$ type compounds. It was found that, for example, 6 mol % of As$_2$F$_6$ resulted in the decomposition of 53 mol % of the SF$_2$NF$_2$ starting material and in the formation of 6 mol % of N$_2$F$^+$AsF$_3^-$. It thus appears that the SF$_2$NF$_2$ decomposition requires only catalytic amounts of As$_2$F$_6$, but that the relatively slow SF$_2$NF$_2$ decomposition reaction comes to a halt when all the available As$_2$F$_6$ is converted by cis-NF$_2$F in a faster reaction to solid N$_2$F$^+$AsF$_3^-$. For the RNF$_2$ type compounds, obviously larger amounts of As$_2$F$_6$ are required because of the quantitative formation of FNO and its fast and quantitative conversion to solid NO$^+$AsF$_3^-$. The fact that only As$_2$F$_6$, but not AsF$_3^-$, catalyzes the RNF$_2$ decomposition was demonstrated by the fact that CINF$_2$ was recovered unchanged when exposed to a stoichiometric amount of N$_2$F$_3^+$AsF$_3^-$ for 2 days at ambient temperature.

Finally, the different behavior of N$_2$F$_3$ and the difluoromino compounds toward strong Lewis acids needs to be discussed. Whereas the difluorination compounds of this study appear to form fluorescent-bridged donor-acceptor complexes, N$_2$F$_3$ forms ionic N$_2$F$_3^+$AsF$_3^-$. This different behavior is attributed to the fact that in N$_2$F$_3$, removal of a fluoride anion is greatly facilitated by the availability of a free valence-electron pair on the vicinal N atom. This free pair can migrate to form an N=N double bond, thus yielding an energetically favorable, stable cation (eq 8). In the case of CF$_3$NF and SF$_2$NF$_2$, the C and S atoms, respectively, do not possess a free valence-electron pair that by migration could stabilize a corresponding R$=\text{NF}^+$ cation. Therefore, for RNF$_2$:

$$\text{CF}_3\text{NF} + \text{AsF}_3^- \rightarrow \text{CF}_3\text{NF}^-$$


the reaction analogous to (8) stops at the thermally unstable intermediate donor–acceptor stage, which on warm-up can decompose to the observed products by attack of a negatively polarized fluoride atom bound to As on the positively polarized central atom of the R group (eq 9). Such a mechanism, involving

\[
\begin{align*}
\text{F} & \quad \text{As} \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

the formation of NF radicals, could explain the formation of both cis- and trans-N₂F₃ isomers and could also account for the observation of side reactions, as in the case of CINF₂.

In summary, this study has shown that (i) strong Lewis acids, which are good fluoride acceptors, catalyze the decomposition of difluoramino compounds, (ii) the thermally unstable intermediates, which are initially formed, appear for RNF₃ compounds with highly electronegative R groups to be fluoride-bridged donor–acceptor complexes, and (iii) the exact nature of the final products is governed by their relative stabilities.

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Registry No. II, 93782-55-9; SF₅NF₃, 13693-10-2; KrF₃SbF₅, 52708-44-8; KrF₃AsF₅, 50859-36-4; CF₃NF₃, 335-01-3; KrF₃, 13773-81-4; AsF₅, 7784-36-3; SF₅ONF₃, 14521-09-6; CF₃ONF₃, 4217-93-0; CINF₃, 13637-87-1; SF₅Br, 15607-89-3; Cl₃, 7782-50-5.
Synthesis and Characterization of NF₄CrF₆ and Reaction Chemistry of CrF₅

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NF₄CrF₆, a new stable NF₄⁺ salt containing an energetic counterion, was prepared by treatment of CrF₅ with an excess of NF₃·HF, in HF solution. The composition and ionic nature of NF₄CrF₆ was established by elemental analysis, vibrational and ¹⁹F NMR spectroscopy, and its X-ray powder pattern. Reactions of CrF₅ with H₂O in HF, CIF₅, FNO, C₆H₆, CFCl₃, and KrF₅ were studied to determine its acidity and oxidizing power. With FNO, a stable 1:1 adduct is formed, which on the basis of its vibrational spectra has the ionic structure NO⁺CrF₅⁻. The reaction of NOCrF₅ with NO produced (NO)⁺CrF₅⁻, which by controlled pyrolysis was converted to NO⁺CrF₆⁻. With stoichiometric amounts of H₂O in HF, CrF₅ did not form a stable OH⁺CrF₅⁻ salt but the reaction resulted in hydrolysis to CrF₅(OH). The influence of the strong Lewis acids AsF₅ and SbF₅ on the oxidizing power of CrF₅ was also investigated. On the basis of the fact that CrF₅-SbF₅ mixtures can oxidize O₂ (IP = 12.06 eV) but not NF₃ (IP = 13.00 eV), the following qualitative oxidizer strength scale is proposed: KrF₅ > PrF₅ > SbF₅ > F₂ > activation energy > CrF₅-SbF₅. The results of a normal-coordinate analysis of CrF₅⁺ and CrF₅⁻ show the expected decrease in force constants with increasing negative charge.

Introduction

Chromium pentafluoride is a known, powerful oxidizer capable of fluorinating, for example, Xe to XeF₆ and XeF₄.²,³ Furthermore, it is known that the oxidizing power of CrF₅ can be enhanced by the addition of a strong Lewis acid, such as SbF₅.⁴ Thus, these CrF₅-Lewis acid mixtures can oxidize O₂ to O₃⁺ and therefore are assigned an electron affinity comparable to that of PrF₅.⁵ In view of this demonstrated high oxidizing power of CrF₅, the known existence of the CrF₅⁺ anion,⁶ and the exceptional stability of NF₄⁺ salts,⁷ the synthesis of the new oxidizer NF₄CrF₆ is appeared feasible.

Experimental Section

Apparatus. Volatile materials were manipulated in stainless-steel vacuum lines equipped with Teflon-FEP U-traps, 316 stainless-steel bellows-seal valves, and a Hense Bourdon tube-type pressure gauge.⁸ Either quartz or sapphire tubes or Teflon-FEP ampules, equipped with stainless-steel valves, were used as reaction vessels. The lines and other hardware used were passivated with CIF₅ and, if HF was to be used, with HF. Nonvolatile or marginally volatile materials, such as SbF₅ and CrF₅, were handled in the dry N₂ atmosphere of a glovebox. Antimony pentafluoride was added to the reactors with a Teflon-needle syringe, and CrF₅, due to its tarsiness at ambient temperature, was preferably handled after it had been cooled by liquid nitrogen. Metathetical reaction and solvolysis studies were carried out in HF solution by using an apparatus consisting of two Teflon-FEP U-traps interconnected through a coupling containing a porous Teflon filter.⁹

High-pressure, high-temperature reactions were carried out in 95- or 1000-cm³ Monel cylinders equipped with Monel valves. The loaded cylinders were placed into an oven set at the desired reaction temperature. Decomposition studies were carried out in a sapphire reactor (Tyco Co.). The reactor was connected to a stainless-steel valve by a Swagelok compression fitting using Teflon ferrulas. The reactor was heated by immersion into a stirred oil bath.

Infrared spectra were recorded in the range 4000-200 cm⁻¹ on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or Ag₃P₅ windows in an Eisco press (EISCO Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed quartz, Teflon-FEP, or sapphire tubes were used as sample containers in the transverse-viewing-transverse-excitation mode. A previously described device was used for recording the low-temperature spectra. The ¹⁹F NMR spectra of the samples contained in sealed, 5-mm-d. Teflon-FEP tubes (Wilnald Glass Co.) were recorded at 46 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. X-ray diffraction patterns of the powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-5 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Philips camera.

Elemental analyses were performed by Mikroanalytische Laboratorium, Elbach, West Germany.

Mass spectra were obtained by using the syntheses of NF₃·HF, ¹⁴NF₄⁺, CrF₅⁺, KrF₅⁺, KrF₅SbF₅, and FNO⁺ and for the drying of HF."
NOCrF₆ and CrF₃

Nitrogen trifluoride (rocketyne), F₂ (Air Products), NO₂, O₂, CIF₃, Cr₁₋ₓSbₓF₄ (Matheson), CrF₅, SF₆, AsF₃ (Ozark-Mahoning), CrF₅H₂O (Baker and Adamson), and Cr powder (Sargent, 100 mesh) were commercially available. Anhydrous CrF₃ was also obtained by dehydrating the hydrate at 200 °C. The purity of the volatile compounds was checked by gas chromatography prior to use. CrF₃ was isolated by fractional condensation. The CFC₁₁ (Du Pont) was dried by storage over P₂O₅ and transferred by distillation without further purification.

Synthesis of CrF₃. It was found that the synthesis of CrF₃ can be carried out under reaction conditions milder than those previously reported. In a typical preparation, CrF₃ (91.75 mmol) was loaded in the drybox into a preassembled I-L Monel high-pressure reactor. The reactor was connected to the vacuum line, and F₂ (947.66 mmol) was added at -196 °C. After 45 hr at 25 °C, the remaining F₂ was removed at -196 °C, and CrF₃ (81.82 mmol, 92.8% yield based on CrF₃ pumped off) was pumped at 60-100 °C and trapped in a U-tube maintained at -78 °C.

Attempts to fluorinate Cr powder with CIF₃ in HF solution at room temperature for 16 h were unsuccessful, even in the presence of 2 atm of F₂, and Cr powder was quantitatively recovered.

Preparation of NF,F₃ CrF₅. A mixture of CrF₅ (10.11 mmol) and NF,F₅ (10.15 mmol) was loaded in the drybox into half of a preassembled Teflon double-U metathesis apparatus. Dry HF (~5 mL) was added on the basis of reaction stoichiometry. If containing NF,F₃-CrF₅, and the resulting mixture was stirred for 30 min at 25 °C. After this mixture and the filter were cooled to -78 °C, the metathesis apparatus was inverted and the resulting solution of NF,F₃HF in HF was filtered into the other half of the apparatus. Part of the HF solvent was pumped off during warming to 25 °C, and the resulting solution of NF,F₃HF in HF was added to the HF solution. The apparatus was then cooled to -196 °C and taken into the drybox and CrF₃ (5.34 mmol) added to it. The apparatus was reattached to the vacuum line and warmed to room temperature. The HF solvent was pumped off during warming, and the reaction mixture was kept at 25 °C and 45 atm at 40 °C. Since the weight and the infrared spectrum of the solid residue still indicated the presence of bifluoride species, the solid was transferred to a sapphire tube and heated in a dynamic vacuum for 2 h at 95 °C. The resulting red, solid residue (1.88 mmol, 50.4%) was then washed with HF (2.58 mmol) and a quantitative impurity was isolated as a byproduct. Thus, the reaction mixture was pumped off complete reduction of NF,F₃HF, and NF,F₃HF by fractional condensation. The Raman spectrum of this mixture, recorded at -130 °C, showed only bands due to solid CrF₃ and solid CrF₅.

The Cr₃-CrF₃ System. A mixture of CrF₃ (4.44 mmol) and Cr₂ (6.28 mmol) was heated in a sapphire tube to 127 °C for 57 h. On the basis of the observed material balance, and infrared spectra of the solid residue, only 49% of the CrF₃ was reduced to CrF₅. Heating to higher temperatures resulted in a complete reduction of CrF₃ but also in the formation of some CrFs as a byproduct. Thus, heating of CrF₃ (4.71 mmol) and Cr₂ (4.48 mmol) to 185 °C for 20 h produced 60.03 g of a brown solid (weight calculated for 4.71 mmol of CrF₃, 0.6031 g) and CIF (3.99 mmol) and CIF (about 0.3 mmol). Although the Cr analysis of the solid product was close to that expected for CrF₃, it was not found in the IR spectrum or infrared infrared spectrum showed the presence of some CrF₃.

The KrF₅SF₆-CrF₅ and KrF₅SF₆-CrF₅-HF System. In a sapphire tube a mixture of KrF₅SF₆ (1.09 mmol) and CrF₃ (1.96 mmol) was warmed to the melting point of CrF₃ (14 °C), at which point gas evolution started. On the basis of the observed material balance and vibrational spectra, all KrF₅SF₆ had decomposed to Kr₂, F₂, and SF₆, but no oxidation of CrF₃ to CrF₅ had occurred. Similar results were obtained under these conditions was repeated.

Reaction of CrF₅, SF₆, and O₂. The reaction between CrF₅-SF₆, and O₂ was conducted in a manner similar to that reported by Gard et al., except that it was carried out in a 45-mm Teflon-FEP ampule. A mixture of CrF₅ (2.37 mmol) and SF₆ (6.54 mmol) was dynamically pumped on 15 °C at room temperature in an attempt to reach the previously reported CrF₅·SF₆ composition. The pumping had been stopped before reaching this composition since CrF₅ was pumped off. At this stage with the assumption that only minor amounts of CrF₅ had been removed, the molar ratio of SF₆/CrF₅, approximated 2.47. Oxygen (4.736 mmol) was then admitted into the ampule at 19 °C. When the mixture was warmed to room temperature for 1 h, a brown solid was formed. On the basis of the observed O₂ material balance, about 1 mol of O₂ was taken up per 1 mol of CrF₅. No significant loss of mass was observed by dynamic pumping on the solid at room temperature for 1 h. The presence of SF₆, formed in the solid product was established by Raman spectroscopy and its X-ray powder diffraction pattern.

Reaction of CrF₅-SF₆, with NF,F₅. Chromium pentfluoride (29.30 mmol) was combined in a Teflon-FEP ampule with SF₆ (5.95 mmol). The mixture was outgassed by repeated pumping at -78 °C, followed by
Vibrational spectra of solid NF₄CrF₆: traces A and B, infrared spectra of the powder at 25 °C pressed between AgCl and AgBr disks, respectively; traces C and D, Raman spectra of the solid recorded at -130 °C with 647.1-nm excitation at two different sensitivity levels, respectively. The listed assignments are based on space group T₃₄ for NF₄⁺ (N) and O₃ for CrF₆⁻ (C).

Figure 1. Vibrational spectra of solid NF₄CrF₆: traces A and B, infrared spectra of the powder at 25 °C pressed between AgCl and AgBr disks, respectively; traces C and D, Raman spectra of the solid recorded at -130 °C with 647.1-nm excitation at two different sensitivity levels, respectively. The listed assignments are based on space group T₃₄ for NF₄⁺ (N) and O₃ for CrF₆⁻ (C).

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The use of an excess of NF₄HF₄ in this reaction is advantageous to ensure complete conversion of the CrF₆⁻. Since NF₄HF₄ is thermally unstable, decomposing above room temperature to gaseous NF₄HF and HF, its excess can easily be removed from the solid NF₄CrF₆ product by pumping at 25–100 °C. The NF₄CrF₆ salt is a deep red, crystalline solid, stable in a dynamic vacuum to about 120 °C. It starts to decompose slowly at 125 °C to NF₄F, F₂, and CrF₆⁻. No species such as NF₄CrF₄ (NF₄)₂CrF₆ or CrF₆⁻ was observed when the compound was gradually pyrolyzed under pumping at temperatures ranging from 125 to 145 °C. In HF at 23 °C the NF₄CrF₆ salt is highly soluble at a rate of 6.39 g of NF₄CrF₆/g of HF.

The ionic nature of NF₄CrF₆, both in the solid state and in HF solution, was verified by vibrational and ¹⁹F NMR spectroscopy. The Raman and infrared spectra of the solid, together with the observed frequencies and assignments for tetrahedral NF₄⁺ (T₄) and octahedral CrF₆⁻ (O₃), are shown in Figure 1. The splittings into the three degenerate components observed for ν₁(F₄) of NF₄⁺.

![Graphical representation of vibrational spectra and Raman spectra of NF₄CrF₆.](image-url)
in the Raman spectrum are due to solid-state effects and are frequently observed for NF6 salts.21 For CrF6, only the two infrared-active modes, v1(F2) and v2(F2), have previously been reported for their Ca+ and NO6+ salts.4 In spite of the broadness of the observed bands and the associated difficulty in choosing their band centers, the previously reported frequencies (CaCrF6 ν1 = 600, ν2 = 295 cm⁻¹; NO2CrF6 ν1 = 600, ν2 = 275 cm⁻¹) are in poor agreement with our values for NF6CrF6 and NO6CrF6 (see Figures 1 and 2). The results of a normal-coordinate analysis for CrF6 are given below.

The Raman spectrum of NF6CrF6 in HF solution at ambient temperature showed only minor shifts from the spectrum of the solid for the bands due to CrF6 (ν1 = 640–670, ν2 = 305–348 cm⁻¹). These shifts, together with the surprisingly high solubility of NF6CrF6 in HF (see above) and the 19F NMR observations (see below), suggest strong interaction between CrF6 and the HF solvent.

The 19F NMR spectrum of NF6CrF6 in HF solution at 29 °C showed a triplet of equal intensity at δ = 215.2 with JνF νF = 118 Hz, characteristic for NF5. A very broad line centered at δ = -136 was assigned to the HF solvent in exchange with CrF6, which contains a paramagnetic Cr(V) central atom.

The X-ray powder diffraction pattern of NF6CrF6 was recorded and is given as supplementary material. The observed pattern is very complex and could not be indexed, suggesting that NFO2CrF6 is not isotypic with the previously known tetragonal NF5M2-type (M = P, As, Sb, Bi) salts.23

Synthesis and Characterization of NO6CrF6. (NO)2CrF6 and NO6CrF6. Before this study, only two CrF6 salts had been known, i.e. CaCrF6 and NO2CrF6.4 It was now found that, in addition to NFO2CrF6 (see above), CrF6 also forms a stable 1:1 adduct with FNO. When stoichiometric amounts of CrF6 and FNO are combined in HF solution, the compound NO6CrF6 is formed:

\[ \text{FNO} + \text{CrF}_6 \rightarrow \text{NO}_6\text{CrF}_6 \]  

(2)

Figure 2. Vibrational spectra of solid NO6CrF6; trace A, infrared spectrum of the powder pressed between AgBr disks; trace B, low-temperature Raman spectrum.

Figure 3. Vibrational spectra of solid (NO)2CrF6; trace A, infrared spectrum; trace B, Raman spectrum.

The deep red solid is stable at room temperature and sublimes at higher temperatures. Its X-ray powder diffraction pattern (given as supplementary material) is too complex for indexing and strongly differs from that of cubic NO6AsF6.2 This is a further confirmation that CrF6 salts appear not to be isotypic with their corresponding main group metal(V) salts.

The ionic nature of solid NO6CrF6 was established by vibrational spectroscopy (see Figure 2). The infrared and Raman spectra show a band at about 310 cm⁻¹ characteristic for the NO stretching mode of the NO6 cation, which is in addition to the bands characteristic for the CrF6 anion (see above).

When an HF solution of NO6CrF6 was treated with a stoichiometric amount of NO, the CrF6 anion was reduced to CrF5F3, resulting in the formation of the new (NO)2CrF6 salt:

\[ \text{NO}_6\text{CrF}_6 + \text{NO} \rightarrow (\text{NO})_2\text{CrF}_6 \]  

(3)

This salt is a yellow-brown (pink when finely ground), crystalline solid that is stable at room temperature but decomposes in a dynamic vacuum at 130 °C. Its X-ray powder diffraction pattern is given as supplementary material. The ionic nature of (NO)2CrF6 was established by vibrational spectroscopy (see Figure 3). The NO6 stretching mode is again observed around 2300 cm⁻¹, with the slightly lower frequency, when compared to that of NO6CrF6, being due to the presence of a doubly charged counterion. The bands due to CrF5 are similar to those of CrF6, but are shifted to slightly lower frequencies. This frequency shift is caused by the increased negative charge of the anion (see the normal-coordinate analysis). On the basis of the number of bands and their relative intensities, it appears safe to conclude that CrF5 is also octahedral. The results of a normal-coordinate analysis for CrF5 are given below.

Although the synthesis of K2CrF6 has been reported as early as 1950,24 very little is known about the CrF5- anion.25,26 Furthermore, the reported syntheses involving the fluorination of

When a sample of (NO)\textsubscript{2}CrF\textsubscript{6} was subjected to vacuum pyrolysis at 130 °C, the following stepwise decomposition occurred resulting in the formation of NOCrF\textsubscript{5}, another new compound:

\[
(\text{NO})_2\text{CrF}_6 \xrightarrow{130 \degree C} \text{NOCrF}_5 + \text{NO}
\]

This salt is a brown, crystalline solid that sublimes above 130 °C without further decomposition, thus preempting the use of its pyrolysis as a method for the preparation of CrF\textsubscript{5}. The X-ray powder diffraction pattern of NOCrF\textsubscript{5} is given as supplementary material.

The ionic nature of NO\textsuperscript{+}CrF\textsubscript{5} was established by vibrational spectroscopy (see Figure 4), which showed the presence of the NO\textsuperscript{+} cation (ν\textsubscript{NO} at about 2320 cm\textsuperscript{-1}). On the basis of the CrF\textsubscript{5}\textsuperscript{-} bands to those observed for several GeF\textsubscript{5} salts,\textsuperscript{2} a polymeric cis-fluorine-bridged structure appears most likely for CrF\textsubscript{5}.

Lewis Acid Strength of CrF\textsubscript{5}. On the basis of a previous report, CrF\textsubscript{5} is amphoteric, forming adducts with the Lewis bases CrF\textsubscript{3} and FNO\textsubscript{3}, and the Lewis acid SbF\textsubscript{5}.\textsuperscript{4} The Lewis acid character of CrF\textsubscript{5} was confirmed by the results of this study, which showed that CrF\textsubscript{5} forms stable NO\textsuperscript{+}CrF\textsubscript{5} and NF\textsubscript{3}\textsuperscript{+}CrF\textsubscript{5} salts. Therefore, CrF\textsubscript{5} must be considered a relatively strong Lewis acid.

However, it is significantly weaker than AsF\textsubscript{5}, as shown by the fact that, even at ~78 °C, CrF\textsubscript{5} does not form a stable adduct with ClF\textsubscript{3}, while ClF\textsubscript{3}AsF\textsubscript{5} is marginally stable at ambient temperature.\textsuperscript{10} Similarly, attempts failed to prepare a KrF\textsuperscript{+}CrF\textsubscript{5}.

salt from KF, and CrF, in either the presence or absence of HF as a solvent. For comparison, KrFAsF, is well-known and decomposes only slowly at room temperature.\(^{31}\)

Although a distinct CrF,2SbF, adduct, formulated as CrF,2SbF,11, has previously been reported,\(^{4}\) we could not verify the existence of such an adduct. Attempts to reach this composition through vaporization of SbF, from a CrF, solution in an excess of SbF, as well as vibrational spectra (see Figures 5 and 6), failed to give any evidence for a definite compound and resulted in the simultaneous removal of both components. In our opinion, the spectra of these CrF,2SbF, mixtures are best interpreted in terms of solutions of the two components, with the observed changes in the spectra being due to different degrees of mixed fluorine bridging between the individual components. This view is also supported by the fact that the viscosity of SbF, is strongly decreased by the dissolution of the highly polymeric CrF,11. If a predominantly ionic CrF,SbF,11 adduct were formed, it would be expected in viscosity or formation of a solid would be expected. Liquid AsF, was found to be also an excellent solvent for CrF,, resulting in dark brown solutions of low viscosity.

**Oxidation Reactions with CrF,2** Oxidation reactions involving either neat CrF, or CrF,2-Lewis acid (SbF, or AsF,) mixtures were carried out to determine its relative oxidative power. It was found that neat CrF, does not oxidize CIF, to CIF,. Furthermore, even in the presence of F, it does not oxidize O, to O,+ at 30 °C and NF, to NF,+ at 125 °C. It is capable, however, of oxidizing CCl, to CIF at 120 °C and CCFCl, to Cl, and a mixture of CIF,Cl, ClF, and CIF, at room temperature. In both reactions, CrF, is sublimated in yellow fluorescent fumes. Some brown solid, presumably CrF,27,32 could be sublimed from the crude CrF, + Cl, reaction product in a static vacuum at 185 °C. The sublimation residue was shown by vibrational spectroscopy and X-ray powder diffraction data to contain also some CrF,. The brown sublimate showed a broad, strong Raman line at 780 cm\(^{-1}\), no detectable X-ray diffraction lines, and a broad infrared band ranging from 380 to 740 and 640 to 490 cm\(^{-1}\), respectively. The infrared spectrum is quite distinct from that of CrF, which does not exhibit a band in the 800-cm\(^{-1}\) region. The brown color observed for our sample of CrF, is in good agreement with Wartenberg's original report\(^{12}\) and does not confirm a subsequent report stating that CrF, is dark green and that the brown color is due to an oxide layer generated by exposure to air.\(^{27}\)

The oxidation of CrF, by O, is most probably enhanced by strong Lewis acids, such as SbF, and AsF,. This is not surprising and is generally the case for many oxidizers. Thus, CrF,2SbF, has been reported to oxidize O, to O,+ at room temperature, and the solid reaction product has been formulated as O,(CrF,SbF,).\(^{4}\)

We have confirmed this reaction and \(p\), approximate 1:1 stoichiometry and have identified the solid reaction product as a mixture of O,+SbF, and lower valent chromium fluorides:

\[
\text{O}_2 + \text{CrF}_2\text{SbF}_5 \rightarrow \text{O}_2^+\text{SbF}_5^- + [\text{CrF}_4]^2- \quad (5)
\]

**Extraction of O,+SbF, from the product was possible by treatment with liquid HF.**

The oxidation of O, to O,+ can also be achieved with CrF,2-AsF, mixtures at or below room temperature. By analogy with the corresponding SbF,2 system, the solid reaction product contained O,+AsF,2-.

Attempts were unsuccessful to oxidize NF, to NF,+ using similar conditions, i.e., pressurizing liquid CrF,2SbF, with several atmospheres of NF, at room temperature. On the basis of the facts that CrF,2-Lewis acid mixtures are capable of oxidizing O, and Xe,\(^{4}\) which have ionization potentials of 12.06 and 12.13 eV, respectively, but cannot oxidize NF, with an IP of 13.00 eV, their electron affinity or oxidizing power can be limited to the relatively narrow range of 12.13-13.00 eV. Since PtF,, KrF, and F,-Lewis acid mixtures activated by a suitable activation energy source are all capable of oxidizing NF, to NF,+ under comparable conditions,\(^{13}\) CrF,2-Lewis acid mixtures are a weaker oxidizer than any one of these systems. On the basis of the above and previous\(^{12}\) results, the following order of decreasing oxidizer strength can be proposed for these systems: KrF, salts > PtF, > Lewis acid + F,-activation energy > CrF,2-Lewis acid.

Reactions of CrF, with either KrF, or KrF, salts were carried out in attempts to produce CrF,, but so far all attempts in this direction have been unsuccessful.

**Synthesis and Properties of CrF,2O.** Our attempts to isolate a stable oxonium salt of CrF,2 according to

\[
\text{CrF}_2 + \text{H}_2\text{O} + \text{HF} \rightarrow [\text{OH}^+\text{CrF}_4^-] \quad (6)
\]

were unsuccessful but resulted in the formation of CrF,2O after removal of the HF solvent:\(^{16}\)

\[
[\text{OH}^+\text{CrF}_4^-] \rightarrow \text{CrF}_2\text{O} + 3\text{HF} \quad (7)
\]

The intermediate formation of OH,2CrF,2 was not unequivocally established but appears very likely from the observation of a pink solid and stable pink HF solution. This reaction produces CrF,2O in quantitative yield and is superior to the previously reported\(^{16}\) synthesis, which involves the reaction of CrO, with CIF, followed by multiple treatments with F, at 120 °C. The properties observed for CrF,2O were in good agreement with those previously reported.\(^{14}\) The observed X-ray powder diffraction pattern is given as supplementary material.

**Normal-Coordinate Analyses of CrF,2 and CrF,2**. Since for CrF,2 no vibrational spectra at all and for CrF, only incomplete data\(^{4}\) had previously been reported, normal-coordinate analyses were carried out for these two anions. Modified valence force fields were computed, assuming \(F_0\) as minimum, due to the underdetermined nature of the \(F_0\) block. On the basis of a previous study\(^{33}\) and experience with similar oxonium ions,\(^{34}\) this condition is expected to be a good approximation to a general valence force field. The observed frequencies, their assignments in point group \(O_0\), and the computed force constants are summarized in Table 1.

---

**Table 1. Vibrational Frequencies and Modified Valence Force Fields of CrF,2 and CrF,2**

| Assign in point group \(O_0\) | \(\text{CrF}_2^2-\) \(\text{(NO)}_2\text{CrF}_2\) | \(\text{CrF}_2^2-\) \(\text{(NO)}_2\text{CrF}_2\) | Force const. modyn/Å
<table>
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<tbody>
<tr>
<td>(A_1) (A_2) (A_3)</td>
<td>650 649 537 537 670 310 305 305</td>
<td>608 521 625 308 298 2430 2623 2654</td>
<td>4.714 3.227 3.107 0.2430 0.2654 3.416 3.077 0.248 0.308 0.329</td>
</tr>
</tbody>
</table>

*Assuming \(F_0\) = minimum.

\(33\) Sawodny, W. J. Mol. Spectrosc. 1969, 30, 56.
I. As expected, the Cr–F stretching force constant $f$, decreases from CrF$_6$ to CrF$_6^-$ due to a bond weakening caused by the increased Cr$^{3+}$–F$^-$ polarity of the bonds in CrF$_6^-$.

**Conclusion.** Chromium pentafluoride is a moderately strong Lewis acid capable of forming stable CrF$_6^-$ salts with NF$_4$ and NO$^+$. The NF$_4^+$ salt is of particular interest as an oxidizer because in it an oxidizing anion is combined with a strongly oxidizing cation. Contrary to previous reports, no evidence was found for CrF$_3$ forming a distinct, predominantly ionic CrF$_3$SbF$_5$ adduct with SbF$_5$. The oxidizing power of CrF$_3$ is greatly enhanced by strong Lewis acids but does not match that of PtF$_6$. Chromium(V) salts can selectively be reduced to Cr(IV) salts with NO. In this manner the new Cr(IV) salts (NO)$_2$CrF$_6$ and NOCrF$_3$ can be prepared. Similarly, CrF$_3$ can be reduced to mainly CrF$_4$ with either Cl$_2$ or CFCl$_3$. Reaction of CrF$_3$ with stoichiometric amounts of H$_2$O in HF produces an unstable oxonium salt that decomposes on HF removal to CrF$_3$O, thus providing a convenient new synthesis for this compound.

**Acknowledgment.** The authors are grateful to Drs. C. J. Schack and L. R. Grant and R. D. Wilson for their help and to the U.S. Army Research Office and the Office of Naval Research for financial support. R.B. is also indebted to Dr. W. Kaska and the University of California, Santa Barbara, for their hospitality and to the DRET for financial support.

**Supplementary Material Available:** A table of X-ray powder diffraction patterns for some Cr-containing compounds (1 page). Ordering information is given on any current masthead page.
Communications

Cyanation and Nitrations of Toluene with Cyanamide and Nitramide through Intermediate Cyanodiazonium Ion: Attempted Fluorination of Aromatics with Fluorodiazonium Ion

Summary: Toluene is cyanated and nitrated with cyanodiazonium and nitrodiazonium ion, generated via in situ diazotization of cyanamide and nitramide, respectively, with NO+BF4-. Attempted fluorination with fluorodiazonium ion, prepared from cis-difluorodiazene and arsenic pentafluoride, gave only trace amounts of fluoroaromatics.

Sir: In previous studies from our laboratory aminodiazonium ions were generated by protonation of hydrazoic acid and alkyl azides in superacids and their ability for amination of aromatics was demonstrated. In continuation of our studies we have found that cyanodiazonium tetrafluoroborate (NCNMeBF4, 1) can be generated in situ by reaction of cyanamide with purified NO+BF4- (1:1) at atmospheric pressure in CH2Cl2 at 0 °C and gives in the presence of excess toluene (3-fold) isomeric toluclidines (12 mol % overall yield). The observed isomer distribution of toluclidines is 48% ortho, 17% meta, and 35% para, close to that obtained for amination of toluene with aminodiazonium ion (46-48% ortho, 13-14% meta, and 35-39% para). Slightly better conversion was achieved by using CH3CN as solvent (14-15%) in which both NO+BF4- and HNCN are more soluble.

In control experiments, when NO+BF4- was allowed to react with cyanamide in acetonitrile at room temperature in the absence of toluene, the initial formation of a pale yellow solution was followed by an exothermic reaction (temperature 70-80 °C) with gas evolution (N2, BF3), suggesting that the initial formation of NCNMe or its precursor complex is followed by rapid diazodiation. Alternatively, NCNMe can be "so generated from cyanamide with thionyl chloride and NO+BF4- under argon (500 psi) and reacted with toluene (50% ortho, 15% meta, 35% para).

We have also found that nitrodiazonium tetrafluoroborate O2NNMeBF4- (2) can be generated when a freshly prepared sample of nitramide4 (from ethyl carbonate and amy1 nitrate) is allowed to react with a molar equivalent of purified NO+BF4- in CH2Cl2 at 0 °C. De-

\[
\text{Me} \quad \begin{array}{c}
\text{CN}
\end{array}
\]

\[
\text{Me} \quad \begin{array}{c}
\text{CN}
\end{array}
\]

diazoniatiative nitrations of toluene (4 equiv) gave isomeric nitrotoluenes in 36% overall yield. The observed isomer distribution of nitrotoluenes is 71% ortho, 3.5% meta, and 25.5% para and closely resembles that of electrophilic nitrations of toluene with strongly electrophilic nitrating agents, such as nitronium salts.

In a control experiment when nitramide was added to dry toluene in CH2Cl2 under the experimental condition, no nitrotoluenes were observed after workup and GC analysis, ruling out any possible nitrations of toluene by nitramide itself or by nitric acid formed upon hydrolysis.

Aromatic cyanation via the cyanodiazonium ion 1 is in all probability a concerted reaction, as the cyanyl cation "CN is not expected to be formed, but the reaction could also involve a radical cation pathway. In contrast, diazodiation of the nitrodiazonium ion 2 to the nitronium ion is thermodynamically favorable and thus it cannot be excluded that its formation precedes nitrations of aromatics.

O2NNMeBF4- + NO+BF4- \rightarrow NO2BF4- + N2

(4) (a) Marvel, C. A.; LaBelle, V. R. Greenberg, J. Inorg. Nucl. Chem. 1969, 31, 68. (b) Nitramide was also prepared by the reaction of nitroacetamide (2 equiv) and NO2BF4- (1 equiv) in tetramethylene sulfone/CH2Cl2 solution at 0 °C for 1 h.

\[
\text{CH2Cl2} + \text{NO2BF4-} \rightarrow \text{NO2BF4-} + \text{MeCN} + \text{CF2Cl} + \text{BF3}
\]

As pointed out by a referee, one equimolar amount of water is also formed in the diazotization of nitramide which will hydrolyze nitronium ion, and the de facto nitrating agent may not be the free nitronium ion, although it is still possible that it is also involved in the overall nitration.

The ability of electronegative substituents in stabilizing diazonium ions was also demonstrated previously by the preparation of isolable fluorodiazonium salts, such as hexafluoroantimonate and hexafluoroarsenate, from cis-difluorodiazene and the strong Lewis acid fluorides SbF$_6$ or AF$_6$.

\[
\text{FN} \rightarrow \text{F}^+ + \text{HF} + \text{AF}_6
\]

We have in the course of our studies also attempted fluorination of aromatics such as benzene, toluene, and nitrobenzene with fluorodiazonium hexafluoroarsenate. Clearly FN$_2^+$ is unable to form F$^-$; thus, the reaction is expected to be that of displacement by the aromatics. The reactions were carried out at -78 °C in anhydrous hydrogen fluoride solution with careful addition of the solution of the fluorodiazonium ion to excess of the aromatics. The reaction was found to be extremely exothermic even under these conditions, and only trace amounts of fluorinated aromatics were formed (analyzed by gas-liquid chromatography and NMR spectroscopy). The fluorodiazonium ion thus seems to be a very strong oxidizing agent and of little practical value for aromatic fluorination.

All reported reactions can be best visualized as displacements of the diazonium ions by the aromatics, either giving the substituted products with simultaneous evolution of nitrogen or by competing reaction on nitrogen with subsequent decomposition of the intermediately formed aryldiazonium ions by the counterions (i.e., cyanide, nitrite, or fluoride).

Acknowledgement. Support of the work at USC by the National Science Foundation and the U.S. Army Research Office, Durham, NC, is gratefully acknowledged.

Registry No. 1, 95512-44-2; 2, 95512-46-2; PhCH$_3$, 108-88-3; NO$_2$BF$_4^-$, 14635-75-7; H$_4$NCN, 420-04-2; SOC$_3$, 7719-09-7; NO$_2$NH$_2$, 7782-94-7; NH$_2$C(O)OEt, 51-79-8; CH$_3$(CH$_2$)ONO$_2$, 1002-16-0; NC-o-C$_6$H$_4$Me, 99-19-1; NC-m-C$_6$H$_4$Me, 620-22-4; NC-p-C$_6$H$_4$Me, 104-85-8; NO$_2$-o-C$_6$H$_4$Me, 99-72-2; NO$_2$-m-C$_6$H$_4$Me, 99-99-0; FN, [12005-87-7]; (Z)-FN$=NF$, 13812-43-6; AsF$_6$, 7784-36-3.


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APPENDIX J

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303

Synthesis and Characterization of NF₄⁺BrF₆⁻ and NF₄⁺BrF₆O⁻

Karl O. Christe* and William W. Wilson

Received November 13, 1985

Although the NF₄⁺ cation is known to form salts with a large variety of anions, such as XF₄⁻ (X = H), XF₄⁺ (X = B, Al), XF₄⁻ (X = Ge, Sn, Ti), X₂F₄⁺ (X = P, As, Sb, Bi, Pt, Cr), X₂F₄⁻ (X = Sb, Bi, Pt), X₂F₆⁻ (X = Si, Ge, Sn, Ti, Mn, Ni), X₂F₆⁺ (X = W, U, Xe), X₂F₇⁺ (X = Xe), X₂F₈⁺ (X = W, U), X₂F₈⁻ (X = S), and XOF⁻ (X = Cl),¹ no salts are presently known in which the anion is derived from a halogen fluoride or oxyfluoride. Previous attempts² have been unsuccessful to prepare and isolate, for example, NF₄⁺XF₆O⁻ (X = Br, Cl), by metathesis according to

NF₄SbF₆ + CaXF₆O → NF₄⁺BrF₆O⁻ + CaSbF₆ + NF₄XF₆O (1)

When HF was used as a solvent, solvolysis of CsXF₆O occurred according to

CsXF₆O + HF → CsHF + XF₆O (2)

For CsClF₄O, substitution of HF by BrF, also resulted in a displacement reaction:

CsClF₄O + BrF₃ → CsBrF₆ + ClF₆O (3)

For CsBrF₆O the analogous displacement by BrF, was not observed, and the observation of the correct amounts of CsSbF₆, NF₄⁺BrF₆O⁻, and BrF₆O for reaction 1 indicated the possible formation of NF₄⁺BrF₆O⁻ as an unstable intermediate. These results encouraged us to attempt the isolation and characterization of NF₄⁺BrF₆O⁻ and possibly NF₄⁺BrF₆⁻.

Experimental Section

Materials. Literature methods were used for the syntheses of NF₄⁺, SbF₆⁻, CaBrF₆O⁻,¹ and CaBrF₆⁻. The BrF₃ (Matheson) was treated with

(1) For a compilation of references see: Christe, K. O.; Wilson, W. W.; Schack, C. J.; Wilson, R. D. Inorg. Synth., in press.
(4) Christe, K. O.; Schack, C. J. Inorg. Chem. 1979, 18, 1512
5 at time of F, at 100 °C for 24 h and then purified by fractional condensation through traps kept at -16 and -20 °C, with the material kept at -30 °C being used. These materials are powerful catalysts and contact with organic materials or moisture must be avoided.

Volatile materials used in this work were handled in a glove box (with activated carbon, and/or BF,.) stainless-steel Teflon FEP vacuum line. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. For the transfer of unstable solvents, the cold materials were taken off the dry box and placed under a layer of either liquid N or liquid Nz, on an open dish placed inside a Stroebel-cooled dewar. Metastable reactions were carried out in BF, solvents by using an apparatus consisting of two FEP U-tubes unconnected through a capillary containing a porous Teflon filter.

Infrared spectra were recorded in the range 4000-200 cm through a Perkin-Elmer Model 283 spectrophotometer by placing the chilled powder between two cold plates. The remaining AgCl module was held in a liquid-N, cooled sample holder of an evacuation low-temperature infrared cell with external Cs windows. The Raman spectra were recorded on a Cary Model 82 spectrophotometer using the 488 nm exciting line of an Ar ion laser and a Czerny-Turner for the elimination of plasma lines. Sealed 1-mm-d. quartz tubes were used as sample containers in a previously described low-temperature device.

Preparation of NF. BF, inside the dry box. CaBF, (100 mm) and NF, (40 mm) were loaded into a passivated Teflon FEP double-U-tube metalhasis apparatus. On the vacuum line BF, (100 mm) was added at -16 °C. The mixture was allowed to warm to 10 °C for 24 h and stored at -16 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line pressurized with 2 atm of dry N, and allowed to warm to 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line pressurized at 2 atm of dry N, and allowed to warm to 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line, washed with dry N, and allowed to warm to 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line, washed with dry N, and allowed to warm to 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line, washed with dry N, and allowed to warm to 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line, washed with dry N, and allowed to warm to 10 °C for 8 days with periodic agitations.

Preparation of NF. BF, The preparation was analogous to that of NF. BF, except for the following modifications. The reaction mixture of NF. BF, (50 mm) and BF,, was allowed to warm to 10 °C for 24 h, then kept at 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line, washed with dry N, and allowed to warm to 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line, washed with dry N, and allowed to warm to 10 °C for 8 days with periodic agitations. The cold apparatus was connected to the vacuum line, washed with dry N, and allowed to warm to 10 °C for 8 days with periodic agitations.

Bands and Assignments
The first examples of NF. bands with halogen fluoride and halogen oxofluoride analogs were prepared by the following low-temperature metalhasis reactions in BF, solution:

\[
\text{NF}_2 \text{BF}_4 + \text{CaBF}_3 \rightarrow (\text{NF}_2 \text{BF}_4 \cdot \text{CaBF}_3)_n
\]

Both NF. bands are white solids that are unstable at room temperature. The NF. BF, soln. is more stable than NF. BF, as evidenced by the fact that even at room temp. a very small but constant and measurable amount of NF. was evolved during removal of the BF, solvent in a dynamic vacuum. This renders the synthesis of NF. BF, time-consuming unless 90% purifying

Figure 1 A vibrational spectra of solid NF. BF, trace A Infrared spectrum trace B Raman spectrum recorded at two different conditions: 

- Time and requires close temperature control. The NF. BF, solid is stable at 22 °C, thus permitting a more rapid BF, removal.
- The thermal decomposition of the two solids follows a different path:

\[
\text{NF. BF,} \rightarrow \text{NF} + \text{BF}_3
\]

Whereas NF. is a strong enough base to reduce the oxofluoride BF, to BF, it is not capable of reducing BF, to either BF, or BF, in solution.

The composition of the NF. BF, and NF. BF, solids was established by the material balances observed for both the syntheses and decomposition reactions and by the temperature Raman and infrared spectroscopy. The observed spectra are shown in Figures and 1, and the frequencies and their assignments are summarized in Table 1. Since the vibrational spectra of the NF. BF, and BF, products are well established, the discussion of the above results can be separated into two parts, both of which are the decomposition of the solid NF. BF, the NF. BF, and its products, is an excellent model for the decomposition of other NF. compounds.

The number of fundamental vibrations and their frequencies observed for the BF, bands in NF. BF, agree within 10% with previous observations made in BF, or BF, solvents. However, the BF, bands in NF. BF, do not show the characteristic bands for a square planar BF, or a BF, solvents. The following bands of the square planar NF. BF, or BF, solvents have been assigned to: A (B) and B (A) bands. This strongly suggests that the BF, bands in NF. BF, is not square planar but rather existent as 3D, d, symmetry, the nature of which is not known. The bands of BF, in NF. BF, are given.
Table I. Vibrational Spectra of NF₄BrF₂ and NF₄BrF₂O

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assignments (point group)

NF₄⁺ (Tₐ)  | BrF₂⁺ (C₆)  | BrF₂O⁻ (C₆)

*Uncorrected Raman intensities (peak heights)

agreement with those previously observed for Cs⁺BrF₂O⁻ and
were assigned correspondingly.

In conclusion, the above results show that the NF₄⁺ cation is
capable of forming marginally stable salts with certain halogen
fluoride or oxyfluoride anions. The synthesis of such salts is
difficult and requires the use of a solvent that is (i) sufficiently
polar to dissolve ionic salts, (ii) sufficiently volatile to allow solvent
removal at low temperature, (iii) stable toward the strongly-
oxidizing NF₄⁺ cation, and (iv) incapable of undergoing a solvolytic
reaction with the starting materials. So far, the only solvent known
to meet or approximate these requirements is BrF₂.

Acknowledgment. The authors are indebted to C. J. Schach,
R. D. Wilson, and L. R. Grant for help and to the Army Research
Office and the Office of Naval Research for financial support.
APPENDIX K

2. CHLORYL FLUORIDE

\[ 6\text{NaClO}_3 + 4\text{ClIF} \rightarrow 6\text{NaF} + 2\text{Cl}_2 + 3\text{O}_2 + 6\text{ClO}_3\text{F} \]

Submitted by KARL O. CHRISTIE,* RICHARD D. WILSON,* and CARL J. SCHACK*
Checked by D. D. DESMARTEAU†

†The checker used one-half the amounts of starting materials in a 150 mL Monel cylinder and obtained the same yield.

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Chloryl fluoride is the most common chlorine oxyfluoride. It is always encountered in reactions of chlorine mono-, tri-, or pentafluorides with oxides, hydroxides, or poorly passivated surfaces. It was first obtained in 1942 by Schmitz and Schumacher by the reaction of ClO₂ with F₂. Other methods involve the reaction of KClO₃ with either BrF₃ or CIF₃. The simplest method involves the reaction of NaClO₃ with CIF₃, resulting in the highest yields and products that can readily be separated.

Procedure

**Caution.** The hydrolysis of ClO₂F can produce shock-sensitive ClO₂.

Therefore, the use of a slight excess of CIF₃ is recommended for the synthesis to suppress any ClO₂ formation. Chlorine trifluoride is a powerful oxidizer and ignites most organic substances on contact. The use of protective face shields and gloves is recommended when working with these materials.

In the dry box, dry sodium chlorate (30 mmol, 3.193 g) is loaded into a 30-mL high-pressure stainless steel Hoke cylinder equipped with a stainless steel Hoke valve. The cylinder is connected to a stainless steel-Teflon FEP vacuum manifold (Fig. 1) that has been well passivated with CIF₃ (Ozark-Mahoning) until the CIF₃, when condensed at −196°, shows no color. The cylinder is then evacuated and CIF₃ (21.5 mmol) is condensed into the cylinder at −196°. The cylinder is allowed to warm to room temperature and is kept at this temperature for 1 day.

The cylinder is then cooled back to −196°, and during subsequent warm-up of the cylinder the volatile products are separated by fractional condensation under dynamic vacuum through a series of U-traps kept by liquid N₂ slush baths at −95° (toluene), −112° (CS₂), and −126° (methylcyclohexane). The trap at −95° contains only a trace of chlorine oxides, the trap at −112° contains most of the ClO₂F (29 mmol), and the trap at −126° (7 mmol) contains mainly Cl₂ and some ClO₂F. The yield of ClO₂F is almost quantitative based on the limiting reagent NaClO₃ (29.4 mmol, 98%).

The purity of the material is checked by infrared spectroscopy in a well-passivated Teflon or metal cell equipped with AgCl windows. The product should not show any impurities. A small amount of chlorine oxides, which can be readily detected by their intense color if present or if formed during handling of ClO₂F, can readily be removed by conversion to ClO₂F with elemental F₂ or will decompose to Cl₂ and O₂ during storage at ambient temperature. Chloryl fluoride can be stored in a metal vessel at room temperature for long time periods without significant decomposition.

†The checker used one-third of the stated scale and obtained ClO₂F in a yield of 95%.
Fig. 1. Typical metal-Teflon vacuum system used for handling strongly oxidizing or corrosive fluorine compounds. As the vacuum source, a good mechanical pump (10⁻¹⁰ torr or better) is normally sufficient. The use of a fluorocarbon oil, such as Halocarbon [Halocarbon Products] as a pump oil is strongly recommended for safety reasons. B. glass waste trap with glass or Teflon stopcocks and a detachable bottom; only fluorocarbon grease [Halocarbon Products] should be used for the stopcocks and joint; the trap is kept cold by a Dewar flask with liquid nitrogen; great care must be taken, and a face shield and heavy leather gloves must be worn when pulling off the cold lower half of the waste trap for disposal of the trapped material by evaporation in a fume hood. The glass waste trap can be connected to the metal line by a glass-metal joint, or metal-to-metal seal, or most conveniently by a quick-coupling compression fitting with Viton O-ring seals. C. scrubber for removal of fluorine; the scrubber consists of a glass tower packed with alternating layers of NaCl and soda lime that are held in place by plugs of glass wool at either end. The glass waste trap can be connected to the metal line by a glass-metal joint, or metal-to-metal seal, or most conveniently by a quick-coupling compression fitting with Viton O-ring seals. D. Teflon-FEP (fluoroethylene-propylene copolymer (Zeus)) or PFA (polytetrafluoroethylene) U-traps made from ⅛- or ¼-in. o.d. commercial-wall tubing; all metal lines are made from either 316 or 321 stainless steel or Monel tubing, except for the lines from the U-traps to the Heise gage (Dresser) J, for which ¼-in. o.d. tubing is preferred. Stainless steel bellows valves E such as Hoke Model 4200 series, are used throughout the entire line, metal-metal or metal-Teflon connections are all made with either flare or compression (Swagelok, Crawford Fitting, or Gyrolok) fittings. F. lecture bottle of CIF, [Ozark-Mahoning] used for preservation of the vacuum line. G. He gas inlet H F, gas inlet I connectors for attaching reaction vessels, reagent containers, etc. J. Heise Bourdon tube pressure gage (0-1000 mm Hg or 0-150 atm). K. crude pressure gage (0-5 atm). L. 2 L. steel bulbs used for either measuring or storing larger amounts of gases. M. ¼-in. o.d. metal U-tubes to permit condensation of gases into the storage bulbs L. N. infrared cell for gases. Teflon head with condensing tip, 5 cm path length. AgCl windows. The four U-traps D connected in series, constitute the fractionation train used routinely for the separation of volatile materials by fractional condensation employing slush baths of different temperatures. The volumes of each section of the vacuum line are carefully calibrated by PVT measurements using a known standard volume.
Fluorine-Containing Compounds

Properties

Chloryl fluoride is a colorless liquid boiling at \(-6^\circ\). The IR spectrum of the gas' shows the following major bands: 1271 (vs), 1106 (ms), 630 (s), and 547 (ms) cm\(^{-1}\). The \(^1^F\) NMR spectrum of the liquid at \(-80^\circ\) consists of a singlet at 315 ppm downfield from external CFCl_3.

References

2. A. A. Woolf, J. Chem. Soc. 1496, 1113
APPENDIX L

12. TUNGSTEN TETRAFLUORIDE OXIDE

\[ 2WF_6 + SiO_2 \rightarrow 2WOF_4 + SiF_4 \]

Submitted by WILLIAM W. WILSON* and KARL O. CHRISTI**
Checked by ROLAND BOUGON†

Tungsten tetrafluoride oxide can be prepared by numerous methods, such as the fluorination of WO_3 at 300°.\(^1\) slow hydrolysis of WF_6;\(^2\) the direct fluorination of W in the presence of O_2 at 300°;\(^3\) the reaction of WF_6 with WO_3 at 400°;\(^4\) the reaction of WOCl_3 with HF;\(^5\) or oxygen-fluorine exchange between WF_6 and B_2O_3.\(^6\) The method given below is a modification of the method of Paine and McDowell, who used stoichiometric amounts of SiO_2 and WF_6 in anhydrous HF for the controlled hydrolysis of WF_6.\(^2\) In our experience,\(^7\) the use of stoichiometric amounts of SiO_2 and WF_6 leads to the formation of some [H,\(\text{O}\)]\(^{-}\)[WO\(_3\)]\(^{+}\) and [H,\(\text{O}\)]\(^{-}\)[W\(_2\)O\(_5\)F\(_4\)]\(^{+}\) as by-products that are difficult to separate from WOF_4. This problem can, however, be minimized by the use of an excess of WF_6. Tungsten tetrafluoride oxide is a starting material for the syntheses of numerous WOF_4 salts.

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L - 1
Procedure

Caution. Anhydrous HF causes severe burns. Protective clothing and safety glasses should be worn when working with liquid HF.

Quartz wool [Preiser Scientific] (1.048 g, 17.44 mmol) is placed into a ½-in. o.d. Teflon FEP (fluoroethylene propylene copolymer) ampule [Zeus] equipped with a Teflon-coated magnetic stirring bar and a stainless steel valve. The ampule is connected to a metal-Teflon vacuum system and evacuated, and dry HF [Matheson] (19 g) and WF₆ [Alfa] (22.102 g, 74.21 mmol) are condensed into the ampule at −196°. The contents of the ampule are allowed to warm to room temperature and are kept at this temperature for 15 hr with stirring.

All material volatile at room temperature is pumped off (10⁻⁴ torr) for 12 hr, leaving behind 9.723 g of a white solid (weight calcd. for 34.89 mmol WOF₂ is 9.624 g). This crude product usually still contains CHO[W₂O₂F₂]⁻ (IR spectrum of the solid pressed as a AgCl disk: 3340, 3100, 1625, 1040, 1030, 908 cm⁻¹) and can be purified by vacuum (10⁻⁴ torr) sublimation in an ice water-cooled Pyrex sublimator at 55°, resulting in 4.245 g of sublimate.

The purity of the sublimate is verified by vibrational spectroscopy of the solid (IR spectrum as a AgCl disk: 1054 (vs), 733 (s), 666 (vs), and 550 (vs) cm⁻¹. Raman: 1058 (10), 740 (1.9), 727 (6.3), 704 (0+), 668 (0+), 661 (0.9), 559 (0+), 518 (0.7), 325 (sh), 315 (sh), 311 (5), 260 (0+), 238 (0.7), 212 (0.5), 185 (0+), 110 cm⁻¹). Anal. Calcd. for WOF₂: W, 66.65; F, 27.55. Found: W, 66.5; F, 27.7.

Properties

Tungsten tetrafluoride oxide is a white hygroscopic solid (mp 104.7 at 25 torr, bp 185.9°) which can be sublimed readily. It is soluble in HF and in propylene carbonate. The ¹⁹F NMR spectrum in propylene carbonate solution consists of a singlet at 65.2 ppm downfield from external CFCl₃, with two satellites with JₓF = 69 Hz.¹⁰

References

13. TETRAFLUOROAMMONIUM SALTS

Submitted by KARL O. CHRISTE,* WILLIAM W. WILSON,* CARL J. SCHACK,* and RICHARD D. WILSON*

Checked by R. BOUGON†

Since \([\text{NF}_4]^+\) is a coordinatively saturated complex fluoro cation, the syntheses of its salts are generally difficult.\(^1\) A limited number of salts can be prepared directly from \(\text{NF}_3\), and these salts can then be converted by indirect methods into other \([\text{NF}_4]^+\) salts that are important for solid propellant \(\text{NF}_3\)-\(\text{F}_2\) gas generators or reagents for the electrophilic fluorination of aromatic compounds.

The two direct methods for the syntheses of \([\text{NF}_4]^+\) salts are based on the reaction of \(\text{NF}_3\) with either \([\text{KrF}]^+\) salts\(^2\)

\[
\text{NF}_3 + [\text{KrF}][\text{AsF}_6] \rightarrow [\text{NF}_4][\text{AsF}_6] + \text{Kr}
\]

or \(\text{F}_2\) and a strong Lewis acid in the presence of an activation energy source \(E\).\(^3\)

\[
\text{NF}_3 + \text{F}_2 + \text{XF}_n \xrightarrow{E} [\text{NF}_4][\text{XF}_{n+1}]
\]

For the chemist interested in synthesis, the second method\(^3\) is clearly superior, due to its high yields, relative simplicity, and scalability.

Four different activation energy sources have been used for the direct synthesis of \([\text{NF}_4]^+\) salts:

1. Heat\(^4-7\): \([\text{NF}_4][\text{BiF}_6], [\text{NF}_4][\text{SbF}_6], [\text{NF}_4][\text{AsF}_6], [\text{NF}_4][\text{TiF}_6 \cdot n\text{TiF}_4]\)
2. Glow discharge\(^8-9\): \([\text{NF}_4][\text{AsF}_6], [\text{NF}_4][\text{BF}_4]\)
3. UV photolysis\(^10,11\): \([\text{NF}_4][\text{SbF}_6], [\text{NF}_4][\text{AsF}_6], [\text{NF}_4][\text{PF}_6], [\text{NF}_4][\text{GeF}_3], [\text{NF}_4][\text{BF}_4]\)
4. Bremsstrahlung\(^12\): \([\text{NF}_4][\text{BF}_4]\)

Of these, the thermal synthesis of \([\text{NF}_4][\text{SbF}_6]\) is most convenient (Synthesis A) and provides the starting material required for the synthesis of other \([\text{NF}_4]^+\) salts by indirect methods. For the synthesis of pure \([\text{NF}_4]^+\) salts on a small scale, low-temperature UV photolysis is preferred (Synthesis B).\(^11\)

The following indirect methods for the interconversion of \([\text{NF}_4]^+\) salts are known:

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M - 1
1. Metathesis reaction:

\[ n[\text{NF}_4][\text{XF}_6] + [\text{Cs}]_n[\text{MF}_{m+n}] \rightarrow [\text{NF}_4]_n[\text{MF}_{m+n}] + n[\text{Cs}][\text{XF}_6] \downarrow \]

where typically \( X = \text{Sb} \) and the solvent is anhydrous HF or \( \text{BrF}_5 \). This method is limited to anions that are stable in the given solvent and results in an impure product. Typical compounds prepared in this manner include \([\text{NF}_4][\text{BF}_4]\),\(^6,13,14\) \([\text{NF}_4][\text{HF}_2]\) (Synthesis C),\(^5\) \([\text{NF}_4][\text{SO}_2\text{F}]\),\(^6\) \([\text{NF}_4][\text{ClO}_4]\),\(^5\) and \([\text{NF}_4][\text{MF}_6] (M = \text{Sn},\ ^{17} \text{Ti},\ ^{18} \text{Ni},\ ^{19} \text{Mn}) \) (Synthesis D).

2. Reaction of solid \([\text{NF}_4][\text{HF}_2],x\text{HF}\) with a weak Lewis acid: When the MG\(^{7+}\) anion is unstable in a solvent, such as HF, and the Lewis acid MG\(^m\) is volatile, the equilibrium

\[ n[\text{NF}_4][\text{HF}_2],x\text{HF} + MG_m \Leftrightarrow [\text{NF}_4]_n[MF_{m+n}] + n(x+1)\text{HF} \]

can be shifted to the right by the use of an excess of MG\(^m\) and continuous removal of HF with the excess of MG\(^m\). Typical salts prepared in this manner include \([\text{NF}_4][\text{SiF}_6]^{21}\) (Synthesis E) and \([\text{NF}_4][\text{MF}_6] (M = \text{U},\ ^{22} \text{W},\ ^{23} \text{Xe})\).

3. Reaction of \([\text{NF}_4][\text{HF}_2]\) with a nonvolatile polymeric Lewis acid: When, in the metathesis (1), all the materials except \([\text{NF}_4][\text{XF}_6]\) are insoluble, product separation becomes impossible. This problem is avoided by digesting the Lewis acid in a large excess of \([\text{NF}_4][\text{HF}_2]\) in HF solution, followed by thermal decomposition of the excess \([\text{NF}_4][\text{HF}_2]\) at room temperature.

\[ [\text{NF}_4][\text{HF}_2] + MG_n \rightarrow [\text{NF}_4][MF_{n+1}] + HF \]

Salts prepared in this manner include \([\text{NF}_4][\text{MOF}_3] (M = \text{U},\ ^{24} \text{W},\ ^{25} \text{Xe}) \) (Synthesis F), \([\text{NF}_4][\text{AlF}_4],^{26}\) and \([\text{NF}_4][\text{Be}_2\text{F}_5].^{26}\)

4. Displacement reaction: Displacement of a weaker Lewis acid by a stronger Lewis acid can be carried out easily, as demonstrated for \([\text{NF}_4][\text{PF}_6].^{11}\)

\[ [\text{NF}_4][\text{BF}_4] + \text{PF}_3 \rightarrow [\text{NF}_4][\text{PF}_6] + \text{BF}_3 \]

5. Rearrangement reaction: When \([\text{NF}_4][\text{GeF}_5]\) is treated with anhydrous HF, the following equilibrium is observed:

\[ \text{+HF} \]

\[ 2[\text{NF}_4][\text{GeF}_5] \Leftrightarrow [\text{NF}_4],_2[\text{GeF}_6] + \text{GeF}_4 \]

\[ +\text{GeF}_6 \]
This equilibrium can be shifted to the right by repeated treatments of \([\text{NF}_4][\text{GeF}_4]\) with HF and GeF\(_4\) removal, and to the left by treatment of \([\text{NF}_4]_2[\text{GeF}_6]\) with GeF\(_4\).\(^{11}\)

A. TETRAFLUOROAMMONIUM HEXAFLUOROANTIMONATE(V)

\[
\text{NF}_3 + 2\text{F}_2 + \text{SbF}_3 \rightarrow [\text{NF}_4][\text{SbF}_6] \\
\text{at 250°}
\]

Procedure

- **Caution.** High-pressure fluorine reactions should be carried out only behind barricades or in a high-pressure bay using appropriately pressure-temperature-rated nickel or Monel reactors that have been well passivated with several atmospheres of \(\text{F}_2\) at the described reaction temperature. Stainless steel reactors should be avoided owing to the potential of metal fires. All \([\text{NF}_4]^+\) salts are moisture-sensitive and must be handled in a dry atmosphere. They are strong oxidizers—contact with organic materials and fuels must be avoided.

A prepassivated (with \(\text{ClF}_3\)), single-ended 95-mL Monel cylinder [Hoke, rated for 5000 psi working pressure], equipped with a Monel valve [Hoke 3232 M4M or equivalent], is loaded in the dry nitrogen atmosphere of a glove box with \(\text{SbF}_3\) [Ozark-Mahoning] (31 mmol). The cylinder is connected to a metal vacuum system,\(^{27}\) evacuated, vacuum leak tested, and charged with \(\text{NF}_3\) [Air Products and Chemicals] (65 mmol) and \(\text{F}_2\) [Air Products and Chemicals] (98 mmol) by condensation at \(-196°\). The barricaded cylinder is heated for 5 days to 250°. The cylinder is allowed to cool by itself to ambient temperature and is then cooled to \(-196°\). The unreacted \(\text{F}_2\) and \(\text{NF}_3\) are pumped off at \(-196°\) (the pump must be protected by a fluorine scrubber\(^{28}\)); during the subsequent warm-up of the cylinder to ambient temperature, \([\text{NF}_4][\text{SbF}_6]\) (10.1 g, 31 mmol, 100% yield based on \(\text{SbF}_3\)) is left behind as a solid residue. The product is either scraped out of the cylinder in the dry box or, more conveniently, dissolved in anhydrous HF that has been dried over \(\text{BiF}_3\).\(^{17}\) Small amounts of \(\text{Ni}[\text{SbF}_6]_2\) and \(\text{Cu}[\text{SbF}_6]_2\), formed as impurities in the attack of the Monel reactor by \(\text{F}_2\) and \(\text{SbF}_3\), are only sparingly soluble in HF and are removed from the \([\text{NF}_4][\text{SbF}_6]\) solution by filtration using a porous Teflon filter [Pallflex]. If desired, the \(\text{SbF}_3\), starting material can be replaced by \(\text{SbF}_3\) [Ozark-Mahoning] without changing the remaining procedure.

**Anal.**\(^{29}\) Calcd. for \([\text{NF}_4][\text{SbF}_6]\): \(\text{NF}_3, 21.80; \text{Sb}, 37.38\). Found: \(\text{NF}_3, 21.73; \text{Sb}, 37.41\).
Properties

Tetrafluoroammonium hexafluoroantimonate(V) is a hygroscopic, white crystalline solid that is stable to about 270°. It is highly soluble in anhydrous HF (259 mg per g of HF at -78°) and moderately soluble in BrF₅. Its ¹⁹F NMR spectrum in anhydrous HF solution consists of a triplet of equal intensity at 214.7 ppm downfield from CFC₁₃ (JNF₃ = 231 Hz) for [NF₄]⁺. The vibrational spectra of the solid exhibit the following major bands: IR (pressed AgCl disk): 1227 (mw), 1162 (vs), 675 (vs), 665 (vs), 609 (m) cm⁻¹. Raman 1160(0.6), 1150(0.2), 843(7.0), 665(1), 648(10), 604(3.9), 569(0.9), 437(1.5), and 275(3.8) cm⁻¹.

B. TETRAFLUROAMMONIUM TETRAFLUOROBORATE(III)

\[
NF₃ + F₂ + BF₃ \xrightarrow{hv} [NF₄][BF₄]
\]

Procedure

- Caution. Ultraviolet goggles should be worn for eye protection when working with higher power UV lamps, and the work should be carried out in a fume hood. [NF₄][BF₄] is a strong oxidizer: contact with organic materials, fuels, and moisture must be avoided.

The low-temperature UV photolysis reaction is carried out in a quartz reactor with a pan-shaped bottom and a flat top consisting of a ~5-cm diameter optical grade quartz window (Fig. 1). The vessel has a side arm connected by a Teflon O-ring joint to a Fischer-Porter Teflon valve to facilitate removal of solid reaction products. The depth of the reactor is about 4 cm, and its volume is about 140 mL. The UV source consists of a 900-W, air-cooled, high pressure mercury arc (General Electric Model B-H6) positioned 4 cm above the flat reactor surface. The bottom of the reactor is kept cold by immersion in liquid N₂. Dry gaseous N₂ is used as a purge gas to prevent condensation of atmospheric moisture on the flat top of the reactor. As a heat shield, a 6-mm thick quartz plate is positioned between the UV source and the top of the reactor.

Premixed NF₃ [Air Products] and BF₃ [Matheson] (27 mmol of each are condensed into the cold bottom of the quartz reactor. Fluorine [Air Products, 19 mmol] is added, and the mixture is photolysed at 196° for 1 hr. After termination of the photolysis, volatile material is pumped out of the reactor through a scrubber during its warm-up to room temperature. The nonvolatile white solid residue (10 g) is pure [NF₄][BF₄]. Instead of the pan-shaped reactor, a simple round quartz bulb can be used with a [NF₄][BF₄] yield of about 85% hr.
13. Tetrafluoroammonium Salts

**Fig. 1** Apparatus for synthesis of $[\text{NF}_3][\text{BF}_4]$.  

**Anal.** Calcd. for $[\text{NF}_3][\text{BF}_4]$: $\text{NF}_3$, 40.16; B, 6.11. Found: $\text{NF}_3$, 40.28; B, 6.1

**Properties**

Tetrafluoroammonium tetrafluoroborate(III) is a hygroscopic white crystalline solid that is stable up to about 150°. It is highly soluble in anhydrous HF and moderately soluble in BrF$_3$. Its $^1$H NMR spectrum in anhydrous HF solution consists of a sharp triplet of equal intensity at $\delta$ 220 ppm downfield from CFCI, $\nu_{\text{HF}} = 230$ Hz) for $[\text{NF}_3]^+$ and an exchange broadened singlet at $\delta$ -158 ppm upfield from CFCI, for $[\text{BF}_4]^-$. The vibrational spectra of the solid exhibit the following major bands: IR (pressed AgCl disk): 1298 (ms), 1222 (mw), 1162 (vs), 1057 (vs), 809 (s), and 522 (s) cm$^{-1}$. Raman: 1179(0.6), 1148(0.6), 1055(0.2), 844(10), 772(3.2), 609(6.3), 524(0.4), 443(2.6), 350(0.9) cm$^{-1}$.

**C. TETRAFLUOROAMMONIUM (HYDROGEN DIFLUORIDE)**

$$[\text{NF}_3][\text{SbF}_5] + \text{CsF} \xrightarrow{\text{M-5}} \text{Cs}[\text{SbF}_6] \downarrow + [\text{NF}_3][\text{HF}_2]$$
**Procedure**

**Caution.** Anhydrous HF causes severe burns. Protective clothing should be worn when working with this material. The HF solutions of \(\text{[NF}_4\text{]}^+\) salts are strongly oxidizing; contact with fuels must be avoided.

A mixture of dry CsF [Kawecki Berylco] (2.361 g, 15.54 mmol) and \(\text{[NF}_4\text{]}\text{[SbF}_6\text{]}\) (5.096 g, 15.64 mmol) is placed inside the dry box into trap I of the leak-checked and passivated (with ClF_3 and dry HF) Teflon FEP Monel metathesis apparatus shown in Fig. 2. The CsF is dried by fusion in a platinum crucible, immediately transferred to the dry box, cooled, and finely ground. The apparatus is attached to a metal Teflon vacuum system by two flexible corrugated Teflon tubes [Pennrube Plastics], and the connections are vacuum leak-checked and passivated. The system is repeatedly exposed to anhydrous HF [Matheson], until the HF is colorless when frozen out at \(-196^\circ\) in a Teflon U-trap of the vacuum system to avoid contamination of the product with any chlorine fluorides that may be adsorbed onto the walls of the metal vacuum system. Anhydrous HF (16.2 g, 810 mmol) is added to trap I, and the mixture is stirred magnetically for 1 hr at room temperature. The metathesis apparatus is cooled with powdered Dry Ice to \(-78^\circ\) for 1 hr and then inverted. The HF solution that contains the
[\text{NF}_4][\text{HF}_2] \text{ is separated from the Cs}[\text{SbF}_6] \text{ precipitate by filtration. To facilitate the filtration step, trap I is pressurized with 2 atm of dry N}_2 \text{ after inversion. A pressure drop in trap I indicates the completion of the filtration step. If desired, repressurization of trap I may be repeated to minimize the amount of mother liquor held up in the filter cake. The desired HF solution of } [\text{NH}_4][\text{HF}_2] \text{ is collected in trap II. It contains about 94\% of the original } [\text{NF}_4]^+ \text{ values, with the remainder being adsorbed on the Cs}[\text{SbF}_6] \text{ filter cake. The } [\text{NF}_4][\text{HF}_2] \text{ solution has a purity of about 97 mole } \% \text{ and contains small amounts of Cs}[\text{SbF}_6] \text{ (solubility of Cs}[\text{SbF}_6] \text{ in HF at } -78^\circ \text{ is 1.8 mg/g HF)}^{13} \text{ and } [\text{NF}_4][\text{SbF}_6] \text{ (if a slight excess of } [\text{NF}_4][\text{SbF}_6] \text{ has been used in the reaction to suppress, by the common ion effect, the amount of dissolved Cs}[\text{SbF}_6]).}

An unstable solid having the composition } [\text{NF}_4][\text{HF}_2] \text{ nHF } (n = 2-10) \text{ can be prepared by pumping off as much HF as possible below } 0^\circ.

\textbf{Properties}

Tetrafluoroammonium (hydrogen difluoride) is stable in HF solution at room temperature but decomposes to NF\(_3\), F\(_2\), and HF on complete removal of the solvent.\(^{13}\) The \(^{19}\text{F} \text{ NMR spectrum of the solution shows a triplet of equal intensity of } \phi \text{ 216.2 ppm downfield from CFCl}_3 \text{ with } J_{\text{NF}} = 230 \text{ Hz. The Raman spectrum of the HF solution has bands at } 1170 \text{ (w), 854 (vs), 612 (m), and 448 (mw) cm}^{-1}\text{.}

\textbf{D. BIS(TETRAFLUOROAMMONIUM)

HEXAFLUOROMANGANATE(IV)}

\[
2[\text{NF}_4][\text{SbF}_6] + \text{Cs}_2[\text{MnF}_6] \rightarrow 2\text{Cs}[\text{SbF}_6] + [\text{NF}_4]_2[\text{MnF}_6]
\]

\(-78^\circ\)

\textbf{Procedure}

\textbf{Caution.} Anhydrous HF can cause severe burns; protective clothing should be worn when working with this solvent. [\text{NF}_4]_2[\text{MnF}_6] \text{ is a strong oxidizer; contact with water and fuels must be avoided.}

The same apparatus is used as for synthesis C. In the dry N\(_2\) atmosphere of a glove box, a mixture of [\text{NF}_4][\text{SbF}_6] \text{ (37.29 mmol) and Cs}_2[\text{MnF}_6]^{20} \text{ (18.53 mmol)} \text{ is placed in the bottom of a prepassivated (with CIF\(_3\)) Teflon FEP (fluoroethylene propylene copolymer) double U-tube metathesis apparatus. Dry HF}\(^{13}\) \text{ (20 mL of liquid) is added at } -78^\circ \text{ on the vacuum line,}\(^{27}\) \text{ and the mixture is warmed to } 25^\circ \text{ for } 30 \text{ min with stirring. The mixture is cooled to } -78^\circ \text{ and}

\text{M- 7}
pressure-filtered at this temperature. The HF solvent is pumped off at 30° for 12 hr, resulting in 14 g of a white filter cake (mainly Cs[SbF₆]) and 6.1 g of a yellow filtrate residue having the approximate composition (weight %): [NF₄][MnF₆], 92, [NF₄][SbF₆], 4, Cs[SbF₆], 4. Yield of [NF₄][MnF₆] is 87% based on Cs₂[MnF₆].

**Properties**

Bis(tetrafluoroammonium) hexafluoromanganate(IV) is a yellow crystalline solid that is stable at 65° but slowly decomposes at 100° to NF₄, F₂, and MnF₂. It is highly soluble in anhydrous HF and reacts violently with water. Its ¹⁹F NMR spectrum in anhydrous HF solution shows a broad resonance at δ 218 ppm below CFCI₁ due to [NF₄]⁺. The vibrational spectra of the solid show the following major bands: IR (pressed AgCl disk): 1221 (m), 1160 (vs), 620 (vs), and 338 (s) cm⁻¹. Raman: 855 (m), 593 (vs), 505 (m), 450 (w), and 304 (s) cm⁻¹.

**E. BIS(TETRAFLUOROAMMONIUM) HEXAFLUOROSILICATE(IV)**

\[2[\text{NF}_4][\text{HF}_2] \cdot n\text{HF} + \text{SiF}_4 \rightarrow [\text{NF}_4]_2[\text{SiF}_6] + 2(n + 1)\text{HF}\]

**Procedure**

- **Caution.** Anhydrous HF can cause severe burns, and protective clothing should be worn when working with liquid HF. All [NF₄]⁺ salts are strong oxidizers, and contact with fuels and water must be avoided.

A solution of [NF₄][HF₂] (27 mmol) in anhydrous HFa is prepared at -78° by synthesis C. Most of the HF solvent is pumped off during warm-up toward 0° until the first signs of decomposition of [NF₄][HF₂] are noted from the onset of gas evolution. The resulting residue is cooled to -196°, and SiF₄ [Matheson] (33 mmol) is added. The mixture is allowed to warm to ambient temperature while providing a volume of about 1 L in the vacuum line for expansion. During warm-up of the apparatus, the SiF₄ evaporates first and, upon melting of the [NF₄][HF₂]·nHF phase, a significant reduction in the SiF₄ pressure is noted, resulting in a final pressure of about 400 torr. A clear, colorless solution is obtained without any sign of solid formation. The material volatile at 0° is pumped off and separated by fractional condensation through traps at -126 and -196°. The SiF₄ portion (about 22 mmol), trapped at -196°, is condensed back into the reactor, which contains a white fluffy solid. After this mixture has been kept at 25° for 24 hr, all volatile material is pumped off at 25° and the SiF₄ is separated again from the HF. The solid residue is treated again with the unreacted SiF₄ at
25° for 14 hr. The materials volatile at 25° are pumped off again. They contain less than 1 mmol of HF at this point. The solid residue is heated in a dynamic vacuum to 50° for 28 hr or until no further HF evolution is noticeable. The white solid residue (about 3.8 g, 80% yield) has the approximate composition (weight %): \([\text{NF}_4]_2[\text{SiF}_6]\) 95.0, Cs[\text{SbF}_6] 2.2, \([\text{NF}_4][\text{SbF}_6]\) 2.3.

**Properties**

Bis(tetrafluoroammonium) hexafluorosilicate(IV) is a white crystalline solid that is stable at 25° but slowly decomposes at 90° to \(\text{NF}_3\), \(\text{F}_2\), and \(\text{SiF}_4\). The vibrational spectra of the solid show the following major bands: IR (pressed AgCl disk): 1223 (mw), 1165 (vs), 735 (vs, br), 614 (m), 609 (mw), 478 (s), and 448 (w) cm\(^{-1}\). Raman: 1164 (1.5), 895 (0+), 885 (0+), 859 (10), 649 (3.2), 611 (5.8), 447, 441 (3.8), and 398 (1) cm\(^{-1}\).

**F. TETRAFLUOROAMMONIUM PENTAFLUOROOXOTUNGSTATE(VI)**

\[
\text{[NF}_4\text{][HF}_2\text{]} + \text{WOF}_4 \rightarrow \text{[NF}_4\text{][WOF}_3\text{]} + \text{HF}
\]

**Procedure**

- **Caution.** Anhydrous HF can cause severe burns. Protective clothing should be worn when working with liquid HF. All \([\text{NF}_4]^+\) salts are strong oxidizers, and contact with fuels and water should be avoided.

A solution of 20 mmol of \([\text{NF}_4][\text{HF}_2]\) in 16 mL of dry HF\(^{13}\) is prepared at \(-78°\) by synthesis C and pressure-filtered into the second half of the metathesis double U-tube containing 14.6 mmol of WOF\(_4\).\(^{13}\) The mixture is stirred with a magnetic stirring bar for 30 min at 25°. The volatile material is pumped off at 25° for 12 hr. The solid residue (about 5 g, 86% yield based on WOF\(_4\)) has the approximate composition (weight %): \([\text{NF}_4][\text{WOF}_3]\) 96, Cs[\text{SbF}_6] 2, \([\text{NF}_4][\text{SbF}_6]\) 2.

**Properties**

Tetrafluoroammonium pentafluorooxotungstate(VI) is a white crystalline solid that is stable at 55° but slowly decomposes at 85° to yield \(\text{NF}_3\), \(\text{OF}_2\), \(\text{WF}_6\), and \([\text{NF}_4][\text{W}_2\text{O}_2\text{F}_6]\).\(^{25}\) The vibrational spectra of the solid show the following major bands: IR (pressed AgCl disk): 1221 (mw), 1160 (vs), 991 (vs), 688 (vs), 620 (vs, br), and 515 (vs) cm\(^{-1}\). Raman: 1165 (0.7), 996 (10), 852 (8.4), 690 (5.4), 613 (4.9), 446 (1.6), 329 (6.8), and 285 (0.5) cm\(^{-1}\).
References

APPENDIX N

14. CESIUM HEXAFLUOROMANGANATE(IV)

\[ 2\text{CsF} + \text{MnCl}_2 + 7\text{F}_2 \rightarrow \text{Cs}_2[\text{MnF}_6] + 2\text{ClF}, \]

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Several methods have been described in the literature for the syntheses of alkali metal hexafluoromanganates(IV). The reactions of $K_2[\text{MnO}_4]$, $\text{MnO}_4^-$, and KF mixtures, or $\text{KMnO}_4$ and 30% $\text{H}_2\text{O}_2$ with aqueous HF produce $K_2[\text{MnF}_4]$. However, the yields and product purities are low. Pure alkali metal hexafluoromanganates(IV) are obtained in high yield by fluorination with $F_2$ in a flow system of either $\text{MnCl}_2 + 2\text{MCl}$ at 375 to 400°, $\text{MnF}_3 + 2\text{KF}$ in a rotating $\text{Al}_2\text{O}_3$ tube at 600°, or $\text{MnCl}_2 + 2\text{KCl}$ at 275°, or by the fluorination of a $\text{KMnO}_4$, $\text{KCl}$ mixture with $\text{BrF}_3$. The method described below is based on the fluorination of a stoichiometric mixture of CsF and $\text{MnCl}_2$ in a static system at 400°. Hexafluoromanganate(IV) salts have interesting spectroscopic properties. $\text{Cs}_4[\text{MnF}_6]$ is a starting material for the metathetical synthesis of $(\text{NF}_4)_2[\text{MnF}_6]$.

**Procedure**

- **Caution.** Safety barricades must be used for carrying out high-pressure fluorination reactions. The $\text{CIF}_2$-$\text{CIF}_3$ by-products are strong oxidizers. Contact with fuel, water, or reducing agents must be avoided.

Commercially available $\text{MnCl}_2$-$4\text{H}_2\text{O}$ (Alfa) is dehydrated by heating in a Pyrex flask to 255° under vacuum (10⁻⁴ torr) for 24 hr. The completeness of the dehydration step is verified by recording the infrared spectrum, which should not show any water bands. Commercially available CsF (Kaweco, Berycol) is dried by fusion in a platinum crucible and is immediately transferred to the dry box.

A mixture of finely ground dry CsF (7.717 g, 50.80 mmol) and $\text{MnCl}_2$ (3.150 g, 25.40 mmol) is placed inside the dry box into a pressurized (with $\text{CIF}_3$) 95-mL high-pressure Monel cylinder (Hoke Model 4HSM, rated for 5000 psi working pressure) equipped with a Monel valve (Hoke, Model 3212M4M). The cylinder is attached to a metal-Teflon vacuum system, evacuated, and cooled to −196° with liquid $\text{N}_2$. Fluorine* (262 mmol) is condensed into the cylinder. The cylinder is disconnected from the vacuum line, heated in an oven to 400° for 36 hr, and then cooled again to −196° on the vacuum line. Unreacted $F_2$ is pumped off at −196° through a fluorine scrubber, and the $\text{CIF}_2$-$\text{CIF}_3$ by-products are pumped off during the warm-up of the cylinder toward room temperature. The yellow solid residue (11.045 g, 100% yield) is pure $\text{Cs}_4[\text{MnF}_6]$.

**Anal.** Calcd. for $\text{Cs}_4[\text{MnF}_6]$: Cs, 61.14; Mn, 12.63. Found: Cs, 61.2; Mn, 12.5.

*Air Products and Chemicals* Prior to use, the fluorine should be passed through a NaF scrubber to remove any HF present, which would promote attack of the Monel reactor as evidenced by the formation of some Cs$_2\text{NiF}_5$.
Properties

Cesium hexafluoromanganate(IV) is a stable yellow solid that decomposes only slowly in moist air. The IR spectrum of the solid as a dry powder pressed between AgCl plates shows the following major absorptions: 620 (vs) (antisymmetric stretch) and 338 (s) (antisymmetric deformation) cm\(^{-1}\). The Raman spectrum of the solid shows bands at 590 (vs) (symmetric in-phase stretch), 502 (m) (symmetric out-of-phase stretch), and 304 (s) (symmetric deformation) cm\(^{-1}\). The compound Cs\(_3\)[MnF\(_6\)] crystallizes at room temperature in the cubic K\(_2\)[PtCl\(_6\)] system with \(a = 8.92\) Å.\(^a\)

References

Synthesis and Characterization of CrF₄O, KrF₂-CrF₄O, and NO*CrF₃O⁻

Karl O. Christe, William W. Wilson, and Roland A. Bougon

Received January 14, 1986

Chromium(VI) tetrfluoride oxide can be prepared in high yield and purity from CrO₃F₂ and KrF₂ in HF solution. The vibrational spectra of gaseous, solid, and matrix-isolated CrF₄O and its KrF₂ and HF solutions are reported, as well as the ¹⁹F NMR spectra of the BrF₂ and SO₂ClF solutions. The data confirm for gaseous, matrix-isolated, and dissolved CrF₄O a monomeric, square-pyramidal structure of symmetry C₄, and for solid CrF₄O a fluorine-bridged polymeric structure. CrF₄O is a strong Lewis acid and with FNO it forms a stable NO*CrF₃O⁻ salt, which was characterized by vibrational spectroscopy. With KrF₂, it forms an unstable 1:1 adduct that has in the solid phase an essentially covalent structure containing a Kr-F-Cr bridge but is completely dissociated in SO₂ClF solution. With AsF₅, it does not form a stable adduct at temperatures as low as -78 °C, indicating that CrF₄O is a weak Lewis base. It was also shown that CrF₃O is a weak Lewis base and does not form a stable adduct at -78 °C.

Introduction

Chromium tetrfluoride oxide, CrF₄O, was first described by Edwards in 1963 as a byproduct in the direct fluorination of metallic chromium, and its unit cell dimensions were reported in 1974. Edwards and co-workers published an improved synthesis from CrO₃ and F₂ at 220 °C and gave the melting point, boiling point, vapor pressure, and description of a solid-solid transition at 24 °C. Reference was made in this paper to unpublished work indicating that the low-temperature phase of CrF₄O has an endless fluorine-bridged chain structure, similar to those of MoF₅O and ReF₅O⁻. The only other report on CrF₄O is a recent paper by Ogden and co-workers, who studied its infrared and UV visible

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spectra in N$_2$ matrices. From a measurement of the chromium isotopic shift and relative intensities, they concluded that monomeric CrF$_2$O$_3$ has a square-pyramidal structure of symmetry $C_4$ and an OCrF bond angle of about 106°. In addition, they found that CrF$_2$O$_3$ forms with CrF and thus the resulting 1:1 adduct has infrared bands at 955 cm$^{-1}$ (v(Cr=O)) and 650-720 cm$^{-1}$ (v(Cr-F)). In this paper, we present the results from an independent study that was undertaken in our laboratory before the paper of Ogden et al. appeared. It includes a new synthesis for CrF$_2$O$_3$ and vibrational and $^{19}$F NMR spectra and its melting point (35 °C) and vapor pressure.

Synthesis of NO$^*$CrF$_4$O. Into a passivated 0.5 in. o.d. Teflon-FEP U-tube, attached to two Teflon valves, were condensed CrF$_2$O$_3$ (0.957 mmol) and FNO (2.15 mmol) at −196 °C. The contents of the tube were allowed to warm to ambient temperature. At first, green powder turned into a red powder, which then turned progressively lighter and finally resulted in a pink color. The material was pumped off and was found to be NO$^*$CrF$_4$O (1.19 mmol), leaving behind 185.3 mg (weight calculated for 0.957 mmol of NO$^*$CrF$_4$O 184.7 mg) of a pink solid that was characterized by vibrational spectroscopy as NO$^*$CrF$_4$O and according to its DSC analysis starts to decompose exothermically at about 237 °C. Its X-ray powder pattern showed the following d spacings (A): 6.51, 5.94, 5.12, 4.84 vs. 4.66, 4.02 vs. 3.89 vs. 3.54 vs. 3.05 w, 2.82 w, 2.31 ms, 2.01 w, 1.99 w, 1.94 w, 1.91 w, 1.85 w, 1.79 w, 1.77 w, 1.71 w, 1.67 w, 1.58 w, 1.51 w, 1.43 w, 1.42 w, 1.40 w.

The CrF$_2$O-AsF$_5$ System. Into a 0.5 in. o.d. Teflon valve, tube, capped off by a Teflon valve, were condensed CrF$_2$O (0.370 mmol) and AsF$_5$ (0.515 mmol) at −196 °C. The temperature of the mixture was cycled several times between −196 and 25 °C. In contrast with pure CrF$_2$O, which exhibits a purple color in the gas phase, the gaseous AsF$_5$-CrF$_2$O mixture did not show any detectable color at 25 °C and the color of the solid in the bottom of the tube had changed from the dark purple of CrF$_2$O to a red-brown. The mixture was cooled to −78 °C, and the volatile material was pumped off. It consisted of AsF$_5$ (0.50 mmol). The residue, non-volatile at −78 °C, consisted of CrF$_2$O (0.37 mmol), indicating that CrF$_2$O does not form a stable adduct with AsF$_5$, except at temperatures as low as −196 °C.

The CrF$_2$O-AsF$_5$ System. When CrF$_2$O (obtained from the reaction of CrF$_2$O-HF mixtures in stainless-steel equipment) was treated with an excess of AsF$_5$, as described above for the CrF$_2$O-AsF$_5$ system, all the AsF$_5$ starting material was quantitatively recovered by pumping on the mixture at −78 °C.

Results and Discussion

CrF$_2$O Synthesis. The reaction of CrF$_2$O$_3$ with KrF$_6$ in anhydrous HF solution at room temperature provides a new synthesis for CrF$_2$O. The reaction proceeds quantitatively according to

$$2\text{CrF}_2\text{O}_3 + 2\text{KrF}_6 \xrightarrow{\text{HF}} 2\text{CrF}_2\text{O} + 4\text{KrF}_3 + \text{O}_2$$

The reaction is initially slow, as can be judged from the color of the HF solution, but once started it proceeds faster. The use of steel equipment should be avoided for this reaction because a mixture of HF and CrF$_2$O rapidly attacks steel with formation of CrF$_2$O.

The use of a twofold excess of KrF$_6$; in the above reaction did not result in additional oxygen-fluorine exchange and concomitant CrF$_2$O formation. Instead, the formation of an unstable 1:1 adduct between CrF$_2$O and KrF$_6$ was observed. When it was warmed to room temperature, the KrF$_6$ adduct decomposed with the formation of KrF$_3$ and CrF$_2$O. The nature of the adduct was studied and will be discussed below. In view of the tendency of CrF$_2$O to form an adduct with an excess of KrF$_6$, and the relative ease of separating CrF$_2$O from CrF$_2$O$_3$, by fractional condensation using trapping temperatures of −31 °C (bromomethane slush bath) for CrF$_2$O and −78 °C for CrF$_2$O$_3$, the use of a slight excess of KrF$_6$ is preferable for the synthesis of CrF$_2$O.

The previously reported method for the synthesis of CrF$_2$O involved the fluorination of CrF$_3$ with F$_2$ at elevated temperature and pressure in a Monel reactor with a water cooled exit. This method requires careful temperature control. The recommended conditions are 400 °C with yields of 2% of CrF$_2$O and 1% of CrF$_3$ (15). If the reaction temperature is increased, the yield of CrF$_2$O increases but CrF$_3$ is obtained as a byproduct that is difficult to separate from CrF$_2$O. One may take advantage of the previous method of more reactivity with the starting material (CrF$_3$) + F$_2$ + CrF$_3$ are embittered by lower yields of more complete product recovery and more difficult product purification.

Properties. CrF$_2$O was identified by its vapor pressure melting point (35 °C) and vibrational spectra. Its vapor pressure is lower than that of CrF$_2$O$_3$ at 25 °C, CrF$_2$O$_3$ at 35 °C, and CrF$_2$O$_3$ at 45 °C, as observed in the previous work (16, 17).
CrF₄, KrF₂-CrF₄, and NO⁺CrF₄⁻

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Table I. Vibrational Spectra (cm⁻¹) of Monomeric and Polymeric CrF₄O Compared to Those of MoF₄O

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</tbody>
</table>

*References 13, 14. Approximately frequencies from ref. 3. Reference 19, for the solid two different spectra were obtained depending on whether the sample had been prepared by sublimation or by solidification of the melt. *Obscured by BrF₄ solvent band.

* Ca narrow singlet (~20 Hz) at about 485 ppm downfield from external CFCI₃. This suggests that all four fluorines are equivalent as expected for a monomeric, square-pyramidal CrF₄O molecule. This was also confirmed by Raman spectroscopy (see below).

Vibrational Spectra and Structure. The square-pyramidal tetrafluoride oxides of Mo, W, and Re are rare exceptions to the Gillespie-Nyholm valence shell electron pair repulsion (VSEPR) theory, which predicts for pentacoordinated XF₄O molecules Cₛₚ symmetry, i.e., a trigonal-bipyramidal structure. Whereas the square-pyramidal structures of monomeric WF₄O and MoF₄O are well-establishe by electron diffraction studies, the only previous evidence for CrF₄O having an analogous Cₛₚ structure was based on a recent infrared matrix isolation study. The results of our study confirm the previous matrix data and provide additional data on the infrared spectrum of the gas, the Raman spectra of its solutions, and the infrared and Raman spectra of solid, polymeric CrF₄O.

We were in the process of studying the infrared spectra of CrF₄O in nitrogen and neon matrices when we learned of the independent work at the University of Southampton. Since our data for the N₂ matrices were in excellent agreement with the results of the Southampton group, we discontinued that part of our study. Our results for the neon matrices raise, however, one minor question concerning the splitting of ν₁(E) into two components in the N₂ matrix. This splitting has been attributed to a matrix site effect. Since in the neon matrix a similar splitting is observed for ν₂ alternate explanations might have to be considered.

The infrared spectra of gaseous CrF₄O (see Figures 1 and 2 and Table I) provide further evidence for a monomeric CrF₄O molecule of symmetry Cₛₚ. A six-atom XF₄O molecule of symmetry Cₛₚ has nine fundamental vibrations, which are classified as 1A + 2B + 2E, of which only the A and the E modes are infrared active. Of the six infrared active modes three are strong vibrations and are the only ones expected to occur above the cutoff frequency of the AgI windows used. As can be seen from Figure 1 three bands were observed and their frequencies are in good agreement with the matrix data. Additional evidence for the Cₛₚ structure comes from the observed Raman spectra.
Figure 2). Although these contours are complicated by the presence of four chromium isotopes (\(^{52}\)Cr, 4.5%; \(^{53}\)Cr, 83.8%; \(^{54}\)Cr, 9.4%; \(^{53}\)Cr, 2.3%), the PR branch splittings of about 18-19 cm\(^{-1}\) for the A\(_1\) parallel bands and of about 12 cm\(^{-1}\) for the perpendicular band of species \(E\) are in good agreement with a previous analysis for square-pyramidal MoF\(_6\), WF\(_6\), and ReF\(_6\). In all infrared spectra of gaseous CrF\(_4\) we have observed a weak infrared band at 826 cm\(^{-1}\) of constant relative intensity. This band is probably due to a combination band or overtone of CrF\(_4\) but at the present time cannot positively be assigned.

Since CrF\(_4\) is highly soluble in both BrF\(_5\) and HF, it was possible to obtain partial Raman spectra for solutions. In agreement with the \(^{19}\)F-NMR data (see above), the Raman data (see Table I) suggest that CrF\(_4\) is monomeric in BrF\(_5\) solution. Within experimental error the Cr=O stretching frequency for the BrF\(_5\) solution is identical with those of the gas and the matrix-isolated species. Although the symmetric CrF\(_4\) stretching mode, \(v_2\)(A\(_1\)), was observed by an intense BrF\(_5\) band, two deformation modes were observable at 340 and 269 cm\(^{-1}\). The latter was polarized, thus confirming its assignment to the symmetric CrF\(_4\) deformation mode, \(v_1\)(A\(_1\)), as previously proposed.

For the HF solution of CrF\(_4\), a relatively broad band at 1008 cm\(^{-1}\) and a very intense band at 677 cm\(^{-1}\) were observed in the Cr=F and Cr=O stretching mode regions, respectively. Their frequencies are intermediate between those of monomeric CrF\(_4\) (see Table 1) and CrF\(_4\) (see below). Therefore, it is not unreasonable to attribute these observed bands to a polyanion such as [CrF\(_4\)]\(^{2-}\) formed according to

\[
2\text{CrF}_4\text{O} + 2\text{HF} = \text{H}_2\text{F}^+ + \text{CrF}_4\text{O}_2^-
\]

This interpretation is in accord with previous results obtained for the HF-MoF\(_6\) and HF-WF\(_6\) systems and is further supported by the observation of a broad weak Raman band at about 580 cm\(^{-1}\), similar to that observed at 576 cm\(^{-1}\) for MoF\(_6\).\(^{15}\)

The \(^{19}\)F-NMR spectrum of the HF solution of CrF\(_4\) at -30 \(^\circ\)C was also recorded and showed in addition to the HF signal at \(\phi = 199\) a very broad unresolved signal at \(\phi = 467\). The upfield shift of 21 ppm relative to monomeric CrF\(_4\) in BrF\(_5\) (see above) parallels that previously observed for WF\(_6\) and W\(_2\)F\(_5\).\(^{17}\)

The infrared and Raman spectra of solid CrF\(_4\)O are shown in Figure 3. A comparison of the observed spectra to those of solid MoF\(_6\) and WF\(_6\) (see Table I) shows close similarities, indicating similar structures for the two compounds, i.e., endless cis-fluorine-bridged chains of XF\(_6\)O pseudo-octahedrons.\(^{3}\) For solid MoF\(_6\), two slightly different Raman spectra have been reported for sublimed MoF\(_6\) and the solidified melt, respectively (see Table I). Although CrF\(_4\)O is known\(^{17}\) to undergo a solid-solid phase transition at 24 \(^\circ\)C, the Raman spectra of sublimed CrF\(_4\)O and of the solidified melt were found to be identical within experimental error. It appears that the polymorphism observed for both MoF\(_6\) and CrF\(_4\)O may involve only slightly different packings of the chains and that the packings in MoF\(_6\) may differ from those in CrF\(_4\)O as indicated by the fact that sublimed MoF\(_6\)\(^{18}\) and CrF\(_4\)O have vastly different unit cells and X-ray powder patterns.

Amphoterism Nature. By analogy with MoF\(_6\)\(^{19}\) and WF\(_6\), and on the basis of its vibrational spectra (see above), monomeric CrF\(_4\)O has a square-pyramidal structure of symmetry C\(_2v\). This square-pyramidal-type structure differs only very little in energy from that of the more common trigonal bipyramidal.\(^{14}\) Since trigonal-bipyramidal molecules generally exhibit a very pronounced tendency to form both tetrahedral cations and octahedral anions (organic and inorganic), it is possible to postulate a square-pyramidal structure for the molecule.\(^{18}\)

The infrared spectrum of the solid at 6 K on a CaF\(_2\) window (see above) showed a broad weak band at 177 cm\(^{-1}\) and a more intense broad band at 467 cm\(^{-1}\). The band at 177 cm\(^{-1}\) was assigned to the Cr=F stretching vibration. This vibration is also observed in the infrared spectrum of the solid at -30 \(^\circ\)C. The band at 467 cm\(^{-1}\) is probably due to a combination band of the Cr=O stretching vibration and a bending vibration of the Cr=O bond. The band at 467 cm\(^{-1}\) is also observed in the infrared spectrum of the solid at -30 \(^\circ\)C.

The Raman spectrum of the solid at 24 \(^\circ\)C shows a very intense band at 177 cm\(^{-1}\) and a weak band at 467 cm\(^{-1}\). The band at 177 cm\(^{-1}\) is probably due to the Cr=F stretching vibration. The band at 467 cm\(^{-1}\) is probably due to a combination band of the Cr=O stretching vibration and a bending vibration of the Cr=O bond. The band at 467 cm\(^{-1}\) is also observed in the Raman spectrum of the solid at -30 \(^\circ\)C.

The Lewis basicity of CrF\(_4\)O was also studied. With AsF\(_5\), it does not form a stable adduct at temperatures as low as -30 \(^\circ\)C. This indicates that CrF\(_4\)O is a rather weak Lewis base. A similar behavior has previously been found for MoF\(_6\), WF\(_6\), and ReF\(_6\). For example, MoF\(_6\) and WF\(_6\) form with the strong Lewis acid SbF\(_5\) only marginally stable 1:1 adducts that consist of either fluoride-bridged zigzag chains (MoF\(_6\)SbF\(_5\)) or dimers containing eight-membered rings with two Re, two Nb, and four Lewis atoms (ReF\(_6\)OsBF\(_5\)).\(^{15}\) It therefore appears that all these square-pyramidal molecules are strong fluoride nonacceptors (Lewis acids) but relatively weak donors (Lewis bases).

NO\(_3\)CrF\(_4\) (Vibrational and Spectral Properties). CrF\(_4\)O combines with NO\(_3\) in a 1:1 ratio to yield the solid adduct NO\(_3\)CrF\(_4\)O. The compound is a stable crystalline form used as a nonaqueous fuel.
Table II. Vibrational Spectra (cm$^{-1}$) of CrF$_3$O Compared to Those of MoF$_3$O and WF$_3$O

<table>
<thead>
<tr>
<th>assign in point group C$_{3v}$</th>
<th>NO*CrF$_3$O</th>
<th>NO*MoF$_3$O</th>
<th>NO*WF$_3$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>n(A1) $\delta$(XO)</td>
<td>980 s</td>
<td>965 (7.2)</td>
<td>980 s</td>
</tr>
<tr>
<td>n(A1) $\delta$(XF)</td>
<td>520 sh</td>
<td>662 mw</td>
<td>548 m</td>
</tr>
<tr>
<td>n(A1) $\gamma$(XF$_2$)</td>
<td>302 m</td>
<td>293 (1)</td>
<td>292 sh</td>
</tr>
<tr>
<td>n(B1) $\delta$(XF$_2$)</td>
<td>557 m</td>
<td>557 (0.6)</td>
<td>591 (0.4)</td>
</tr>
<tr>
<td>n(B1) $\gamma$(XF$_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n(C) $\delta$(XO)</td>
<td>586 vs. br</td>
<td>650 vs. br</td>
<td>605 vs. br</td>
</tr>
<tr>
<td>n(C) $\gamma$(XO)</td>
<td>330 m</td>
<td>317 (6.2)</td>
<td>327 (5.9)</td>
</tr>
<tr>
<td>n(E) $\delta$(XO)</td>
<td>279 m</td>
<td>252 s</td>
<td>242 s</td>
</tr>
</tbody>
</table>

*Reference 17  **Reference 22

Figure 4. Vibrational spectra of solid NO*CrF$_3$O. (A) infrared spectrum of a mixture of NO*CrF$_3$O and NO*CrF$_3$O·CrF$_3$O between AgCl disks at room temperature; (B) infrared spectrum of NO*CrF$_3$O; (C) Raman spectrum of solid NO*CrF$_3$O in a glass capillary recorded at $-144^\circ$C with 647$\mu$m excitation.

was established by infrared and Raman spectroscopy (see Figure 4 and Table II), which shows the characteristic NO* stretching mode at about 2310 cm$^{-1}$. The assignments for CrF$_3$O in point group C$_{3v}$ were made by analogy with those previously reported$^{11,22}$ for MoF$_3$O and W$_2$F$_6$O (see Table II) and show plausible trends if the corresponding mass and coupling effects are taken into consideration. Of the given assignments, those for $v_1$, $v_2$, and $v_3$ are firm while those for $v_4$, $v_5$, $v_6$, and $v_7$ are somewhat tentative.

A comparison of the vibrational spectra of NO*CrF$_3$O with the two previously reported infrared bands$^2$ for Cs*CrF$_3$O shows substantial frequency differences. The drop in the Cr=O stretching frequency by 25 cm$^{-1}$ from NO*CrF$_3$O (980 cm$^{-1}$) to Cs*CrF$_3$O (955 cm$^{-1}$) is larger but similar to those previously found$^{12,22}$ for the corresponding NO*-Cs$^+$ couples of MoF$_3$O and W$_2$F$_6$O and most likely is caused to some extent by the different degree of anion-cation interaction. The large frequency increase of about 100 cm$^{-1}$ for the antisymmetric CrF$_3$ stretching mode from NO*CrF$_3$O to Cs*CrF$_3$O is more difficult to explain. This band is generally very broad and the choice of the band center can be difficult. However, in this case the shift is opposite to that reported for the NO*MoF$_3$ and Cs*MoF$_3$ couple and the

reported Cs*CrF$_3$O value 1650-720 cm$^{-1}$ is outside the range (550-650 cm$^{-1}$) of this band in NO*CrF$_3$O but falls within the range observed for the polyanion CrF$_3$O·CrF$_3$O (see below). A comparison of the data of Table II shows that for the NO* and Cs* salts of MoF$_3$O and W$_2$F$_6$O, there are also some large frequency shifts for the bands assigned to the X-F stretching mode n(A1)$^2$ At this time it is difficult to say to what extent these shifts are real.

The infrared spectrum of a mixture of NO*CrF$_3$O and NO*CrF$_3$O·CrF$_3$O obtained by controlled pyrolysis at NO* CrF$_3$O in a DSC cell is shown in Figure 4. Composed to that of NO*CrF$_3$O the spectrum shows the expected changes between the Cr=O and CrF$_3$ stretching modes are shifted toward higher frequencies which are intermediate between those of CrF$_3$O and solid CrF$_3$O. These data indicate that a mechanism
spectra of NMR was Vilridoal Spectra The low-temperature infrared and Raman structural identification of this adduct was facilitated to replace the CrF,0 adduct. This adduct formation rendered the removal of the excess KrF quite difficult. The adduct was found to be a purple solid that at room temperature reversibly dissociates to KrF, and CrF,0. The formation of a KrF,2CrF,0 adduct is not surprising in view of the fact that both WF,0 and MoF,0 form adducts with KrF, and the formation of a KrF,2CrF,0 was established by low-temperature infrared, Raman, and 39F NMR spectroscopy.

Vibrational Spectra. The low-temperature infrared and Raman spectra of KrF,2CrF,0 were recorded and are shown in Figure 5. The observed frequencies are summarized in Table III. The structural identification of this adduct was facilitated by the fact that the analogous KrF,MoF,0 and KrF,WF,0 adducts had previously been thoroughly characterized by Holloway and Schrobilgen. These investigators have established by nuclear magnetic resonance and vibrational spectroscopy that these adducts are predominantly covalent, containing a Kr-F-metal bridge in a position trans to the oxygen ligand:

A comparison of the vibrational spectra of KrF,2CrF,0 to those of KrF,MoF,0 and KrF,WF,0 shows smooth trends for this series and the values are presented in Table III.

Table III. Vibrational Spectra (cm⁻¹) and Relative Intensities* of Solid KrF,2CrF,0 Compared to Those of KrF,2 MoF,0, and KrF,2WF,0

<table>
<thead>
<tr>
<th>IR (gas)</th>
<th>RA (gas, solid)</th>
<th>IR (−196 °C)</th>
<th>RA (−144 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1011 m</td>
<td>1011 (1.1)</td>
<td>1034 (1.2), 1025 (3.3)</td>
<td>1041 (0.8), 1034 (4.5)</td>
</tr>
<tr>
<td>723 w</td>
<td>736 (0.05)</td>
<td>702 (0.5)</td>
<td></td>
</tr>
<tr>
<td>704 s</td>
<td>718 (0.2)</td>
<td>698 (0.7)</td>
<td></td>
</tr>
<tr>
<td>668 s</td>
<td>671 (10)</td>
<td>691 (6.3)</td>
<td>706 (1.8)</td>
</tr>
<tr>
<td>655 vs</td>
<td>650 (0.1)</td>
<td>661 (0.2)</td>
<td></td>
</tr>
<tr>
<td>550 sh</td>
<td>550 (0.7)</td>
<td>582 (1.6)</td>
<td>611 (0.3)</td>
</tr>
<tr>
<td>342 vs</td>
<td>550 (0.7)</td>
<td>579 (5.3)</td>
<td>581 (4.5)</td>
</tr>
<tr>
<td>588 vs</td>
<td>550 (0.7)</td>
<td>566 (10)</td>
<td></td>
</tr>
</tbody>
</table>

*Relative RA intensities based on peak heights and not peak areas.  
Reference 24.  
Reference 25.  
Fw = terminal fluorine.  
Ko = bridging fluorine.

NO CF,0 exist and are thermally more stable than NO CF,0.

KOF,2CrF,0. During preparations of CrF,0 from CrO,F2 and an excess of KrF,2 it was noticed that KrF,2 was not only unable to replace the second oxygen of CrO,F2 by two fluorines but also formed a CrF,0-KrF,2 adduct. This adduct formation rendered the removal of the excess KrF quite difficult. The adduct was found to be a purple solid that at room temperature reversibly dissociates to KrF,2 and CrF,0. The formation of a KrF,2-CrF,0 adduct is not surprising in view of the fact that both WF,0 and MoF,0 form adducts with KrF,2. The nature of KrF,2-CrF,0 was established by low-temperature infrared, Raman, and 39F NMR spectroscopy.

Vibrational Spectra. The low-temperature infrared and Raman spectra of KrF,2-CrF,0 were recorded and are shown in Figure 5. The observed frequencies are summarized in Table III. The structural identification of this adduct was facilitated by the fact that the analogous KrF,2-MoF,0 and KrF,2-WF,0 adducts had previously been thoroughly characterized by Holloway and Schrobilgen. These investigators have established by nuclear magnetic resonance and vibrational spectroscopy that these adducts are predominantly covalent, containing a Kr-F-metal bridge in a position trans to the oxygen ligand:

A comparison of the vibrational spectra of KrF,2-CrF,0 to those of KrF,2-MoF,0 and KrF,2-WF,0 shows smooth trends for this series and the values are presented in Table III.

Table IV. Frequencies (cm⁻¹) of the KrF,2 Stretching Modes of KrF,2 Adducts

<table>
<thead>
<tr>
<th>KrF,2</th>
<th>KrF,2MoF,0</th>
<th>KrF,2WF,0</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(F,Kr)</td>
<td>r(F,Kr)</td>
<td>r(F,Kr)</td>
</tr>
<tr>
<td>581, 581</td>
<td>581, 581</td>
<td>581, 581</td>
</tr>
<tr>
<td>469, 450</td>
<td>469, 450</td>
<td>469, 450</td>
</tr>
</tbody>
</table>

*Reference 24.  
Reference 25.
F_2CrF_4O exhibits the smallest frequency separation, suggesting that the covalency of the KrF_2XF_4O adducts increases on going from X = W to X = Cr.

\(^{19}\)F NMR Spectra. The increase in covalency for KrF_2CrF_4O was further supported by \(^{19}\)F NMR spectroscopy. Whereas KrF_2XF_4O (X = Mo, W) show unequivocal NMR evidence for a fluorine-bridged adduct in SO_2ClF solution, the corresponding KrF_2CrF_4O adduct in SO_2ClF showed in the temperature range -120 to -10 °C only two sharp signals due to CrF_4O and KrF_2 without any sign of coupling. The chemical shift of the CrF_4O resonance exhibited relatively little temperature dependence and occurred in the range 482-486 ppm. However, the chemical shift of KrF_2 showed a very pronounced temperature dependence varying from about 63 ppm at -118 °C to about 82 ppm at -10 °C. A similarly pronounced temperature dependence of the chemical shift of KrF_2 has previously been observed for BrF_4 solutions (68 ppm at -150 °C and 78 ppm at 27 °C) and was attributed to solvation effects.

Conclusion. The structure and physical and chemical properties of CrF_4O resemble those of WF_4O and MoF_4O. Thus, CrF_4O is also a strong Lewis acid and forms a stable NO\(^{+}\)CrF_4O\(^{-}\) salt. With KrF_2 it forms an unstable, highly covalent 1:1 adduct which in SO_2ClF solution, contrary to those of WF_4O and MoF_4O, is completely dissociated to KrF_2 and CrF_4O. The major difference between CrF_4O and MoF_4O and WF_4O is the strong increase in oxidizing power from WF_4O to CrF_4O with the latter being capable of oxidizing O_2 to O_2^+ and NF_3 to NF_3^+.

Acknowledgment. We are grateful to Drs. C. J. Schack and L. R. Grant and R. D. Wilson for their help and to the U.S. Army Research Office and the Office of Naval Research for financial support. R.A.B. is also indebted to Dr. W. Kaska and the University of California, Santa Barbara, CA, for their hospitality and to the DRET for financial support.

Registry No. CrF_4O, 22376-90-4; CrO_2F_n, 7788-96-7; HF, 7664-39-3; NO\(^{+}\)CrF_4O, 102110-04-3; AsF_5, 7784-36-3; CrF_4O, 43997-25-7; KrF_2CrF_4O, 102110-05-4.

(27) Christe, K. O.; Wilson, W. W., unpublished data.
ESTIMATION OF THE N–F BOND DISTANCE IN NF₂* FROM ITS GENERAL VALENCE FORCE FIELD

(Received 12 October 1985; accepted 31 January 1986)

Abstract—The estimate of the bond length in NF₂* from the published general valence force field was revised and a value of 1.31 Å is suggested.

Although the NF₂ cation has been known for two decades [1, 2], so far all attempts have failed to obtain a crystal structure of one of its salts and thus a value for its N–F bond length. Based on its known general valence force field, the N–F bond length of NF₂* has been estimated as 1.24 Å [3]. Since this value is unusually short and disagrees with that of 1.32 Å recently predicted by ab initio studies [4], the basis for the previous estimate of 1.24 Å was reexamined.

For the previous estimate of \( r_{\text{NF}} \) of NF₂* from its stretching force constant \( f_s \) (6.15 N/cm), a linear extrapolation was used which was based on only two data points (FNO, \( r = 1.512 \) Å, \( f_s = 2.151 \) N/cm; and NF₃, \( r = 1.365 \) Å, \( f_s = 4.311 \) N/cm). If additional NF compounds for which reliable bond distances and force constants are available (NF, \( r = 1.3173 \) Å [5], \( f_s = 5.90 \) N/cm [6]; FNO₂, \( r = 1.467 \) Å [7], \( f_s = 2.678 \) N/cm [8]) are included in the bond length extrapolation, it becomes obvious (see Fig. 1) that the previous linear extrapolation is a poor approximation. As has previously been shown for other bonds, the plots of \( f_s \) against \( r \) are nonlinear [9] and resemble that of Fig. 1. Using the curve of \( f_s \) value of 6.15 N/cm, the N–F bond length of NF₂* is estimated as about 1.31 Å. This value is in excellent agreement with the ab initio value of 1.32 Å and clearly is a better estimate than the previously published value of 1.24 Å.

Acknowledgement—The author is indebted to the U.S. Army Research Office and the Office of Naval Research for financial support.

REFERENCES

Chemical Synthesis of Elemental Fluorine

Sir:

The chemical synthesis\(^1\) of elemental fluorine has been pursued for at least 173 years\(^2\) by many notable chemists, including Davy,\(^3\) Fremy,\(^4\) Moissan,\(^5\) and Ruff.\(^6\) All their attempts have failed, and the only known practical synthesis of F\(_2\) is Moissan’s electrolysis.

Although in principle the thermal decomposition of any fluoride is bound to yield fluorine, the required reaction temperatures and conditions are so extreme that rapid reaction of the evolved fluorine with the hot reactor walls preempts the isolation of significant amounts of fluorine. Thus, even in the well-publicized case of K\(_2\)PbF\(_4\), only trace amounts of fluorine were isolated.\(^7\)

These failures, combined with the fact that fluorine is the most electronegative element and generally exhibits the highest single bond energies in its combinations with other elements,\(^8\) have led to the widely accepted\(^11\) belief that it is impossible to generate fluorine by purely chemical means.

The purpose of this communication is to report the first purely chemical synthesis of elemental fluorine in significant yield and concentration. This is based on the fact that thermodynamically unstable high-oxidation-state transition-metal fluorides can be stabilized by anion formation. Thus, unstable NiF\(_2\), CuF\(_2\), or MnF\(_2\) can be stabilized in the form of their corresponding MF\(_4^2-\) anions. Furthermore, it is well-known that a weaker Lewis acid, such as MF\(_2\), can be displaced from its salts by a stronger Lewis acid, such as SbF\(_5\).

\[
\text{K}_2\text{MF}_2 + 2\text{SbF}_5 \rightarrow 2\text{KSbF}_6 + [\text{MF}_2^-] \quad (1)
\]

If the liberated MF\(_2\) is thermodynamically unstable, it will spontaneously decompose to a lower fluoride, such as MF\(_2\) or MF\(_2^+\), with simultaneous evolution of elemental fluorine.

\[
[\text{MF}_2^-] \rightarrow \text{MF}_2 + \text{F}_2 \quad (2)
\]

Since a reversal of (2) is thermodynamically not favored, fluorine can be generated even at relatively high pressures.

Consequently, the chemical generation of elemental fluorine might be accomplished by a very simple displacement reaction, provided a suitable complex fluoro anion is selected which can be prepared without the use of elemental fluorine and is derived from a thermodynamically unstable parent molecule. The salt selected for this study was K\(_2\)MnF\(_6\). It has been known\(^1\) since 1899 and is best prepared from aqueous HF solution.\(^10\)

\[
2\text{KMnO}_4 + 2\text{KF} + 10\text{HF} + 3\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{MnF}_6 + 8\text{H}_2\text{O} + 3\text{O}_2 \quad (3)
\]

The literature yield of 30% was increased to 73% and can probably be improved further by refining the washing procedure (use of acetone instead of HF).\(^11\) The other starting materials, SbF\(_5\), can be prepared\(^12\) in high yield from SbCl\(_5\) and HF.

\[
\text{SbCl}_5 + 5\text{HF} \rightarrow \text{SbF}_5 + 5\text{HCl} \quad (4)
\]

Since both starting materials, K\(_2\)MnF\(_6\) and SbF\(_5\), can be readily prepared without the use of F\(_2\) from HF solutions, the reaction

\[
2\text{K}_2\text{MnF}_6 + 2\text{SbF}_5 \rightarrow 2\text{KSbF}_6 + \text{MnF}_2 + \text{F}_2 \quad (5)
\]

represents a truly chemical synthesis of elemental fluorine.

The displacement reaction between K\(_2\)MnF\(_6\) and SbF\(_5\) was carried out in a passivated Teflon-stainless-steel reactor at 150°C for 1 h. The gas, volatile at -196°C, was measured by PVT and shown by its reaction with mercury and its characteristic odor to be fluorine. The yield of fluorine based on (5) was found to be reproducible and in excess of 40% but most likely can be improved upon significantly by refinement of the experimental conditions. Fluorine pressures of more than 1 atm were generated in this manner.

In summary, the purely chemical generation of elemental fluorine can be achieved in high yield and concentration by a very simple displacement reaction between starting materials that can:

be prepared in high yields from HF solutions and have been known for 80 years or longer. As in the cases of noble gas or NF
chemistry, the successful chemical synthesis of elemental fluorine demonstrates that one should never cease to critically challenge accepted dogmas.

Acknowledgment. The author is grateful to R. D. Wilson for his assistance with some of the experiments, to Drs. C. J. Schack, W. W. Wilson, and L. R. Grant for help, and to the U.S. Army Research Office and Office of Naval Research for financial support.


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APPENDIX R


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PREPARATION AND CHARACTERIZATION OF Ni(SbF$_6$)$_2$

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SUMMARY

Ni(SbF$_6$)$_2$ was prepared from Ni powder, F$_2$ and SbF$_5$ at
270°C and 250 atm pressure. The yellow, crystalline material
is stable to at least 230°C and was characterized by elemental
analysis, x-ray powder data, and vibrational spectroscopy.
The crystal structure of Ni(SbF$_6$)$_2$, (hexagonal, a = 5.16Å,
c = 27.90Å, Z = 3), can be related to the rhombohedral-hexagonal
LiSbF$_6$ structure by occupation of only every second Li$^+$ site
with Ni$^{2+}$ and by the concomitant doubling of the c-axis of its
hexagonal unit cell.

INTRODUCTION

In high temperature fluorination reactions involving
elemental fluorine and a strong Lewis acid in a metal cylinder,
the metal cylinder is usually strongly attacked by the reagents.
To minimize these side reactions, cylinders made from either
nickel or nickel-copper alloys, such as Monel, are generally
used. Even under these conditions the attack on the cylinder
is still appreciable and often can compete with the desired
reactions [1-3]. Although it has repeatedly been stated that
the side products in F$_2$-MF$_5$(M=As,Sb,Bi) reactions in nickel
reactors are Ni(MF$_6$)$_2$ salts [1-3], very few data have been

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published for these compounds. For Ni(AsF$_6$)$_2$, only its x-ray powder pattern and vibrational spectra [4] and, for Ni(SbF$_6$)$_2$, only its magnetic moment [5] have been published. In view of the fact that these salts are very common impurities in most high-temperature, high-pressure fluorination reactions involving these Lewis acids and fluorine, a better characterization of these nickel salts was highly desirable.

EXPERIMENTAL

Apparatus

Fluorine (Air Products) was handled in a conventional stainless steel-Teflon FEP vacuum line. Solids and SbF$_5$ (Ozark Mahoning, purified by vacuum distillation prior to use) were handled in the dry nitrogen atmosphere of a glove box. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrometer. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1 nm exciting line of a Kr-ion laser and melting point capillaries as sample containers. X-ray diffraction patterns were obtained using 0.5 mm quartz capillaries, a General Electric Model XRD-6 diffractometer, Ni-filtered CuK$_\alpha$ radiation, and a 114.6 mm diameter Phillips camera.

Ni(SbF$_6$)$_2$

Nickel powder (7.968 mmol) was placed into a 20 mL nickel cylinder equipped with a nickel valve. The cylinder containing the Ni powder was passivated at ambient temperature with 2 atm of gaseous F$_2$ for 2.5 hr. The F$_2$ was pumped off and distilled SbF$_5$ (53.80 mmol) was added to the cylinder in the dry box. The cylinder was connected to a stainless steel vacuum line, evacuated and cooled to -196°C. Fluorine (60.5 mmol) was condensed into the cylinder, and the cylinder was allowed to warm to ambient temperature behind a barricade. The cylinder was placed into an oven and heated...
to 270°C for 88 hr, cooled, and then reconnected to the vacuum line. The excess of F₂ was pumped off at room temperature, and the reactor was heated in a dynamic vacuum to 180°C for 7 hr. The yellow crystallinic residue (14.257g, weight calcd. for 26.90 mmol of Ni(SbF₆)₂ = 14.262g) did not lose any weight on heating to 230°C for 4 hr in a dynamic vacuum. Anal. Calcd for Ni(SbF₆)₂: Ni, 11.07; Sb, 45.93; F, 43.00. Found: Ni, 11.22; Sb, 46.20; F, 42.67.

RESULTS AND DISCUSSION

Synthesis and Properties of Ni(SbF₆)₂

The reaction of F₂ and SbF₅ with nickel powder was carried out in a nickel reactor at 270°C and about 250 atm pressure. It resulted not only in a quantitative conversion of the nickel powder to Ni(SbF₆)₂, but also in an attack on the walls of the nickel vessel until the limiting reagent, SbF₅, was completely consumed by formation of Ni(SbF₆)₂. The product was a finely divided, pale yellow, hygroscopic, crystalline powder which is stable in a dynamic vacuum up to at least 230°C. Its composition was established by the observed material balance and elemental analysis. It readily dissolves in water with the green color characteristic for aqueous solutions of Ni²⁺. With CH₃CN it forms a bright blue solid and solution. By analogy with the known [6] compound [Ni(CH₃CN)₆]²⁺(BF₄⁻)₂, the blue color suggests the formation of the corresponding [Ni(CH₃CN)₆]²⁺(SbF₆⁻)₂ complex. In anhydrous HF, Ni(SbF₆)₂ is quite soluble. Large cube-shaped crystals were grown from this solvent. However, they tended to be multiple crystals, thus preempting a crystal structure determination.

X-Ray Diffraction Data

Due to the lack of suitable single crystals, only powder data could be recorded for Ni(SbF₆)₂. The observed pattern (see Table I)
closely resembles those previously reported for the hexagonal-
trigonal AMF₆-type compounds LiBiF₆ and NaBiF₆ [7]. These
compounds are isotypic with LiSbF₆ whose structure is well known
from single crystal data and can be considered as a tetragonal
distorted, face-centered cubic NaSbF₆-type structure [8].

Replacement of the singly charged Li⁺ cations by doubly
charged Ni²⁺ cations in the LiSbF₆ lattice results in half of
the cation sites becoming vacant. The distribution of the Ni²⁺
sites and vacancies could be either ordered or disordered. If it
is ordered, Ni²⁺ sites alternate with vacancies, and therefore
the unit cell dimensions of LiSbF₆ must be doubled for Ni(SbF₆)₂.

A closer inspection of the powder pattern of Ni(SbF₆)₂
reveals indeed the presence of a weak line at 4.03Å. This
line can only be indexed if the value of the c-axis of the
hexagonal (Z = 3) LiSbF₆ unit cell is doubled, resulting in
the following unit cell parameters for Ni(SbF₆)₂: a = 5.16Å,
c = 27.90Å, V = 643.3Å³, and Z = 3. Other super-structure lines
were not observed, but their relative intensities might be very
low. If the Ni(SbF₆)₂ pattern is indexed based on this doubled
hexagonal cell, the trigonal condition, -h + k + l = 3n,
obviously is no longer met.

On the other hand, if the distribution of the Ni²⁺ and
vacancy sites were disordered, no super-structure lines should
be observable. Consequently, the x-ray powder diffraction data
of Ni(SbF₆)₂ are best interpreted in terms of a LiSbF₆-type
structure with an ordered occupation of the Li⁺ sites by Ni²⁺
and vacancies.

In LiSbF₆ each Li is surrounded by six F from six different
SbF₆⁻ octahedra [8]. Thus, both Li and Sb are hexacoordinated
<table>
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<tr>
<th>d(obsd), Å</th>
<th>d(calcld), Å</th>
<th>Intens.</th>
<th>h</th>
<th>k</th>
<th>l</th>
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<td>1.257</td>
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<td>1.223</td>
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<td>1.214</td>
<td>mw</td>
<td>1</td>
<td>2</td>
<td>16</td>
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</tbody>
</table>

*Hexagonal; a = 5.16 Å, c = 27.90 Å, Z = 3, V = 643.3 Å³
CuKα radiation, Ni filter.
with respect to fluorine, and each fluorine has one nearest Sb and Li neighbor. In Ni(SbF\textsubscript{6})\textsubscript{2} half of the Li sites of LiSbF\textsubscript{6} have been substituted with Ni while the other half is vacant. Assuming an ordered distribution of Ni sites and vacancies, only three of the six fluorines of each SbF\textsubscript{6}\textsuperscript{-} anion can form fluorine bridges to Ni\textsuperscript{2+} cations. Furthermore, a close inspection of the LiSbF\textsubscript{6} structure suggests that for Ni(SbF\textsubscript{6})\textsubscript{2} the three bridging fluorines of each SbF\textsubscript{6}\textsuperscript{-} anion must be cis with respect to each other, i.e. share a common face of the SbF\textsubscript{6} octahedron. Consequently, the site symmetry of the Sb atom in Ni(SbF\textsubscript{6})\textsubscript{2} may not be higher than C\textsubscript{3v}.

A comparison of the unit cell of Ni(SbF\textsubscript{6})\textsubscript{2} with those of numerous other AMF\textsubscript{6} type compounds [9] shows excellent agreement. The ionic radius of Ni\textsuperscript{2+} (0.69Å) [10] is similar to that of Li\textsuperscript{+} (0.60Å) [9], and all the LiMF\textsubscript{6} type compounds of [9] possess the rhombohedral-hexagonal LiSbF\textsubscript{6} structure. As discussed above, the Ni(SbF\textsubscript{6})\textsubscript{2} structure can be derived directly from the LiSbF\textsubscript{6} structure by converting the unimolecular rhombohedral LiSbF\textsubscript{6} cell to its corresponding trimolecular hexagonal cell, and then doubling the c-axis of the latter to accomodate a whole number of both, Ni\textsuperscript{2+} cation and vacancy sites.

A comparison of the powder pattern of Ni(SbF\textsubscript{6})\textsubscript{2} with that published for Ni(AsF\textsubscript{6})\textsubscript{2} [4] shows that the two compounds are not isotypic. This is unexpected because LiAsF\textsubscript{6} and NaAsF\textsubscript{6} are both isotypic with LiSbF\textsubscript{6} [9]. The pattern of Ni(AsF\textsubscript{6})\textsubscript{2} has previously been indexed [4] for a pseudo-cubic (a/c = \sqrt{2}), tetragonal unit cell with a = 13.62, c = 9.63Å, and Z = 8.

Vibrational Spectra

In A\textsuperscript{+}MF\textsubscript{6}\textsuperscript{-} type compounds, the nature and extent of the cation-anion interaction are of particular interest [4]. For B\textsuperscript{2+}(MF\textsubscript{6}\textsuperscript{-})\textsubscript{2} type compounds, this interaction becomes even more interesting because only half of the fluorines can participate in bridges and the increased positive charge of the cations should result in stronger anion-cation attractions. As a consequence, the high symmetry of the MF\textsubscript{6}\textsuperscript{-} anions in a compound such as LiSbF\textsubscript{6} [8] is
destroyed and vibrational spectroscopy should be well suited for
the study of this problem.

According to the above x-ray data, the site symmetry of the
\( \text{SbF}_6^- \) anions in \( \text{Ni(SbF}_6)_2 \) must be \( C_{3v} \) or lower and further
splittings of bands are possible because the unit cell contains
six \( \text{SbF}_6^- \) anions. The number of the possible fundamental
vibrations and their expected infrared and Raman activities
are shown in Table II for symmetry \( C_{3v} \) and the appropriate sub-
groups. However, without knowledge of the space group and factor
group of \( \text{Ni(SbF}_6)_2 \), a detailed analysis is not possible.

### TABLE II

Correlation table for \( \text{SbF}_6^- \) IN \( \text{Ni(SbF}_6)_2 \)

<table>
<thead>
<tr>
<th>( \nu_{\text{sym}} ) in phase</th>
<th>free ( \text{SbF}_6^- )</th>
<th>( \text{SbF}_6^- ) distorted by 3F bridges</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{\text{sym}} ) out of phase</td>
<td>( O_h )</td>
<td>( C_{3v} )</td>
</tr>
<tr>
<td>( \nu_{\text{asym}} )</td>
<td>( A_{1g} )</td>
<td>( A_{1} )</td>
</tr>
<tr>
<td>( \delta_{\text{sym}} )</td>
<td>( E_g )</td>
<td>( E )</td>
</tr>
<tr>
<td>( \delta_{\text{sym}} ) in plane</td>
<td>( F_{1u} )</td>
<td>( A_{1} )</td>
</tr>
<tr>
<td>( \delta_{\text{sym}} ) out of plane</td>
<td>( F_{2g} )</td>
<td>( E )</td>
</tr>
<tr>
<td>IR active</td>
<td>( F_{1u} )</td>
<td>( A_{1}, E )</td>
</tr>
<tr>
<td>RA active</td>
<td>( A_{1g}, E_g, F_{2g} )</td>
<td>( A_{1}, E )</td>
</tr>
</tbody>
</table>
The observed infrared and Raman spectra are shown in Fig. 1, and the frequencies are summarized in Table III. In the frequency range expected for Sb-F stretching vibrations (500-750 cm$^{-1}$), at least eight infrared and seven Raman bands are observed which are not mutually exclusive. These data clearly indicate that SbF$_6^-$ in Ni(SbF$_6$)$_2$ is not octahedral, but strongly distorted. The number of observed Sb-F stretching modes exceeds not only that (four) expected for either C$_{3v}$ or C$_3$ symmetry, but also that (six) predicted for either C$_s$ or C$_1$ symmetry, and is attributed to a low site symmetry of SbF$_6^-$ and a dynamic coupling of the anions in the unit cell.

Based on frequency and intensity arguments, the following tentative assignments are proposed for the Sb-F stretching modes (see Table III). The three nonbridging fluorines should have higher frequencies and narrower and more intense Raman bands than the bridging ones. Furthermore, the symmetric stretching modes should be more intense in the Raman and the antisymmetric ones more intense in the infrared spectra. The relative sharpness of the nonbridging SbF$_3$ Raman bands lends additional support to our assumption of an ordered structure for Ni(SbF$_6$)$_2$.

For a disordered structure we would expect even more bands and, in particular, more diffuse Raman bands due to the irregularities in the fluorine bridging.

The bands in the 170 to 320 cm$^{-1}$ frequency range are assigned to the Sb-F deformation modes. As for the stretching modes, the frequency range covered by these vibrations is again considerably wider than, for example, for free SbF$_6^-$ [11,12]. This effect is attributed to the influence of the fluorine bridges which will weaken the bridging Sb-F and strengthen the nonbridging Sb-F bonds. The frequency of a medium intensity infrared band with a very weak Raman counterpart in the 350 cm$^{-1}$ region appears high for an Sb-F deformation mode, but is in the range expected for the Ni...FSb stretching mode and, therefore, is assigned accordingly.

R-8
Fig. 1. Vibrational Spectra of Solid Ni(SbF₆)₂. Traces A and B, infrared spectra as KBr and AgCl pellets, respectively. The broken line in trace A probably contains a contribution from K₃SbF₆ generated by interaction of KBr with Ni(SbF₆)₂. The broken line in B is due to absorption by the AgCl window material. Trace C, Raman spectrum, recorded with a slit width of 5 cm⁻¹.
TABLE III

Vibrational frequencies and assignments for Ni(SbF₆)₂

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<th>I r</th>
<th>Assignment</th>
</tr>
</thead>
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<td>742(1)</td>
<td>vₐ SbF₃ out of phase</td>
</tr>
<tr>
<td>716s</td>
<td>717(12)</td>
<td>vₐ SbF₃ in phase</td>
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<tr>
<td>708s</td>
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<td>vₛₐ SbF₃ out of phase</td>
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<tr>
<td>673ms</td>
<td>674(100)</td>
<td>vₛₐ SbF₃ in phase</td>
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<tr>
<td>615sh</td>
<td>618(5)</td>
<td>vₛₐ SbF₃ out of phase</td>
</tr>
<tr>
<td>583s</td>
<td></td>
<td>vₐ SbF₃ out of phase</td>
</tr>
<tr>
<td>568sh</td>
<td>568(2)</td>
<td>vₐ SbF₃ in phase</td>
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<td>521m</td>
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<tr>
<td>354m</td>
<td>348(0+)</td>
<td>Ni...Fsb stretching</td>
</tr>
<tr>
<td>331w</td>
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</tr>
<tr>
<td></td>
<td>308(24)</td>
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</tr>
<tr>
<td>302w</td>
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<td>267vs</td>
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<td>130sh</td>
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*Uncorrected Raman intensities based on relative peak heights*
CONCLUSION

The above data demonstrate that, compared to Ni(AsF$_6$)$_2$ [3], Ni(SbF$_6$)$_2$ is thermally much more stable and is readily formed in high pressure-high temperature fluorination reactions involving SbF$_5$ in nickel reactors. X-ray powder diffraction data and vibrational spectra show that the Ni(SbF$_6$)$_2$ structure can be derived from the rhombohedral-hexagonal LiSbF$_6$ structure by substitution of the Li$^+$ cations by half as many Ni$^{2+}$ cations and vacancies. The observation of a super-structure line in the x-ray powder data and the well defined and sharp Raman spectra support a structural model in which the Ni$^{2+}$ sites and vacancies are ordered.

ACKNOWLEDGEMENT

The authors are grateful to Mrs. M. Lance, Mr. J. Isabey, Dr. C. J. Schack and Mr. R. D. Wilson for their help, to the US Army Research Office and the Office of Naval Research for financial support, and to Dr. R. Bau of the University of Southern California for the examination of Ni(SbF$_6$)$_2$ crystals by x-ray diffraction.

REFERENCES

APPENDIX S

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303

On the Condensed Phases of Difluoramine and its Alkali Metal Fluoride Adducts

Karl O. Christe* and Richard D. Wilson

Abstract

Infrared and Raman spectra of HNF$_2$ and DNF$_2$ in the liquid and the solid phases show that the compounds are associated through hydrogen bridges between the nitrogen atoms. Raman spectra of the KF, RbF and CsF adducts and infrared spectra of the RbF adduct of difluoramine are interpreted in terms of strongly hydrogen bridged [F...HNF$_2$]$^-$ anions. For the CsF and RbF adducts evidence was obtained for the existence of a distinct second modification of the [F...HNF$_2$]$^-$ anion with a significantly stronger hydrogen bridge. The reactions of KF·HNF$_2$ with TeF$_5$OF, OF$_2$, FONO$_2$ and FOCIO$_3$ were studied and resulted in the fluorination of HNF$_2$ to HF and N$_2$F$_4$.

Introduction

Although HNF$_2$ (difluoramine or fluorimide) has been known$^{1,2}$ since 1959, the literature on this interesting compound is sparse. This lack of data may be attributed to the fact that HNF$_2$ is a vicious explosive.$^3$ While studying alkali metal fluoride catalyzed$^5$ reactions of HNF$_2$ with various inorganic hypofluorites, we became interested also in the nature of the MF·HNF$_2$ adducts...
(K, Rb, Cs). The existence of these adducts was reported in 1965, and it was shown that KF·HNF₂, RbF·HNF₂ and CsF·HNF₂ are stable up to about -90°, -72° and -64°C, respectively. Whereas KF·HNF₂ and RbF·HNF₂ undergo smooth dissociation on warmup, CsF·HNF₂ invariably explodes before reaching room temperature. The nature of these adducts has previously been studied by low-temperature infrared spectroscopy, and it was postulated that CsF·HNF₂ possesses a structure different from those of the other MF·HNF₂ adducts. However, the experimental evidence in support of either structure was not convincing due to strong interference from water and impurity bands. In order to obtain more reliable data on these interesting adducts, we have recorded their low-temperature Raman and infrared spectra. Since for difluoramine only gas phase and partial, low resolution, solid phase infrared spectra had previously been reported, it became also necessary to record its infrared and Raman spectra in the condensed phases. This allowed a better distinction between MF·HNF₂ bands and those due to associated HNF₂ and provided some insight into the nature of the association of HNF₂ in the condensed phases.

**Experimental Section**

**Caution:** Difluoramine is highly explosive, and protective shielding and clothing should be used during handling operations. The compound was always condensed at -142°C, and the use of a -196°C bath for condensing HNF₂ should be avoided. Furthermore, the CsF·HNF₂ adduct invariably explodes before reaching 0°C. The hypofluorites FOClO₃, FONO₂ and TeF₅OF are also shock-sensitive and must be handled with the same precautions.
Materials and Apparatus

Difluoramine was handled in either a glass or all Teflon-FEP and -PFA vacuum line to avoid metal fluoride catalyzed HF elimination. Other volatile materials were handled in a stainless steel vacuum line equipped with Teflon-FEP U-traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge. Nonvolatile materials were handled in the dry N₂ atmosphere of a glove box.

Difluoramine was prepared by hydrolysis of difluorourrea using a literature method. For the synthesis of DNF₂, a previously reported method involving H-D exchange between HNF₂ and a large excess of D₂O produced only a low yield of DNF₂, and the sample still contained 14% of HNF₂. Essentially pure DNF₂ was obtained in high yield by the method used for the preparation of HNF₂, but substituting NH₂CONH₂, H₂O and H₂SO₄ by their deuterated analogues. The alkali metal fluorides were dried by fusion in a platinum crucible, followed by immediate transfer of the hot clinkers to the dry N₂ atmosphere of a glove box.

The RbF crystal (Semi-Elements Inc.) used for the low-temperature infrared study of the RbF*HNF₂ adduct was freshly cleaved with a razor blade in the dry box and mounted in a dry N₂ atmosphere into the tip of the helium refrigerator. Small amounts of moisture absorbed onto the surface of the RbF crystal were completely removed by pumping on the crystal in the infrared beam for 24 hrs at 10⁻⁶ torr. Literature methods were used for the syntheses of FONO₂, TeF₅OF, and FOClO₃. OF₂ (Allied Chemical) was purified by fractional condensation at -210° prior to its use. The alkali metal fluoride-difluoramine adducts were generally prepared by condensing an excess of HNF₂ onto the alkali metal fluoride at -142°, warming the mixture to -78° for several hours, and then removing the excess of HNF₂ in a dynamic vacuum at -64°, -78° and -95° for CsF*HNF₂.
RbF-HNF$_2$, and KF-HNF$_2$, respectively. The composition of the resulting adducts generally approached a 1:1 mole ratio.

Infrared spectra were recorded in the range 4000-200 cm$^{-1}$ on a Perkin-Elmer Model 283 spectrophotometer. The spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The low-temperature infrared spectra were obtained at various temperatures with an Air Products Model DE 202S helium refrigerator equipped with an internal RbF and external CsI windows. The Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. Sealed, 3mm o.d., quartz tubes were used as sample containers in the transverse-viewing-transverse-excitation mode. For neat HNF$_2$ the tip of the tube was drawn out to a smaller diameter to minimize the sample size. A previously described device was used for recording the low-temperature spectra.

The TeF$_5$OF-KF-HNF$_2$ System. A passivated (with ClF$_3$), 0.5 in. o.d. Teflon-FEP ampule equipped with a Teflon-PFA valve (Galtex Corp.) was loaded in the drybox with finely powdered, dry KF (2.0g). On the glass vacuum line, HNF$_2$ (3.2 mmol) was added to the ampule at -142$^\circ$ and the mixture was kept at -78$^\circ$ for 1 hr. On the steel-Teflon vacuum line, TeF$_5$OF (1.57 mmol) was added at -196$^\circ$. The ampule was slowly warmed to -78$^\circ$ for 87 hr by means of a CO$_2$-liquid N$_2$ slush bath, and then to -64$^\circ$ for 1 hr. The material volatile at -64$^\circ$ was fractionated through a series of traps kept at -78$^\circ$, -95$^\circ$, -126$^\circ$ and -196$^\circ$ and consisted of N$_2$F$_4$ (1.55 mmol) and traces of TeF$_6$, TeF$_5$OTeF$_5$ and FNO. Then the ampule was allowed to warm to 25$^\circ$, and the volatile material was fractionated through traps kept at -78$^\circ$, -126$^\circ$ and -196$^\circ$. It consisted of N$_2$F$_4$ (0.05 mmol), TeF$_5$OH (0.35 mmol) and traces of TeF$_6$, HF and TeF$_5$OTeF$_5$. The vibrational spectra of the white solid residue showed the presence of HF$_2^-$ and TeF$_5$O$^-$. 

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The OF₂-KF·HNF₂ System. The KF·HNF₂ adduct was prepared as described above from KF (7.3 mmol) and HNF₂ (4.2 mmol), and OF₂ (2.95 mmol) was added at -196°. After slow warmup to -78° no noticeable reaction had occurred. Repeating the reaction at -22° for 1 hr resulted in a 73% consumption of the OF₂ and the formation of N₂F₄ (1.0 mmol) as the main product.

The FOCIO₃-KF·HNF₂ System. A mixture of FOCIO₃ (5.65 mmol) and KF·HNF₂ (KF 69 mmol, HNF₂ 7.44 mmol), when warmed slowly from -196° to -78°, resulted in an explosion.

The FONO₂-KF·HNF₂ System. A mixture of FONO₂ (0.92 mmol) and KF·HNF₂ (KF 172 mmol, HNF₂ 1.22 mmol), when warmed slowly from -142° to -78° and then to 25° during fractionation of the volatile material, produced N₂F₄ (0.5 mmol) with NO₂, FNO₂ and some O₂ as the major volatile by-products.

Results and Discussion

Vibrational Spectra of Difluoramine. Infrared spectra were recorded for gaseous HNF₂ and DNF₂ and solid HNF₂. Raman spectra were measured for the liquid and solid phases of HNF₂ and DNF₂. The spectra are given in Figures 1 to 3, and the observed frequencies and their assignments are summarized in Table 1.

The infrared spectrum of gaseous HNF₂ was in excellent agreement with previous results by Lide and coworkers⁹ and requires no further comment. These authors also reported four fundamental vibrations for gaseous DNF₂ which were measured on a partially deuterated sample. In our study using a completely deuterated sample,
a fifth fundamental, $v_4 (a')$, was observed at 498 cm$^{-1}$. Furthermore, we prefer to assign the center of the $v_5 (a^*)$ band to 1028 cm$^{-1}$ and not to the maximum at 1042 cm$^{-1}$ which, we believe, represents the maximum of the R branch of $v_5$ (see trace A of Figure 2). This preference is based on the reasonable assumption of similar band contours for $v_5$ in HNF$_2$ and DNF$_2$. Similarly, the band center of $v_3 (a')$ of DNF$_2$ is preferably assigned to 962 cm$^{-1}$ instead of the previously proposed$^9$ value of 972 cm$^{-1}$. The 962 cm$^{-1}$ value is also supported by the observation of the $(v_3 + v_6)(a^*)$ combination band at 1849 cm$^{-1}$ (calcd for 962 + 888 = 1850 cm$^{-1}$). It is also noteworthy that our revised frequency values for DNF$_2$ result in a better match with those obtained by Pulay and co-workers by ab initio calculations from the HNF$_2$ values.$^{17}$

The liquid phase frequencies are almost identical to the gas phase values (see Table 1) indicating only weak association for liquid difluoramine. The only remarkable feature is the splitting of the NH and the ND stretching mode, $v_1 (a')$, into two components. These splittings and their relative Raman intensities and polarization ratios are similar for both HNF$_2$ and DNF$_2$ and do not permit their attribution to combination bands in Fermi resonance with $v_1$. Similar splittings have been observed for the symmetric stretching modes of liquid NH$_3$ and ND$_3$$^{18}$ and solid HO$_2$F$^{19}$ and have been attributed to aggregates.$^{19,20}$ Therefore, this explanation is also preferred for difluoramine.

For solid difluoramine the previously reported infrared spectrum had been recorded with only low precision in the NaCl region$^{10}$ and deviates significantly from that given in Figure 3. Compared to the liquid phase values, the NH stretching frequency of solid HNF$_2$ decreased by about 40 cm$^{-1}$ and the NH deformation frequencies increased by about 23 cm$^{-1}$. Furthermore, all these modes are split into two
components each and bands due to libration and lattice modes appear below 310 cm\(^{-1}\). All these features suggest an increased degree of association. Since the N-H modes are shifted and split relative to the gas phase, and those of the NF\(_2\) group are not, the association must involve intermolecular N-H\(\cdots\)N and not N-H\(\cdots\)F bridges. This surprising result is discussed elsewhere in more detail.\(^{21}\) The fact that in HNF\(_2\) the nitrogen is a better electron donor than fluorine is in accord with the previous report by Craig that the weak HNF\(_2\)BF\(_3\) and HNF\(_2\)BCl\(_3\) donor-acceptor adducts contain B-N and not B-F bridges.\(^{10}\) By analogy with the known structure of solid HF,\(^{21}\) a zig-zag chain structure, such as

![diagram](image)

is most likely for (HNF\(_2\))\(_n\), but without additional structural support a more detailed interpretation of the vibrational data appears unwarranted.

**Vibrational Spectra and Structure of the MF\(\cdots\)HNF\(_2\) Adducts.** Adducts of both HNF\(_2\) and DNF\(_2\) with KF, RbF and CsF were prepared as previously described.\(^6\) When an excess of HNF\(_2\) was used in the syntheses, followed by removal of unreacted HNF\(_2\) at low temperature, the combining ratios approximated 1:1. Low-temperature Raman spectra were measured for all these adducts (Figures 4 and 5). Low-temperature infrared spectra were recorded only for RbF\(\cdots\)HNF\(_2\) (Figure 3) due to the limited availability of the corresponding alkali metal fluoride windows and the treacherous explosiveness of the CsF\(\cdots\)HNF\(_2\) adduct on warmup to ambient temperature which caused severe damage to the cryostats.
The Raman spectra of MF-HNF$_2$ (M=K and Rb) and MF-DNF$_2$ (M=K, Rb and Cs) were completely analogous (see Figure 3 and Table II), suggesting essentially identical structures for these adducts. Compared to the spectra of free HNF$_2$ (see above), the frequency of the N-H stretching mode has decreased by about 600 cm$^{-1}$ and consists of numerous broad bands. The two N-H deformation frequencies have increased by about 100 cm$^{-1}$ and are also split, whereas the three NF$_2$ modes exhibit only relatively small frequency decreases with νasNF$_2$ also being split. These observations are thoroughly consistent with an adduct involving a strong hydrogen bridge between HNF$_2$ and the fluoride anion [F…H−N<sup>P</sup>−F$^-$], similar to those previously reported for CsF·HONO$_2$ and KF·(CH$_2$COOH)$_2$.

The minor frequency decrease of the NF$_2$ vibrations can be explained by the electron density release from F$^-$ to HNF$_2$ which increases the partial negative charges on the two fluorines of the NF$_2$ group, causing an increase of the HN−F bond polarity and decrease of the N−F force constants.

The Raman spectra of the corresponding DNF$_2$ adducts are completely analogous and show the expected N−H:N−D frequency ratio of about 1.35 to 1.40. In addition to these major effects, all the spectra exhibit some more subtle features. For example, the NF$_2$ modes show a frequency decrease of about 10 cm$^{-1}$ on going from KF·HNF$_2$ to CsF·HNF$_2$. This can be ascribed to the higher negative charge on F$^-$ in CsF, relative to that in KF.

In addition to the internal modes of the HNF$_2$ subunit in the [F…H−N<sup>P</sup>−F$^-$] anion, we would also expect librational modes due to the F…H−N bridge, i.e. one F−H stretch and two F…H−N deformation modes. Furthermore, bands due to the interaction between the alkali metal cations and the fluoride anions should be observable. All these modes should occur at relatively low frequencies and indeed
numerous bands below 350 cm\(^{-1}\) were observed. By analogy with the N-H modes, the F\(\cdots\)H modes are probably broad and of low Raman intensity and therefore difficult to observe in the Raman spectra. In the infrared spectra of RbF\(\cdots\)HNF\(_2\) (traces C and D of Figure 3) there is clear evidence for a strong absorption at about 330 cm\(^{-1}\), and this could be one of the F\(\cdots\)H libration modes. The sharper features observed in the 240-190 cm\(^{-1}\) region of the Raman spectra do not exhibit the large deuterium isotopic shifts expected for the F\(\cdots\)H-N bridge modes and therefore are probably due to modes involving mainly fluoride ion motions in the lattice.

The Raman spectra of CsF\(\cdots\)HNF\(_2\) showed the following interesting additional features. Two different sets of bands were observed which exhibited similar overall patterns but pronounced frequency shifts from each other, as shown by traces A and B of Figure 5. The spectrum depicted as trace A is very similar, although not quite analogous, to those of all the adducts given in Figure 4. The spectrum of trace B shows very pronounced frequency shifts (decrease of \(\nu_{\text{NH}}\) by about 300 cm\(^{-1}\), increase of the N-H deformations by about 40 cm\(^{-1}\), decrease of the NF\(_2\) modes by about 10-30 cm\(^{-1}\), and increase of the librational frequencies) relative to trace A. These shifts are best attributed to a hydrogen bonded [F\(\cdots\)HNF\(_2\)]\(^{-}\)adduct which is very similar to that discussed above for the other adducts, but contains a significantly stronger hydrogen bridge. No evidence was observed for the existence of adducts showing frequencies intermediate between those of traces A and B, thus suggesting the presence of two distinct structures and not a progressive variation of the hydrogen bond strength.
In the case of HF addition to the fluoride anion, each free valence electron pair of the fluoride can form a hydrogen bridge, resulting in the \([F(\cdot\cdot\cdot HF)\_n]^\text{-}\) polyanions where \(n\) can range from 1 to 4.\(^{25-28}\) The interpretation of the second, more strongly hydrogen bridged \(F(\cdot\cdot\cdot H N F\_2)\) type adduct in terms of an analogous \([F(\cdot\cdot\cdot H N F\_2)\_n]^\text{-}\) anion can be ruled out because the observed frequency changes (decrease of the N-H and NF\(_2\) stretching modes) are opposite to those predicted for these polyanions.

Further evidence for the existence of a second, distinct, more strongly hydrogen bonded adduct was obtained from the low-temperature infrared spectra of RbF\(\cdot\cdot\cdot\)HNF\(_2\) (see below). This demonstrates that the occurrence of a second, more strongly bridged HNF\(_2\) adduct is not limited to CsF, but also occurs for RbF.

For the low-temperature infrared spectra of RbF\(\cdot\cdot\cdot\)HNF\(_2\), difluoramine was condensed at -220°C onto an RbF single crystal window. After recording the spectrum of the solid HNF\(_2\) deposit (Figure 3, trace B), the temperature of the RbF window was warmed briefly to -110°C in a static vacuum. Volatile material was pumped off quickly at -110°C, and the window was cooled back again to -220°C. The infrared spectrum of the resulting product (Figure 3, trace C) showed the absence of any unreacted HNF\(_2\) and corresponded well to the low-temperature Raman spectra of the MF\(\cdot\cdot\cdot\)HNF\(_2\) adducts shown in Figure 4. When the temperature of the infrared sample was briefly cycled through -105°C and cooled down again to -220°C, additional bands were observed which are marked in trace D of Figure 3 by a dagger. The frequencies of these bands are almost identical to the major Raman bands of the more strongly hydrogen bonded modification of the CsF\(\cdot\cdot\cdot\)HNF\(_2\) adduct shown in trace B of Figure 5 and were assigned accordingly (see Table II). Cycling of the RbF\(\cdot\cdot\cdot\)HNF\(_2\) sample from -220°C through ambient temperature in a dynamic vacuum resulted in the
disappearance of the bands attributed to these RbF•HNF₂ adducts.

Comparison of the results from this work with those from a previous low-temperature infrared study⁶ show only fair to poor agreement. This disagreement can be attributed to the poor quality of the previously reported data which is no surprise in view of the great experimental difficulties encountered. Although the existence of two different types of compounds, one a hydrogen bonded MF•••HNF₂ and the other an MNF₂•HF adduct, had been postulated, this conclusion was based more on the then known reaction chemistry of the adducts than on the spectroscopic data. The MNF₂•HF structure had been proposed to account for the fact that only CsF•HNF₂ exhibited a propensity to explode on warming toward room temperature. The present study demonstrates that the KF•HNF₂, RbF•HNF₂ and CsF•HNF₂ adducts exhibit the same structural features involving a strong hydrogen bridge between the HNF₂ and the fluoride anion of the alkali metal fluoride, and that the existence of a second, distinct modification which differs from the first one only in the strength of its hydrogen bridge is not unique for CsF. Although this second modification appears to form more readily with CsF, it was also observed for RbF and therefore might not necessarily be the main reason for the explosive nature of CsF•HNF₂. Other factors, such as the higher affinity of CsF for HF, might be significant contributors. No evidence was obtained in this study for the presence of a distinct NF₂⁻ anion which should exhibit vibrational spectra very different from those observed.

**Reaction Chemistry of MF•HNF₂ Adducts.** Since MF•HNF₂ adducts are known to react with perfluoroalkyl hypofluorites according to

\[ R_fOF + MF\cdot HNF_2 \rightarrow R_fOF_2 + HNF_2 \]
the analogous reactions were studied for several hypofluorites for which the corresponding -ONF$_2$ derivatives are still unknown. The hypofluorites studied included TeF$_5$OF, FOCI$_3$ and FONO$_2$. In the case of TeF$_5$OF the observed reaction products are best explained by the oxidation of HNF$_2$ by TeF$_5$OF.

$$\text{TeF}_5\text{OF} + 2\text{KF*HNF}_2 \rightarrow -64^\circ \rightarrow \text{TeF}_4\text{O} + 2\text{KF} + 2\text{HF} + N_2F_4$$

followed by the competing reactions

$$\text{TeF}_4\text{O} + \text{HF} \rightarrow \text{TeF}_5\text{OH}$$
$$\text{TeF}_4\text{O} + \text{KF} \rightarrow K\text{TeF}_5\text{O}$$
$$\text{HF} + \text{KF} \rightarrow K\text{HF}_2$$

The reaction of OF$_2$ with KF•HNF$_2$ required a considerably higher temperature and even at -22°C was still incomplete after one hour. Again the main reaction was the oxidation of HNF$_2$ to N$_2$F$_4$.

$$20\text{F}_2 + 4\text{KF*HNF}_2 \rightarrow 2N_2F_4 + 4\text{KHF}_2 + \text{O}_2$$

In the case of FOCI$_3$ and KF•HNF$_2$, the mixture exploded when warmed from -196°C toward -78°C. For FONO$_2$, the reaction could be sufficiently controlled, but again N$_2$F$_4$ was formed in almost quantitative yield with NO$_2$, O$_2$ and FNO$_2$ as the major by-products. It thus appears that with hypofluorites which are powerful oxidizers, fluorination of HNF$_2$ to N$_2$F$_4$ and HF is favored over XONF$_2$ formation.

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Diagram Captions

**Figure 1.** - Raman spectra of liquid and solid HNF$_2$.

**Figure 2.** - Vibrational spectra of DNF$_2$: trace A, infrared spectrum of the gas at 270 torr in a 5 cm path length cell; traces B and C, Raman spectra of liquid and solid DNF$_2$, respectively.

**Figure 3.** - Infrared spectra of solid HNF$_2$ and of the RbF·HNF$_2$ adduct at -220°C: trace A, background of the RbF·HNF$_2$ window; trace B, solid HNF$_2$; trace C, RbF·HNF$_2$ adduct generated by cycling the deposit of trace B through -110°C; the bands marked by an asterisk are due to cell background; trace D, spectrum produced by cycling deposit of trace C through -105°C; the new set of bands marked by a dagger are ascribed to the second, more strongly hydrogen bridged species; trace E, cell background after cycling through 25°C with pumping.

**Figure 4.** - Raman spectra of KF·HNF$_2$ (traces A, A'), KF·DNF$_2$ (trace B), RbF·HNF$_2$ (traces C and C'), RbF·DNF$_2$ (trace D), and CsF·DNF$_2$ (traces E and E'), all recorded at -140°C. The traces A', C' and E' were recorded at a higher sensitivity setting.

**Figure 5.** - Raman spectra of the two modifications of CsF·HNF$_2$ at -140°C. Traces A and A' show the spectrum of the more weakly hydrogen bridged adduct at two different sensitivity levels, respectively, and traces B and B' those of the stronger hydrogen bridged adduct.
<table>
<thead>
<tr>
<th>Assignment</th>
<th>Approx Description</th>
<th>HNF₂ (Gas, IR)</th>
<th>HNF₂ (Liquid, IR)</th>
<th>HNF₂ (Solid)</th>
<th>DNF₂ (Gas, IR)</th>
<th>DNF₂ (Liquid, IR)</th>
<th>DNF₂ (Solid)</th>
<th>DNF₂ (Calc)</th>
</tr>
</thead>
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<tr>
<td>C₅</td>
<td>ν(NH)</td>
<td>3193vw</td>
<td>3210(0.8)p</td>
<td>3215w</td>
<td>3163(0.8)</td>
<td>[2333]C</td>
<td>2388(1)p</td>
<td>2353(3.2)</td>
</tr>
<tr>
<td>2ν₂ (a')</td>
<td></td>
<td>27390vw</td>
<td></td>
<td></td>
<td>2650w</td>
<td></td>
<td></td>
<td>2107(0+)</td>
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<tr>
<td>ν₂ + ν₅ (a')</td>
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<td>1850mυ</td>
<td>1850sh</td>
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<td></td>
<td>1897vw</td>
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<td>2ν₅ (a')</td>
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<td>1429(0.9)dp</td>
<td>1446(0.3)</td>
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<td>1043(0.8)dp</td>
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<td>1310(0.7)p</td>
<td>1304(0.5)</td>
<td>1009s</td>
<td>1007(2)p</td>
<td>1003(1.2)</td>
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<td>ν₂ + ν₄ (a')</td>
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<td>1008sh</td>
<td>1006mυ</td>
<td>1110(0+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₅ (a')</td>
<td>6s F₂ NH</td>
<td>972ms</td>
<td>974(10)p</td>
<td>978(10)</td>
<td>962ms</td>
<td>970(10)p</td>
<td>977(10)</td>
<td>961</td>
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<tr>
<td>ν₆ (a')</td>
<td>vs NF₂</td>
<td>888vs</td>
<td>869(4.0)dp</td>
<td>875vs</td>
<td>888vs</td>
<td>866(3.6)dp</td>
<td>868(3.3)</td>
<td>888</td>
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<tr>
<td>ν₄ (a')</td>
<td>6s NF₂</td>
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<td>504(0.2)p</td>
<td>503m</td>
<td>505(5.4)</td>
<td>498mυ</td>
<td>501(8.4)p</td>
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(a) Uncorrected Raman intensities (peak heights).
(b) Data from ref. 17, calculated by ab initio from HNF₂ values.
(c) Estimated value from ref. 9; not observed in this study because of its low intensity.
Table II. Vibrational Spectra of the Alkali Metal Fluoride - Difluoramine Adducts

<table>
<thead>
<tr>
<th>Assignment for</th>
<th>KF·HNF₂</th>
<th>KF·DNF₂</th>
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<th>RbF·DNF₂</th>
<th>CsF·HNF₂</th>
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<td></td>
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<td>IR(II)</td>
<td>Ra</td>
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<td>[F···H-N]</td>
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<tr>
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<td>2160(0.3)</td>
<td>3050(0.1)</td>
<td>3050m</td>
<td>2160(0+)</td>
<td>3060(0.2)</td>
<td>2080(0+)</td>
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<td>2600(0.3)</td>
<td>1936(0.2)</td>
<td>2640(0.6)</td>
<td>1932(0.2)</td>
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<td></td>
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<td>1474w</td>
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<td>1412(0.4)</td>
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<td>1420m</td>
<td>1076(0.2)</td>
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<td>944(10)</td>
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<td>943(10)</td>
<td>951(10)</td>
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<td>858(1.7)</td>
<td>852(1.7)</td>
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| (a) I and II refer to the two modifications (see text for explanation). All Raman spectra were recorded at -140°C, infrared spectra at -220°C.
| (b) Uncorrected Raman intensities (peak heights).
| (c) For the NF·DNF₂ adducts, assignments involving the N-O group have been listed in the N-H rows.
APPENDIX T

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303

New, One Step Syntheses of BrF₃O and BrF₄O⁻ Salts
and the Preparation and Characterization of RbBrF₄O and NaBrF₄O

WILLIAM W. WILSON and KARL O. CHRISTE

Received...

ABSTRACT

The reactions of an excess of BrF₅ with the alkali metal nitrates NaNO₃, KNO₃, RbNO₃ and CsNO₃ provide new, simple, high yield syntheses of the corresponding BrF₄O⁻ salts and FNO₂. The NaBrF₄O and RbBrF₄O salts have been prepared for the first time and were characterized by vibrational spectroscopy, DSC and their x-ray powder diffraction patterns. The reaction of LiNO₃ with an excess of BrF₅ does not result in the formation of a stable LiBrF₄O salt but produces free BrF₃O in high yield. This provides a simple, one step synthesis of BrF₃O from commercially available starting materials.

INTRODUCTION

The existence of KBrF₄O was discovered in 1976 both by Bougon and coworkers¹ and by Gillespie and Spekkens.² It was prepared either by the reaction¹ of KBrO₃ with a large excess of BrF₅ at 80°C in the presence of F₂ or by the reaction² of KBrF₆ with KBrO₃ in CH₃CN solution. Both methods have drawbacks. Although Bougon's method¹ can yield a pure product, the course of the reaction is difficult to control and frequently KBrF₄ is obtained as the only product.³ Gillespie's method² produces a mixture of KBrF₂O₂ and KBrF₄O which must be separated by numerous extractions with CH₃CN.
An improved synthesis of BrF$_4$O$^-$ salts was reported by Christe and coworkers$^3$ who reacted BrO$_4^-$ salts with BrF$_5$ and F$_2$. In addition to KBrF$_4$O, the latter authors also prepared and characterized CsBrF$_4$O. Although this method results in a pure product in essentially quantitative yield,$^3$ the required BrO$_4^-$ starting materials are difficult to prepare.$^4$ Except for NF$_4^+$BrF$_4$O$^-$$^5$ no other BrF$_4$O$^-$ salts have been reported.

Three methods have previously been reported for the synthesis of BrF$_3$O. Bougon and Bui Huy$^6$ reacted KBrF$_4$O with O$_2$AsF$_6$ in BrF$_5$ solution.

$$\text{KBrF}_4\text{O} + \text{O}_2\text{AsF}_6 \rightarrow \text{KAsF}_6 + \text{BrF}_3\text{O} + \text{O}_2 + \frac{1}{2}\text{F}_2 \quad (1)$$

Gillespie and Spekkens$^2$ dissolved KBrF$_4$O in anhydrous HF,

$$\text{KBrF}_4\text{O} + \text{HF} \rightarrow \text{KHF}_2 + \text{BrF}_3\text{O} \quad (2)$$

and extracted the formed BrF$_3$O with BrF$_5$ at low temperature. Adelhelm and Jacob$^7$ obtained BrF$_3$O, together with FBrO$_2$, by treatment of a mixture of BrF$_2$OPtF$_6$ and BrO$_2$PtF$_6$ with FNO$_2$.

$$\text{BrF}_2\text{OPtF}_6 + \text{FNO}_2 \rightarrow \text{NO}_2\text{PtF}_6 + \text{BrF}_3\text{O} \quad (3)$$

$$\text{BrO}_2\text{PtF}_6 + \text{FNO}_2 \rightarrow \text{NO}_2\text{PtF}_6 + \text{FBrO}_2 \quad (4)$$

All three methods are elaborate and involve several steps and exotic starting materials. The development of a new, simple, one-step synthesis of BrF$_3$O from commercially available starting materials was therefore highly desirable.
EXPERIMENTAL

Materials. Commercial LiNO₃ (J. T. Baker, 99.7%), NaNO₃ (J. T. Baker, 99.5%), KNO₃ (J. T. Baker, 99.1%), and RbNO₃ (K & K Labs, Inc., 99.9%) were dried in a vacuum oven at 120°C for one day prior to their use. The CsNO₃ was prepared from Cs₂CO₃ and HNO₃ and dried in the same manner. The BrF₅ (Matheson) was treated with 35 atm of F₂ at 100°C for 24 hr and then purified by fractional condensation through traps kept at -64 and -95°C, with the material retained at -95°C being used. BrF₅ and BrF₃O are powerful oxidizers and contact with organic materials or moisture must be avoided.

Apparatus. Volatile materials used in this work were handled in a well-passivated (with BrF₅ until it was recovered as a white solid at -196°C) stainless steel Teflon FEP vacuum line. Non-volatile materials were handled in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000-200 cm⁻¹ on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed glass tubes were used as sample containers in the transverse-viewing-transverse-excitation mode. X-ray diffraction patterns of the powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Phillips camera. DSC measurements were carried out with a Perkin-Elmer Model DSC-1B using crimp sealed aluminum pans and a heating rate of 10°C/min.
Preparation of $\text{M}^+\text{BrF}_4\text{O}^-$ ($\text{M}$=Cs, Rb, K, Na). Inside the dry box, a weighed amount (typically about 3 mmol) of MF was loaded into a prepassivated reactor (either a 30 mL stainless steel cylinder or a 0.75" o.d. Teflon-FEP ampule) which was closed by a valve. The reactor was connected to the vacuum line and a fivefold excess of BrF$_3$ was added at -196°. The reactor was warmed to a given temperature for a specified period of time with occasional agitation, followed by fractional condensation of the volatile products through a series of two U-traps kept at -142° (BrF$_5$) and -196° (FNO$_2$). The material balances were determined from the weight gain of the solid residue in the reactor and the amounts of volatiles collected in the cold traps. All materials were identified by vibrational spectroscopy. The reaction conditions and product yields for the various BrF$_4$O$^-$ salts are summarized in Table I.

Preparation of BrF$_3$O. Inside the dry box, LiNO$_3$ (2.12 mmol) was loaded into a passivated 30 mL stainless steel cylinder. On the vacuum line, BrF$_5$ (31.93 mmol) was added at -196°, and the cylinder was stored at 0° for 20 days with occasional agitation. The cylinder was reconnected to the vacuum line, cooled to -196° and did not contain any material volatile at this temperature. While allowing the cylinder to slowly warm toward ambient temperature, the volatile material was separated in a dynamic vacuum by fractional condensation through a series of traps kept at -64, -142 and -196°. The -64° trap contained BrF$_3$O (2.01 mmol, 95% yield based on LiNO$_3$), the -142° trap collected the excess of BrF$_5$ and a small amount of BrF$_3$O, and the -196° trap retained the FNO$_2$ (2.05 mmol, 97% yield based on LiNO$_3$). The white, solid residue (about 0.06g, weight calcd for 2.12 mmol of LiF = 0.055g) was identified by its x-ray powder pattern as LiF. Its powder pattern and vibrational spectra did not exhibit any lines attributable to either LiNO$_3$ or a BrF$_4$O$^-$ salt. When the duration of this reaction was shortened to 4 hr, the conversion of LiNO$_3$ and the concomitant yield of BrF$_3$O decreased to 70%.
RESULTS AND DISCUSSION

Syntheses of BrF_4^- Salts and BrF_3O. The reaction of an excess of BrF_5 with the alkali metal nitrates CsNO_3, RbNO_3, KNO_3, or NaNO_3 proceeds in high yield according to (5).

\[ \text{MNO}_3 + \text{BrF}_5 \rightarrow \text{MBrF}_4O + \text{FNO}_2 \]  \hspace{1cm} (5)

The reactivity of MNO_3 decreases from Cs to Na. Thus, the reaction of CsNO_3 is complete within one hour at -31°C (see Table I, run 1). For KNO_3, a 31% conversion to KBrF_4O was obtained under the same conditions (run 5), but thereafter the reaction progressed only very slowly. Because tripling the amount of BrF_5 did not significantly increase the conversion of KNO_3 (run 6), and since the solubility of KBrF_4O in BrF_5 is quite low, coating of the solid KNO_3 phase by product was suspected as the principal cause for the observed fall-off in the reaction rates. This suspicion was confirmed. Fine grinding of the product, followed by a second treatment with BrF_5, almost doubled the yield of KBrF_4O (run 5). Complete conversion of KNO_3 to KBrF_4O was achieved at ambient temperature by ball milling the reagents during the reaction (run 8). Alternatively, complete conversion of KNO_3 to KBrF_4O could be achieved by heating to 100°C (run 10). Run 11 shows that these reactions do not require a fivefold excess of BrF_5, but also go to completion with lower BrF_5 to metal nitrate ratios.

The reactions of NaNO_3 with BrF_5 differed somewhat from those of CsNO_3, RbNO_3 and KNO_3 which produced exclusively the corresponding BrF_4^- salts. At a reaction temperature of 0°C, some free BrF_3O was always isolated in addition to NaBrF_4O (run 13). When the reaction temperature was increased to 25°C, the solid products contained significant amounts of BrF_4^- and BrO_2F_2^- salts (run 14). The formation of BrF_4^- and BrO_2F_2^- at 25°C is not surprising.
BrF₃O is known to decompose above 0° to BrF₃ + O₂, and reaction of BrF₃O with a second mole of NaN₃ can generate BrO₂F. Both, BrF₃ and BrO₂F, can then react with NaF to give the corresponding anions, as shown in equations (6) to (10).

\[
\begin{align*}
\text{NaNO}_3 + \text{BrF}_5 & \rightarrow \text{NaF} + \text{BrF}_3\text{O} + \text{FNO}_2 \\
\text{NaNO}_3 + \text{BrF}_3\text{O} & \rightarrow \text{NaF} + \text{BrO}_2\text{F} + \text{FNO}_2 \\
\text{NaF} + \text{BrO}_2\text{F} & \rightarrow \text{NaBrO}_2\text{F}_2 \\
2\text{BrF}_3\text{O} & \rightarrow 2\text{BrF}_3 + \text{O}_2 \\
\text{NaF} + \text{BrF}_3 & \rightarrow \text{NaBrF}_4
\end{align*}
\]  

(6) (7) (8) (9) (10)

A rationale for the formation of free BrF₃O in the NaNO₃-BrF₅ system will be given below.

The isolation of some free BrF₃O from the NaNO₃-BrF₅ reaction suggested the possibility of preparing BrF₃O in a simple, one step synthesis from a metal nitrate whose metal fluoride does not form a stable BrF₄O⁻ salt at 0° or below. This concept was verified for LiNO₃. When LiNO₃ is reacted with an excess of BrF₅ at 0°, BrF₃O is formed in essentially quantitative yield according to (11).

\[
\text{LiNO}_3 + \text{BrF}_5 \rightarrow \text{LiF} + \text{BrF}_3\text{O} + \text{FNO}_2
\]  

(11)

Ballmilling of the solid reagents during the reaction, as in run 8, might also be advantageous for this system if shorter reaction times are desired.

When BrF₅ was reacted for 1 hr at either -31 or 25°C with an excess of CsNO₃, a quantitative conversion of BrF₅ to CsBrF₄O and FNO₂ was observed. The solid product consisted exclusively of CsBrF₄O and unreacted CsNO₃. With an excess of LiNO₃, however, the course of the reaction was very different and will be reported in a separate paper.

The above described syntheses of MBBrF₄O and BrF₃O offer numerous advantages over the previously used methods. Among these are:

(i) the starting materials, BrF₅ and MNO₃, are commercially...
available and relatively inexpensive; (ii) the yields are essentially quantitative; (iii) the reactions can be carried out at convenient temperatures and at autogenous pressures; and (iv) these syntheses are one step reactions requiring only simple equipment. In addition to being useful methods for the preparation of MBrF₄₀ and BrF₃₀, these reactions also can be used as a convenient new laboratory method for the preparation of FNO₂ under mild conditions. The yields of FNO₂ are quantitative, and product separation is very easy. The FNO₂ is much more volatile than the other products and can readily be isolated in high purity by either fractional condensation or removal in vacuo at low temperature (BrF₅ stops at -95°, whereas FNO₂ still passes through a -142° trap but stops at -196°).

Some interesting questions concerning the mechanism of the MNO₃-BrF₅ reactions are raised by the following facts. For the NaNO₃-BrF₅ system at 0° some BrF₃₀ was obtained as a by-product besides NaBrF₄₀, and at 25° the formed BrF₃₀ underwent either fast decomposition to BrF₃ + O₂ or further reaction with NaNO₃ to BrO₂F, followed by complexing with NaF to form the corresponding sodium salts. In marked contrast to these observations, the heavier alkali metal salts (K, Rb and Cs) form, even at reaction temperatures as high as 100°, the corresponding MBrF₄₀ salts in quantitative yield. As shown below, NaBrF₄₀ is stable up to about 160°. Therefore the free BrF₃₀ could not have formed by decomposition of NaBrF₄₀, but must have been generated from a less stable intermediate which is capable of generating either BrF₃₀ + MF + FNO₂ or MBrF₄₀ + FNO₂.

A logical candidate for this intermediate is the [NO₃·BrF₅]⁻ polyanion. BrF₅ is well known to exhibit some Lewis acidity and forms, for example with F⁻, an octahedral BrF₆⁻ anion in which the free valence electron pair on bromine occupies a sterically inactive s orbital.¹⁰ Therefore, the formation of
an analogous [NO₃·BrF₅]⁻ anion is quite plausible. Decomposition of the resulting M⁺[NO₃·BrF₅]⁻ salt could involve either FNO₂ elimination from the anion resulting in the direct formation of M⁺BrF₄O⁻ (12), or F⁻ abstraction from the [NO₃·BrF₅]⁻ anion by M⁺ followed by FNO₂ elimination from an unstable BrF₄ONO₂ molecule thus producing free BrF₃O (13). Whether (10) or (13) dominates should depend on the F⁻ ion affinity of M⁺ and the thermal stability of M⁺[NO₃·BrF₅]⁻. Sodium is expected to form the least stable M⁺[NO₃·BrF₅]⁻ salt and therefore should be most prone to decomposition to MF and BrF₄ONO₂. Based on these arguments, the following mechanism is proposed to explain the observed reaction chemistry.

\[
\begin{align*}
\text{(12)} & \quad M^+\text{NO}_3^- + \text{BrF}_5 \rightarrow M^+\left[\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\text{F} \\
\text{F}
\end{array}\right]^- + \text{FNO}_2 \\
\text{(13)} & \quad M^+\text{NO}_3^- + \text{BrF}_5 \rightarrow [\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\text{F} \\
\text{F}
\end{array}]^- \rightarrow M^+\text{F} + [\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\text{F} \\
\text{F}
\end{array}]^{-2} \rightarrow \text{BrF}_3\text{O}
\end{align*}
\]

For M = Na, dissociation of the intermediate M⁺[NO₃·BrF₅]⁻ salt to MF and BrF₄ONO₂ would be faster than intramolecular FNO₂ elimination, while the reverse could be said for M = Cs, Rb, or K.

Attempts were unsuccessful to isolate the proposed [NO₃·BrF₅]⁻ intermediate anion by condensation of BrF₅ onto an excess of CsNO₃ at -196°, brief warming of the mixture to the mp of BrF₅ (-60.5°), and recooling it to -196°. Low-temperature Raman spectra of the resulting product showed only CsBrF₄O, FNO₂ and unreacted BrF₅.
Properties of the MBrF₄O Salts. The only previously known BrF₄⁻ salts were KBrF₄O,² CsBrF₄O³ and NF₄BrF₄O.⁵ It was therefore of interest to characterize the two new salts, NaBrF₄O and RbBrF₄O.

All these alkali metal BrF₄O⁻ salts are white, stable crystalline solids. Based on DSC data, the onset of thermal decomposition occurs at the following temperatures: NaBrF₄O, 161°; KBrF₄O, 221°; RbBrF₄O, 226°; CsBrF₄O, 189°. The x-ray powder diffraction patterns were also recorded for these salts. It was found that RbBrF₄O is isotypic with KBrF₄O and its diffraction pattern (see Table II) was indexed for a tetragonal cell by analogy to that previously published for KBrF₄O.¹ Many of the lines in the powder patterns of CsBrF₄O and NaBrF₄O (see Table III) can be indexed for similar tetragonal cells, however, the correspondence is not as good and in view of the large unit cells involved, our confidence in such an indexing is low.

The vibrational spectra of BrF₄⁻ salts are interesting. For KBrF₄O¹ and CsBrF₄O³ numerous splittings of degenerate modes into their components were observed which made assignments³ difficult. The vibrational spectra of RbBrF₄O (see Figure 1) are similar to those of CsBrF₄O and also exhibit these pronounced splittings. However, the spectra of NaBrF₄O (see Figure 2) are much simpler and therefore can be used to examine the correctness of the previous assignments.³ As can be seen from Table IV, the Raman spectrum of NaBrF₄O allows unambiguous assignments for ν₁, ν₂, ν₃, ν₄, ν₆ and ν₉. The extra Raman bands in the spectra of KBrF₄O¹, CsBrF₄O³ and RbBrF₄O are due to splittings of the degenerate E modes into their components, accompanied by significant gains in intensity, and have previously been assigned³ correctly. The minor frequency differences between RbBrF₄O and NaBrF₄O are normal for salts with different cations and are as expected, i.e. strongest interaction of the anion with the smallest cation.

Acknowledgement. The authors are indebted to Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson for their help and to the Army Research Office and the Office of Naval Research for financial support.
REFERENCES


Diagram Captions

Figure 1. Vibrational spectra of solid RbBrF₄O: trace A, infrared spectrum of a sample in an AgCl disk; trace B, Raman spectrum.

Figure 2. Vibrational spectra of solid NaBrF₄O: trace A, infrared spectrum of a sample in an AgBr disk; trace B, Raman spectrum.
Table I. Reaction Conditions and Yields for the Syntheses of MBrF$_4$O Salts

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<td>25</td>
<td>67</td>
<td>5.0</td>
<td>53$^g$</td>
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(a) reactor: 0.75" o.d. Teflon FEP ampule; (b) reactor: 30 ml stainless steel cylinder; (c) sample was reground after 4 hr reaction time; (d) sample was reground after 5 hr reaction time; (e) reactants were subjected to ball milling during reaction; (f) volatile products contained 14% free BrF$_3$O and solid residue showed the presence of a trace of NaBrO$_2$F$_2$; (g) volatile products contained BrF$_3$O$^-$ and BrF$_3$ and solid residue BrO$_2$F$_2^-$ and BrF$_4^-$ as by-products.
Table II. X-Ray Powder Data for RbBrF$_4$\textsuperscript{a}

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<th>$d_{\text{obsd}}, $Å</th>
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\(\text{a) Cu Kα radiation and Ni filter; tetragonal; } a = 14.43Å,\)
\(c = 15.86Å, Z = 32, V = 3302Å^3, d \text{ (calcd)} = 4.14 \text{ gcm}^{-3}.\)

T-13
### Table III. X-Ray Powder Data for NaBrF₄O and CsBrF₄O

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<td>1.717</td>
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</table>

(a) Cu Ka radiation and Ni filter
Table IV. Vibrational Spectra\(^a\) of NaBr\(_4\)O and RbBr\(_4\)O

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<tr>
<th>IR(^c)</th>
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<td>1015vw</td>
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<td></td>
<td></td>
<td>(\nu_2 + \nu_7(E))</td>
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<tr>
<td>930s</td>
<td>929(7.0)</td>
<td>943s</td>
<td>941(7.0)</td>
<td>(\nu_1(A_1), \nu(\text{BrO}))</td>
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<tr>
<td>505sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>570-450vs,br</td>
<td>482(8.7)</td>
<td>590-450vs,br</td>
<td>456(6)</td>
<td>(\nu_7(E), \nu\text{as(Br}_4\text{)})</td>
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<tr>
<td>513(10)</td>
<td>528(10)</td>
<td>(\nu_2(A_1), \nu\text{as(Br}_4\text{)}) in phase</td>
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<td></td>
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<tr>
<td>431(7)</td>
<td>421(6.7)</td>
<td>(\nu_4(B_1), \nu\text{as(Br}_4\text{)}) out of phase</td>
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<tr>
<td>420sh</td>
<td>419(6)</td>
<td>410sh</td>
<td></td>
<td>(\nu_8(E), \delta(O\text{Br}_4\text{)})</td>
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<tr>
<td>392mw</td>
<td>393sh</td>
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<td></td>
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<td>309(1.2)</td>
<td>320m</td>
<td>303(0.4)</td>
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<td>(\nu_3(A_1), \delta\text{s(Br}_4\text{)}) out of plane</td>
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<td>242(2.2)</td>
<td>262(1.9)</td>
<td>(\nu_6(B_2), \delta\text{s(Br}_4\text{)}) in plane</td>
<td></td>
<td></td>
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<tr>
<td>189(0.9)</td>
<td>172(1.2)</td>
<td>(\nu_9(E), \delta\text{as(Br}_4\text{)}) in plane</td>
<td></td>
<td></td>
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</table>

\(^a\) All spectra recorded at ambient temperature.
\(^b\) Uncorrected Raman intensities (peak heights).
\(^c\) AgCl disk.
\(^d\) AgBr disk.
Dinitrogen pentoxide, the anhydride of nitric acid, was first prepared in 1849 from the reaction of Cl₂ with dry AgNO₃ at 60°C. Subsequent methods involve either the dehydration of concentrated nitric acid by phosphorous pentoxide or the oxidation of N₂O₄ with ozone. Since N₂O₅ is unstable at ambient temperature and decomposes to N₂O₄ and O₂, the above methods require the use of an efficient ozone generator to suppress the formation of N₂O₄. Dinitrogen pentoxide is also formed when a mixture of oxygen and nitrogen is passed through an electric arc at high voltages and in the reactions of POCl₃ or NO₂Cl with AgNO₃.

The gas phase structure of N₂O₅ has been established by electron diffraction and consists of two -NO₂ groups joined by an oxygen atom. The N-O-N bond angle is 111.8° and the -NO₂ groups undergo large amplitude torsional motions about a point of minimum energy corresponding to C₂ symmetry. In the solid phase, N₂O₅ has the ionic structure NO₂⁺NO₃⁻, which was supported by vibrational spectroscopy and was subsequently confirmed by an x-ray diffraction study. The latter indicated linear symmetric NO₂⁺ cations with an N-O bond length of 1.154±0.01Å.

In a recent study we have shown that BrF₅ interacts with an excess of LiNO₃ to give BrONO₂ and FNO₂:

\[ \text{BrF}_5 + 3\text{LiNO}_3 \rightarrow 3\text{LiF} + \text{BrONO}_2 + \text{O}_2 + 2\text{FNO}_2 \]
However, when the ratio of LiNO₃:BrF₅ was significantly higher than three, N₂O₅ was produced instead of FNO₂, implying (2) as a secondary reaction.

\[ FNO₂ + LiNO₃ \rightarrow LiF + N₂O₅ \]  

(2)

Since the methods generally used for the synthesis of N₂O₅ require an efficient ozone generator and, particularly when HNO₃ is the starting material, involve cumbersome purification steps, we examined reaction (2) for its potential as a simple, new synthesis of pure N₂O₅.

During the characterization of N₂O₅, its laser Raman spectrum was also recorded. Although the observed spectrum confirms the ionic NO₂⁺NO₃⁻ structure of solid N₂O₅, previously unreported bands were observed which are incompatible with a completely linear NO₂⁺ cation.

Experimental

**Materials and Apparatus.** The FNO₂ was prepared from BrF₅ and alkali metal nitrates, as previously described.¹⁸ The LiNO₃ (J. T. Baker, 99.7%) was dried in vacuo at 120°C for 12 hr before use. Volatile materials were handled in a well passivated (with ClONO₂) stainless steel Teflon-FEP vacuum line.¹⁹ Non-volatile materials were handled in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000-200 cm⁻¹ on a Perkin-Elmer Model 283 spectrophotometer. Raman spectra were taken on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser and a previously described²⁰ device for recording the low-temperature spectra. Sealed glass tubes were used as sample containers in the transverse-viewing-transverse-excitation mode.
Preparation of $\text{N}_2\text{O}_5$. A prepassivated 30mL stainless steel cylinder was loaded in the drybox with LiNO$_3$ (2.85 mmol). The cylinder was connected to the vacuum line and FNO$_2$ (1.34 mmol) was condensed in at -196°C. The cylinder was slowly warmed from -196 to 0°C and kept at this temperature for 24 hours. It was then cooled back to -196°C and checked for noncondensible material ($\text{O}_2$), but none was observed. The material volatile at 20°C was then separated by fractional condensation in a dynamic vacuum through traps kept at -142 and -196°C while the cylinder was allowed to warm up from -196 to 20°C. The -142°C trap contained a white solid (146mg, weight calc'd for 1.34 mmol of N$_2$O$_5$ = 145mg) which was shown by low-temperature Raman spectroscopy to be pure N$_2$O$_5$. The -196°C trap contained nothing. The nonvolatile residue in the cylinder consisted of a white solid (140mg, weight calc'd for 1.51 mmol of LiNO$_3$ and 1.34 mmol of LiF = 139mg) which was spectroscopically identified as a mixture of LiNO$_3$ and LiF.

Results and Discussion

Synthesis of N$_2$O$_5$. Nitryl fluoride reacts with an excess of LiNO$_3$ to provide pure N$_2$O$_5$ in quantitative yield. By limiting the reaction temperature to 0°C and using well passivated equipment, decomposition or hydrolysis of N$_2$O$_5$ is avoided and the need for an ozone generator is eliminated. Furthermore, the product separation is extremely simple because N$_2$O$_5$ is the only volatile material.

Raman Spectrum and Structure of N$_2$O$_5$. During the characterization of the N$_2$O$_5$ prepared by the above method from FNO$_2$ and LiNO$_3$, its low-temperature laser Raman spectrum was also recorded. The observed spectrum (see Figure 1 and Table 1) exhibited more bands than previously reported$^{13,14}$ and predicted from the known crystal structure$^{16}$ and a factor group analysis (see Table 2). To verify
that these additional Raman bands belonged indeed to $\text{N}_2\text{O}_5$, a sample of $\text{N}_2\text{O}_5$ was also prepared from $\text{N}_2\text{O}_4$ and ozone and its Raman spectrum was recorded. The observed spectrum was identical to that of Figure 1.

According to the previous x-ray crystal study, $\text{N}_2\text{O}_5$ crystallizes in the space group $D_{6h}^4$ (C6/mmc) with $Z=2$ and trigonal planar $\text{NO}_3^-$ anions in $D_{3h}$ sites and linear symmetric $\text{NO}_2^+$ cations in $D_{3d}$ sites. The structure was based on 64 non-zero reflections with a final $R$ value of 0.120. The refinement of this structure was subsequently confirmed by Cruickshank and coworkers but raised a question concerning the bond lengths of the $\text{NO}_2^+$ cations in $\text{NO}_2^+\text{NO}_3^-$ and $\text{NO}_2^+\text{ClO}_4^-$. Although the symmetric $\text{NO}_2^+$ stretching modes are practically identical in both compounds, the bondlengths differed by 0.049 Å and rotational oscillation corrections were suggested as a possible explanation for this large discrepancy.

Returning to the Raman spectrum of solid $\text{N}_2\text{O}_5$, the only two previous studies were carried out with Toronto arc excitation. Only two Raman lines at about 1400 and 1050 cm$^{-1}$ were observed and correctly attributed to the symmetric $\text{NO}_2^+$ and $\text{NO}_3^-$ stretching modes, respectively. We have now also observed (see Figure 1 and Table 1) the antisymmetric stretch and the in-plane deformation modes for $\text{NO}_3^-$ at 1350 and 722 cm$^{-1}$, respectively, and the deformation mode for $\text{NO}_2^+$ at 534 cm$^{-1}$. Whereas the Raman activity of $\nu_3$ and $\delta$ in-plane of $\text{NO}_3^-$ is in accord with the results of the factor group analysis (see Table 2), the latter cannot explain the intense Raman band observed for the $\text{NO}_2^+$ deformation mode.

The Raman and infrared activities and relative intensities of the $\text{NO}_2^+$ modes in $\text{NO}_2^+\text{NO}_3^-$ closely resemble those in $\text{NO}_2^+\text{ClO}_4^-$, which contains a slightly bent ($\angle\text{ONO} = 175.2\pm1.4^\circ$) $\text{NO}_2^+$ cation. Our data for $\text{NO}_2^+\text{NO}_3^-$, therefore, suggest that the $\text{NO}_2^+$ cation in solid $\text{N}_2\text{O}_5$ might be similarly bent. The failure of the x-ray crystal structure study to detect this nonlinearity of $\text{NO}_2^+$
for NO$_2^+$NO$_3^-$ might be attributed to facts such as the low precision of the x-ray study (64 reflections, $R = 0.12$)$^{16}$ or, more likely, rotational oscillation of the NO$_2^+$ cation$^{21}$ which could result in an averaged linear structure for a slightly nonlinear ion. Such an averaging would not be observable on the vibrational spectroscopy time scale.

In addition to the above discussed fundamental vibrations, several very weak bands were observed in the Raman spectrum of solid NO$_2^+$NO$_3^-$. The three bands at 1087, 1079 and 1065 cm$^{-1}$ can be attributed to the first overtone of the NO$_2^+$ deformation mode in Fermi resonance with the symmetric stretching mode. The splitting into three components can be explained by the assumption of an $E_{2u}$ component for the deformation mode which is inactive in both the infrared and Raman spectra but whose overtone and combination bands are Raman active (see Table 2). The weak band at 687 cm$^{-1}$ is attributed to a combination band of the NO$_2^+$ deformation with the 161 cm$^{-1}$ lattice mode. For the very weak band at 1028 cm$^{-1}$ we do not have, at the present time, a plausible explanation.

Acknowledgement. The authors thank Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson for their help and the U.S. Army Research Office and the Office of Naval Research for financial support.
References

(3) Berthelot, M. Bull. soc. chim. 1874, 21, 53.
(4) Russ, F.; Pokorny, E. Monatsh. 1913, 34, 1051.
(10) Ehrlich, V.; Russ, F. Monatsh. 1911, 32, 917.
(11) Odet, M.; Vignon, L. Compt. rend. 1869, 69, 1142, and 1870, 70, 96.
Table 1. Vibrational Spectra of Solid N$_2$O$_5$

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<td></td>
<td>vs, v$_1$(Σg$^+$)</td>
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(a) In view of the uncertainty about the actual symmetry of the ions, the idealized D$_{oh}$ and D$_{3h}$ symmetries were used for NO$_2^+$ and NO$_3^-$, respectively.

(b) Values from ref. 15.
Table 2. Correlation for the Intramolecular Vibrations of $\text{NO}_2^+$ and $\text{NO}_3^-$ in the $\text{NO}_2^+\text{NO}_3^-$ Crystal between their Point Groups, Site Groups and Factor Groups and their Infrared and Raman Activities

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<th>site group</th>
<th>factor group</th>
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<td>$A_1'(R)$</td>
<td>$A_{lg}(R)$</td>
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<td>$A_2''(IR)$</td>
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<td></td>
<td></td>
<td>$B_{2g}$ -</td>
</tr>
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<td>$E'(R,IR)$</td>
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<td>$E_{2g}(R)$</td>
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<td>$E'(R,IR)$</td>
<td>$E_{1u}(IR)$</td>
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<td></td>
<td></td>
<td>$E_{2g}(R)$</td>
</tr>
<tr>
<td>$\text{NO}_2^+$ symmetric stretch</td>
<td>$D_{∞h}$</td>
<td>$D_{3d}$</td>
<td>$D_{6h}$</td>
</tr>
<tr>
<td></td>
<td>$Σg^+(R)$</td>
<td>$A_{lg}(R)$</td>
<td>$A_{lg}(R)$</td>
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<tr>
<td>antisymmetric stretch</td>
<td>$Σu^+(IR)$</td>
<td>$A_{2u}(IR)$</td>
<td>$A_{2u}(IR)$</td>
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<tr>
<td></td>
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<td>$B_{1u}$ -</td>
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<tr>
<td>deformation</td>
<td>$Πu(IR)$</td>
<td>$E_u(IR)$</td>
<td>$E_{1u}(IR)$</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>$E_{2u}$ -</td>
</tr>
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</table>

$2\times$ deformation ($D_{6h}$)

\[
\begin{align*}
2E_{1u} &= A_{lg} + A_{2g} + E_{2g}(R) \\
2E_{2u} &= A_{lg} + A_{2g} + E_{2g}(R) \\
E_{1u} \cdot E_{2u} &= B_{lg} + B_{2g} + E_{lg}(R)
\end{align*}
\]
Figure 1. Low-temperature laser Raman spectrum of solid $\text{N}_2\text{O}_5$. 
ABSTRACT

The reaction of FNO$_2$ with an excess of LiNO$_3$ at 0°C provides a new, simple and quantitative synthesis for N$_2$O$_5$. It eliminates some of the drawbacks of previously used syntheses such as the need for an efficient ozone generator and cumbersome purification steps. The laser Raman spectrum of solid N$_2$O$_5$ was recorded and suggests that, contrary to a previous low-precision x-ray crystal structure study, the NO$_2^+$ cation in solid N$_2$O$_5$ might not be completely linear.
APPENDIX V

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303

Bromine Nitrates
William W. Wilson and Karl O. Christie

Abstract

The reaction of BrF$_5$ with a large excess of LiNO$_3$ at 0°C produces LiF, BrONO$_2$, N$_2$O$_5$ and O$_2$ as the principal products. The infrared spectra of BrONO$_2$ in the gas and solid phases and in N$_2$ and Ne matrices, and the Raman spectrum of the solid phase were recorded. With the exception of the N-OBr torsional mode, all fundamental vibrations of BrONO$_2$ can be assigned and support a planar structure for this molecule. The fundamental vibrations involving the NO$_2$ group exhibit pronounced frequency shifts on going from the gas to the solid indicating association in the solid phase. With N$_2$O$_5$ the BrONO$_2$ molecule forms an unstable adduct which was shown by Raman spectroscopy to possess the ionic structure NO$_2^+$$[\text{Br(NO}_2)_2]^-$. Based on a comparison of our results with those found in the literature and three unpublished dissertations, it is concluded that the previously reported compounds BrO$_2$·3NO$_2$, Br(NO$_3$)$_3$ and BrNO$_3$·N$_2$O$_5$ are all identical with our material and therefore must be assigned the composition NO$_2^+$$[\text{Br(NO}_2)_2]^-$. For comparison, Cs$^+$$[\text{Br(NO}_2)_2]^-$ was also prepared, and its vibrational spectra were recorded and assigned.

Introduction

In a recent study from our laboratory it was shown that the reactions of an excess of BrF$_5$ with the nitrates of Na, K, Rb and Cs provide simple, high yield, one step syntheses for the corresponding BrF$_4$O$^-$ salts and FNO$_2$. Since lithium does not
form a stable BrF$_4$O$^-$ salt, the use of LiNO$_3$ as a starting material in the above reaction afforded a direct, one step synthesis of BrF$_3$O.$^1$ During the study of the LiNO$_3$-BrF$_5$ system, it was found that the use of an excess of LiNO$_3$ in this reaction dramatically altered its course and produced bromine nitrate containing material.

Very few papers dealing with bromine nitrates have previously been published. The first report on the existence of bromine nitrates was published in 1961 by Schmeisser and Taglinger.$^2$ From the reaction of BrF$_3$ with N$_2$O$_5$ they obtained a compound believed to be Br(NO$_3$)$_3$. By reaction with iodine this material was converted to BrONO$_2$ which was also prepared from BrCl and ClONO$_2$. Ozonization of BrONO$_2$ resulted in the formation of O$_2$BrONO$_2$.$^2$ The only other published reports on these compounds were a confirmation$^3$ of the BrONO$_2$ + O$_3$ reaction and a study of the stratospheric significance of BrONO$_2$ in which its gas phase ultraviolet and infrared spectra and some physical properties were also reported.$^4$ In addition, the synthesis and a partial infrared spectrum were reported for [N(CH$_3$)$_4$]$^+$(Br(ONO$_2$)$_2$]$^-$, which was prepared from [N(CH$_3$)$_4$]$^+$(Cl)$_2$ Br$^-$ and ClONO$_2$.5

Toward the end of our study, Professor Naumann from the University of Dortmund, Germany, kindly provided us with copies of three unpublished dissertations$^6$-$^8$ which were carried out between 1963 and 1977 under the late Professor Schmeisser. The pertinent results of these studies are summarized in the following three paragraphs.

In 1963 Schuster$^6$ found that the interaction between Br$_2$ and ClONO$_2$ at room temperature can produce two different products. At short reaction times BrONO$_2$ was obtained in good yield, whereas at extended reaction times the principal product was BrONO$_2$·N$_2$O$_5$. The latter compound was also obtained by reaction (1),

\[
\text{BrONO}_2 + \text{N}_2\text{O}_5 \rightarrow \text{BrONO}_2\cdot\text{N}_2\text{O}_5 \quad (1)
\]
and found in the residue from the partial decomposition of Taglinger's "\(Br(\text{NO}_3)_3\)." Furthermore, it was shown that the compound trinitrobromine dioxide, \(\text{BrO}_2\cdot3\text{NO}_2\), reported in 1953 by Pflugmacher, was identical with \(\text{BrONO}_2\cdot\text{N}_2\text{O}_5\). Although no structural information on \(\text{BrO}_2\cdot3\text{NO}_2\) and \(\text{BrONO}_2\cdot\text{N}_2\text{O}_5\) was available, their compositions were firmly established by elemental analyses, and the possibility of the ionic structure \(\text{NO}_2^+\left[\text{Br(\text{NO}_3)_2}\right]^->\) was suggested.

Holthausen confirmed for \(\text{BrONO}_2\cdot\text{N}_2\text{O}_5\) the ionic \(\text{NO}_2^+\left[\text{Br(\text{NO}_3)_2}\right]^->\) structure by low-temperature infrared spectroscopy and by the metathetical reaction (2).

\[
\text{NO}_2^+\left[\text{Br(\text{NO}_3)_2}\right]^-> + [\text{N(CH}_3)_4]^+\text{NO}_3^- + [\text{N(CH}_3)_4]^+[\text{Br(\text{NO}_3)_2}]^- + \text{N}_2\text{O}_5
\]

The \([\text{N(CH}_3)_4]^+[\text{Br(\text{NO}_3)_2}]^-\) salt was also prepared according to reactions (3), (4) and, interestingly, (5).

\[
[\text{N(CH}_3)_4]^+\text{BrCl}_2^- + 2\text{ClONO}_2 \rightarrow [\text{N(CH}_3)_4]^+[\text{Br(\text{NO}_3)_2}]^- + 2\text{Cl}_2 \quad (3)
\]
\[
[\text{N(CH}_3)_4]^+\text{NO}_3^- + \text{BrONO}_2 \rightarrow [\text{N(CH}_3)_4]^+[\text{Br(\text{NO}_3)_2}]^- \quad (4)
\]
\[
[\text{N(CH}_3)_4]^+\text{NO}_3^- + \text{"Br(\text{NO}_3)_3"} \rightarrow [\text{N(CH}_3)_4]^+[\text{Br(\text{NO}_3)_2}]^- \quad (5)
\]

Attempts to prepare \(\text{NO}_2^+\left[\text{Br(\text{NO}_3)_2}\right]^->\) and \(\text{Cs}^+\left[\text{Br(\text{NO}_3)_2}\right]^->\) were either unsuccessful or resulted in an impure product, respectively. The low temperature infrared spectrum of \(\text{BrONO}_2\) was also recorded and showed the following absorptions (cm\(^{-1}\)):

\begin{itemize}
  \item 1655s
  \item 1615vs
  \item 1260vs
  \item 830vs
  \item 725s
  \item 630s
  \item 395s
\end{itemize}

Stosz repeated the previous preparations of \(\text{BrONO}_2\), \(\text{NO}_2^+\left[\text{Br(\text{NO}_3)_2}\right]^->\), and \(\text{"Br(\text{NO}_3)_3"}\), recorded their low-temperature Raman spectra and redetermined some physical properties, such as melting points and vapor pressures (\(\text{BrONO}_2\): mp = -28°C, \(\Delta H_{\text{vap}} = 8.0\) kcal/mol). He showed that the Raman spectra of \(\text{NO}_2^+\left[\text{Br(\text{NO}_3)_2}\right]^->\)
and "Br(NO₃)₃" were identical and concluded that NO₂⁺[Br(NO₃)₂]⁻ actually was Br(NO₃)₃. Attempts to prepare K⁺[Br(NO₃)₂]⁻ were unsuccessful.

Based on the above data, the identity of BrONO₂ appeared well established; however, serious doubts existed concerning the exact nature of either BrO₂·3NO₂, BrONO₂·N₂O₅, NO₂⁺[Br(NO₃)₂]⁻, or Br(NO₃)₃. The fact that all four compounds represent one single species has been well established. However, the recent Raman spectroscopic identification of this species as Br(NO₃)₃ by Stosz could not explain the results of both Schuster and Holthausen and required a thorough reexamination.

**Experimental**

**Materials.** Commercial LiNO₃ (J. T. Baker, 99.7%) and CsBr (Aldrich, 99.9%) were dried in a vacuum oven at 120°C for one day prior to their use. The BrF₅ (Matheson) was treated with 35 atm of F₂ at 100°C for 24 hr and then purified by fractional condensation through traps kept at -64 and -95°C, with the material retained at -95°C being used. The Br₂ (J. T. Baker, purified) was stored over P₂O₅ prior to its use. The CsBrCl₂ was prepared from CsBr and Cl₂ in CH₃CN solution. After addition of about the stoichiometric amount of Cl₂ to the CsBr-CH₃CN solution, a small amount of undissolved white solid was removed by filtration in a dry N₂ atmosphere. The clear, yellow filtrate was pumped to dryness at ambient temperature. The resulting yellow solid was identified as CsBrCl₂ by its strong Raman band at 294 cm⁻¹. The synthesis of ClONO₂ has previously been described.

**Apparatus.** Volatile materials used in this work were handled in a well-passivated (with BrF₅ until it was recovered as a white solid at -196°C or with ClONO₂ when no fluoride coatings were desired) stainless steel Teflon FEP vacuum line.
volatile materials were handled in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000-200 cm\(^{-1}\) on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The low-temperature infrared spectra of solid and matrix-isolated materials were obtained with an Air Products Model DE202S helium refrigerator equipped with CsI windows. For the matrix isolation spectra of BrONO\(_2\), the N\(_2\) or Ne matrix gas was swept through a Teflon FEP U-tube containing BrONO\(_2\) at -31°C.

Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed glass tubes were used as sample containers in the transverse-viewing-transverse-excitation mode. A previously described\(^{13}\) device was used for recording the low-temperature spectra.

**Preparation of BrONO\(_2\).** Since the reaction of BrCl with ClONO\(_2\) gives only low yields of BrONO\(_2\),\(^2,4,6\) the reaction of Br\(_2\) with ClONO\(_2\) was used for its synthesis.\(^6,8\) In a typical experiment, dry Br\(_2\) (10.43 mmol) and ClONO\(_2\) (31.82 mmol) were successively condensed into a prepassivated (with ClONO\(_2\)) 75mL stainless steel cylinder. The cylinder was warmed from -196°C to 25°C and was kept at this temperature for 1.5 hr with frequent agitation. It was then cooled to -196°C and contained no noncondensible material (no O\(_2\) evolution). The cylinder was allowed to slowly warm to 25°C while separating the volatile material by fractional condensation in an oil pump vacuum through a series of traps kept at -31°C (bromobenzene...
slush), -45° (chlorobenzene slush), and -196°C. The trap at
-45° contained 3.90 mmol of a yellow solid which was identified
by its vibrational spectra as BrONO₂ (18.6% yield based on Br₂).
The -196° trap contained the Cl₂ by-product and the unreacted
Br₂ and ClONO₂.

When the reaction between Br₂ and ClONO₂ is carried out for
prolonged time periods at room temperature, the main product
becomes NO₂⁺[Br(ONO₂)₂]⁻. Separation of BrONO₂ from NO₂⁺
[Br(ONO₂)₂]⁻ can be achieved by pumping on a mixture of the
two kept at -35°C. The NO₂⁺[Br(ONO₂)₂]⁻ is less volatile and
remains as a white or very pale yellow residue, whereas the
BrONO₂ can be collected as a yellow sublimate.

Preparation of Cs⁺[Br(NO₃)₂]⁻. A prepassivated (with ClONO₂)
30mL stainless steel cylinder was loaded in the drybox with
CsBrCl₂ (2.432 mmol). On the vacuum line, ClONO₂ (19.68 mmol)
was added at -196°C. The cylinder was allowed to warm to 0°C
and was kept at this temperature for 4 hr with occasional
agitation. The cylinder was cooled to -196°C and contained no
noncondensible gas. The material volatile at 0°C was pumped
off and separated by fractional condensation through traps
kept at -112° and -196°C during warm up of the cylinder from
-196° to 0°C. The -196° trap contained Cl₂ (4.51 mmol),
whereas the -112° trap had unreacted ClONO₂ (14.78 mmol). The
cylinder contained 743 mg of a white solid which based on its
vibrational spectra was Cs⁺[Br(ONO₂)₂]⁻ containing a small
amount of CsNO₃. The latter was formed by slow decomposition
of Cs⁺[Br(ONO₂)₂]⁻ at ambient temperature which was shown to
yield CsNO₃ and BrONO₂ as the primary products, followed by
decomposition of BrONO₂ to Br₂, N₂O₅, NO₂ and O₂. Attempts
to prepare Cs⁺[Br(ONO₂)₂]⁻ directly with CsBr and ClONO₂ at
0°C were unsuccessful and produced only a product consisting of
CsNO₃ and an unidentified cesium polyhalide which was also
obtained from the reaction of CsBr with Cl₂ in aqueous
solution. Its solid phase Raman spectrum showed the following bands, 340vw, 230sh, 215s, 203vs, 142m, 126w, 108w, 80m, 62mw, and resembled that of CsIBr$_2^{14}$, except for significant shifts to higher frequencies.

The LiNO$_3$-BrF$_5$ System. A prepassivated (with BrF$_5$) 30mL stainless steel cylinder was loaded in the drybox with LiNO$_3$ (20.065 mmol). On the vacuum line, BrF$_5$ (2.485 mmol) was added at -196°C. The cylinder was kept at 0°C for 3.5 days and then cooled to -196°C. The material volatile at -196°C consisted of O$_2$ (2.481 mmol). The cylinder was allowed to slowly warm to 25°C while the volatile material was separated in a dynamic vacuum by fractional condensation through two traps kept at -142 and -196°C. The -196°C trap contained a trace of FNO$_2$, whereas the -142°C trap had 894 mg of a white solid consisting of an equimolar mixture of NO$_2$+[Br(ONO$_2$)$_2$]$^-$ and N$_2$O$_5$ (weight calcd for 2.485 mmol NO$_2$+[Br(ONO$_2$)$_2$]$^-$ and 2.485 mmol of N$_2$O$_5$ = 889 mg). The white solid residue (851 mg) in the cylinder consisted of LiF and LiNO$_3$ (weight calcd for 12.423 mmol of LiF and 7.643 mmol of LiNO$_3$ = 849 mg). Separation of NO$_2$+[Br(ONO$_2$)$_2$]$^-$ from N$_2$O$_5$ was achieved by fractional condensation. The NO$_2$+[Br(ONO$_2$)$_2$]$^-$ was trapped at -35°C whereas the N$_2$O$_5$ slowly passed. Vibrational spectroscopy was used for the identification of the materials.

When the ratio of LiNO$_3$ to BrF$_5$ was less than five, the formation of some free FNO$_2$ was observed together with a decreased yield of N$_2$O$_5$.

Results and Discussion

In this section, we will first present our results on the syntheses and characterization of BrONO$_2$, Cs$^+$[Br(ONO$_2$)$_2$]$^-$ and NO$_2$+[Br(ONO$_2$)$_2$]$^-$. 
followed by a critical review of the presently known bromine nitrate chemistry based on our data and the unpublished dissertations of Schuster, Holthausen and Stosz.

Syntheses. When \( \text{BrF}_5 \) is reacted with a threefold amount of \( \text{LiNO}_3 \), the main products are \( \text{BrONO}_2 \) and \( \text{FNO}_2 \) (6).

\[
3\text{LiNO}_3 + \text{BrF}_5 \rightarrow 3\text{LiF} + \text{BrONO}_2 + 2\text{FNO}_2 + \text{O}_2 \quad (6)
\]

At a mole ratio of \( \text{LiNO}_3 \) to \( \text{BrF}_5 \) above five, \( \text{BrONO}_2 \) and \( \text{N}_2\text{O}_5 \) (or their adduct, depending on the temperature) become the main products (7).

\[
5\text{LiNO}_3 + \text{BrF}_5 \rightarrow 5\text{LiF} + \text{BrONO}_2 + 2\text{N}_2\text{O}_5 + \text{O}_2 \quad (7)
\]

Subtraction of equation (6) from (7) implies reaction (8) which was experimentally verified and will be reported on separately.

\[
2\text{LiNO}_3 + 2\text{FNO}_2 \rightarrow 2\text{LiF} + \text{N}_2\text{O}_5 \quad (8)
\]

Furthermore, it was found that, in agreement with Schuster and Holthausen, \( \text{BrONO}_2 \) forms with \( \text{N}_2\text{O}_5 \) the 1:1 adduct \( \text{BrONO}_2 \cdot \text{N}_2\text{O}_5 \) (1) which has, as shown below, the ionic structure \( \text{NO}_2^+ [\text{Br(ONO}_2)_2]^-. \) Since our vibrational spectra for \( \text{NO}_2^+ [\text{Br(ONO}_2)_2]^-. \) (see below) were almost identical to those attributed by Stosz to "\( \text{Br(NO}_3)_3 \)" additional synthetic work was carried out to resolve some of the previously reported discrepancies. For example, \( \text{BrONO}_2 \) was prepared by Schuster's method (9)

\[
\text{Br}_2 + 2\text{ClONO}_2 \rightarrow 2\text{BrONO}_2 + \text{Cl}_2 \quad (9)
\]

and was characterized. For the unambiguous identification of the \( [\text{Br(ONO}_2)_2]^-. \) anion, the \( \text{Cs}^+ [\text{Br(ONO}_2)_2]^-. \) salt was prepared according to (10) and characterized.

\[
\text{CsBrCl}_2 + 2\text{ClONO}_2 \rightarrow \text{Cs}^+ [\text{Br(ONO}_2)_2]^-. + 2\text{Cl}_2 \quad (10)
\]
Characterization of BrONO₂

Physical Properties. BrONO₂ is the best characterized bromine nitrate. It is a yellow solid with a melting point of -28°C. This value agrees well with that reported by Stosz, but is significantly higher than those of -42° and -33° reported previously. These low values were probably due to the presence of some impurities. It has a vapor pressure of 114mm at 23°C and slowly decomposes at ambient temperature to Br₂, N₂O₅, NO₂, and O₂.

Vibrational Spectra and Structure. Only limited data were previously available on the vibrational spectra and structure of BrONO₂. A partial infrared spectrum of the gas had been published, and one of the dissertations contained a Raman spectrum of the solid whose frequencies deviated significantly from the gas-phase values. No conclusions were reached whether the bromine atom is coplanar or perpendicular to the O₂NO-plane. For the closely related ClONO₂ molecule, the question concerning its planarity was hotly disputed and finally settled in favor of a planar structure. In view of the scarcity of data for BrONO₂, we have recorded its infrared spectra in the gas phase and in N₂ (see Figure 1) and Ne matrices, and the infrared and Raman spectra of the neat solid (see Figure 2). The observed frequencies are summarized in Table 1.

Vibrational Assignments. A comparison of the fundamental vibrations of BrONO₂ with those of the closely related molecules ClONO₂, FONO₂, CH₃ONO₂, and HONO₂ shows excellent agreement both with respect to frequencies and relative infrared and Raman intensities (see Table 2). Since the planarity of ClONO₂, CH₃ONO₂, and HONO₂ is well established, the data of Table 2 strongly supports a planar structure for BrONO₂ as well.
The assignments of the observed fundamental vibrations to the individual modes is straightforward. A planar BrONO₂ molecule has symmetry $C_s$. The irreducible representation for the intramolecular vibrations is $\Gamma = 7A' + 2A''$. The intense 1714, 1288, 806, and 564 cm⁻¹ infrared gas-phase bands are characteristic for all covalent nitrates and are due to the antisymmetric NO₂ stretching, the symmetric NO₂ stretching, the NO₂ scissoring, and the ONO₂ antisymmetric in plane deformation vibrations, respectively.²¹

The N-O stretching mode has very high Raman intensities in all the covalent nitrates listed in Table 2 and occurs in FONO₂ and ClONO₂ at 457 and 436 cm⁻¹, respectively.²¹ Therefore, this mode is assigned to the very intense Raman band at 397 cm⁻¹ in solid BrONO₂.

A cursory inspection of Table 2 might raise questions of why the N-O stretching modes should be of such high Raman intensities, exhibit negligible $^{14}$N-$^{15}$N isotopic shifts, and have surprisingly low frequencies. A comparison with the well known and analyzed vibrational spectra of FNO₂ provides the answer to these questions. The FNO₂ molecule is a good approximation to the ONO₂ part of the XONO₂ compounds, but due to its higher symmetry and lower number of fundamental vibrations is much more amenable to a thorough normal coordinate analysis. Thus, the $A_1$ block of FNO₂ contains only three fundamental vibrations at about 1308, 810 and 555 cm⁻¹ which are best assigned to the symmetric NO₂ stretching, the NO₂ scissoring and the NF stretching mode, respectively.²¹,²²,²³,²⁹ The observed frequencies, intensities, and $^{14}$N-$^{15}$N isotopic shifts are similar to those of the corresponding ONO₂ modes in XONO₂. The potential energy distribution (Set I in Table VII of Mirri et al.)³⁸ shows that the highest frequency is almost pure NO₂ stretching, the intermediate frequency is mainly an antisymmetric combination of the NO₂...
scissoring motion and the NF stretching motion with some contribu-
tion from NO$_2$ stretching, while the lowest frequency is best
described as a symmetric combination of NF stretching and some
NO$_2$ stretching. These results account nicely for the experimental
observations and should be directly transferrable to the XONO$_2$
molecules of this study. A normal coordinate analysis for BrONO$_2$,
however, would be of little value in view of the grossly under-
determined nature of the problem (28 symmetry force constants
from seven frequencies in the A' block) and the expected strong
coupling effects.

It should be noted that in the infrared spectrum of solid BrONO$_2$
the N-O stretching mode becomes quite intense (see 400 cm$^{-1}$ band
in trace A of Figure 2). This increase in intensity for the neat
solid is attributed to pronounced association effects (see below).

The N-O-Br in plane bending mode should result in an intense
Raman band between 300 and 200 cm$^{-1}$ and therefore can readily
be assigned to the strong Raman band at 244 cm$^{-1}$. The N-ObBr
torsional mode should occur below 140 cm$^{-1}$ and cannot be assigned
with confidence based on the available data.

The only two fundamental vibrations yet unaccounted for are the
ONO$_2$ out of plane deformation and the O-Br stretching modes. The
O-Br stretching mode should be of high Raman and low infrared
intensity, whereas the 6ONO$_2$ out-of-plane mode should be of medium
IR and low Raman intensity and occur in the 700 to 770 cm$^{-1}$ region.
Based on these predictions, the intense Raman band at 761 cm$^{-1}$
with a weak matrix infrared counterpart at 750 cm$^{-1}$ is assigned
to vO-Br, and the medium strong matrix infrared band at 725 cm$^{-1}$
with a very weak Raman counterpart at 738 cm$^{-1}$ to the δ out of
plane ONO$_2$ mode. This accounts for all the nine fundamental
vibrations of BrONO$_2$ and provides consistent frequency and
intensity trends for the series HONO$_2$, CH$_3$ONO$_2$, FONO$_2$, ClONO$_2$, and
BrONO₂ (see Table 2). Essentially all of the observed weak bands can be assigned in terms of overtones and combination bands of these fundamental vibrations (see Table 1).

Association in the Solid Phase. As mentioned above, some of the fundamental vibrations in solid BrONO₂ significantly deviate from those of the gas and the matrix isolated molecule. From the fundamental vibrations involved and the magnitudes and directions of the shifts, conclusions can be drawn concerning the nature of the association. The involvement of the NO₂ group in the bridging is indicated by a lowering of its stretching frequencies (Δvₛ = -98, Δvₛ = -23 cm⁻¹) and an increase of its in-plane deformation frequencies (Δs₆ = 77, Δs₆ = 34 cm⁻¹). The fact that the δ out-of-plane ONO₂ frequency is essentially unshifted, suggests that the bridging occurs in the ONO₂ plane and does not directly involve the nitrogen atom. Hence, the NO₂ group should bridge to either the bromine or the oxygen atom of the O-Br group of another BrONO₂ molecule. Of these two alternatives, bromine definitely is the better acceptor as shown by the existence of the [Br(ONO₂)₂]⁻ anion. Since in this anion the nitrate ligands are monodentate, we prefer for solid BrONO₂ a model involving intermolecular BrON(O)O--→BrONO₂ bridges which are also monodentate.

Characterization of Cs⁺[Br(ONO₂)₂]⁻ and NO₂⁺[Br(ONO₂)₂]⁻

Physical Properties. Cs⁺[Br(ONO₂)₂]⁻ is a white crystallinic solid. It is only marginally stable at room temperature and dissociates to CsNO₃ and BrONO₂ with the latter decomposing further to Br₂, N₂O₅, NO₂, and O₂. Therefore it is difficult to obtain samples which are completely free of CsNO₃.

NO₂⁺[Br(ONO₂)₂]⁻ is a white crystallinic solid which can be purified by vacuum sublimation. It is stable at -35°C and can be trapped at this temperature. At 23°C it has a dissociation pressure of about 130 torr and decomposes to BrONO₂ and N₂O₅.
which can then undergo further slow decomposition to \( \text{Br}_2 + \text{N}_2\text{O}_5 + \text{O}_2 \) and \( \text{N}_2\text{O}_4 + \text{O}_2 \), respectively. It melts at about 46°C with decomposition.

**Vibrational Spectra.** The vibrational spectra of \( \text{Cs}^+\{\text{Br(ONO}_2\}_2\}^- \) and \( \text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^- \) are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are summarized in Table 3. A cursory inspection of Figures 3 and 4 reveals that the main features in the spectra of both materials are very similar, except for three extra bands in \( \text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^- \). These extra bands occur at 1395 cm\(^{-1}\) in the Raman and at 2370 cm\(^{-1}\) and 566-551 cm\(^{-1}\) in the infrared spectra. These bands are characteristic for the \( \text{NO}_2^+ \) cation\(^{40,41}\) and establish the ionic structure \( \text{NO}_2^+ \{\text{Br(ONO}_2\}_2\}^- \) for this \( \text{BrONO}_2\cdot\text{N}_2\text{O}_5 \) adduct.

The first question which must be answered with respect to the \( \{\text{Br(ONO}_2\}_2\}^- \) anion is the nature of the nitrato groups. These groups could be either ionic or covalent. From the complexity of the observed spectra and the absence of bands characteristic for a free \( \text{NO}_3^- \) anion,\(^{40}\) it can be concluded that the nitrato groups must be covalent.

A covalent nitrato ligand could be either mono- or bi-dentate. Based on previous thorough vibrational analyses,\(^{42,43}\) covalent bidentate nitrato ligands should exhibit in the 900-1700 cm\(^{-1}\) range three groups of Raman bands at about 1600 (\( \text{vN-O} \)), 1200 (\( \text{vs NO}_2 \)) and 1000 cm\(^{-1}\) (\( \text{vs NO}_2 \)) with their intensities decreasing in the order \( I_1 > I_2 > I_3 \). On the other hand, covalent monodentate nitrato groups should exhibit two bands in the 900-1700 cm\(^{-1}\) frequency range at about 1700 (\( \text{vas NO}_2 \)) and 1300 cm\(^{-1}\) (\( \text{vs NO}_2 \)) with the 1300 cm\(^{-1}\) band being more intense in the Raman spectrum.\(^{17-22}\) For molecules containing more than one nitrato ligand, coupling of the vibrations of these ligands is expected which should result in splittings due to in-phase and out-of-phase motions. Furthermore, the formal negative charge in the ion is predicted to increase

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the polarity of the nitrogen-oxygen bands, thereby lowering their frequencies somewhat. Inspection of Figures 3 and 4 shows that the observed spectra are in accord with these predictions for strongly coupled monodentate ligands and therefore will be assigned in this manner.

The next question is how are the two nitrato ligands in [Br(ONO$_2$)$_2$]$^-$ most likely arranged with respect to each other? Treating the -ONO$_2$ group as a pseudo-halide, the O-Br-O part of [Br(ONO$_2$)$_2$]$^-$ is expected to be, for practical purposes, linear. Since the N-O-Br angle should be close to tetrahedral (109°), the two nitrato ligands could be either cis or trans to each other, or form a dihedral angle. If the nitrato ligands would be trans to each other, the [Br(ONO$_2$)$_2$]$^-$ anion would possess a symmetry center, and the infrared and Raman bands should be either mutually exclusive or at least differ dramatically in intensity. Since this is not the case, a trans-configuration can be ruled out. Since mutual repulsion arguments mitigate against a cis-isomer, we prefer a configuration with a dihedral angle. Such an anion would possess symmetry C$_2$, with the twofold rotation axis passing through the Br atom at a right angle to the O-Br-O axis and splitting the dihedral angle in half.

The irreducible representation for the intramolecular vibrations of [Br(ONO$_2$)$_2$]$^-$ of symmetry C$_2$ is $\Gamma = 10A + 11B$, where the A modes are symmetric and the B modes antisymmetric to the twofold axis. Of these 21 modes, 9 belong to the O-Br-O skeleton and 12 involve motions of the nitrato ligands. A breakdown into the individual modes is given in Table 4. Since the unit cells of these [Br(ONO$_2$)$_2$]$^-$ salts might contain more than one molecule, additional splittings might be observed in the actual spectra due to ion coupling and anion-cation interactions.
Tentative assignments for some of the fundamental vibrations of \[\text{Br}(\text{ONO}_2)_2\] can be made on the following basis. The four groups of bands between 900 and 1600 cm\(^{-1}\) should represent the four NO\(_2\) stretching modes. Of these, the symmetric, in-phase NO\(_2\) stretch should be very strong in both the Raman and the infrared spectra and therefore must be assigned to either the 1280 or the 1530 cm\(^{-1}\) group. Since in BrONO\(_2\) (see above) the symmetric NO\(_2\) stretch is about 370 cm\(^{-1}\) lower than the anti-symmetric one, the 1280 cm\(^{-1}\) group in the spectra of \[\text{Br}(\text{ONO}_2)_2\] is assigned to the symmetric, in-phase NO\(_2\) stretch. This leaves the 1530 cm\(^{-1}\) group for assignments to one of the two anti-symmetric NO\(_2\) stretches. From these two, the out-of-phase mode should be of much higher infrared intensity than the in-phase mode and therefore the 1530 cm\(^{-1}\) group is assigned to the anti-symmetric, out-of-phase NO\(_2\) stretch. Based on its low infrared intensity, the 1100 cm\(^{-1}\) group is assigned to the antisymmetric, in-phase NO\(_2\) stretch, leaving the 950 cm\(^{-1}\) group for assignment to the symmetric, out-of-phase NO\(_2\) stretch.

Two comments are required with respect to these NO\(_2\) stretching bands: (i) for NO\(_2^+\)[Br(ONO\(_2\))\(_2\)]\(^-\) the Raman bands show additional splittings into 3 components for the antisymmetric and 2 components for the symmetric modes and also their frequencies significantly deviate in most cases from those of their infrared counterparts. This is attributed to the influence of the NO\(_2^+\) counterion which is less symmetrical than Cs\(^+\) thus causing stronger cation-anion interactions in the solid; and (ii) for Cs\(^+\)[Br(ONO\(_2\))\(_2\)]\(^-\) the failure to observe a Raman band around 1130 cm\(^{-1}\) might be due to the lower signal to noise ratio in the spectrum.

There is a group of three distinct bands in the 690 to 790 cm\(^{-1}\) region which are assigned by analogy with the spectra of solid BrONO\(_2\) (see above) to the scissoring, the out-of-plane, and the
antisymmetric in-plane deformation modes of the NO₂ groups (see Table 3). No detectable splittings due to in-phase and out-of-phase coupling were observed for these modes.

The O-N torsional mode is expected to be of low frequency and to occur in the frequency range of the skeletal modes. Therefore, no attempt was made to assign this mode.

The assignments for the NOBrON skeletal modes are more difficult because few data are available for comparable systems. If the nitrato group is treated as a pseudo-halide, the known spectra of certain [BrHal₂]⁻ species will give us an estimate for the frequency range to be expected for the OBrO vibrations. In BrF₂⁻, BrCl₂⁻ and Br⁺⁻ the symmetric stretching vibration has frequencies of 442, 272, and 162 cm⁻¹ respectively. Furthermore, the N-O stretching vibration in the halogen nitrates occurs between 390 and 460 cm⁻¹ (see Table 2). Therefore, it seems reasonable to assume that the NOBrON skeletal modes should occur in similarly low frequency ranges and not be assignable to the bands observed in the 700-800 cm⁻¹ range. Based on these comparisons, we tentatively assign the strong Raman bands at 317 and 298 cm⁻¹ in Cs⁺[Br(ONO₂)₂]⁻ to the symmetric in-phase N-O stretch and the symmetric BrO₂ stretch, respectively, and the weak Raman bands at about 460 and 400 cm⁻¹ to the corresponding antisymmetric stretching motions, respectively. Due to the overlap of the frequency ranges of the skeletal deformation modes and the lattice vibrations, no assignments are proposed at this time for the lower frequency bands.

Critical Review of Bromine Nitrate Chemistry. A combination of our results with those of Taglinger,² Schuster,⁶ Hothausen,⁷ Stosz,⁸ and Pflugmacher⁹ allows the following conclusions concerning the presently known bromine nitrates: (i) the compound obtained originally from BrF₃ and N₂O₅ and ascribed to "Br(NO₂)₃"²
is actually $\text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^-$. Stosz$^8$ repeated the original synthesis$^2$ and recorded a low temperature Raman spectrum which is identical to that obtained by us for $\text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^-$. Furthermore, the physical and chemical properties reported$^2,8$ for "Br(NO$_3$)$_3$" are practically identical to those of $\text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^-$. Schuster had previously shown$^6$ that Pflugmacher's "BrO$_2$.3NO$_2$" is identical to "BrNO$_3$.N$_2$O$_5$", which has been shown by this study to be $\text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^-$. Therefore the previously reported compounds "Br(NO$_3$)$_3$", "BrO$_2$.3NO$_2$", and "BrNO$_3$.N$_2$O$_5$" are all one and the same compound, i.e. $\text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^-$; and (ii) based on the fact that "Br(NO$_3$)$_3$" is actually $\text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^-$, we have critically reviewed the known reaction chemistry of the bromine nitrates. The most important reactions are presented in Scheme 1. The formation of $\text{NO}_2^+\{\text{Br(ONO}_2\}_2\}^-$ from BrF$_3$
and N₂O₅ in the original "Br(NO₃)₃" preparation² can readily be explained in terms of reactions (11) through (14).

\[
\begin{align*}
\text{BrF}_3 + \text{N}_2\text{O}_5 & \rightarrow 2\text{F(NO}_2) + \text{BrFO} & (11) \\
2\text{BrFO} & \rightarrow \text{FBrO}_2 + \text{BrF} & (12) \\
\text{BrF} + \text{N}_2\text{O}_5 & \rightarrow \text{BrONO}_2 + \text{FNO}_2 & (13) \\
\text{BrONO}_2 + \text{N}_2\text{O}_5 & \rightarrow \text{NO}_2^+\{\text{Br(ONO}_2\}^2_2 & (14)
\end{align*}
\]

Experimental support for this sequence was obtained by Stosz⁸ who demonstrated the formation of FBrO₂ as a by-product in this system. Similarly, BrONO₂ does not disproportionate according to (15),⁸ but produces NO₂⁺[Br(ONO₂)₂]⁻ according to (16) and (17).

\[
\begin{align*}
3\text{BrONO}_2 & \rightarrow \text{Br(ONO}_2\}^3_3 + \text{Br}_2 & (15) \\
2\text{BrONO}_2 & \rightarrow \text{Br}_2 + \text{N}_2\text{O}_5 + \text{O}_2 & (16) \\
\text{BrONO}_2 + \text{N}_2\text{O}_5 & \rightarrow \text{NO}_2^+\{\text{Br(ONO}_2\}^2_2 & (17)
\end{align*}
\]

The formation of NO₂⁺[Br(ONO₂)₂]⁻ from Br₂ and ClONO₂ at room temperature and extended reaction times can similarly be explained by (9), followed by (16) and (17) resulting in (18)

\[
\text{Br}_2 + 6\text{ClONO}_2 \rightarrow 2\text{NO}_2^+\{\text{Br(ONO}_2\}^2_2 + 3\text{Cl} + \text{O}_2 & (18)
\]

as the overall reaction. By limiting the reaction time of (9) to about one hour, the thermal decomposition of BrONO₂ (16) and NO₂⁺[Br(ONO₂)₂]⁻ formation (17) can be minimized and (9) becomes a useful BrONO₂ synthesis.

From a historical point of view it is interesting to note that the original misidentification² of "Br(NO₃)₃" was not recognized...
inspite of all the experimental evidence by Schuster, Holthausen, and Stosz. None of them questioned the correctness of the claim for "Br(NO$_3$)$_3$" and, ironically, the last one of these investigators even concluded that NO$_2^+$(Br(ONO)$_2$)$_2^-$ actually was "Br(NO$_3$)$_3$".

Acknowledgement. The authors are indebted to Drs. C J. Schack and L. R. Grant and Mr. R. D. Wilson for their help, to Prof. D. Naumann for providing us with copies of the theses of L. Taglinger, E. Schuster, R. Holthausen, and A. Stosz, and to the Army Research Office and the Office of Naval Research for financial support.
REFERENCES

(16) Wilson, W. W.; Christe, K. O. to be published.
**DIAGRAM CAPTIONS**

**Figure 1.** Infrared spectra of BrONO$_2$. Trace A, N$_2$ matrix (MR=300) isolated sample at 5°K; trace B, infrared spectrum of the gas at 120 and 10mm pressure in a 5cm path length cell.

**Figure 2.** Vibrational spectra of solid BrONO$_2$. Trace A, infrared spectrum of the neat solid on a CsI window at 5°K; traces B and C, Raman spectra of the neat solid in a glass tube at -135°C, recorded at two different sensitivity settings.

**Figure 3.** Vibrational spectra of solid Cs$^+$[Br(ONO$_2$)$_2$]$^-$. Trace A, infrared spectrum of the solid as an AgCl disk at 20°C; the absorptions shown with a broken line are due to CsNO$_3$ formed by slow decomposition of the compound at this temperature; trace B, Raman spectrum of the solid at -134°C.

**Figure 4.** Vibrational spectra of solid NO$_2$$^+$[Br(ONO$_2$)$_2$]$^-$. Trace A, infrared spectrum of the solid at -186°C between CsI windows; trace B, Raman spectrum of the solid at -132°C.
### Table 1. Vibrational Spectra of Gaseous, Matrix-Isolated, and Solid BrONO$_2$

<table>
<thead>
<tr>
<th>Gas</th>
<th>Infrared</th>
<th>Raman</th>
<th>Assignment in point group C$_2v$</th>
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<td>Ne Matrix</td>
<td>Solid</td>
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<td>2982vw</td>
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<td>2565vw</td>
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<td></td>
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<tr>
<td>2273vw</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1719 vs</td>
<td>1702vs</td>
<td>1709vs</td>
<td>1616vs</td>
</tr>
<tr>
<td>1709 vs</td>
<td>1683m</td>
<td></td>
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<tr>
<td>1610vw</td>
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<td>1468vw</td>
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<td>1449vw</td>
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<td>1292 vs</td>
<td>1285vs</td>
<td>1285vs</td>
<td>1265vs</td>
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<tr>
<td>1288 vs</td>
<td>1279w</td>
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<td>1112vw</td>
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<td>958vw</td>
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<td>825sh</td>
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<td>810</td>
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<td>805vs</td>
<td>802vs</td>
<td>839vs</td>
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<td>750w</td>
<td>765vw</td>
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<td>735m</td>
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<td>574</td>
<td>563s</td>
<td>642s</td>
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<td>559</td>
<td>569</td>
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<td>637(sh)</td>
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</table>

(*) the splittings observed for these three bands are attributed to matrix effects. In the neon matrix, for example, only a single band was observed for $v_5$. 
Table 2. Fundamental Vibrations of Covalent Nitrites

<table>
<thead>
<tr>
<th></th>
<th>CH₃ONO₂</th>
<th>FONO₂</th>
<th>ClONO₂</th>
<th>BrONO₂</th>
<th>assignments in point group C₃ and approx description of mode</th>
</tr>
</thead>
<tbody>
<tr>
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<td>gas</td>
<td>solid</td>
<td>gas</td>
<td>gas</td>
<td>liquid gas matrix solid solid</td>
</tr>
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<td>1708 cm⁻¹</td>
<td>1646 vs</td>
<td>1625 w, dp</td>
<td>1669 vs</td>
<td>1634 w, dp</td>
<td>[39]1759 vs</td>
</tr>
<tr>
<td>1325 cm⁻¹</td>
<td>1256 vs</td>
<td>1203 w, p</td>
<td>1283 s, dp</td>
<td>1293 s, p</td>
<td>1292(59), p</td>
</tr>
<tr>
<td>1099 cm⁻¹</td>
<td>958 s</td>
<td>926 s, p</td>
<td>654 s</td>
<td>860 s, dp</td>
<td>800(17), p</td>
</tr>
<tr>
<td>1017 cm⁻¹</td>
<td>310 s</td>
<td>341 w, p</td>
<td>101 s</td>
<td>933 s, p</td>
<td>929(67), p</td>
</tr>
<tr>
<td>1057 cm⁻¹</td>
<td>707 s</td>
<td>612 w, dp</td>
<td>657 s</td>
<td>664 s, p</td>
<td>636(31), dp</td>
</tr>
<tr>
<td>949 cm⁻¹</td>
<td>722 s</td>
<td>677 s, p</td>
<td>578 s</td>
<td>578 s, p</td>
<td>457(100), p</td>
</tr>
<tr>
<td>866 cm⁻¹</td>
<td>340 s</td>
<td>351 w, p</td>
<td>304(33), p</td>
<td>270 vvw</td>
<td>267(47), p</td>
</tr>
<tr>
<td>773 cm⁻¹</td>
<td>773 s</td>
<td>(771) C</td>
<td>759 s</td>
<td>(761)</td>
<td>708(0.6)</td>
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<tr>
<td>737 cm⁻¹</td>
<td>737 s</td>
<td>485 w</td>
<td>152 vvw</td>
<td>165(4), dp</td>
<td>140(2), dp</td>
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</tbody>
</table>

(a) ref 34.
(b) Numbers in brackets ¹⁴N-¹⁵N isotopic shifts.
(c) Frequency in parentheses calculated from overtones.
(d) ref 33.
(e) ref 19-21; the previously reported polarization data for v₇ are questionable due to the extremely low Raman intensities of this mode.
(f) ref 33.
(g) Based on the observed ¹⁴N-¹⁵N (Ref. 19) and ³⁵Cl-³⁷Cl (Ref. 31) isotopic shifts, these two vibrations are strongly mixed.
| Cs\(^+\)Br(ONO\(_2\))\(_2\)\(^-\) | NO\(_2^+\)Br(ONO\(_2\))\(_2\)\(^-\) |
|-----------------|-----------------|-----------------|
| Ra | Ir | Ra | Ir |
| 1530(12) | 1520vs | 1569(1) | 2370m | vas NO\(_2^+\) |
| 1529(26) | 1493(1) | 1530vs | vas NO\(_2\), out-of-phase |
| 1395(35) | 1308(2) | 1567(21) | vs NO\(_2^+\) |
| 1283(14) | 1285vs | 1265vs | vas NO\(_2\), in-phase |
| 975(4) | 964(14) | 965sh | vas NO\(_2\), in-phase |
| 960sh | 955s | 964(14) | vs NO\(_2\), out-of-phase |
| 982(4) | 930vs | 930vs | δ sciss NO\(_2^+\) |
| 791(2) | 786s | 787(1) | 782s | δas NO\(_2\) in-plane |
| 732(63) | 735s | 747(100) | 750s | δas NO\(_2\) in-plane |
| 697(1) | 699s | 700(4) | 706s | δ NO\(_2^+\) |
| 460(0+),br | 480(0+),br | 566ms | 551ms | vas O-N |
| 400(0+),br | 400(2),br | | | vas BrO\(_2\) |
| 317(71) | 315(63) | | | vs O-N |
| 298(35) | | | | vs BrO\(_2\) |
| 230(10) | | | | |
| 157(47) | 162(32) | 175(33) | 162(32) | |
| 128sh | 126(21) | | | |
| 110(64) | 105(100) | | | |
| 87(100) | 93(5) | | | |
| 53sh | 80(57) | | | |
Table 4. Summary of the 21 Fundamental Vibrations
Expected for [Br(ONO$_2$)$_2$]$^-$ in Point Group $C_2$

NOBrON Skeletal Modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
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<tbody>
<tr>
<td>$\nu$ BrO$_2$</td>
<td>(B)</td>
</tr>
<tr>
<td>$\nu$ O-N in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\nu$ O-N out-of-phase</td>
<td>(B)</td>
</tr>
<tr>
<td>$\delta$ BrON in-plane, in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\delta$ BrON in-plane, out-of-phase</td>
<td>(B)</td>
</tr>
<tr>
<td>$\delta$ OBrO out-of-plane</td>
<td>(B)</td>
</tr>
<tr>
<td>$\tau$ Br-O in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\tau$ Br-O out-of-phase</td>
<td>(B)</td>
</tr>
</tbody>
</table>

NO$_2$ Modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
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</thead>
<tbody>
<tr>
<td>$\nu$ NO$_2$, in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\nu$ NO$_2$, out-of-phase</td>
<td>(B)</td>
</tr>
<tr>
<td>$\nu$ NO$_2$, in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\nu$ NO$_2$, out-of-phase</td>
<td>(B)</td>
</tr>
<tr>
<td>$\delta$ sciss NO$_2$, in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\delta$ sciss NO$_2$, out-of-phase</td>
<td>(B)</td>
</tr>
<tr>
<td>$\delta$ ONO$_2$ out-of-plane, in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\delta$ ONO$_2$ out-of-plane, out-of-phase</td>
<td>(B)</td>
</tr>
<tr>
<td>$\delta$ as ONO$_2$ in-plane, in-phase</td>
<td>(A)</td>
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<tr>
<td>$\delta$ as ONO$_2$ in-plane, out-of-phase</td>
<td>(B)</td>
</tr>
<tr>
<td>$\tau$ O-N, in-phase</td>
<td>(A)</td>
</tr>
<tr>
<td>$\tau$ O-N, out-of-phase</td>
<td>(B)</td>
</tr>
</tbody>
</table>
Figure 1.
Figure 3.

V-30
APPENDIX W

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303

Solid Propellant Based Pure Fluorine Gas Generators

Karl O. Christe* and Richard D. Wilson
Received . . .

Abstract

Solid propellant based gas generators are described which can rapidly produce pure fluorine at superatmospheric pressure. These generators are based on the in situ formation of a thermodynamically unstable transition metal fluoride from its stable anion by a simple displacement reaction with a stronger Lewis acid. The formed unstable transition metal fluoride undergoes spontaneous decomposition to a stable lower oxidation state fluoride and elemental fluorine. The given examples include K₂NiF₆, Cs₂CuF₆ or Cs₂MnF₆ as the transition metal salts and BiF₅, TiF₄ or mixtures thereof as the Lewis acids.

Introduction

The storage and handling of either cryogenic liquid or high-pressure gaseous fluorine frequently presents safety and logistics problems. These problems can be overcome by the use of solid propellant, fluorine gas generators. During the past fifteen years numerous fluorine gas generators were developed which are based on NF₄⁺ salts.¹ In these systems, a highly overoxidized grain, consisting mainly of an NF₄⁺ salt and several percent of a fuel, such as powdered aluminum, is burned. The heat, Q, generated in the burning process dissociates the bulk of the NF₄⁺ salt, as shown in (1).

\[
\text{NF}_4\text{MF}_6 + Q \rightarrow \text{NF}_3 + \text{F}_2 + \text{MF}_5
\] (1)

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If the heat $Q$ is high enough, some of the NF$_3$ is also dissociated as shown in (2).

$$2\text{NF}_3 \xrightarrow{+Q} \text{N}_2 + 3\text{F}_2$$  \hspace{1cm} (2)

Although impressive fluorine yields were achieved with these generators, they suffer from the disadvantage of producing NF$_3$ and some N$_2$ as by-products. Whereas in many cases these by-products can be tolerated, there are certain applications which require pure F$_2$. Consequently, the development of solid propellant systems capable of generating pure fluorine gas was highly desirable.

**Experimental**

**Materials.** BiF$_5$ and K$_2$NiF$_6$ (both from Ozark Mahoning Co.) were of high purity and used without further purification. TiF$_4$ (Allied Chemical) was treated in a Monel cylinder for 2 days at 250°C with F$_2$ at 70 atm to eliminate some impurities formed by hydrolysis during prolonged storage of the material. The syntheses of Cs$_2$CuF$_6$ and Cs$_2$MnF$_6$ have previously been described.

Prior to its use, CoF$_3$ (Ozark Mahoning Co.) was prefluorinated for 3 days with 8 atm of F$_2$ at 300°C.

**Apparatus and Procedure**

All solid propellant F$_2$ gas generation reactions were carried out in a well passivated (with 2 atm of F$_2$ at 200°C) stainless steel apparatus consisting of a 30 ml Hoke cylinder equipped with a cross fitting and a feed-through for a sheathed thermocouple which almost touched the bottom of the cylinder. A pressure transducer (Validyne DP-15) and a Hoke valve leading to a stainless steel vacuum line were connected to the two remaining sides of the cross. Weighed amounts of the transition metal fluoride salt and the Lewis acid were thoroughly mixed in the
dry nitrogen atmosphere of a glove box and loaded into the apparatus. The apparatus was then connected to the vacuum line, evacuated, and leak checked. The bottom of the cylinder was rapidly heated by the hot air stream from a heat gun, and the pressure evolution and inside temperature of the reactor were followed on a strip chart recorder. The evolved fluorine was measured by standard PVT methods and analyzed for its purity by reacting it with mercury. The material balance was further cross-checked by weighing the reactor before the reaction and after removal of the evolved fluorine.

The CoF₃ decomposition experiments were carried out in either a Monel reactor with an Al₂O₃ boat as a sample container or a sapphire tube (Tyco). Pressure and temperature were monitored as described above. The reactors were heated by a fluidized sand bath.

**Results and Discussion**

**Generation of F₂ by Reversible Reactions.** Since certain transition metal fluorides, such as CoF₃, are known to decompose at elevated temperatures to a lower fluoride and fluorine, the equilibrium

\[
2\text{CoF}_3 \rightleftharpoons 2\text{CoF}_2 + \text{F}_2
\]  

(3)

was examined for its potential as a fluorine gas generator. The CoF₃ system was found to exhibit the following drawbacks: (i) relatively high temperatures (in excess of 500°C) were required for the generation of even moderate fluorine pressures (about 268 torr at 514°C); (ii) long reaction times were required to reach equilibrium; (iii) on cooling of the system, the back reaction to CoF₃ consumed most of the fluorine formed; (iv) reaction of the fluorine with the hot reactor walls was difficult.
to suppress; and (v) the yields of fluorine were disappointingly low. These drawbacks appear to be generally true for equilibrium reactions of this type and therefore render these reversible systems unattractive for fluorine gas generator applications.

Generation of F\textsubscript{2} by Irreversible Reactions. Most of the above drawbacks of the reversible reactions can be avoided by the use of irreversible reactions. This principle has been applied by us in previous work.\textsuperscript{1} For example, the thermal decomposition of NF\textsubscript{4}BF\textsubscript{4} (4) in an NF\textsubscript{3}-F\textsubscript{2} gas generator is irreversible,

\begin{equation}
\text{NF}_4\text{BF}_4 \rightarrow \text{NF}_3 + \text{F}_2 + \text{BF}_3 \quad (4)
\end{equation}

i.e. NF\textsubscript{3}, F\textsubscript{2} and BF\textsubscript{3}, even at elevated temperature and pressure, do not reform NF\textsubscript{4}BF\textsubscript{4}.\textsuperscript{4} This concept of irreversibility was further exploited\textsuperscript{2,5} by replacing the BF\textsubscript{4}\textsuperscript{-} anion in the NF\textsubscript{4}\textsuperscript{+} salt by anions such as NiF\textsubscript{6}\textsuperscript{2-} or MnF\textsubscript{6}\textsuperscript{2-} which themselves are stable but are derived from thermodynamically unstable parent molecules. In the thermal decomposition of these (NF\textsubscript{4}\textsuperscript{+})\textsubscript{2}MF\textsubscript{6}\textsuperscript{2-} type salts, thermodynamically unstable MF\textsubscript{4} molecules are formed (5) which then decompose in a second irreversible step to a stable lower fluoride and F\textsubscript{2} (6).

\begin{equation}
(N\text{F}_4\textsuperscript{+})_2\text{MF}_6^{2-} \rightarrow 2\text{NF}_3 + 2\text{F}_2 + [\text{MF}_4] \quad (5)
\end{equation}

\begin{equation}
[\text{MF}_4] \rightarrow \text{MF}_{(4-x)} + \frac{x}{2}\text{F}_2 \quad (6)
\end{equation}

The concept of generating a thermodynamically unstable fluoride from its stable anion, followed by its irreversible decomposition with spontaneous fluorine evolution, has recently been utilized for the purely chemical generation of elemental fluorine.\textsuperscript{6} Using starting materials, i.e. K\textsubscript{2}MnF\textsubscript{6} and SbF\textsubscript{5}, which can be prepared from HF, elemental fluorine was generated by the simple displacement reaction (7), followed by the irreversible decomposition of
the unstable MnF$_4$ (8).

$$K_2\text{MnF}_6 + 2\text{SbF}_5 \rightarrow 2\text{KSbF}_6 + [\text{MnF}_4] \tag{7}$$

$$2[\text{MnF}_4] \rightarrow 2\text{MnF}_3 + \text{F}_2 \tag{8}$$

If in this scheme, the liquid Lewis acid SbF$_5$ is replaced by a solid Lewis acid of sufficient strength and suitable melting or sublimation point, a pure fluorine, solid propellant based gas generator is obtained, as demonstrated by equations (9) and (10),

$$A_2\text{MF}_6 + 2\text{BiF}_5 \rightarrow 2\text{ABiF}_6 + \text{MF}(4-x) + \frac{x}{2} \text{F}_2 \tag{9}$$

$$A_2\text{MF}_6 + \text{TiF}_4 \rightarrow A_2\text{TiF}_6 + \text{MF}(4-x) + \frac{x}{2} \text{F}_2 \tag{10}$$

where A can be an alkali metal and M can be Ni, Cu or Mn. The results of five typical experiments are summarized in Table 1. Although no systematic effort was made to maximize the F$_2$ yields, the results of Table 1 show that the F$_2$ yields are generally very good. From both yield and molecular weight considerations, K$_2\text{NiF}_6$ appears to be the most attractive starting material. Of the two Lewis acids tested, BiF$_5$ (mp 151.4°C, bp 230°C) appears to be superior to TiF$_4$ (subl. p 283.1°C), although on a weight basis, the considerably lighter bifunctional acid TiF$_4$ might be attractive, particularly as an additive to other Lewis acids as shown by run 5 of Table 1.

The starting materials used in this study can be readily premixed at ambient temperature and stored safely. When heated to about 60 to 70°C, fluorine evolution starts. The fluorine evolution was measured as a function of time and temperature and a typical curve for the K$_2$NiF$_6$-BiF$_5$ system is shown in Figure 1. The fluorine evolution is rapid, the gas can be generated at super-atmospheric pressure, and there is no evidence for any reversible

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reactions. Furthermore, the $F_2$ is evolved at such moderate temperatures that reaction of the fluorine with the container walls is of no concern. The purity of the generated fluorine was shown to be in excess of 99% by its quantitative reaction with mercury.

**Conclusion.** Application of the same principle which was recently used for the chemical synthesis of elemental fluorine, to solid Lewis acids results in useful, solid propellant based, pure fluorine gas generators. The validity of the concept has been demonstrated for $A_2MF_6$ salts ($A = K$ or $Cs$ and $M = Ni$, Cu or Mn) and $BiF_5$ or $TiF_4$ as the Lewis acids. Further improvements in the attainable fluorine yields are anticipated by variation of the starting materials and Lewis acids and an optimization of the stoichiometries and reaction conditions.

**Acknowledgement.** The authors are grateful to Drs. L. R. Grant, C. J. Schack, and W. W. Wilson for their help, and to the U.S. Army Research Office and the Office of Naval Research for partial financial support.
Table 1. Results from Solid Propellant, Pure Fluorine, Gas Generator Experiments

<table>
<thead>
<tr>
<th>Run #</th>
<th>starting materials (mmol)</th>
<th>F₂ generated (mmol)</th>
<th>peak pressure (torr)</th>
<th>F₂ yield (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K₂NiF₆ (1.47) BiF₅ (4.51)</td>
<td>1.1</td>
<td>990</td>
<td>75ᵃ</td>
</tr>
<tr>
<td>2</td>
<td>Cs₂CuF₆ (2.01) BiF₅ (3.95)</td>
<td>0.9</td>
<td>836</td>
<td>46ᵃ</td>
</tr>
<tr>
<td>3</td>
<td>Cs₂MnF₆ (4.86) BiF₅ (14.85)</td>
<td>1.0</td>
<td>929</td>
<td>41ᵇ</td>
</tr>
<tr>
<td>4</td>
<td>K₂NiF₆ (6.31) TiF₄ (6.25)</td>
<td>0.87</td>
<td>810</td>
<td>14ᵃ</td>
</tr>
<tr>
<td>5</td>
<td>K₂NiF₆ (1.94) TiF₄ (1.94) BiF₅ (1.94)</td>
<td>0.88</td>
<td>820</td>
<td>45ᵃ</td>
</tr>
</tbody>
</table>

(a) yields based on the limiting reagent and the following stoichiometry:

\[ \text{A}_2\text{MF}_6 + 2\text{BiF}_5 \rightarrow 2\text{ABiF}_6 + \text{MF}_2 + \text{F}_2 \]

(b) yield based on the limiting reagent and the following stoichiometry:

\[ \text{Cs}_2\text{MnF}_6 + 2\text{BiF}_5 \rightarrow 2\text{CsBiF}_6 + \text{MnF}_3 + 0.5\text{F}_2 \]
References


Diagram Caption

Figure 1. Pressure and temperature versus time curves for the $K_2NiF_6-BiF_5$ system.
APPENDIX X

ON THE EXISTENCE OF A CrF$_4$O·SbF$_5$ ADDUCT

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SUMMARY

CrF$_4$O is capable of forming a stable adduct with SbF$_5$. Based on its low-temperature Raman spectrum, this adduct has a predominantly covalent, fluorine bridged structure, similar to that of MoF$_4$O·SbF$_5$.

INTRODUCTION

In a recent paper the amphoteric nature of CrF$_4$O has been investigated. It was shown that CrF$_4$O is a very strong Lewis acid, but only a rather weak Lewis base and does not form a stable adduct with AsF$_5$ at temperatures as low as -78°C [1]. In view of the fact that the closely related MoF$_4$O, WF$_4$O and ReF$_4$O molecules can form stable 1:1 adducts with SbF$_5$ [2], it was interesting to study the interaction between CrF$_4$O and SbF$_5$.

EXPERIMENTAL

Materials. Literature methods were used for the synthesis of CrF$_4$O [1] and the drying of the HF solvent [3]. SbF$_5$ (Ozark Mahoning) was distilled prior to its use.
Apparatus. Volatile materials were manipulated in stainless-steel vacuum lines equipped with Teflon-FEP U-traps, 316 stainless steel bellows-seal or Teflon-PFA (Fluoroware, Inc.) valves, and a Heise Bourdon tube-type pressure gauge [4]. The vacuum lines and other hardware employed were passivated with ClF₃ and HF. Nonvolatile or low volatility materials were handled in the dry nitrogen atmosphere of a glove-box. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. The sample was contained in a sealed 1 mm o.d. quartz capillary, and the spectra were recorded at -140°C using a previously described device [5].

Reaction of CrF₄O with SbF₅- A passivated 0.5" o.d. Teflon-FEP U-tube, closed by two valves, was loaded in the dry-box with SbF₅ (0.89 mmol). The U-tube was connected to the vacuum line and HF (1.08g) and CrF₄O (0.31 mmol) were condensed in at -196°C. The contents of the tube were warmed to room temperature resulting in a light red solution. All material volatile at room temperature was pumped off and passed through a -78°C and a -196°C trap. Nothing was trapped at -78°C, but the -196°C trap contained the HF solvent. The residue was a dark red-brown liquid which upon heating to 55°C for 15 hr in a dynamic vacuum condensed on the colder parts of the tube. The volatile material trapped at -78°C was white and consisted of SbF₅. The condensate (143 mg) consisted of dark red droplets and crystals. The appearance of some liquid material can be accounted for by the fact that, based on the material balance, the condensate still contained 31 mg (0.14 mmol) of SbF₅ in excess over that required for the 1:1 adduct CrF₄O·SbF₅. The crystals were characterized by low-temperature Raman spectroscopy, but were not suitable for a crystal structure determination because of twinning or disorder.
RESULTS AND DISCUSSION

CrF₄O, when combined with an excess of SbF₅ in anhydrous HF solution, forms after removal of the solvent a dark brown-red liquid adduct. In a dynamic vacuum at 55°C, most of the excess SbF₅ can be pumped off. As the CrF₄O·SbF₅ mol ratio approaches 1:1, dark red crystals are obtained which are stable at 55°C. Attempts to determine their structure by single crystal x-ray diffraction techniques failed because of twinning or disorder. However, their low-temperature Raman spectrum (see Figure 1) indicates that their structure closely resembles those of the mainly covalent MoF₄O·SbF₅ and WF₄O·SbF₅ adducts [2], (see Table 1). The minor differences

![Figure 1. The Raman Spectrum of CrF₄O·SbF₅ at -140°C](image)
TABLE 1.
Raman Spectrum of CrF₄O·SbF₅ Compared to Those of MoF₄O·SbF₅,
WF₄O·SbF₅ and Their Parent Molecules

<table>
<thead>
<tr>
<th>observed frequencies (cm⁻¹) and relative intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>1061 vs</td>
</tr>
<tr>
<td>758 mw</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>710 s</td>
</tr>
<tr>
<td>670 s</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>556 vw</td>
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</tr>
<tr>
<td></td>
</tr>
<tr>
<td>334 w</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>312 w</td>
</tr>
<tr>
<td>279 w</td>
</tr>
<tr>
<td>242 vw</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>133 vw</td>
</tr>
</tbody>
</table>
in the observed spectra can be attributed to (i) the low temperature at which the \( \text{CrF}_4 \cdot \text{SbF}_5 \) spectrum was recorded which may cause some additional splittings, (ii) the mass and force constant differences between Cr, Mo, and W, and (iii) the increasing ionicity of the metal-F bonds from Cr to W which causes the relative Raman intensity of the metal oxygen vibrations to increase with respect to those of the metal-fluorine vibrations. Thus, the above results show that CrF\(_4\)O is also capable of forming a stable adduct with SbF\(_5\) and that the resulting adduct has a mainly covalent, fluorine bridged structure similar to that of MoF\(_4\)O-SbF\(_5\) [2].

ACKNOWLEDGEMENTS

The authors are grateful to Drs. R. Bougon, C. Schack and L. Grant and Mr. R. Wilson for their help, to Dr. R. Bau for the examination of the crystals by x-ray diffraction, and to the Office of Naval Research and the Army Research Office for financial support.

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APPENDIX Y

SELF-ASSOCIATION IN HOF AND HNF₂. WHICH ATOMS ARE THE BETTER PROTON ACCEPTORS, FLUORINE, OXYGEN OR NITROGEN?

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SUMMARY

The infrared and Raman spectra of solid HOF and HNF₂ are best interpreted in terms of hydrogen bridged aggregates involving the oxygen or nitrogen atoms, respectively, and not fluorine as proton acceptors. This result is contrary to intuition and the conclusions previously reached for solid HOF [1,2].

INTRODUCTION

The vibrational spectra of solid HOF have recently been studied [1,2]. A detailed analysis of the data was presented [2] in which it was tacitly assumed that the intermolecular hydrogen bridges involve the fluorine and not the oxygen atom. A more recent study of the vibrational spectra of solid HNF₂ in this laboratory provided experimental evidence for intermolecular hydrogen bridging through the nitrogen atoms [3]. Since both, NF₂ and OF, are paraelements of F [4] and

Y-1
therefore should exhibit similar properties [4], the basis for the previous conclusion concerning the (HOF)$_n$ structure was critically reviewed in the light of our data.

DISCUSSION

General Considerations

Very polar molecules of the type HX, where X is a highly electronegative group or atom, exhibit a pronounced tendency to associate in the solid phase through hydrogen bridges. If X is either a single atom, such as fluorine, or is a group, such as -OH or -NH$_2$, which contains only one highly electronegative atom, there is no ambiguity as to which atom is the proton acceptor. Thus, the self-association of water obviously involves hydrogen bridges between oxygen atoms. If however the X group, as for example in -OF or -NF$_2$, contains two or more different atoms of high electronegativity, ambiguity arises as to which of these atoms is the better proton acceptor. Although a wealth of information exists on hydrogen bonded systems [5], the more specific problem of competing proton acceptors has found only little attention.

A priori, it is difficult to predict for self-associated HOF whether oxygen or fluorine is the better proton acceptor. In systems, such as (HOF)$_n$, which involve moderately strong hydrogen bonds between uncharged polar molecules, numerous factors contribute to the strength of the hydrogen bond. Among these factors, five main contributions which are of similar magnitude, have been proposed: (a) electrostatic or coulomb energy, (b) exchange repulsion, (c) polarization energy, (d) charge transfer energy or covalent contribution, and (e) dispersion energy. Although these contributions are superpositioned
in a complicated manner, there is general agreement that considerable molecular orbital overlap occurs between the involved atoms leading to preferred geometries, such as the linearity of the hydrogen bridge [6]. In addition to the molecular orbital overlap, the charge distribution in the molecule is also very important because of its strong influence on the coulomb energy. In view of these complications and the difficulties encountered with carrying out reliable molecular orbital computations for relatively large systems, it is not surprising that either empirical or intuitive approaches have frequently been used to choose the most likely proton acceptor site.

With respect to the (HOF)$_n$ problem, there are two pieces of information available which suggest that oxygen might be the better proton acceptor. First, the charge distribution in HOF has been determined by ab initio calculations as roughly $+0.50\ -0.31\ -0.19$ O----F [7,8], indicating that a hydrogen bridge to oxygen should result in the largest coulomb energy. Second, an MO study of the proton affinities of oxygen and fluorine in HOF favored oxygen by 10 kcal/mol [9]. These data and our experimental results for (HNF$_2$)$_n$ which suggest nitrogen protonation [3], prompted the examination of whether the previously published vibrational spectra of (HOF)$_n$ [1,2] can be reinterpreted in terms of oxygen protonation.

Vibrational Spectra of (HOF)$_n$ and (HNF$_2$)$_n$

The previous studies [1,2] on solid HOF showed the following salient features. The O-F stretching vibration appeared as a sharp, unsplit band, which was virtually unshifted from its gas phase value. The O-H stretching band, on the other hand, was quite broad and appeared as a doublet, red shifted from the gas-phase by about 200 cm$^{-1}$. The HOF
bending mode was unsplit and blue shifted by 42 cm\(^{-1}\). In addition to these three internal vibrational modes, intermolecular modes were observed in the infrared spectrum at 628 and 448 cm\(^{-1}\) which exhibited large shifts on deuteration. In the Raman spectra six low-frequency bands were seen which showed no significant deuterium isotope shifts.

The vibrational spectra of solid HNF\(_2\) showed the following salient features. The two NF\(_2\) stretching and the NF\(_2\) scissoring modes were sharp, unsplit and essentially unshifted from the gas phase values. The N-H stretching mode was a sharp doublet, red shifted from the gas-phase by about 43 cm\(^{-1}\). The two HNF\(_2\) bending modes were split and blue shifted by about 30 cm\(^{-1}\). In addition to these six internal vibrational modes, five low-frequency Raman bands were observed which exhibited only small shifts on deuteration.

**Interpretation of the Spectra**

A comparison of the two sets of spectra reveals that HOF and HNF\(_2\) exhibit the same characteristic changes on going from the gas phase to the solid phase. The pronounced frequency shifts of the modes involving motions of the hydrogens establish the presence of hydrogen bridging for both molecules. For HNF\(_2\) the lack of frequency shifts, splittings or line broadening for the NF\(_2\) modes indicates that the hydrogen bonds must involve the nitrogen and not one of the two fluorines. If the hydrogen would be bridging to one of the two fluorine atoms, the latter would become non-equivalent causing significant shifts and splittings. The failure to observe evidence for two nonequivalent fluorine atoms might be explained in terms of a bifurcated structure, such as 

\[
\begin{array}{c}
\text{F} \\
\text{H-N} \\
\text{F}
\end{array}
\]

However, such a structure is
highly unlikely from molecular orbital arguments which favor linear hydrogen bridges [6]. Assuming smooth trends for the paraelements -OF and -NF₂ and accepting the spectroscopic evidence for N···H-N bridging in HNF₂, we can then conclude that, contrary to the previous interpretation [2], (HOF)ₙ should be oxygen and not fluorine bridged. The observed vibrational spectra with an undisturbed O-F mode lend strong support to this interpretation, as do the above given, theoretical arguments, i.e. proton affinity [9] and charge distribution [7,8].

In the absence of crystal structure data for solid HNF₂ and HOF, there is no point in assigning the low-frequency modes observed for the two compounds. Based on analogy to similar systems [6], structures containing zig-zag chains or large rings would seem most probable:

\[ \text{Conclusions} \]

The fact that the oxygen in HOF and the nitrogen in HNF₂ are better proton acceptors than fluorine seems reasonable for the following reasons: (a) in both molecules the hydrogen atoms are attached to O and N, respectively, thus releasing electron
density to them which is only partially transferred to the fluorine ligands. Thus, most of the negative charge resides on O and N (note the charge distribution in HOF [7,8]) rendering the -OH and -NH groups more basic than the fluorine ligands, and (b) the molecular orbitals of the free valence electrons on fluorine are more contracted than those on N or O due to its increased nuclear charge, and therefore provides less overlap energy with the hydrogen orbital. It thus appears that the negative charge density and the size of the free valence pair orbitals of an atom are more important than factors, such as its number of free valence electron pairs or its electronegativity, which might be chosen intuitively as a measure for its proton acceptor strength.

ACKNOWLEDGEMENT

The author wishes to thank Drs. C. J. Schack and W. W. Wilson for helpful discussions and the Army Research Office and the Office of Naval Research for financial support.

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APPENDIX AA


Chiste et al. [45] Oct. 18, 1983

[54] NF₃-F₂ GAS GENERATOR COMPOSITIONS [5] Improved compositions are described for solid propellant NF₃-F₂ gas generators using (NF₃)ₓTiF₄ and clinkering agents derived from LiF, KF, and NaF, either alone or in mixtures.

[75] Inventors: Karl O. Chiste, Calabasas; William W. Wilson, Canoga Park, both of Calif. [52] U.S. Cl. 149/109.4; 149/119

[73] Assignee: The United States of America as represented by the Secretary of the Army, Washington, D.C.


[22] Filed: Mar. 25, 1982

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Primary Examiner—Edward A. Miller
Attorney, Agent, or Firm—Robert P. Gibson; Anthony T. Lane; Jack W. Voigt

[57] ABSTRACT

Improved compositions are described for solid propellant NF₃-F₂ gas generators using (NF₃)ₓTiF₄ and clinkering agents derived from LiF, KF, and NaF, either alone or in mixtures.

6 Claims, No Drawings
1

NF₃-F₂ GAS GENERATOR COMPOSITIONS

DEDICATORY CLAUSE

The invention described herein was made in the course of or under a contract or subcontract thereunder with the Government and may be manufactured, used, and licensed by or for the Government for governmental purposes without the payment to us of any royalties thereon.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to improved compositions for solid propellant NF₃-F₂ gas generators, useful, for example, in chemical HF-DF lasers.

2. Description of Prior Art

NF₄⁺ salts are key ingredients for solid propellant NF₃-F₂ gas generators, as shown by D. Pilipovich in U.S. Pat. No. 3,963,542. These propellants consist of a highly oxidized grain using NF₄⁺ salts as the oxidizer. Burning these propellants with a small amount of fuel, such as aluminum powder, generates sufficient heat to thermally dissociate the bulk of the oxidizer. This is shown for NF₂BF₄ in the following equation:

NF₂BF₄ - NF₄⁺ + F₂ + BF₃

As can be seen from the equation the gaseous combustion products contain the volatile Lewis acid BF₃. This disadvantage of a volatile Lewis acid byproduct is shared by most known NF₄⁺ compositions. These volatile Lewis acids possess a relatively high-molecular weight and a low γ-value (γ = C_v/C_m), relative to the preferred diluent helium and frequently act as a desiccator for the chemical HF-DF laser. Consequently, these volatile Lewis acids must be removed from the generated gas prior to its use in an efficient chemical laser. Based on the state of the art, heretofore, this would be achieved by adding a clinker forming agent, such as KF, to the solid propellant formulation. The function of this additive served to convert the volatile Lewis acid, such as BF₃, to a non-volatile salt as shown by the following equation:

KF + BF₃ → KBF₄

Since the addition of KF significantly increases the weight of the formulation while the amount of evolved NF₃ and F₂ remains the same, the yield of NF₃ and F₂ per pound of formulation is decreased. For NF₂BF₄ based formulations, the replacement of KF by the lighter alkali metal fluorides NaF or LiF would theoretically improve the obtainable NF₃-F₂ yield, but was found to be impractical due to the insufficient thermal stability of NaBF₄ and LiBF₄, resulting in incomplete clinking of the BF₃.

The use of self-clinkering formulations based on (NF₄)₂TiF₆ has previously been proposed by Christe et al. (U.S. Pat. No. 4,152,406) as means of increasing the theoretically obtainable NF₃-F₂ yield relative to that of the state of the art NF₂BF₄-1.2KF formulation. However, test firings of (NF₄)₂TiF₆ based formulations showed that the relatively high volatility of TiF₄ (boiling point of 234°C) resulted in the deposition of TiF₄ throughout the whole gas generator system. To eliminate TiF₄ from the generated gas, KF had to be added to the (NF₄)₂TiF₆ based formulations. This necessary

KF addition lowered the theoretically obtainable NF₃-F₂ yield to a value of 39.5 weight % which is comparable to that of 38.5 weight % of the KF clinkered NF₂BF₄ system and thus eliminated most of the improvement offered by the use of (NF₄)₂TiF₆.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

The above described problem of obtaining an (NF₄)₂TiF₆ based formulation of significantly higher performance than that offered by the state of the art NF₂BF₄-1.2KF system is overcome by the present invention. We have found that, contrary to NF₂BF₄, (NF₄)₂TiF₆ forms thermally stable clinkers with the lighter alkali metal fluorides NaF and LiF and that less than stoichiometric amounts of these alkali metal fluorides are required for the formation of a stable clinker due to the ability of TiF₄ to form polytitanate anions. The improvements resulting from this concept are summarized in Table 1.

<table>
<thead>
<tr>
<th>System</th>
<th>F Yield (Weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NF₄)₂TiF₆-1.2KF</td>
<td>39.5</td>
</tr>
<tr>
<td>(NF₄)₂TiF₆-2.4KF</td>
<td>39.3</td>
</tr>
<tr>
<td>(NF₄)₂TiF₆-4KF</td>
<td>42.9</td>
</tr>
<tr>
<td>(NF₄)₂TiF₆-4LiF</td>
<td>47.0</td>
</tr>
<tr>
<td>(NF₄)₂TiF₆-4NaF</td>
<td>48.4</td>
</tr>
<tr>
<td>(NF₄)₂TiF₆-8LiF</td>
<td>50.9</td>
</tr>
</tbody>
</table>

Accordingly, it is an object of the present invention to provide high performing solid propellant NF₃-F₂ gas generator formulations based on (NF₄)₂TiF₆ and low molecular weight alkali metal fluorides. This and other objects and features of the present invention will be apparent from the following examples. It is understood, however, that these examples are merely illustrative of the invention and should not be considered as limiting the invention in any sense.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLE 1

A formulation containing 81.44 weight % (NF₄)₂TiF₆, 14.71 weight % LiF and 3.83 weight % Al was fired in a typical gas generator. Smooth burning was observed. Disassembly of the generator after completion of the test showed that the desired clinker had formed in the combustion chamber with essentially no TiF₄ deposited in the coolant pack section of the generator. The clinker was shown by chemical analysis and vibrational spectroscopy to consist mainly of M₂TiF₆ where M is Li.

EXAMPLE 2

A formulation containing 85.2 weight % (NF₄)₂TiF₆, 3.8 weight % LiF, 8.5 weight % KF and 2.5 weight % Al was fired in a typical gas generator. Again essentially complete clinkering of the TiF₄ was observed and the clinker was shown by elemental and spectroscopic analysis to consist mainly of M₂TiF₆(F₄) where M is Li and/or K.

EXAMPLE 3

A formulation containing 86.0 weight % (NF₄)₂TiF₆, 7.3 weight % NaF, 6.7 weight % KF and 2.5 weight % Al was fired in a typical gas generator. Again essentially
NF₃-F₂ GAS GENERATOR COMPOSITIONS

DEDICATORY CLAUSE

The invention described herein was made in the course of or under a contract or subcontract thereunder with the Government and may be manufactured, used, and licensed by or for the Government for governmental purposes without the payment to the owner of any royalties thereon.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to improved compositions for solid propellant NF₃-F₂ gas generators, useful, for example, in chemical HF-DF lasers.

2. Description of Prior Art

NF₄⁺ salts are the key ingredients for solid propellant NF₃-F₂ gas generators, as shown by D. Pilipovich in U.S. Pat. No. 3,963,542. These propellants consist of a highly over-oxidized grain using NF₄⁺ salts as the oxidizer. Burning these propellants with a small amount of fuel, such as aluminum powder, generates sufficient heat to thermally dissociate the bulk of the oxidizer. This is shown for NF₃BF₄ in the following equation:

NF₃BF₄ → NF₃ + F₂ + BF₃

As can be seen from the equation the gaseous combustion products contain the volatile Lewis acid BF₃. This disadvantage of a volatile Lewis acid byproduct is shared by most known NF₄⁺ compositions. These volatile Lewis acids possess a relatively high-molecular weight and a low γ value (γ = C_p/C_v), relative to the preferred diluent helium and frequently act as a deactivator for the chemical HF-DF laser. Consequently, these volatile Lewis acids must be removed from the generated gas prior to its use in an efficient chemical laser. Based on the state of the art, heretofore, this would be achieved by adding a clinker forming agent, such as KF, to the solid propellant formulation. The function of this additive served to convert the volatile Lewis acid, such as BF₃, to a non-volatile salt as shown by the following equation:

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The use of self-clinkerizing formulations based on (NF₄)₂TiF₆ has previously been proposed by Christe et al. (U.S. Pat. No. 4,152,406) as means of increasing the theoretically obtainable NF₃-F₂ yield to a value of 39.5 weight % which is comparable to that of 38.5 weight % of the KF clinker NF₃BF₄ system and thus eliminated most of the improvement offered by the use of (NF₄)₂TiF₆.

NF₃BF₄ → NF₃ + F₂ + BF₃

Accordingly, it is an object of the present invention to provide high performing solid propellant NF₃-F₂ gas generator formulations based on (NF₄)₂TiF₆ and low molecular weight alkali metal fluorides.

This and other objects and features of the present invention will be apparent from the following examples. It is understood, however, that these examples are merely illustrative of the invention and should not be considered as limiting the invention in any sense.

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A formulation containing 81.44 weight % (NF₄)₂TiF₆, 14.71 weight % LiF and 3.83 weight % Al was fired in a typical gas generator. Smooth burning was observed. Disassembly of the generator after completion of the test showed that the desired clinker had formed in the combustion chamber with essentially no TiF₄ deposited in the coolant pack section of the generator. The clinker was shown by chemical analysis and vibrational spectroscopy to consist mainly of M₂TiF₆ where M is Li.

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complete clinkering of the TiF$_4$ was observed and the clinker was shown by elemental and spectroscopic analyses to consist mainly of $M_2Ti_2F_{10}$ where $M$ is Na and/or K.

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

We claim:

1. Solid propellant NF$_3$-F$_2$ gas generator composition comprising (NF$_4$)$_2$TiF$_6$ with LiF as a clinker forming agent.

2. Solid propellant NF$_3$-F$_2$ gas generator compositions according to claim 1 wherein the mole ratio of LiF to (NF$_4$)$_2$TiF$_6$ is from 1 to 2.4.

3. Solid propellant NF$_3$-F$_2$ gas generator composition comprising (NF$_4$)$_2$TiF$_6$ with NaF as a clinker forming agent.

4. Solid propellant NF$_3$-F$_2$ gas generator compositions according to claim 3 wherein the mole ratio of NaF to (NF$_4$)$_2$TiF$_6$ is from 1 to 2.4.

5. Solid propellant NF$_3$-F$_2$ gas generator compositions comprising (NF$_4$)$_2$TiF$_6$ with mixtures of LiF with heavier alkali metal fluorides MF, where $M$ is selected from Na and K, as a clinker forming agent.

6. Solid propellant NF$_3$-F$_2$ gas generator compositions according to claim 5 wherein the mole ratio of LiF and MF to (NF$_4$)$_2$TiF$_6$ is from 1 to 2.4.
United States Patent

[4,421,727]

Wilson et al.


[54] NF$_2$, WF$_2$ AND NF$_3$, UF$_3$ AND METHODS OF PREPARATION

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Primary Examiner—Edward A. Miller
Attorney, Agent, or Firm—R. F. Beers, K. E. Walden; R. D. Johnson

ABSTRACT

Salts of the formula NH$_2$M$_2$— are produced by the following reaction

\[ \text{NF}_2 + \text{WF}_2 = \text{NF}_2 + \text{WF}_2 + \text{HF} \]

wherein M is uranium (U) or tungsten (W).

8 Claims, No Drawings
SUMMARY OF THE INVENTION

Accordingly an object of this invention is to provide methods which permit the synthesis of new NF₄⁺ salts containing anions derived from very weak Lewis acids.

Another object of this invention is to provide new energetic NF₄⁺ compositions which are useful in explosives and solid propellants.

A further object of this invention is to provide new compositions for solid propellant NF₄⁻F₂ gas generators for chemical HF-DF lasers which deliver a maximum of F₂ and F⁻ while not producing any gases which deactivate the chemical laser.

Yet another object of this invention is to provide NF₄ fluorotungstates which on burning with tungsten powder can produce hot WF₆ gas in high yield.

These and other objects of this invention are achieved by providing:

Salts of the formula NF₄⁺MₓFₙ⁻ by the following reaction

\[ \text{NF₄HF}_2 \cdot n\text{HF} \rightarrow M\text{F}_x \cdot (n+1)\text{HF} \]

wherein M is uranium (U) or tungsten (W). These salts are useful as ingredients in solid propellants and in high detonation pressure explosives.

A method of generating hot WF₆ gas by burning a mixture of NF₄WF₇ and tungsten metal.

DETAILS DESCRIPTION OF THE PREFERRED EMBODIMENT

Surprisingly, it has now been found that the salts NF₄UF₇ and NF₄WF₇ can be prepared from the very weak and volatile Lewis acids UF₆ and WF₆. The salts are prepared by the following methods.

First, readily available NF₄SbF₆ salt is converted by metathesis into NF₄HF₂ according to the reaction

\[ \text{NF₄SbF₆} + \text{HF} \rightarrow \text{NF₄HF₂} + \text{SbF₅} \]


The NF₄HF₂ produced by the above procedure will be complexed with HF and can be represented by the formula NF₄HF₂ₙHF. Because HF is a stronger Lewis acid than either UF₆ or WF₆, as much HF as possible has to be removed from the NF₄HF₂ without decomposing the NF₄HF₂. This can be achieved by judicious pumping at about 0 °C. This is continued until a solid having the composition NF₄HF₂ₙHF wherein n is from about 0.5 to about 10.0 is obtained.

NF₄UF₆ and NF₄WF₇ are produced by the following reactions:

\[ \text{NF₄HF₂} + \text{HF} \rightarrow \text{NF₄UF₆} + (n+1)\text{HF} \]
\[ \text{NF₄HF₂} + \text{HF} \rightarrow \text{NF₄WF₇} + (n+1)\text{HF} \]

These reactions may be run at ambient (25 °C) temperature. Repeated treatments of NF₄HF₂ₙHF with a large excess of UF₆ or WF₆, followed by the removal of the
volatile products at ambient temperatures, surprisingly shifted the equilibrium in reaction (2) and the equilibrium in reaction (3) quantitatively to the right. This is probably due to the thermal stability of NF₅UF₇ and of NF₅WF₇ being significantly higher than that of NF₅UF₆.

The addition of UF₆ or WF₆ and subsequent evacuation of volatile reaction products is continued until the conversion of NF₅UF₆+H₆F to NF₅UF₇ or NF₅WF₇ is substantially completed. This will be the point at which no significant amount of UF₆ or WF₆ is taken up and no significant amount of volatile reaction products (e.g., HF gas) is generated. Thus, by monitoring the gases evacuated from the reaction chamber, the progress of the reaction may be monitored.

Examples 1 and 2 further illustrate these procedures. NF₅UF₇ and NF₅WF₇ are useful as key ingredients for solid propellant NF₅–F₂ gas generators and for high density pressure explosives.

NF₅WF₇ is of particular interest as an ingredient for hot WF₆ gas generators. Hot WF₆ is an excellent electron capturing agent and therefore useful for reducing radar signatures. For example, formulations based on 6NF₄WF₇+5W=11WF₆+3N₂(4)
can theoretically produce up to 97 weight percent of WF₆ with flame temperatures in excess of 2000°C. A pyrotechnic mixture of finely powdered NF₅WF₇ and tungsten in approximately a 6:5 molar ratio may be used.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood that the invention is not limited to these examples but is susceptible to various modifications that will be recognized by one of ordinary skill in the art.

EXAMPLE 1
Preparation of NF₅WF₇

Dry CaF₂ (15.0 mmol) and NF₅SbF₆ (15.0 mmol) were loaded in a drybox into one half of a prepassivated Teflon double U-metathesis apparatus. Dry HF (15 ml) liquid was added on the vacuum line and the mixture was stirred with a Teflon coated magnetic stirring bar for 15 minutes at 25°C. After cooling the apparatus to -78°C, it was inverted and the NF₅HF₇ solution was filtered into the other half of the apparatus. Tungsten hexafluoride (22.5 mmol) was condensed at -196°C onto the NF₅WF₇. The mixture was warmed to ambient temperature, and two immiscible liquid phases were observed. After vigorous stirring for 30 minutes at 25°C, the lower WF₆ layer dissolved in the upper HF phase. Most of the volatile products were pumped off at ambient temperature until the onset of NF₅HF₇ decomposition became noticeable (NF₅ evolution). An additional 8.0 mmol of WF₆ was added at -196°C to the residue. When the mixture was warmed to ambient temperature, white solid product appeared in the form of a slurry. All material volatile at -31°C was pumped off for 1 hour and consisted of HF and some NF₃. An additional 14.3 mmol of WF₆ was added to the residue and the resulting mixture was kept at 25°C for 14 hours. All material volatile at -13°C was pumped off for 2 hours and consisted of HF and WF₆. The residue was kept at 22°C for 2.5 days and pumping was resumed at -13°C for 2.5 hours and at 22°C for 4 hours. The volatiles collected at -210°C consisted of some HF and small amounts of NF₃ and WF₆. The white
(3) allowing the WF₆ to react with the NF₄HF₂nHF;
(4) pumping off the volatile products of the reaction;
and
(5) repeating steps (2) through (4) until the
NF₄HF₂nHF is substantially converted to
NF₄WF₄.

7. The process of claim 6 wherein n is from about 0.5
to about 10.0.
8. The process of claim 6 wherein steps (2), (3), and
(4) are performed at ambient temperature.

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BB-4
A process for introducing a fluorine atom into an aromatic hydrocarbon by effecting a substitution reaction between an aromatic hydrocarbon and an NF₄⁺ cation containing salt.
METHOD FOR INTRODUCING FLUORINE INTO AN AROMATIC RING

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

FIELD OF THE INVENTION

This invention relates to fluorocarbons and to a novel method for their synthesis. In a more particular aspect, this invention concerns itself with a novel method for introducing a fluorine atom into an aromatic ring.

Aromatic fluorocarbons are a well known class of chemical compounds that find wide utility for a variety of industrial applications and in the fabrication of various commercial products. They are useful as solvents, electrical fluids, heat transfer fluids and as components in the manufacture of resins, waxes, greases and oils. However, presently known methods for synthesizing such compounds by introducing a fluorine atom into an aromatic ring are severely limited.

The classic Balz-Schiemann reaction, for example, and methods such as the decarboxylation of fluoroformates are useful for the introduction of a single fluorine atom, but are generally less useful for multiple fluorine atom substitution. The use of elemental fluorine or electrochemical fluorination methods result mainly in addition and not in substitution. Halogen fluorides, such as CIF3, BrF3, or IF3 produce, in addition to fluorine substituted compounds, large amounts of the corresponding halogen substituted compounds and also some addition products. The yield of substitution products obtainable with halogen fluorides can be improved by the use of strong Lewis acids. However, the extreme reactivity of the resulting compounds, such as CIF2+BF4- or CIF2+SF6-, makes control of their reactions with organic compounds extremely difficult and unsafe. The utilization of transition metal fluorides, such as CoF3 or CeF7 results in addition and saturation, requiring subsequent rearomatization. Therefore, this method is limited to highly or perhalogenated aromatics. Pyrolysis of aliphatic fluorocarbons, such as CFBF3, can also produce fluorocarbons. However, this method is limited again to the synthesis of perfluorinated aromatics. Halogen exchange reactions, such as F- versus F-, using HF, alkali metal or metal fluorides are useful, but are restricted to systems strongly activated towards nucleophilic attack by fluoride ion. Hypofluorites, such as CF3OF, are useful for electrophilic and photolytic fluorinations. The electrophilic fluorinations are limited again to activated aromatics, whereas the free radical photolytic fluorinations often lack selectivity resulting in —OCF3 substituted by-products and side chain fluorination. The xenon fluorides and especially XeF2 are promising reagents for electrophilic aromatic substitution reactions, but full extent of their usefulness is still unknown. The limited availability of xenon, its high price, and the treacherous explosiveness of their hydrolysis product, XeO3, are drawbacks curtailting its extensive use.

The above listing of some of the known methods of preparing aromatic fluorine compounds, although not extensive, clearly illustrates the problems prevalent in this area of technology and points out the need for a reliable, readily available and economically feasible reagent for accomplishing the electrophilic fluorine substitution of aromatic ring compounds. Therefore, a research effort was undertaken in an attempt to satisfy the need for a generally usable reagent.

In theory, the ideal reagent for electrophilic substitution would be a salt containing the F+ cation. Unfortunately, such salts do not exist. As an alternative, salts containing complex fluoro cations of the type XFPn+ could be used. However, to be a strong electrophile, such a cation should possess high electronegativity. Since highly electronegative fluorine compounds generally are very strong oxidizers, most of these cations react too violently with organic compounds to be of practical interest. As a consequence, the research effort referred to above proved to be unsuccessful. Additional research, however, proved to be fruitful and culminated in the discovery that the NF4+ cation constitutes an exception to the general rule that such cations react too violently with organic compounds. As a result of the present invention, therefore, it was found that aromatic ring compounds, such as benzene, toluene, and nitrobenzene, interact rapidly with NF4BF4 in anhydrous HF to give, almost exclusively, fluorine substituted aromatic derivatives.

SUMMARY OF THE INVENTION

The present invention concerns itself with a method for introducing fluorine into an aromatic ring structure by using NF4BF4 as a reaction reagent. The introduction is accomplished by an electrophilic substitution reaction in which up to five hydrogen atoms in the aromatic ring can be substituted by fluorine atoms. The reaction can be carried out by either adding the aromatic compound, such as benzene in vapor form, to a cooled solution of NF4BF4 in HF or, alternatively, by adding slowly a solution of NF4BF4 to a solution of benzene in HF.

Accordingly, the primary object of this invention is to provide a novel method for introducing a fluorine atom into an aromatic ring structure.

Another object of this invention is to provide a method for substituting fluorine atoms for the hydrogen atoms in an aromatic ring structure.

Still another object of this invention is to provide for the synthesis of fluorine containing aromatic ring compounds by effecting a reaction between a non-fluorine containing aromatic compound and salts containing an NF4+ cation.

A further object of this invention is to provide a method for introducing a fluorine atom into an aromatic ring by using NF4BF4 as a reaction reagent in the electrophilic substitution of a fluorine atom for a hydrogen atom in an aromatic ring structure.

The above and still further objects and advantages of the present invention will become more readily apparent upon consideration of the following detailed description thereof.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Pursuant to above-defined objects, the present invention concerns itself with a novel method for introducing fluorine atoms into an aromatic ring compound through the electrophilic substitution of a hydrogen atom by a fluorine atom. The known methods for introducing fluorine into an aromatic ring are quite limited and are often not generally applicable. A widely applicable reagent for carrying out electrophilic substitution reac-
Hydrogen fluoride was used as a solvent because of the high solubility of NF4+ salts in it and also because the diluent and heat dissipation properties of a solvated system were found to be beneficial in the anticipated vigorous fluorination. As stated herebefore, the reaction was carried out by either adding benzene vapor to a cooled solution of NF3BF4 in HF or by adding slowly a solution of NF3BF4 to a solution of benzene in HF. On contact gas evolution was noted. When rapid addition occurred some apparent charring occurred. The stepwise substitution of H by F was observed according to the following general equation:

$$\text{aNF3BF}_4 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_4\text{F}_a\text{BF}_4 + \text{HF}$$

The evolved gas was removed under vacuum and trapped at -196° C. It was found to be NF3 and the amount corresponded to that expected on the basis of one mole of NF3 per mole of NF3BF4. Hexafluorobenzene was not observed although all other substitution products from mono- to penta-fluorobenzene were obtained. Almost no saturated or partially saturated fluorocarbons were produced which makes this process of formation was noted. Hexafluorobenzene was not observed. It was found that NF3BF4 could be of practical interest. The NP+. cation, however, was not in the products generally are very strong oxidizers, most Ut-p5am product distribution. However, at these higher NF4+ ion contents, the mixture corresponded to essentially pure material. The simplest aromatic hydrocarbon studied in the previously referred to research effort was benzene. With NF4+ substrate mole ratios of about three, up to five hydrogens were substituted by F as shown in the following generalized equation:

$$\text{aNF3BF}_4 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_4\text{F}_a\text{BF}_4 + \text{HF} \text{ (where } a = 1-5)$$

However, at these higher NF4+ to substrate ratios, the reaction was more difficult to control and more "char" formation was noted. Hexafluorobenzene was not observed as a product. If significant amounts had been formed, it would have easily been detected by mass spectrometry since its base peak is the parent ion. Only trace quantities of partially saturated species, C2F4H2 and C3F5H were observed, indicating that very little addition occurred.

In order to determine the nature of the reaction, benzene, C6H5CH3 and C6H5NO2 were also studied. These were chosen for their well known ability to differentiate between an electrophilic and a free radical reaction path, based on the observed ortho-meta-para product distribution. In the toluene reaction, the ratio of NF4+ to toluene was in the range 2:4:1. Thus, an excess of fluorine was available (assuring one F/NF4+ is available for substitution) and multishielding was expected. The result of a very rapid reaction is illustrated by the following equation:

$$\text{C}_6\text{H}_5\text{CH}_3 + \text{aNF3BF}_4 \rightarrow \text{C}_6\text{H}_4\text{F}_a\text{BF}_4 + \text{HF} \text{ (where } a = 1-5)$$

In carrying out the reactions of this invention, the nonvolatile materials were manipulated in a well-passivated (with CIF3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seals valves and a Hense Bourdon tube-type pressure gauge.

The mass spectra of the products strongly indicate that no side chain fluorination had occurred, in agreement with other spectroscopic evidence. Typical isomer distributions for the ring substitution were: f-F(15), m-F(8), p-F(15), 2,4-di-F(30), and mixed di- and tri-F(25). Obviously, o- and p-products predominate for this electrophilic substitution reaction.
For the nitrobenzene reaction, a 3:10 mole ratio of NF4BF4 substrate was used. Even under these conditions, this reaction was less vigorous than those of benzene or toluene, as exemplified by a slightly slower NF3 evolution and the lack of "darkening" of the solution until the mixture was finally warmed to about 0°C. Fluorine substitution occurred to give C6F5H3,2NO2 (where n = 1-4) compounds. Minor amounts of FNO2(H)F were formed and traces of C6F5H3,2NO species were observed, but overwhelmingly the NO2 group was not displaced. The observed products were mainly monosubstituted with the following isomer distribution: o-F(16), m-F(62), and p-F(7). The observation of predominantly ortho and para substitution and the lack of side chain fluorination in toluene, and the meta substitution in nitrobenzene establishes these NF4BF4 reactions as electrophilic substitutions.

For nitrobenzene, the yield of fluorinated products was not determined due to separation problems caused by the low volatility of the products and the large excess of nitrobenzene used. However, in view of the high relative amount of mono-F species, and the limited amounts of charring, it is estimated that the yield of substituted products was high. For the much more reactive C6H4 and C6F5H3,2CH3 yields varied widely. Volatile, fluorinated species were observed equivalent to 30-60% of the aromatic starting compounds.

The following examples are presented in order to point out the invention with greater detail. The examples, however, are illustrative only and are not to be construed as limiting the invention in any way.

EXAMPLE I

C6H5NO2. To a stirred solution of C6H5NO2 (10 mmol) in 5 ml HF at -78°C was added dropwise over 30 min. a solution of NF4BF4 (2.88 mmol) in 5 ml HF. Reaction of the NF4BF4 was shown by an increase in pressure due to NF3 evolution. When all the NF4BF4 had been added, the reaction was gradually warmed to 0°C and left overnight. During the warming, the reaction solution changed from pale yellow to dark brown. Keeping the reaction amon on at -45°C, the NF3, HF, and other volatile materials were pumped away through a -78°C and -196°C traps. After the majority of the HF was removed, the reactor was maintained at 0°C. The material passing the -78°C fraction consisted of a few droplets of a liquid with a low vapor pressure at ambient temperature. Mass spectroscopy of the vapor from the drops showed minor amounts of aromatic fluorocarbons which did not contain NO2 substituents. These were of the empirical formula C6F5Hn,1NO (n = 1-6). The principal ion peaks observed were m/e (assign): 85(NO2;HF), 49 (NOF), and 30(NO). Examination of the liquid non-volatiles at 0°C, which remained in the reactor, by NMR spectroscopy, showed that five fluorinated compounds were present and all were found to be substituted nitrobenzenes by comparison of the observed chemical shifts with reported values. By measurement of the area of the resonances the amount of each compound was calculated: o-C6F5H4NO2 (14%), m-C6F5H4NO2 (62%), p-C6F5H4NO2 (6%), 2,6-or 3,5-difluoronitrobenzene (14%), and 2,4-difluoronitrobenzene. The large excess of C6H5NO2 employed, and still present, masked the 1H spectra of these products and thus the 19F spectra were relied on for identification.

EXAMPLE II

C6H5CH3, Toluene and NF4BF4 (1.4 molar ratio) were reacted by condensing the hydrocarbon onto the stirred HF solution of the salt at -78°C. Alternatively, toluene in HF at -78°C was treated dropwise with a solution of NF4BF4 (1.2 molar ratio). In either case, instantaneous reaction occurred and the solution became black. After warming to 0°C for a few hours, these reactions were worked up in the usual manner. Much tar like residue remained in the reactor in each case. Infrared spectroscopic examination of the volatile products, trapped at -78°C, showed strong bands near 1500 cm⁻¹ confirming the presence of aromatic species. Mass spectra of these fractions showed at both experiments that only aromatic substitution products were present, these were of the empirical formula C6F5Hn,1NO (n = 1-6). The low intensity of the m/e 69 and 51 peaks indicated the absence of CF3 or CF2H groups in these compounds with the observed intensities of these peaks being due to C6F5H2 and C6F5H4 ions. From the reaction using a higher ratio of NF4BF4 to toluene, a significant amount of C6F5H2 NO was found indicating some displacement of CH3 from the ring. The NMR spectra of these products confirmed that various fluorotoluenes were present approximately in the amounts given (%): o-C6F5H4NOCH3 (15%), p-C6F5H4NOCH3 (16%), m-C6F5H4NOCH3 (8%), 2,4-difluorotoluene (30%), other di- and tri-fluorotoluenes (25%), and 2,4,5,6-tetrafluorotoluene (7%).

EXAMPLE III

C6H5. Benzene and NF4BF4 were reacted using the same two techniques described for toluene. It was not possible to prevent charring and blackening of the benzene. Nevertheless, isolation of the volatile products condensable at -78°C and examination of their mass spectra showed that substantial substitution of H by F had occurred, resulting in the formation of C6F5Hn,1NO (n = 1-5). C6F6 was not observed and only minor amounts of the addition products C6F5H2 and C6F5H3 were observed.

In consideration of the aforementioned detailed description, it is obvious that the present invention provides a novel method for substituting fluorine atoms for hydrogen atoms in an aromatic ring structure without affecting saturated or oxidized substituents. The results of this invention clearly demonstrate the utilization of NF4+ ion containing salts as powerful reagents for the introduction of fluorine atoms into aromatic rings by electrophilic substitution. Up to five hydrogens can be substituted in aromatic systems by a rapid substitution reaction, found to be highly efficient and relatively safe, before a much slower addition reaction takes over.

This slower fluorine addition reaction was also studied and found to produce the corresponding cyclo-hexasdiene and benzene. The addition reactions are novel and offer a controlled, high yield path to dienes which have previously only been obtained as parts of complex mixtures.

To obtain more data on the reactions of aromatics with NF4+ salts, an examination of aromatic systems, which were already highly fluorinated, was carried out. It was found that these starting materials are more inert toward the strongly fluorinating NF4BF4 thus allowing better control of the reaction. Experiments were carried out using tetra-, penta-, and hexa-fluoronitrobenzene as starting materials. All reacted gradually at, or near, ambient
temperature. All solutions and products were colorless throughout the reactions. Liberated NF₃ and excess, unreacted NF₃BF₄ were recoverable. The products were identified spectroscopically and most of them have been reported in the literature, making their identification unequivocal. The overall results are shown by the equations.

\[
\begin{align*}
\text{NF}_3BF_4 \xrightarrow{\text{HF}, 153^\circ C} & \quad \text{F} \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

(94%)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

(72%)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

(24%)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

(53%)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

(35%)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

(47%)

For these three highly fluorinated benzenes, the addition of the first two fluorines occurs in para position to each other (1,4 addition) and ortho to any hydrogen, if present. The addition of a second pair of fluorines cannot proceed by a 1,4 mechanism without changing the ring into a bicyclic form, which is generally encountered only under photolytic conditions. Thus, the second pair of fluorines undergoes a 1,2 addition to yield a cyclohexane.

For pentafluorobenzene, some substitution was also observed. It is not clear whether this is the result of a true substitution or of an addition-elimination reaction. In the case of p-C₆F₅H₂, the second F₂ addition produces the 1H,4H-octafluorocyclohexene which has two possible geometric isomers. Trace quantities of the saturated product, C₆F₁₅H₂, were also detected by mass spectroscopy.

In order to provide greater detail in connection with the addition reactions referred to above, Examples IV, V and VI are presented. In these addition reactions, almost no hydrogen substitutions occurred. The addition of the first pair of fluorine atoms always gave 1,4-cyclohexadiene in which the CF₂ group was ortho to hydrogen on the ring. The addition of the second pair of fluorine atoms results in the formation of cyclohexenes. These reactions occurred in high yield. All products were characterized spectroscopically and by comparison to literature data.

**EXAMPLE IV**

C₆F₆H. A sample of NF₃BF₄ (4.07 mmol) contained in a Teflon (FEP) ampoule was dissolved in anhydrous HF (4 ml) and cooled to −78 °C. Hexafluorobenzene (1.25 mmol) was condensed into the ampoule, which was then warmed gradually while stirring magnetically. After being kept overnight at 0°–10 °C, the clear, colorless solution was cooled to −78 °C and the volatile material quickly removed by condensation into a −196 °C trap. The −196 °C trap contained NF₃ (1.24 mmol) contaminated with traces of HF as shown by infrared spectroscopy. The reaction was allowed to continue for another day at room temperature. While maintaining the reaction ampoule at 0 °C, the volatile products and HF were separated by fractional condensation in a series of U-traps cooled at −45°, −78°, and −196°. The −196 °C fraction, NF₃ and HF, was discarded and the −45 °C trap was empty. The −78 °C trap contained a white solid, which melted to a colorless liquid above 0 °C. Examination of this material by infrared and gas chromatography showed it to be 1,4-perfluorocyclohexadiene (1.18 mmol, 94.3% yield, based on C₆F₆) with a slight amount (2–3%) of unreacted C₆F₆. Intense ions in the mass spectrum were observed at m/e (assign.) 224(C₆F₆), 205(C₆F₆), 186(C₆F₄), 174(C₆F₃), 155(C₆F₃, base), 136(C₆F₄), 124(C₆F₃), 117(C₆F₃), 105(C₆F₃), 93(C₆F₃), 86(C₆F₃), 74(C₆F₂), 69(CF₃), 55(CF₂), and 31(CF). The 19F NMR spectrum showed two equal area multiplets at 113.1 and 158.3 ppm in agreement with the literature for 1,4-C₆F₆.

A white solid remained in the reaction ampoule and was shown by Raman spectroscopy to be NF₃BF₄ (1.48 mmol).

**EXAMPLE V**

C₆F₆H. As before, a mixture of NF₃BF₄ (4.29 mmol) and C₆F₃H (1.35 mmol) in HF was stirred and warmed during several hours from −78 °C toward ambient temperature where it was kept for 12 hours. Evolved NF₃ (3.3 mmol) was monitored. After several more hours of stirring at room temperature, the products were separated by vacuum fractionation through U-traps cooled at −45°, −78°, and −196° C. All material passed the −45 °C trap except for a small amount of NF₃BF₄ remaining in the reactor. The −196 °C fraction was discarded. The −78 °C trap contained 1.24 mmol of a colorless liquid whose infrared spectrum indicated that it was composed of more than one cyclohexene [1170(\text{~m~}), 1740(\text{~s~}), and 1720 cm⁻¹(\text{~v~})], as well as unreacted C₆F₃H. Gas chromatography showed three components which were analyzed individually by mass spectroscopy. In order of elution they were: (1) 1,4-C₆F₄, 26.1%, (2) 1H-heptafluorocyclohexa-1,4-diene, 66.3%, and (3) C₆F₃H, 7.6% with the composition based on GC peak areas. The mass spectra of the fractions agreed very well with published data for the assigned compounds. In addition, the 19F NMR spectra confirmed the formulated structures. For 1H-heptafluorocyclohexa-1,4-diene, a literature report of the NMR spectrum could not be found, but by comparison with related compounds it was apparent that the observed resonances and area ratios were reasonable for that structure. Chemical shifts of H or F, ppm or δ (rel. F peak area): 1-H, 5.93; 2-F, 12.77(1); 3-F, 115.2(2); 4-F, 160.1; 5-F, 155(1), 6-F, 167.7(2). The conversion of C₆F₆H was 92%. The composition of the product was 28% 1,4-C₆F₄ and 72% 1,4-C₆F₃H, with a total of 91% of the organic material being recovered.

CC-5
EXAMPLE VI

-p-CF₄H₂. A mixture of NF₄BF₄(4.18 mmol) and p-CF₄H₂(1.43 mmol) in 4 ml HF at -78° C. was stirred
and warmed to 0° C. over 3 hours, followed by over-
night stirring at 0°-20° C. Fractional condensation at 
-78° C. and -196° C. was used to separate HF and
NF₃ from the products which were retained in the -78° C.
trap. No unreacted NF₄BF₄ remained in the reactor.
The original -78° C. fraction was further separated by
refractionation through -45° and -78° C. traps. The
former contained 0.21 mmol of a colorless liquid whose
infrared spectrum showed a strong band at 1710 cm⁻¹
typical for the double bond of a -CF=CH— group.
Analyses using GC/MS procedures showed this mate-
rial to be 1H,4H-hexafluorocyclohexa-1,4-diene. Prom-
inent mass spectral peaks were found at m/e (assign.):
188(C₆F₁₂H₂), 169(C₅F₁₁H₂), 150(C₅F₁₀H₂),
138(C₅F₁₀H₂), 137(C₅F₁₀H₂, base),
99(C₄F₁₀H₂), 94(C₄F₉H₂), 93(C₄F₉),
81(C₄F₈H₂), 80(C₄F₈H₂), 75(C₃F₇H₂),
69(CF₆), 68(C₅F₄H₂), 61(C₅H),
57(C₅F₃H₂), 56(C₅F₃H₂), 51(CF₃H),
50(CF₂),
44(C₃F₂H), and 31(CF). The ²¹F NMR spectrum for
this compound agreed with published data. Similar analyses
of the -78° C. fraction showed it to be a mixture of 
unreacted p-CF₄H₂, the above described 1H,4H cy-
clohexa-1,4-diene, and a compound of empirical for-
mula C₆F₁₂H₂. An infrared spectrum of the latter com-
 pound showed bands at cm⁻¹ (intens.): 3070(w),
2960(w), 1710(m), 1380(s), 1355(w), 1260(m),
1150(s), 1065(m), 1030(m), 743(mw),
637(w), 580(w), and
582(w). The bands near 3000 cm⁻¹ are assignable to
the carbon-hydrogen stretches of -C—C—M and C—H
groups while the 1710 cm⁻¹ peak is typical of a
-CF=CH— stretching vibration. Strong ion peaks in
the mass spectrum were at m/e (assign.):
226(C₆F₁₂H₂), 207(C₅F₁₁H₂), 186(C₅F₁₀H₂), 157(C₅F₁₀H₂)
144(C₅F₁₀H₂), 137(C₅F₁₀H₂), 119(C₅F₁₀H₂),
117(C₅F₁₀H₂),
113(C₅F₁₀H₂), 94(C₅F₁₀H₂), 93(C₅F₁₀),
75(C₅F₁₀H₂),
69(CF₆), 57(C₅F₃H₂), 51(CF₃H), and 50(CF₂). The
NMR spectra of the -78° C. fraction confirmed the
presence of p-CF₄H₂, 1H,4H-hexafluorocyclohexa-1,4-
diene, and 1H,4H-octafluorocyclohexene; chemical
shift of H or F, ppm or δ (rel. area) of
1H,4H—C₆F₁₂H₂: 1-H,5.1(1); 2-F, 121.5(1), 3-F, 11
5.1(2).
The conversion of starting material was 78%.
The com. 

New energetic salts NF₄XeF₇ and (NF₄)₂XeF₄ are prepared by reacting NF₄HF₂ with XeF₆ and exposing NF₂XeF₇ to blue 4880Å laser light.

1 Claim, No Drawings
PERFLUOROMAMMONIUM SALT OF NF3APFLUOROXENON ANION

BACKGROUND OF THE INVENTION

This invention relates to energetic inorganic salts and more particularly to salts containing the NF4+ cation.

NF4+ salts are key ingredients for solid propellant NF3—F2 gas generators, as shown by D. Filipovich in U.S. Pat. No. 3,946,542, and for high detonation pressure explosives, as shown by K. O. Christe in U.S. Pat. No. 4,207,124. The synthesis of NF4+ salts is unusually difficult because the parent molecule NF3 does not exist and the salts must be prepared from NF3 which amounts formally to a transfer of F+ to NF3 according to:

\[
\text{NF}_3 + \text{F}^+ \rightarrow \text{NF}_4^+
\]

Since fluorine is the most electronegative of all elements, F+ cannot be generated by chemical means. This difficult synthetic problem was overcome by K. O. Christe, et al. as shown in U.S. Pat. No. 3,503,719. By the use of an activation energy source and a strong volatile Lewis acid, such as AsF5, the conversion of NF3 and F2 to an NF4+ salt became possible:

\[
\text{NF}_3 + \text{F}_2 + \text{AsF}_5 \rightarrow \text{NF}_4^+ \text{AsF}_5^-
\]

However, only few Lewis acids are known which possess sufficient strength and acidity to be effective in this reaction. Therefore, other indirect methods were needed which allowed conversion of the readily accessible NF4+ salts into other new salts. Two such methods are presently known. The first one involves the displacement of a weaker Lewis acid by a stronger Lewis acid, as shown by K. O. Christe and C. J. Schack in U.S. Pat. No. 4,172,881 for the system:

\[
\text{NF}_4^+\text{BF}_4^- + \text{PF}_5^- \rightarrow \text{NF}_4^+\text{PF}_6^- + \text{BF}_3
\]

but is again limited to strong Lewis acids. The second method is based on metathesis, i.e., taking advantage of the different solubilities of NF4+ salts in solvents such as HF or BrF3. For example, NF4+SBF6 can be converted to NF4+BF4 according to:

\[
\text{NF}_4^+\text{SBF}_6 + \text{BF}_3 \rightarrow \text{NF}_4^+\text{BF}_4^- + \text{BrF}_3
\]

This method has successfully been applied by K. O. Christe, et al. as shown in U.S. Pat. Nos. 4,108,965; 4,152,406; and 4,172,884 to the synthesis of several new salts. However, this method is limited to salts which have the necessary solubilities and are stable in the required solvent. The limitations of the above two methods are quite obvious and preclude the synthesis of NF4+ salts of anions which are either insoluble in these solvents or are derived from Lewis acids weaker than the solvent itself and therefore are displaced from their salts by the solvent.

SUMMARY OF THE INVENTION

The limitations of the previously known reactions for the synthesis of NF4+ salts are overcome by the present invention. It was found that NF4+ salts derived from very weak and volatile Lewis acids, such as XeF6, which are weaker than the solvent itself, can be prepared by the following method. A solid having the composition NF4+HF2 nHF, where n ranges from about 0.5 to 10, was obtained as described by K. O. Christe et al. in Inorganic Chemistry, 19, 1494 (1980). Repeated treatments of NF4+HF2 nHF, with a large excess of XeF6 followed by removal of the volatile products at ambient temperature, permitted to shift the following equilibrium:

\[
\text{NF}_4^+\text{HF}_2 + \text{XeF}_6 \leftrightarrow \text{NF}_4\text{XeF}_6 + (n + 1) \text{HF}
\]

quantitatively to the right.

For applications, such as solid propellant NF3—F2 gas generators for chemical HF-DF lasers, the NF4+—F2 yields must be as high as possible and no volatile products which would deactivate the excited species can be tolerated. The highest usable fluorine content theoretically available from the thermal decomposition of a previously known sufficiently stable NF4+ salt were 64.6 and 59.9 weight percent for (NF4)2NF3 and (NF4)2MF6, respectively. Although these fluorine yields are high, the solid NF3 and MF3 byproducts render their formulations difficult to burn and require higher fuel levels thus reducing the practically obtainable fluorine yields. Consequently, NF4+ salts decomposing exclusively to NF3, F2 and inert diluents, such as noble gases or nitrogen, were highly desirable. The new NF4+XeF salt, described in this invention, fulfills all of these requirements and provides a theoretical usable fluorine yield of 62.9 weight percent. On decomposition, it produces only NF3, F2 and inert Xe. A further increase in the usable fluorine yield to 71.7 weight percent, the highest presently known value, was achieved by converting NF4+XeF into (NF4)2XeF6 according to:

\[
\text{NF}_4^+\text{XeF}_2 \rightarrow (\text{NF}_4)_2\text{XeF}_6
\]

This conversion was achieved by irradiating the yellow NF4+XeF salt with blue 4880 Å light from an Ar ion laser. The yellow NF4+XeF strongly absorbs the blue light and is photolytically decomposed to (NF4)2XeF6 and gaseous XeF6. Since (NF4)2XeF6 is white it does not absorb the blue light and is not further decomposed. Therefore, this invention also provides a new, selective, laser-induced, photolitic method for converting NF4+XeF into (NF4)2XeF6. The latter compound not only provides the highest NF3—F2 yield of any presently known compound, but also gives the highest theoretical detonation pressures in explosive formulations (about 50 kbar higher than corresponding formulation containing (NF4)2NF3).

Accordingly, an invention of this invention is to provide a new compound.

Another object of this invention is to provide new energetic NF4+ compositions which are useful in explosives, and solid propellants.

A further object of this invention is to provide NF4+ compositions for solid propellant NF3—F2 gas generators for chemical HF-DF lasers which deliver a maximum of NF3 and F2 while not producing any gases which deactivate the chemical laser.

Still another object of the invention is to provide a novel method of preparing new energetic compounds.
fractional condensation through traps kept at -64°C. Evidence for undisolved

(17.87 mmol) was stirred with liquid for 45 minutes. The mixture was recycled into the reactor. The HF collected in the -64°C trap was discarded, but the XeF6 collected in the -196°C trap was inverted and the white filter cake (5.78 g, weight caled for 15.54 mmol of CsSbF6) was taken to the drybox. It was confirmed by vibrational and 19F NMR spectroscopy, pyrolysis and analysis of the pyrolysis residue for NF4XeF7, Cs+ and SbF6-. Based on these results, the reaction product had the following composition (weight %): NF4XeF (98.01), NF4SbF6 (0.88) and CsSbF6 (0.11). The NF4XeF7 salt was identified by its Raman spectrum which exhibited the bands characteristic for NF4XeF7 (1159, 1149, (v3), 841, (v1), 603 (v4), 440 (v2) and 25°C, which exhibited the bands characteristic for NF4XeF7 (558, 495, 464, 233, 212 cm⁻¹).

EXAMPLE 2

A sample of NF4XeF7 was exposed at room temperature for prolonged time to blue 4880 Å laser light. Photolytic decomposition of NF4XeF7 occurred resulting in (NF4)2XeF4 formation (time of exposure depends upon the intensity and power of the light source).

\[2NF4XeF7 \rightarrow h\nu_{4880\AA} \rightarrow (NF4)2XeF4 + XeF6\]

The (NF4)2XeF4 salt was identified by its Raman spectrum which exhibited the bands characteristic for NF4XeF7 (1158, 1145, 841, 602, 440 cm⁻¹) and XeF6 (500, 433, 416, 380, 374 cm⁻¹).

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described. What is claimed is:

1. NF4XeF7.

4.428,913
APPENDIX EE


[34] PERFLUOROAMMONIUM SALTS
FLUOROXENON ANIONS

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[73] Assignee: The United States of America as
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Navy, Washington, D.C.

[21] Appl. No.: 540,951
[22] Filed: Oct. 11, 1983

Related U.S. Application Data
4,428,913.

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[52] U.S. Cl. ........................................... 423/262; 149/119;
423/351; 423/462; 204/157.1 R; 204/157.1 H
[58] Field of Search ...................... 423/262; 204/157.1 R,
204/157.1 H

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Primary Examiner—Herbert T. Carter
Attorney, Agent, or Firm—Robert F. Beers; Thomas M.
Phillips

[37] ABSTRACT
New energetic salts NF₃XeF₇ and (NF₄)₂XeF₂ are pre-
pared by reacting NH₄HF₂ with XeF₆ and exposing
NF₃XeF₇ to blue 4880 Å laser light.

2 Claims, No Drawings
PERFLUOROMETHAMMONIUM SALTS FLUOROXENON ANIONS

This application is a division of application Ser. No. 391,786, filed June 24, 1983 now U.S. Pat. No. 4,428,913.

BACKGROUND OF THE INVENTION

This invention relates to energetic inorganic salts and more particularly to salts containing the NF₄⁺ cation. NF₄⁺ salts are key ingredients for solid propellants NF₃-F₂ gas generators, as shown by D. Filipovich in U.S. Pat. No. 3,963,542, and for high detonation pressure explosives, as shown by K. O. Christe in U.S. Pat. No. 4,207,124. The synthesis of NF₄⁺ salts is unusually difficult because the parent molecule NF₃ does not exist and the salts must be prepared from NF₃ which amounts formally to a transfer of F⁻ to NF₄⁺ according to:

NF₃ + F⁻ → NF₄⁺

Since fluorine is the most electronegative of all elements, F⁻ cannot be generated by chemical means. This difficult synthetic problem was overcome by K. O. Christe, et al as shown in U.S. Pat. No. 3,503,719. By the use of an activation energy source and a strong volatile Lewis acid, such as AsF₅, the conversion of NF₃ and F₂ to an NF₄⁺ salt become possible:

NF₃ + F₂ + AsF₅ → NF₄⁺ + AsF₆⁻

However, only few Lewis acids are known which possess sufficient strength and acidity to be effective in this reaction. Therefore, other indirect methods were needed which allowed conversion of the readily accessible NF₄⁺ salts into other new salts. Two such methods are presently known. The first one involves the displacement of a weaker Lewis acid by a stronger Lewis acid, as shown by K. O. Christe and C. J. Schack in U.S. Pat. No. 4,172,881 for the system:

NF₄BF₄ + PF₃ → NF₄F₃ + BF₃

but is again limited to strong Lewis acids. The second method is based on metathesis, i.e., taking advantage of the different solubilities of NF₄⁺ salts in solvents such as HF or BrF₅. For example, NF₄SbF₆ can be converted to NF₄BF₄ according to:

NF₄SbF₆ + CBF₃ → NF₄BF₄ + SbF₅

This method has successfully been applied by K. O. Christe, et al as shown in U.S. Pat. Nos. 4,108,965; 4,152,406; and 4,172,884 to the synthesis of several new salts. However, this method is limited to salts which have the necessary solubilities and are stable in the required solvent. The limitations of the above two methods are quite obvious and preempted the synthesis of NF₄⁺ salts of anions which are either insoluble in these solvents or are derived from Lewis acids weaker than the solvent itself and therefore are displaced from their salts by the solvent.

SUMMARY OF THE INVENTION

The limitations of the previously known reactions for the synthesis of NF₄⁺ salts are overcome by the present invention. It was found that NF₄⁺ salts derived from very weak and volatile Lewis acids, such as XeF₆, which are weaker than the solvent itself, can be prepared by the following method. A solid having the composition NF₄xF₆nHF, where n ranges from about 0.5 to 10, was obtained as described by K. O. Christe et al in Inorganic Chemistry, 19, 1494 (1980). Repeated treatments of NF₄xF₆nHF with a large excess of XeF₆ followed by removal of the volatile products at ambient temperature, permitted to shift the following equilibrium:

NF₄xF₆nHF + XeF₆ → NF₄xF₆(n+1)HF quantitatively to the right.

For applications, such as solid propellant NF₃-F₂ gas generators for chemical HF-DF lasers, the NF₄xF₂ yields must be as high as possible and no volatile products which would deactivate the excited species can be tolerated. The highest usable fluorine contents theoretically available from the thermal decomposition of a previously known sufficiently stable NF₄⁺ salt were 64.6 and 59.9 weight percent for (NF₄)₂NiF₆ and (NF₄)₂MnF₆, respectively. Although these fluorine yields are high, the solid NiF₂ and MnF₂ byproducts render their formulations difficult to burn and require higher fuel levels thus reducing the practically obtainable fluorine yields. Consequently, NF₄⁺ salts decomposing exclusively to NF₃, F₂ and inert diluents, such as noble gases or nitrogen, were highly desirable. The new NF₄XeF₆⁺ salt, described in this invention, fulfills all of these requirements and provides a theoretical usable fluorine yield of 62.9 weight percent. On decomposition, it produces only NF₃, F₂ and inert Xe. A further increase in the usable fluorine yield to 71.7 weight percent, the highest presently known value, was achieved by converting NF₄XeF₆ into (NF₄)₂XeF₈ according to:

2NF₄XeF₆ → (NF₄)₂XeF₈ + NF₄F₆

This conversion was achieved by irradiating the yellow NF₄XeF₆ salt with blue 4880 Å light from an Ar ion laser. The yellow NF₄XeF₆ strongly absorbs the blue light and is photolytically decomposed to (NF₄)₂XeF₈ and gaseous XeF₆. Since (NF₄)₂XeF₈ is white it does not absorb the blue light and is not further decomposed. Therefore, this invention also provides a new, selective, laser-induced, photolytic method for converting NF₄XeF₆ into (NF₄)₂XeF₈. The latter compound not only provides the highest NF₃-F₂ yield of any presently known compound, but also gives the highest theoretical detonation pressures in explosive formulations (about 50 kbar higher than corresponding formulation containing (NF₄)₁NiF₆). Accordingly, an object of this invention is to provide a new compound.

Another object of this invention is to provide new energetic NF₄⁺ compositions which are useful in explosives, and solid propellants. A further object of this invention is to provide NF₄⁺ compositions for solid propellant NF₃-F₂ gas generators for chemical HF-DF lasers which deliver a maximum of NF₃ and F₂ while not producing any gases which deactivate the chemical laser.
Still another object of this invention is to provide a novel method of preparing new energetic compounds. These and other objects of this invention will become apparent from the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

Example 1

Dry CsF (15.54 mmol) and NF₄SbF₆ (15.65 mmol) were loaded in the drybox into one half of a prepassivated Teflon U metathesis apparatus. Dry HF (9 ml liquid) was added on the vacuum line and the mixture was stirred with a Teflon-coated magnetic stirring bar for 45 minutes at 25°C. After cooling the apparatus to -78°C, it was inverted and the NF₄HF₂ solution was filtered into the other half of the apparatus. Most of the HF solvent was pumped off during warm up from -78°C to room temperature. This mixture was stirred at 25°C for several hours, followed by removal of the volatiles (weight calcd for 15.54 mmol of CsSbF₆=5.72 g) consisted of CsSbF₆. The composition of these solids was confirmed by vibrational and ¹⁹F NMR spectroscopy, pyrolysis and analysis of the pyrolysis residue for NF₄⁺, Cs⁺ and SbF₆⁻. Based on these results, the reaction product had the following composition (weight %): NF₄XeF₇ (98.01), NF₄SbF₆ (0.88) and CsSbF₆ (1.11).

The NF₄XeF₇ salt was identified by its Raman spectrum which exhibited the bands characteristic for NF₄⁺, XeFs⁺ and XeF₆⁻ (558, 495, 464, 233, 212 cm⁻¹).

EXAMPLE 2

A sample of NF₄XeF₇ was exposed at room temperature for prolonged time to blue 4880 Å laser light. Photolytic decomposition of NF₄XeF₇ occurred resulting in (NF₄)₂XeF₆ formation (time of exposure depends upon the intensity and power of the light source).

\[ \text{NF}_4\text{XeF}_7 \xrightarrow{\text{hv}(4880\text{Å})} (\text{NF}_4)_2\text{XeF}_6 + \text{XeF}_6 \]

The (NF₄)₂XeF₆ salt was identified by its Raman spectrum which exhibited the bands characteristic for NF₄⁺ (1158, 1145, 841, 603 cm⁻¹) and XeF₆⁻ (500, 433, 416, 380, 374 cm⁻¹).

Obviously, many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

We claim:
1. (NF₄)₂XeF₆.
2. A method of preparing (NF₄)₂XeF₆ comprising the following steps in order:
   (1) exposing NF₄XeF₇ to a blue 4880 Å laser light source until photolytic decomposition of NF₄XeF₇ occurs resulting in (NF₄)₂XeF₆ formation, and
   (2) isolating the product (NF₄)₂XeF₆.

* * * * *
APPENDIX FF

United States Patent

[19] Schack et al.

[45] Date of Patent: Jul. 31, 1984

[54] SYNTHESIS OF PENTAFUOROTELLURIUM HYPOFLUORITE

[75] Inventors: Carl J. Schack, Chatsworth; William W. Wilson, Simi Valley; Karl O. Christiansen, Calabasas, all of Calif.

[73] Assignee: The United States of America as represented by the Secretary of the Air Force, Washington, D.C.

[21] Appl. No.: 478,581
[22] Filed: Mar. 24, 1983

[51] Int. Cl. 11/24 O'Brien 243/472, 473, 506, 579, 467, 423/472, 641, 642, 643, 512

[56] References Cited

U.S. PATENT DOCUMENTS

OTHER PUBLICATIONS
U.S. Pat. Appl. "Pentafluorotellurium Oxides", Schack et al. identified as AF Inv. No. 15,528, filed of even date herewith.

Primary Examiner—Earl C. Thomas
Assistant Examiner—Jeffrey E. Russel
Attorney, Agent or Firm—Donald J. Singer, William J. O'Brien

[57] ABSTRACT

The present invention concerns itself with a method for synthesizing hypofluorite compounds by utilizing fluorine fluorosulfate as a fluorinating agent and to a novel pentafluorotellurium hypofluorite compound prepared thereby.

4 Claims, No Drawings
SYNTHESIS OF PENTAFLUOROTELLURIUM HYPOFLUORITE

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

BACKGROUND OF THE INVENTION

This invention relates to hypofluorite compounds and to a novel method for their preparation. In a more particular aspect, this invention concerns itself with a novel route for effecting the synthesis of pentafluorotellurium hypofluorite (TeF$_5$OF) using fluorine fluorosulfate as a reaction component.

Hypofluorite compounds are well known and find utility for a wide variety of industrial applications. They are particularly useful as fluorinating agents for introducing fluorine atoms into another compound, and as intermediates in synthetic reactions. At the present time, however, there is no simple and convenient process for producing these compounds. Until recently, the number of elements known to form hypofluorites was limited to the nonmetal main group elements hydrogen, carbon, nitrogen, oxygen, sulfur, selenium, fluorine and chlorine.

Generally, the method heretofore for the synthesis of these hypofluorites involved the fluorination of the corresponding hydroxyl compounds or their metal salts with elemental fluorine. An attempt was made by Seppelt et al., Inorg. Chem. 1973, 12, 2727, to apply this method to the synthesis of the hitherto unknown TeF$_5$OF. The attempt was unsuccessful. An analogous method, however, proved fruitful in synthesizing TeF$_5$OCl which led to the conclusion that TeF$_5$OF is unstable or actually non existent. Additionally, further research efforts, as reported by Christe et al., Inorg. Chem., 1981, 20, 2104, proved to be successful in synthesizing a stable iodine hypofluorite with the observation that hypofluorites are generally more stable than the other hypohalides and the suggestion that TeF$_5$OF should exist and should also be stable.

In line with the observations noted above, additional experimental efforts proved successful and a novel method for synthesizing TeF$_5$OF was discovered. It was found that the hitherto unknown TeF$_5$OF compound could be produced in stable form and in relatively high yield by a process which provided for the use of fluorine fluorosulfate as the fluorinating agent.

SUMMARY OF THE INVENTION

The present invention concerns itself with a novel method for synthesizing hypofluorites by utilizing fluorine fluorosulfate as a fluorinating agent. The method of this invention proved successful in synthesizing in high yield a novel compound, pentafluorotellurium hypofluorite. Synthesis is achieved by effecting a reaction between CsTeF$_5$O and FOSO$_2$F at relatively low temperatures.

Accordingly, the primary object of this invention is to provide a novel method for synthesizing hypofluorite compounds.

Another object of this invention is to provide a method for synthesizing hypofluorite compounds that utilizes fluorine fluorosulfate as a fluorinating agent.

Still another object of this invention is to provide a method for synthesizing the novel compound, pentafluorotellurium hypofluorite.

The above and still other objects and advantages of the present invention will become more readily apparent upon consideration of the following detailed description thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Pursuant to the above-defined objects, the present invention is brought into effect by accomplishing a reaction between CsTeF$_5$O and FOSO$_2$F within a closed environment at temperatures ranging from about -10° to -45° C. The known methods for preparing hypofluorites are quite limited and attempts at using these previously known methods for producing the hitherto unknown TeF$_5$OF have not been successful. For example, the fluorination of either CsTeF$_5$O or KTeF$_5$O with F$_2$ at -45° to -10° C resulted only in the formation of TeF$_6$. However, with the present invention, it was found that a fairly high yield synthesis of TeF$_5$OF could be accomplished by reacting CsTeF$_5$O with FOSO$_2$F at temperatures ranging from about -10° to -45° C. This reaction is illustrated by the following general equation:

$$\text{CsTeF}_5\text{O} + \text{FOSO}_2\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{TeF}_5\text{OF}$$

This novel reaction represents a new synthetic route to the preparation of hypofluorite compounds. Based on the general usefulness of the analogous ClOSO$_2$F reagent for the syntheses of hypochlorites, it would appear that FOSO$_2$F will become a similarly useful, versatile and general reagent for the synthesis of hypofluorite compounds.

When the synthesis of TeF$_5$OF from CsTeF$_5$O and FOSO$_2$F was carried out above -45° C, the amount of TeF$_6$ by-product sharply increased. For example, at -10° C and with a reaction time of 3 days, the TeF$_6$ to TeF$_5$OF ratio in the product increased to 1:1. The use of an excess of CsTeF$_5$O in this reaction was found advantageous for the product purification since it eliminated the need for separating TeF$_6$ from FOSO$_2$F.

The reaction scheme for synthesizing the novel TeF$_5$OF compound of this invention is further illustrated with greater specificity by Example I which follows.

EXAMPLE I

A 30 ml stainless steel Hoke cylinder was loaded with CsTeF$_5$O (3.42 mmol) in the glove box. After evacuation and cooling of the cylinder to -196° C, FOSO$_2$F (2.79 mmol) was added from the vacuum line. The closed cylinder was slowly warmed to -78° C in a liquid nitrogen-CO$_2$ slush bath and finally kept at -45° C for 48 h. Upon recoiling to -196° C about 4-5 cm$^3$ of noncondensable gas was observed to be present. This was pumped away and the condensable products were separated by fractional condensation in a series of traps cooled at -78°, -126°, and -196° C. The -78° C fraction was TeF$_5$OF (0.19 mmol) while the -196° C fraction was TeF$_6$ (0.49 mmol).

A white solid was retained at -126° C, which changed to a colorless glass and melted, over a range of a few degrees, near -80° C to a clear, colorless liquid.

This material was identified as TeF$_5$OF (1.91 mmol, 68% yield) based on its vapor density molecular weight found, 256.2, calcd. 257.6 g/mol. Further identification
was based on its spectroscopic properties and on the preparation of derivatives. The observed weight loss of the solid (0.375 g) agreed with that calculated (0.389 g) for the conversion of 2.79 mmol CsTeF5O to CsSO4F. Vapor pressure-temperature data of TeF5OF were measured: T°C. Pmm: -79.3, 16; -64.2, 45; -57.6, 63; -46.9, 108; -32.5, 210; -23.0, 312.

The TeF5OF compound of Example I is colorless as a gas and liquid. Its vapor pressure-temperature relationship for the range -79° to -23° C. is given by the equation

\[ \log P_{\text{mm}} = -6.9022 - 1101.2/T \]

The extrapolated boiling point is 0.6° C. The derived heat of vaporization is \( H_{\text{vap}} = 5039 \text{ mol}^{-1} \) and the Trouton constant is 18.4 indicating little or no association in the liquid phase. Vapor density measurements showed that in the gas phase the compound is also not associated. A sharp melting point for TeF5OF was not observed because the samples showed a tendency to 20 form a glass near -30° C. The compound appears to be completely stable at ambient temperature and has been stored in stainless steel cylinders for more than four months without any sign of decomposition.

The mass spectrum of TeF5OF is listed in Table I together with the spectra of TeF5OCI and TeF5OH which were measured for comparison. All of the listed fragments showed the characteristic tellurium isotope pattern and therefore the individual m/e listings were omitted for simplicity. The spectra of all three compounds show weak parent ions and TeF5+ as the base peak.

**Table I**

<table>
<thead>
<tr>
<th>TeF5OF</th>
<th>TeF5OCI</th>
<th>TeF5OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>mass</td>
<td>mass</td>
</tr>
<tr>
<td>ion</td>
<td>ion</td>
<td>ion</td>
</tr>
<tr>
<td>TeF5OF</td>
<td>TeF5OCI</td>
<td>TeF5OH</td>
</tr>
<tr>
<td>v</td>
<td>w</td>
<td>v</td>
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<tr>
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</tr>
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<tr>
<td>v</td>
<td>w</td>
<td>v</td>
</tr>
</tbody>
</table>

The infrared spectra of gaseous and of neon matrix isolated TeF5OF and the Raman spectra of liquid and solid TeF5OF were recorded and the observed frequencies are summarized in Table II.

**Table II-continued**

<table>
<thead>
<tr>
<th>VIBRATIONAL SPECTRA OF TeF5OF</th>
</tr>
</thead>
<tbody>
<tr>
<td>obd freq, cm(^{-1}), and ref intens(^{a})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raman</th>
<th>IR (g)</th>
<th>IR (gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid</td>
<td>(solid)</td>
<td>(liquid)</td>
</tr>
<tr>
<td>gas</td>
<td>Ne</td>
<td>-55° C</td>
</tr>
<tr>
<td>1800 v</td>
<td>2v</td>
<td>2v</td>
</tr>
<tr>
<td>1449 v</td>
<td>2v</td>
<td>2v</td>
</tr>
<tr>
<td>1400 w</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>1006 v</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>1006 v</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>60</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>734 w</td>
<td>721(13)</td>
<td>738(5)</td>
</tr>
<tr>
<td>718 v</td>
<td>v1</td>
<td>v1</td>
</tr>
</tbody>
</table>

**Table III**

<table>
<thead>
<tr>
<th>Vibrational Spectra of TeF5OF and their Assignment Compared to Those of TeF5Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>obd freq, cm(^{-1}), and ref intens(^{a})</td>
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</table>

**Table IV**

<table>
<thead>
<tr>
<th>VIBRATIONAL SPECTRA OF TeF5OF</th>
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<tbody>
<tr>
<td>obd freq, cm(^{-1}), and ref intens(^{a})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raman</th>
<th>IR (g)</th>
<th>IR (gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid</td>
<td>(solid)</td>
<td>(liquid)</td>
</tr>
<tr>
<td>gas</td>
<td>Ne</td>
<td>-55° C</td>
</tr>
<tr>
<td>1800 v</td>
<td>2v</td>
<td>2v</td>
</tr>
<tr>
<td>1449 v</td>
<td>2v</td>
<td>2v</td>
</tr>
<tr>
<td>1400 w</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>1006 v</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>1006 v</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>60</td>
<td>2v</td>
<td>v</td>
</tr>
<tr>
<td>734 w</td>
<td>721(13)</td>
<td>738(5)</td>
</tr>
<tr>
<td>718 v</td>
<td>v1</td>
<td>v1</td>
</tr>
</tbody>
</table>

**FF-3**
TABLE III—continued

<table>
<thead>
<tr>
<th>$\nu$ (cm$^{-1}$)</th>
<th>IR (gas)</th>
<th>Raman (liquid)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A^0$ $\nu_{13}$</td>
<td>FXY</td>
<td>908 v</td>
</tr>
<tr>
<td>$A^-$ $\nu_{13}$</td>
<td>FXY</td>
<td>240 m</td>
</tr>
<tr>
<td>$A^-$ $\nu_{14}$</td>
<td>FXY</td>
<td>166 m</td>
</tr>
</tbody>
</table>

*Uncorrected Raman measurements (peak regions)*

In preparing and testing the novel hypofluorite compound of this invention, the volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP (a polyfluoropropylene propylene copolymer) traps and 316 stainless steel bellows-seal valves and a Heise Bourdon tube-type pressure gauge. Telluric acid was prepared by the literature method of Mathers et al., Inorg. Syn., 1950, 3, 145, and also purchased from Cerac, Inc., and from Pfaltz and Bauer. Fluorosulfuric acid obtained from Allied was used both as received (light brown color) and after distillation to obtain the clear colorless material. The fluoride fluorosulfate was synthesized as described by Dudley et al., J. Am. Chem. Soc. 1956, 78, 290. The reaction of TeF$_5$OH with either ClO$_2$F or CIF was used to prepare TeF$_5$OCI. Cesium and potassium chloride were oven dried, then cooled and powdered in the dry N$_2$ atmosphere of a glove box.

Infrared spectra were recorded in the range 4000-200 cm$^{-1}$ on a Perkin-Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points, and the reported frequencies are believed to be accurate to ±2 cm$^{-1}$. The spectra of gases were obtained using either a Teflon cell of 5-cm path length equipped with AgCl windows or a 10-cm stainless steel cell equipped with polyethylene windows which were seasoned with CIF$_3$. The spectra of matrix isolated TeF$_5$OF and TeF$_5$OCI were obtained at 6K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research grade Ne(Matheson) was used as a matrix material in a mole ratio of 400:1.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488 nm exciting line of an Ar-ion laser and a Claassen filter for the elimination of plasma lines. Quartz tubes (3 mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A device described in Miller et al., Appl. Spectrosc. 1970, 24, 271 was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al. in J. Appl. Spectrosc. 1969, 23, 8.

From an examination of the above, it can be seen that the FOSOF$_2$F is a useful reagent for the synthesis of hypofluorites. Furthermore, it is shown that TeF$_5$OF, as expected from comparison with TeF$_5$OCI, TeF$_5$OBr and FOIF$_4$, indeed exists and is a stable molecule.

What is claimed is:

1. The compound pentfluorotellurium hypofluorite.
2. A method for synthesizing pentfluorotellurium hypofluorite which comprises the steps of:
   (a) effecting a reaction between (1) CsTeF$_5$O and (2) FOSOF$_2$F at a temperature between about −45° to −10° C; and
   (b) continuing said hypofluorite reaction at said temperature for a period of time sufficient to prepare a pentfluorotellurium reaction product; and
   (c) separating said reaction product.
3. A method in accordance with claim 2 wherein said period of time is about 9 days.
4. A method in accordance with claim 2 wherein said temperature is about −45° C.

* * * * *
METHOD FOR INTRODUCING FLUORINE INTO AN AROMATIC RING

Inventors: Karl O. Christe, Calabasas; Carl J. Schack, Chatsworth, both of Calif.

Assignee: The United States of America as represented by the Secretary of the Air Force, Washington, D.C.

Filed: Sep. 20, 1983

Related U.S. Application Data

Division of Ser. No. 343,033, Jan. 27, 1982, Pat. No. 4,423,260.

Abstract

A process for introducing a fluorine atom into an aromatic hydrocarbon by effecting a substitution reaction between an aromatic hydrocarbon and an NF₄⁺ cation containing salt.

4 Claims, No Drawings
METHOD FOR INTRODUCING FLUORINE INTO AN AROMATIC RING

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon. This is a division of application Ser. No. 343,033, filed Jan. 27, 1982, now U.S. Pat. No. 4,423,260.

FIELD OF THE INVENTION

This invention relates to fluorocarbons and to a novel method for their synthesis. In a more particular aspect, this invention concerns itself with a novel method for introducing a fluorine atom into an aromatic ring. Aromatic fluorocarbons are a well known class of chemical compounds that find wide utility in a variety of industrial applications and in the fabrication of organic compounds. They are useful as solvents, electrical fluids, heat transfer fluids and as components in the manufacture of resins, waxes, greases and oils. However, presently known methods for synthesizing such compounds by introducing a fluorine atom into an aromatic ring structure are severely limited.

The classic Balz-Schiemann reaction, for example, and methods such as the decarboxylation of fluoroformates are useful for the introduction of a single fluorine atom, but are generally less useful for multiple fluorine substitution. The use of elemental fluorine or electrochemical fluorination methods result mainly in addition and not in substitution. Halogen fluorides, such as ClF3, BrF3, or IF3, produce, in addition to fluorine substituted compounds, large amounts of the corresponding halogen substituted compounds and also some addition products. The yield of substitution products obtainable with halogen fluorides can be improved by the use of strong Lewis acids. However, the extreme reactivity of the resulting compounds, such as ClF3 BF4− or ClF3+ SBF6−, makes control of their reactions with organic compounds extremely difficult and unsafe. The utilization of transition metal fluorides, such as CoF3 or CeF3 results in addition and saturation, requiring subsequent rearomatization. Therefore, this method is limited to highly or perhalogenated aromatics. Pyrolysis of aliphatic fluorocarbons, such as CF3Br, can also produce fluoroaromatics. However, this method is limited again to the synthesis of perfluorinated aromatics. Halogen exchange reactions, such as Cl versus F, using HF, alkali metal or metal fluorides are useful, but are restricted to systems strongly activated towards nucleophilic attack by fluoride ion. Hypofluorites, such as CF3OF, are useful for electrophilic and photolytic fluoro
ingen reactions. The electrophilic fluoro
genations are limited again to activated aromatics, whereas the free radical photolytic fluoro
ingenations often lack selectivity resulting in -OCF3 substituted by-products and side chain fluoro
genation. The xenon fluorides and especially XeF2 are promising reagents for electrophilic aromatic substitution, but the full extent of their usefulness is still unknown. The limited availability of xenon, its high price, and the treacherous explosiveness of their hydrolysis products, NeO2, are drawbacks curtailing its extensive use.

The above listing of some of the known methods of preparing aromatic fluorine compounds, although not exhaustive, clearly illustrates the problems prevalent in this area of technology and points out the need for a reliable, readily available and economically feasible reagent for accomplishing the electrophilic fluorine substitution of aromatic ring compounds. Therefore, a research effort was undertaken in an attempt to satisfy the need for a generally useful reagent.

In theory, the ideal reagent for electrophilic substitu
tion would be a salt containing the F+ cation. Unfortunately, such salts do not exist. As an alternative, salts containing complex fluoro cations of the type XP(n-1)+ could be used. However, to be a strong electrophile, such a cation should possess high electronegativity. Since highly electronegative fluorine compounds generally are very strong oxidizers, most of these cations react too violently with organic compounds to be of practical interest. As a consequence, the research effort referred to above proved to be unsuccessful. Additional research, however, proved to be fruitful and culminated in the discovery that the NF4+ cation constitutes an exception to the general rule that such cations react too violently with organic compounds. As a result of the present invention, therefore, it was found that aromatic ring compounds, such as benzene, toluene, and nitrobenzene, interact rapidly with NF3BF4 in anhydrous HF to give, almost exclusively, fluorine substituted aromatic derivatives.

SUMMARY OF THE INVENTION

The present invention concerns itself with a method for introducing fluorine into an aromatic ring structure by using NF3BF4 as a reaction reagent. The introduction of fluorine into an aromatic ring structure is accomplished by an electrophilic substitution reaction in which up to five hydrogen atoms in the aromatic ring can be substituted by fluorine atoms. The reaction can be carried out either by adding the aromatic compound, such as benzene in vapor form, to a cooled solution of NF3BF4 in HF or, alternatively, by adding slowly a solution of NF3BF4 to a solution of benzene in HF.

Accordingly, the primary object of this invention is to provide a novel method for introducing a fluorine atom into an aromatic ring structure.

Another object of this invention is to provide a method for substituting fluorine atoms for the hydrogen atoms in an aromatic ring structure.

Still another object of this invention is to provide for the synthesis of fluorine containing aromatic ring compounds by effecting a reaction between a non-fluorine containing aromatic compound and salts containing an NF4+ cation.

A further object of this invention is to provide a method for introducing a fluorine atom into an aromatic ring by using NF3BF4 as a reaction reagent in the electrophilic substitution of a fluorine atom for a hydrogen atom in an aromatic ring structure.

The above and still further objects and advantages of the present invention will become more readily apparent upon consideration of the following detailed description thereof.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Pursuant to above-defined objects, the present invention concerns itself with a novel method for introducing fluorine atoms into an aromatic ring compound through the electrophilic substitution of a hydrogen atom by a fluorine atom. The known methods for introducing fluorine into an aromatic ring are quite limited and are
often not generally applicable. A widely applicable reagent for carrying out electrophilic substitution reactions on aromatic ring systems, therefore, would be highly desirable. As a result, a concentrated research effort was undertaken based on the hypothesis that the use of NF₄⁺ ion containing salts in this regard would be promising. A continued investigation of aromatic hydrocarbon reactions with NF₄⁺ ion containing species confirmed the hypothesis. It was found that a reaction between an aromatic hydrocarbon ring compound, such as benzene, toluene or nitrobenzene with an NF₄⁺ salt accomplished the substitution of up to five hydrogen atoms in the aromatic ring by fluorine atoms.

Hydrogen fluoride was used as a solvent because of the high solubility of NF₄⁺ salts in it and also because the diluent and heat dissipation properties of a solvated system were found to be beneficial in the anticipated vigorous fluorination. As stated hereinbefore, the reactions were found to be beneficial in the anticipated system were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an AEI Quad 300 quadrupole spectrometer and 1H and 19F nmr spectra were determined with a Varian EJ390 spectrometer operating at 84.6 and 90 MHz, using CFC₃ or TMS as internal standards, respectively. Positive chemical shifts are upfield from CFC₃ and downfield from TMS. Raman spectra were recorded on a Cary Model 83 using the 4880 Å exciting line. Gas chromatographic data were obtained using a Varian Aerograph GC with a thermal conductivity detector under isothermal conditions (135°) with a stainless steel column (1/‌8 × 10') packed with Poropak PS. For the GC determination of the quantitative composition of mixtures, uncorrected peak areas were used since response factors were not available for all compounds. The solid NF₄BF₄ was prepared from NF₄BF₄ on F-I°-BF₄ at low temperature using UV activation, which gives analytically pure material.

The simplest aromatic hydrocarbon studied in the previously referred to research effort was benzene. With NF₄⁺ substrate mole ratios of about three, up to five hydrogens were substituted by F as shown in the following generalized equation:

\[ n\text{NF}_4\text{BF}_4 + \text{C}_6\text{H}_6 \xrightarrow{\text{HF}} C_6H_{6-n}F_n + n\text{NF}_3 + n\text{BF}_3 + n\text{HF} \]  
(1)

The evolved gas was removed under vacuum and trapped at -196° C. It was found to be NF₃ and the amount corresponded to that expected on the basis of one mole of NF₄BF₄ per mole of NF₄BF₄. Hexafluorobenzene was not observed although all other substitution products from mono-to-penta-fluorobenzene were obtained. Almost no saturated or partially saturated fluorocarbons were produced which makes this process of special interest in generating aromatic fluorocarbons directly from their hydrocarbon analogues.

The benzene, toluene, and nitrobenzene reactants interacted rapidly with NF₄BF₄ in anhydrous HF to give, almost exclusively, fluorinated substituted aromatic derivatives. With benzene, up to five hydrogens were replaced by fluorine. A maximum of four hydrogens were displaced in C₆H₄CH₃ and C₆H₄NO₂. The direction of substitution in C₆H₄CH₃ and C₆H₄NO₂ and the lack of side chain fluorination in C₆H₄CH₃ support an electrophilic substitution mechanism when using NF₄BF₄ as a reactant. Although highly electronegative fluorine compounds generally react very slowly even with powerful oxidizers, most cations react too violently with organic compounds to be of practical interest. The NF₄⁺ cation, however, was found to be an exception. It combines high electronegativity (oxidation state of -V) with high kinetic stability (it is isoelectronic with CF₄), and its reactions require significant activation energies. Furthermore, NF₄⁺ salts, such as NF₄BF₄, offer the advantage of generating in an electrophilic aromatic substitution reaction only by-products, such as NF₃ and BF₃, which are unreactive toward the organic compounds. In view of these properties and its ready availability, NF₄BF₄ was found to be an ideal candidate for electrophilic aromatic substitution reactions. A vigorous ring hydrogen substitution occurred even at -7.8° C. in HF solution.

In carrying out the reactions of this invention, the nonvolatile materials were manipulated in a well-passivated (with ClF₃) stainless steel vacuum line equipped with Teflon FEP traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube type pressure gauge. Hydrogen fluoride work was carried out in an all Monel and Teflon vacuum system. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an AEI Quad 300 quadrupole spectrometer and 1H and 19F nmr spectra were determined with a Varian EJ390 spectrometer operating at 84.6 and 90 MHz, using CFC₃ or TMS as internal standards, respectively. Positive chemical shifts are upfield from CFC₃ and downfield from TMS. Raman spectra were recorded on a Cary Model 83 using the 4880 Å exciting line. Gas chromatographic data were obtained using a Varian Aerograph GC with a thermal conductivity detector under isothermal conditions (135°) with a stainless steel column (1/‌8 × 10') packed with Poropak PS. For the GC determination of the quantitative composition of mixtures, uncorrected peak areas were used since response factors were not available for all compounds. The solid NF₄BF₄ was prepared from NF₄BF₄ on F-I°-BF₄ at low temperature using UV activation, which gives analytically pure material.

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(1)

However, at these higher NF₄⁺ to substrate ratios, the reaction was more difficult to control and more "char" formation was noted. Hexafluorobenzene was not observed as a product. If significant amounts had been formed, it would have easily been detected by mass spectrometry since its base peak is the parent ion. Only trace quantities of partially saturated species, C₆F₅H₂ and C₆F₄H were observed, indicating that very little addition occurred.

In order to determine the nature of the reaction, two substituted benzenes, C₆H₅CH₃ and C₆H₄NO₂ were also studied. These were chosen for their well known ability to differentiate between an electrophilic and a free radical reaction path, based on the observed ortho-meta-para product distribution.

In the toluene reaction, the ratio of NF₄⁺ to toluene was in the range 2-4:1. Thus, an excess of fluoride was available (assuming one F/NF₄⁺ is available for substitution) and multisubstitution was expected. The result of a very rapid reaction is illustrated by the following equation:

\[ C_6H_5CH_3 + n\text{NF}_4\text{BF}_4 \xrightarrow{\text{HF}} C_6F_5H_3CH_3 \]  
(1)

where \( n \) = 1-4

The mass spectra of the products strongly indicate that no side chain fluorination had occurred, in agreement with other spectroscopic evidence. Typical isomer distributions for the ring substitution were: o-F(15), m-F(8), p-F(15), 2,4 di-F(30), and mixed di- and tri-F(25). Obviously, o- and p- products predominate for...
this electron rich ring, a result which is compatible with an
electrophilic substitution process.

For the nitrobenzene reaction, a 3:10 mole ratio of
NF$_3$BF$_4$:substrate was used. Even under these con-
tions, this reaction was less vigorous than those of ben-
zenes or toluene, as exemplified by a slightly slower NF$_3$
 evolution and the lack of “darkening” of the solution
until the mixture was finally warmed to about 0ºF. Flu-
orine substitution occurred to give C$_6$F$_5$H$_n$-NO$_2$
(where n=1-4) compounds. Minor amounts of NO$_2$
were formed and traces of C$_4$F$_5$H$_n$- species
were observed, but overwhelmingly the NO$_2$ group
was not displaced. The observed products were mainly
monosubstituted with the following isomer distribution:

- o-F(16), m-F(62), and p-F(7). were formed and traces of C$_4$F$_5$.H
  evolution and the lack of
- NFBFF:

The observation of predominantly ortho and para
substitution and the lack of side chain fluorination in
toluene, and the meta substitution in nitrobenzene estab-
ilishes these NF$_3$BF$_4$ reactions as electrophilic substitu-
tions.

For nitrobenzene, the yield of fluorinated products
was not determined due to separation problems caused
by the low volatility of the products and the large ex-
cess of nitrobenzene used. However, in view of the high
relative amount of mono-F species, and the limited
amount of charring, it is estimated that the yield of
substituted products was high. For the much more reac-
tive C$_6$H$_4$ and C$_6$H$_4$CH$_3$, yields varied widely. Volatile,
fluorinated species were observed equivalent to
30-60% of the aromatic starting compounds.

The following examples are presented in order to
point out the invention with greater detail. The exam-
ple, however, are illustrative only and are not to be
construed as limiting the invention in any way.

EXAMPLE I

C$_6$H$_5$NO$_2$. To a stirred solution of C$_6$H$_5$NO$_2$ (10
mmol) in 5 ml HF at -78º was added dropwise over 30
min. a solution of NF$_3$BF$_4$(2.88 mmol) in 5 ml HF.
Reaction of the NF$_3$BF$_4$ was shown by an increase in
pressure due to NF$_3$ evolution. When all the NF$_3$BF$_4$
had been added, the reaction was gradually warmed to
0º C. and left overnight. During the warming, the reac-
tion mixture took on a pale yellow to dark brown tone.
Keeping the reaction ampoule at -45º, the NF$_3$, HF,
and other volatile materials were pumped away
through -78º and -196º C. traps. After the majority of
the HF was removed, the reactor was maintained at 0º
C. The material passing the -78º C. fraction consisted
of a few droplets of a liquid with a low vapor pressure
at ambient temperature. Mass spectrometry of the vapor
from the drops showed minor amounts of aromatic
fluorocarbons which did not contain NO$_2$ substituents.
These were of the empirical formula
C$_6$F$_5$H$_n$-NO$_2$ (n=1-4). The principal ion peaks observed
were m/e (assign.): 85(NO$_2$F HF), 49 (NOF), and
30(NO). Examination of the liquid non-volatiles at 0º C.
which remained in the reactor, by NMR spectroscopy,
showed that five fluorinated aromatics were present
and all were found to be substituted nitrobenzenes by
comparison of the observed chemical shifts with re-
ported values. By measurement of the area of the reso-
nances the amount of each compound was calculated:

- o-C$_6$F$_5$HNO$_2$(14%)
- m-C$_6$F$_5$HNO$_2$(62%)
- p-C$_6$F$_5$HNO$_2$(6%)
- 2,6- or 3,5-difluorinitrobenzene (14%), and
2,4-difluorinitrobenzene. The large excess of
C$_6$H$_5$NO$_2$ C employed, and still present, masked the

$^1$H spectra of these products and thus the $^{19}$F spectra
were relied on for identification.

EXAMPLE II

C$_6$H$_5$CH$_3$. Toluene and NF$_3$BF$_4$(1:4 molar ratio)
were reacted by condensing the hydrocarbon onto the
stirred HF solution of the salt at -78º C. Alternatively,
toluene in HF at -78º C. was treated dropwise with a
solution of NF$_3$BF$_4$ (1:2 molar ratio). In either case,
instantaneous reaction occurred and the solution be-
came black. After warming to 0º C. for a few hours,
these reactions were worked up in the usual manner.

Much tar like residue remained in the reactor in each
case. Infrared spectroscopic examination of the volatile
species, trapped at -78º C., showed strong bands near
1500 cm$^{-1}$ confirming the presence of aromatic species.

Mass spectra of these fractions showed in both experi-
ments that only aromatic substitution products were
present; these were of the empirical formula C$_6$F$_5$H$_n$-NO$_2$
(where n=1-4). The low intensity of the m/e 69 and 51
peaks indicated the absence of CF$_3$ or CF$_2$H groups in
these compounds with the observed intensities of these
peaks being due to C$_6$F$_5$H$_2$ and C$_6$H$_5$F$_2$ ions. From the
reaction using a higher ratio of NF$_3$BF$_4$ to toluene, a
significant amount of C$_6$F$_5$H$_2$NO$_2$, was found indicating
some displacement of CF$_3$ from the ring. The NMR
spectra of these products confirmed that various fluoro-
toluenes were present approximately in the amounts
given (%): o-C$_6$F$_5$H$_2$CH$_3$(15), p-C$_6$F$_5$H$_2$CH$_3$(16), m-
C$_6$F$_5$H$_2$CH$_3$(8), 2,4-difluorotoluene (30), other di-
and tri-fluorotoluenes (25), and 2,4,5,6-tetra-
fluorotoluenes(7).

EXAMPLE III

C$_6$H$_6$. Benzene and NF$_3$BF$_4$ were reacted using the
same two techniques described for toluene. It was not
possible to prevent charring and blackening of the ben-
zen. Nevertheless, isolation of the volatile products
demandable at -78º C. and examination of their mass
spectra showed that substantial substitution had occurred,
and that the solution be.

In consideration of the aforementioned detailed de-
scription, it is obvious that the present invention pro-
vides a novel method for substituting fluorine atoms for
hydrogen atoms in an aromatic ring structure without
affecting saturated or oxidized substituents. The results
of this invention clearly demonstrate the utilization of
NF$_3$F ion containing salts as powerful reagents for the
introduction of fluorine atoms into aromatic rings by
electrophilic substitution. Up to five hydrogens can be
substituted in aromatic systems through highly efficient
and relatively safe substitution reactions, often in a very
short period of time.

This slower fluorine addition reaction was also stud-
ied and found to produce the corresponding cyclo-hex-
dienes and hexenes. The addition reactions are novel
and offer a controlled, high yield path to dienes which
have previously only been obtained as parts of complex
mixtures.

To obtain more data on the reactions of aromatics
with NF$_3$F salts, an examination of aromatic systems,
which were already highly fluorinated, was carried out.
It was found that these starting materials are more inert
than the strongly fluorinating NF$_3$BF$_4$, and thus allow-
better control of the reaction. Experiments were carried
out using tetra-, penta-, and hexafluorobenzene as start-
For these three highly fluorinated benzenes, the addition of the first two fluorines occurs in para position to each other (1,4 addition) and ortho to any hydrogen, if present. The addition of a second pair of fluorines cannot proceed by a 1,4 mechanism without changing the ring into a bicyclo form, which is generally encountered only under photolytic conditions. Thus, the second pair of fluorines undergoes a 1,2 addition to yield a cyclohexene.

For pentafluorobenzene, some substitution was also observed. It is not clear whether this is the result of a true substitution or of an addition-elimination reaction. In the case of p-CF₂H₃ the second F₂ addition produces the 1H,4H-octafluorocyclohexene which has two possible geometric isomers. Trace quantities of the saturated product, C₆F₁₀H₂, were also detected by mass spectrometry.

In order to provide greater detail in connection with the addition reactions referred to above, Examples IV, V and VI are presented. In these addition reactions, almost no hydrogen substitutions occurred. The addition of the first pair of fluorine atoms always gave 1,4-cyclohexadiene in which the CF₂ group was ortho to hydrogen on the ring. The addition of the second pair of fluorine atoms results in the formation of cyclohexenes. These reactions occurred in high yield. All products were characterized spectroscopically and by comparison to literature data.
EXAMPLE VI

p-C_4F_4H. A mixture of NF_4BF (4.18 mmol) and p-
C_4F_4H_2I (1.43 mmol) in 4 ml HF at -78°C was stirred
and warmed to 0°C over 3 hours, followed by over-
night stirring at 0°-20°C. Fractional condensation at
-78°C and -197°C was used to separate HF and
NF_4I from the products which were retained in the
-78°C trap. No unreacted NF_4BF_4 remained in the reactor.
The original -78°-20°C fraction was further separated
by refrac-tionating through -45°C and -78°C traps.
Analysis using GC/MS procedures showed this mate-
rial to be 1H, 4H-hexafluorocyclohexa-1,4-diene. Prom-
inent mass spectral peaks were found at m/e (assign.):
118(C_4F_4H_2I), 169(C_4F_4H_2), 150(C_4F_4H_2),
138(C_4F_4H_2), 137(C_4F_4H), 119(C_4F_4H), base,
99(C_3F_3H), 94(C_3F_3H), 93(C_3F_3), 88(C_3F_3H_2),
81(C_2F_5H), 70(C_2F_5H), 75(C_2F_5H), 69(CF_2), 68(CF_2H),
61(CFH), 57(CF_2H_2), 56(CFH), 51(CFH), 50(CF_2),
44(CF_2H), and 31(CF). The 19F NMR spectrum for this
compound agreed with published data. Similar analysis of
the -78°C fraction showed it to be a mixture of 25
unreacted p-C_4F_4H_2I above described 1H, 4H cy-
clohexa-1,4-diene, and a compound of empirical for-
mula C_4F_4H_2. An infrared spectrum of the latter com-
 pound showed bands at cm^{-1} (intens.): 3070(w),
2960(w), 1710(m), 1380(s), 1355(w), 1260(m), 1150(s),
1068(m), 1030(m), 743(mw), 637(w), 580(w), and
582(w). The bands near 3000 cm^{-1} are assignable to the
carbon-hydrogen stretches of -CH=CH=CH and C-H
groups while the 1710 cm^{-1} peak is typical of a -CF=CH-
stretching vibration. Strong ion peaks in the mass
spectrum were at m/e (assign.): 226(C_4F_4H_2).

What is claimed is:
1. A process for adding fluorine across the double
bonds in a highly halogenated aromatic hydrocarbon
which comprises the step of effecting an addition
reaction between a highly halogenated aromatic hydro-
carbon and a hydrogen fluoride solvent solution of
NF_4BF_4.
2. A process in accordance with claim 1 wherein said
highly halogenated aromatic hydrocarbon is tetra-
fluorobenzene.
3. A process in accordance with claim 1 wherein said
highly halogenated aromatic hydrocarbon is penta-
fluorobenzene.
4. A process in accordance with claim 1 wherein said
highly halogenated aromatic hydrocarbon is hexa-
fluorobenzene.
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