AD/A-006 332

INORGANIC HALOGEN OXIDIZER RESEARCH

K. O. Christe, et al

Rocketdyne
Canoga Park, California

26 February 1975

Rocketdyne Division
Rockwell International
6633 Canoga Avenue
Canoga Park California 91304

R-9662

ANNUAL REPORT
INORGANIC HALOGEN OXIDIZER RESEARCH
(1 January 1974 through 31 December 1974)

25 February 1975

Contract N00014-70-C-0294
G.O. 09263

Office of Naval Research
Power Branch
Code 429

PREPARED BY

K. O. Christe, C. J. Schack,
and R. D. Wilson

Reproduction in whole
or in part is permitted
for any purpose of the
United States Government.

APPROVED BY

B. Tuffly
B. Tuffly
Program Manager
Propellants, Explosives, and Ingredients
Advanced Programs

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
R-9662

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)*
ANNUAL REPORT, INORGANIC HALOGEN OXIDIZER RESEARCH

5. TYPE OF REPORT & PERIOD COVERED
Annual Report, 1 January 1974 through 31 December 1974

6. PERFORMING ORG. REPORT NUMBER
R-9662

7. AUTHOR(s)
K. O. Christe, C. J. Schack, and R. D. Wilson

8. CONTRACT OR GRANT NUMBER(s)
N00014-70-C-0294

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Rocketdyne Division, Rockwell International
6633 Canoga Avenue
Canoga Park, California 91304

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research Power Branch

12. REPORT DATE
26 February 1975

13. NUMBER OF PAGES
260

14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*

15. SECURITY CLASS. *(of this report)*
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Reproduction in whole or in part is permitted for any purpose of the United States Government

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Synthesis, Novel Oxidizers, Perchlorates, Fluorination, Halogen Fluorides, Onium Salts, Infrared and Raman Spectra, nmr Spectra

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The following novel onium salts were synthesized: $NH_2F_2^+AsF_6^-$, $NH_2F_2^+SbF_6^-$, $OH_3^+AsF_6^-$, $OH_3^+SbF_6^-$, $OH_3^+BF_4^-$, $H_2Cl^+SbF_6^-$, and $SH_3^+SbF_6^-$. With the exception of OH_3^+, these cations are novel. Most of these compounds were characterized by nmr and vibrational spectroscopy.

The use of low-temperature uv-photolysis was explored as a new route to energetic oxidizers. This technique resulted in an improved synthesis for known

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

ia UNCLASSIFIED

PRICES SUBJECT TO CHANGE

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

20. ABSTRACT (Continued)

NF_4^+ salts and in the isolation of the novel compound $(NF_4^+)_2GeF_6^{--}$. The novel NF_3^+ radical cation was obtained by low-temperature γ-irradiation of NF_4^+ salts and was identified by esr spectroscopy.

The three new nitrogen oxyfluorides, recently reported by Schumacher, were shown to be well-known compounds. A structural study of $I(ONO_2)_3$, $ClONO_2$, FNO_2, $ClNO_2$, and the isoelectronic pair NF_3O-CF_3O^- was carried out using vibrational spectroscopy.

The use of KrF^+ salts for the synthesis of high oxidation state compounds was studied. BrF_6^+ salts were prepared by this method and their vibrational spectra, force fields, and crystal systems were determined. However, other salts, such as $ClF_6^+MF_6^-$, could not be synthesized by this method. The nmr spectrum, previously assigned by Glemser to ClF_5O, was duplicated using a mixture of ClF_3, ClF_3O, and HF. The synthesis of $FClO_2$ was improved, but its synthesis from ClF and O_2, reported by Jache, could not be duplicated. The field of chlorine oxyfluorides was reviewed for Advances in Inorganic Chemistry and Radiochemistry.

Crystal field effects and relaxation in O_2^+ salts were studied by esr spectroscopy. Low-temperature uv-photolysis was found to be a superior synthetic method for the unstable $O_2^+BF_4^-$ and the novel $(O_2^+)_2GeF_6^{--}$ salts. The vibrational spectra, force fields, and mean square amplitudes of vibration were redetermined for SF_4 and SF_4O.

The reaction of chlorine perchlorate with pentafluoromonochlorobenzene resulted in the addition of 2 moles of $ClOClO_3$ across two of the double bonds of the aromatic ring. An improved synthesis for $CF_2(\overset{O}{\overset{\|}{C}}F)_2$ was discovered using $ClOSO_2F$ as one of the starting materials. Vanadyl perchlorate, $VO(ClO_4)_3$, was prepared from $ClOClO_3$ and $VOCl_3$.

CONTENTS

Appendix H

Appendix I

Appendix J

Appendix K

FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 473, with Lt. R. S. Miller as Scientific Officer. This report covers the period 1 January 1974 through 31 December 1974. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, and Mr. R. D. Wilson. The program was administered by Dr. L. Grant, Manager, Exploratory Chemistry, and Dr. B. Tuffly, Program Manager.

INTRODUCTION

This report covers a 12-month period and describes Rocketdyne's efforts in the area of halogen chemistry. As in the past years, our research was kept diverse and covered areas ranging from the exploration of new synthetic methods and the syntheses of novel compounds to structural studies. As in the past (Ref. 1) we have summarized completed pieces of work in manuscript form suitable for publication. Thus, time spent for report and manuscript writing is minimized, and widespread dissemination of our data achieved.

During the past 12 months, the following papers were published, submitted for publication, or presented at meetings. All of these arose from work sponsored under this program.

PUBLICATIONS DURING PAST CONTRACT YEAR

Papers Published

1. "Vibrational Assignment of SF_4," by K. O. Christe, W. Sawodny, and P. Pulay, J. Mol. Spectrosc., 21, 158 (1974).
2. "Halogen Fluorides," by K. O. Christe, International Union of Pure and Applied Chemistry, Proceedings of XXIVth Internat. Congress, 4, 115 (1974).
3. "Cesium Bis(perchlorato)bromate (I), $Cs^+[Br(OClO_3)_2]^-$," by K. O. Christe and C. J. Schack, Inorg. Chem., 13, 1452 (1974).
4. "Reactions of the $(CF_3)_2NO$ Radical with Strong Oxidizers," by K. O. Christe, C. J. Schack, R. D. Wilson, and D. Pilipovich, J. Fluor. Chem., 4, 423 (1974).
5. "Trifluoromethyl Perchlorate-Preparation and Properties," by C. J. Schack, D. Pilipovich, and K. O. Christe, Inorg. Nucl. Chem. Lett., 10, 449 (1974).
6. "Trifluoromethyl Perchlorate, Infrared and Raman Spectra," by C. J. Schack and K. O. Christe, Inorg. Chem., 13, 2374 (1974).
7. "Halogen Nitrates," by K. O. Christe, C. J. Schack, and R. D. Wilson, Inorg. Chem., 13, 2811 (1974).

8. "Reactions of Ozone with Covalent Hypohalites," by C. J. Schack and K. O. Christe, *Inorg. Chem.*, *13*, 2378 (1974).

9. "Halogen Perchlorates. Reactions with Fluorocarbon Halides," by C. J. Schack, D. Pilipovich, and K. O. Christe, *Inorg. Chem.*, *14*, 145 (1975).

10. "An Improved Synthesis of $FClO_2$," by K. O. Christe, R. D. Wilson, and C. J. Schack, *Inorg. Nucl. Chem. Lett.*, *11*, 161 (1975).

11. "Esr Study of O_2^+ Salts. Influence of Crystal Field Effects and Relaxation," by I. B. Goldberg and K. O. Christe, *Inorg. Chem.*, *14*, 152 (1975).

Papers in Press

12. "Vibrational Spectrum and Force Constants of the XeF_5^+ Cation," by K. O. Christe, E. C. Curtis, and R. D. Wilson, *J. Inorg. Nucl. Chem.*

13. "Titanium Tetraperchlorate and Chromyl Perchlorate," by C. J. Schack, D. Pilipovich, and K. O. Christe, *J. Inorg. Nucl. Chem.*

14. "Chlorine Oxyfluorides," by K. O. Christe and C. J. Schack, *Advances Inorg. Chem. Radiochem.*

15. "The NF_3^+ Radical Cation. Esr Studies of Radiation Effects in NF_4^+ Salts," by S. P. Mishra, M. C. R. Symons, K. O. Christe, R. D. Wilson, and R. I. Wagner, *Inorg. Chem.*

16. "The BrF_6^+ Cation. Infrared Spectrum and Force Field," by K. O. Christe and R. D. Wilson, *Inorg. Chem.*

17. "The CF_3O^- Anion. Vibrational Spectrum of an Unusual CF_3 Compound," by K. O. Christe, E. C. Curtis, and C. J. Schack, *Spectrochim. Acta.*

18. "On the Existence of Several New ONF Compounds," by K. O. Christe, *Z. Anorg. Allg. Chem.*

Papers Presented at Meetings

19. "The CF_3O^- and BrF_6^+ Ions and Novel Onium Salts," by K. O. Christe, C. J. Schack, R. D. Wilson, and E. C. Curtis, 5th European Fluorine Symposium, Aviemore, Scotland (September 1974)

20. "New Energetic Halogen Compounds," by K. O. Christe, Invited lectures at the University of Southern California and the California State University, Los Angeles (1974).

DISCUSSION

PROTONATION STUDIES

During studies of the controlled hydrolysis of $BrF_4^+MF_6^-$ (M = Sb or As) in HF solutions, stable white solids were obtained in high yields. It was shown that instead of the expected reaction

$$BrF_5 + 2H_2O + MF_5 \rightarrow BrO_2^+MF_6^- + 4HF$$

the following reaction took place

$$HF + H_2O + MF_5 \rightarrow H_3O^+MF_6^-$$

These novel oxonium salts were thoroughly characterized by elemental analysis, material balance, infrared, Raman, and nmr spectroscopy, DSC, and X-ray diffraction. The results are summarized in Appendix I. A crystal structure determination of these interesting compounds will be carried out in collaboration with Dr. Charpin of the French Atomic Energy Commission using their neutron diffraction facilities. The extraordinary thermal stability of these oxonium salts suggested the possible existence of other onium salts previously believed not to be able to exist. Consequently, the protonation of the following molecules was studied: NF_3, NHF_2, HCl, H_2S, and Xe.

For H_2S, the stable salt $H_3S^+SbF_6^-$ was isolated and characterized (see Appendix J). Although alkylsulfonium cations have been known for many years and are important industrial chemicals, this is the first synthesis of a salt containing the parent sulfonium cation. This salt should be a useful chemical. For example, it can be used as an H_2S generator according to:

$$H_3S^+SbF_6^- + H_2O \rightarrow H_3O^+SbF_6^- + H_2S$$

In the series of fluoroammonium cations of the composition $NH_nF^+_{4-n}$, previously only the NF_4^+ (Ref. 2 through 11), NH_3F^+ (Ref. 12 and 13), and NH_4^+ (Ref. 14) cations had been known. It was of great interest to establish the stability of the missing two cations, i.e., of NHF_3^+ and $NH_2F_2^+$, because a reasonable stability of these ions would suggest that NF_4^+ salts might be synthesized by direct fluorination of NH_4^+ salts. It was found that $NH_2F_2^+$ salts do indeed exist and are of marginal stability at room temperature. The characterization of these salts was slow and tedious, because these salts behaved as true derivatives of the treacherous difluoramine. In spite of numerous unpredictable explosions, we succeeded to characterize well the $NH_2F_2^+SbF_6^-$ and the $NH_2F_2^+AsF_6^-$ salt. These results are summarized in Appendix K. The decomposition mode of these salts was briefly studied (see Appendix K) since these compounds might be suitable starting materials for HF elimination lasers. For NF_3, no evidence for protonation was found at temperatures as low as -78 C. Furthermore, attempts to fluorinate $NH_4^+AsF_6^-$ in HF solution with F_2 in the temperature range -78 to 25 C did not produce any fluoroammonium cations (see Appendix K). A direct synthesis of fluoroammonium salts is extremely desirable for the following reason. The NF_4^+ salts are the most promising materials for solid propellant fluorine generators for chemical HF lasers, but a cheaper production process is required to make their use economically feasible.

The protonation of HCl in HF-SbF_5 solution produced the unstable salt $H_2Cl^+SbF_6^-$, whereas Xe showed no evidence for protonation at temperatures as low as -78 C. For more details see Appendix J.

NITROGEN FLUORIDES

In view of the importance of NF_4^+ salts for solid-propellant fluorine atom generators, a significant percentage of our effort was spent in this direction. The NF_4^+ salts were discovered by one of us under an ONR contract at Stauffer Chemical (Ref. 15). The concept of a fluorine atom gas generator, based on $NF_4^+BF_4^-$, was developed at Rocketdyne (Ref. 16). Under this program (Ref. 7) a new synthesis for NF_4^+ salts, using uv-photolysis, was discovered. This method is being developed at Rocketdyne on an Air Force contract (Ref. 17) into a process suitable for the production of $NF_4^+BF_4^-$ in pound quantities. Since the Air Force contract is strictly limited to $NF_4^+BF_4^-$, we have explored under this program the synthesis of $NH_4^+AsF_6^-$ and other novel NF_4^+ salts.

It was found that very pure $NF_4^+AsF_6^-$ can be prepared by uv-photolysis at -196 C in a small quartz or steel-sapphire reactor at a rate of ~1.3 g/hr. Since BF_3 might possibly behave as a deactivator in an HF laser, we have investigated the synthesis of novel NF_4^+ salts containing other suitable anions. Using our low-temperature uv-technique, the new salt $(NF_4^+)_2\ GeF_6^{--}$ was synthesized and identified by vibrational spectroscopy. This salt is expected to be an ideal F atom generator candidate. Its full characterization will be carried out during the current year and complete data will be given in the next annual report in manuscript form. For the characterization of $(NF_4^+)_2GeF_6^{--}$, a better knowledge of the GeF_6^{--} anion is required. For this purpose, the salts $(NO^+)_2GeF_6^{--}$ and $(O_2^+)_2\ GeF_6^{--}$ were synthesized and are also being studied.

The mechanism by which NF_4^+ salts are formed and decompose (Ref. 7) are of great importance for our understanding and the development of improved NF_4^+ syntheses. Consequently, we have studied in collaboration with Prof. Symons of the University of Leicester, England, the decomposition of $NF_4^+AsF_6^-$ under the influence of γ-irradiation. It was shown by low-temperature esr spectroscopy that $NF_4^+AsF_6^-$ decomposes to yield the NF_3^+ radical cation in addition to a second slightly less stable radical, which is believed to be $AsF_6^{\bullet}$. These decomposition studies support the mechanism, previously published by Rocketdyne (Ref. 7). A detailed report on this study is given in Appendix B.

NITROGEN OXYFLUORIDES

Sicre and Schumacher from Argentina have recently reported (Ref. 18) the existence of three novel nitrogen oxyfluorides (i.e., FONO, NF_3O_2, and an unknown). In view of their potential as oxidizers, we have examined Schumacher's claim. It was found that the reported compounds actually are the well-known $HONO_2$, $FONO_2$, and covalent N_2O_5. These results were summarized in manuscript form (see Appendix D).

One more effort was made to synthesize the novel $(CF_3)_2NO^+$ cation according to:

$$(CF_3)_2NO + O_2^+AsF_6^- \rightarrow (CF_3)_2NO^+AsF_6^- + O_2$$

A previous study of this system (Ref. 19), carried out in the absence of a solvent, produced the expected O_2, but no $(CF_3)_2NO^+$ salt. This salt would be of interest since it could readily be converted into a CF_3 substituted NF_3O derivative by the following displacement reaction:

$$(CF_3)_2NO^+AsF_6^- + FNO \rightarrow NO^+AsF_6^- + (CF_3)_2FNO$$

The $O_2^+AsF_6^-$-$(CF_3)_2NO$ system was re-examined in the presence of WF_6 as a solvent. The products (i.e., $NO^+AsF_6^-$ and O_2) were identical to those previously obtained by us for the neat $O_2^+AsF_6^-$-$(CF_3)_2NO$ system (Ref. 19). No evidence was observed for the formation of the desired $(CF_3)_2NO^+AsF_6^-$. This re-examination was prompted by [illegible] bstract of a Russian paper scheduled, but not presented, as the 5th European Fluorine Symposium at Aviemore.

The bonding in NF_3O is quite unusual. During work with $Cs^+CF_3O^-$ we have also recorded its vibrational spectrum. It was found that the spectrum of CF_3O^- closely resembled that of isoelectronic NF_3O and that the literature assignment of two fundamentals in NF_3O was probably incorrect. Consequently, the Raman spectra of liquid and gaseous NF_3O were recorded and our suspicion was confirmed. After completion of our work, the Raman spectrum of gaseous NF_3O was published by Selig and coworkers (Ref. 20) who reached the same conclusion. A normal coordinate analysis was carried out for CF_3O^-. It was found that the bonding in CF_3O^- is very unusual and closely resembles that in NF_3O. The results were summarized in manuscript form (see Appendix E).

HALOGEN FLUORIDES

The general usefulness of KrF_2-Lewis acid adducts as oxidative fluorinators for the synthesis of high oxidation state compounds was examined. Schrobilgen's work (Ref. 21) on $BrF_6^+MF_6^-$ salts was confirmed. We have succeeded to characterize better the BrF_6^+ cation. The infrared spectra, force constants, and X-ray powder data were obtained, [illegible] e summarized in Appendix H. Attempts to prepare either $BrF_6^+BF_4^-$ or $ClF_6^+AsF_6$ by this technique were unsuccessful. As yet, we have not had the time to re-examine Bartlett's suspect claim (Ref. 22) for the formation of $XeOF_5^+$ from $XeOF_4$ and KrF^+, although the necessary starting materials have already been prepared.

The ^{19}F nmr spectrum reported in 1972 by Züchner and Glemser (Ref. 23) and attributed to the novel chlorine fluoride oxide, ClF_5O, was duplicated by us using a mixture of ClF_3 and ClF_3O with HF added to enhance the exchange rate. This is further support that Züchner and Glemser's report is incorrect (see Appendix A).

The literature method (Ref. 24) for preparing $FClO_2$ was improved. Furthermore, Jache's claim (Ref. 25) for a high yield synthesis of $FClO_2$ from ClF and O_2 was examined and found to be incorrect. The results from this study are summarized in Appendix F.

A structural study of ClF_3O by microwave spectroscopy in collabroation with Dr. Lovas of NBS gave preliminary data. A more complete study of this molecule will be undertaken in collaboration with Prof. Bodenseh of the University of Ulm, Germany, who is better equipped for handling corrosive oxidizers.

An extensive review was written on chlorine fluoride oxides for Advances in Inorganic and Radiochemistry which was solicited by Prof. Emeleus. The writing of this review greatly benefits from our expertise in this field acquired under ONR sponsorship. The manuscript is given as Appendix A.

In collaboration with Prof. Edwards of the University of Birmingham, England, an X-ray crystal structure determination of $(BrF_2^+)_2\ GeF_6^{--}$ has been completed. The data have been refined and are in the process of being written up in manuscript form.

O_2^+ SALTS

Dioxygenyl salts are of great potential for solid-propellant oxygen generators in chemical lasers. In addition, we were interested in their reaction chemistry. They can be used as a one electron oxidizer (Ref. 19 and 26) and yield interesting species with halogen fluorides (Ref. 1). Since for the latter study, esr spectroscopy was used as a diagnostic tool, the esr spectra of O_2^+ salts had to be investigated first. This work was done in collaboration with Dr. Goldberg from the Rockwell International Science Center and produced interesting results concerning crystal field effects and relaxation. The results are summarized in Appendix G.

In the course of this work we have also discovered an improved synthesis for thermally unstable O_2^+ salts. Previously, these salts had to be prepared from the Lewis acid and the unstable O_2F_2, which in turn had to be synthesized by low-temperature glow-discharge. We have now found that these salts can conveniently be prepared by uv photolysis of O_2-F_2-Lewis acid mixtures at -78 C. By this technique we have prepared the known $O_2^+BF_4^-$ (see Appendix G) and the novel $(O_2^+)_2GeF_6^{--}$ salt.

INORGANIC PERHALATES

Covalent metal perchlorates have potential as burning rate modifiers for solid propellants. In addition to $Ti(ClO_4)_4$ and $CrO_2(ClO_4)_2$ (Ref. 1), we have now synthesized $VO(ClO_4)_3$ according to:

$$VOCl_3 + 3Cl_2O_4 \rightarrow 3Cl_2 + VO(ClO_4)_3$$

This perchlorate is an orange-yellow, viscous liquid at room temperature. Its infrared spectrum is consistent with bidentate bonding of the perchlorate groups. An attempt to obtain a Raman spectrum failed due to the absorption of the laser light by the sample. Thermal degradation at 110 C gave excellent analytical results for decomposition according to the equation:

$$2VO(ClO_4)_3 \rightarrow V_2O_5 + 3Cl_2 + 10.5\ O_2$$

The reaction of $CoCl_3$ and Cl_2O_4 was carried out in an attempt to prepare the novel anhydrous $Co(ClO_4)_3$. After several weeks at -45 and -25 C, it was found that only a small fraction (20-percent) of the expected Cl_2 by-product had formed. This is indicative of a very slow reaction and perhaps also of only a surface reaction of the solid $CoCl_3$. Similar results were obtained with $CrCl_3$ and $NiCl_2$ substrates, while MnF_3 did not react at all. Obviously, a common solvent is required to promote these reactions.

We have also examined the synthesis of fluorine perbromate according to:

$$Cs^+BrO_4^- + F_2 \rightarrow CsF + FOBrO_3$$

Several reactions were carried out at temperatures ranging from -50 to -20 C, but no reaction occurred.

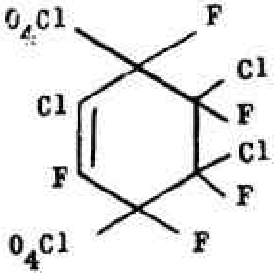
FLUOROCARBON PERCHLORATES

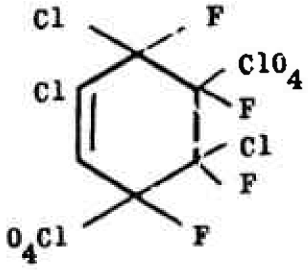
We have continued our studies (Ref. 1) of fluorocarbon perchlorates. These compounds hold promise as energetic plasticizers in solid-propellant formulations. Of particular interest was the reaction of $ClOClO_3$ with aromatic fluorocarbons.

The reaction of C_6F_5Cl and chlorine perchlorate was examined and found to parallel that of C_6F_6. Thus a bis-Cl_2O_4 adduct was obtained.

$$C_6F_5Cl + 2Cl_2O_4 \rightarrow C_6F_5Cl_3(ClO_4)_2$$

This reaction occurs by Cl and ClO_4 addition across two of the "double bonds" of the aromatic ring. The third "double bond" remains unaffected and the product is thus a cyclohexene. In addition to the material balance of the synthetic reaction, the nature of the product was established by its infrared, mass, Raman, and ^{19}F nmr spectra. In particular the ^{19}F nmr spectra shows that five different types of fluorine are present as expected for a single isomeric product. However, the exact position of the various substituents is unknown. The two most likely isomers are:





A sample of the new perchlorate of the empirical formula, $C_6F_5I(ClO_4)_2$, was prepared from C_6F_5I and Cl_2O_4. This solid was slightly yellow and sticky but appeared crystalline. As before (Ref. 1), it proved difficult to handle; a few crystals detonated under the action of a spatula. The Raman spectrum of the compound has now been obtained on a freshly prepared sample using low-temperature conditions to preclude decomposition in the laser source. The spectrum clearly showed the presence of the $I(ClO_4)_4^-$ anion. Thus this iodo bis-perchlorate should actually be formulated as $[(C_6F_5)_2I^+I(ClO_4)_4^-]$. Similar spectral data were previously obtained for the alkyl analogues, $[(i\text{-}C_3F_7)_2I^+I(ClO_4)_4^-]$ and $[(n\text{-}C_7F_{15})_2I^+I(ClO_4)_4^-]$. Therefore, all the iodo-perchlorate adducts isolated to date are in reality, salts of the $I(ClO_4)_4^-$ anion. Detailed results will be given in the next annual report in manuscript form.

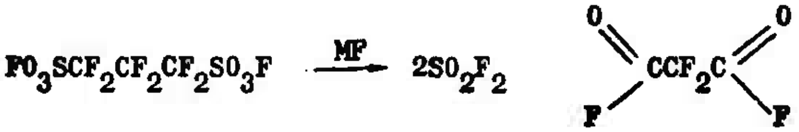
DIFUNCTIONAL FLUOROCARBONS

Difunctional fluorocarbons are important as cross-linking agents for polymers. We have now studied the usefulness of our previously discovered (Ref. 1) chlorine fluorosulfate reaction chemistry for the synthesis of difunctional fluorocarbons.

The reaction of chlorine fluorosulfate and fluorocarbon bromides resulted in:

$$BrCF_2CF_2CF_2Br + 2ClSO_3F \rightarrow FO_3SCF_2CF_2CF_2SO_3F + 2BrCl$$

The fluorosulfate derivative was used in turn to prepare the acyl fluoride:



All materials were identified by infrared, mass and ^{19}F nmr spectra. Detailed results will be given in the next annual report in manuscript form.

MISCELLANEOUS STRUCTURAL STUDIES

A structural study of the covalent halogen nitrates $ClONO_2$ and $I(ONO_2)_3$ was carried out using vibrational spectroscopy. It was shown that in $ClONO_2$, contrary to general belief, the Cl atom is not coplanar with the ONO_2 group. For comparison, the Raman spectra of FNO_2 and $ClNO_2$ were also recorded. These results are summarized in Appendix C.

We have thoroughly re-examined the vibrational spectra of SF_4 and SF_4O. The spectra of these two molecules are still poorly understood. They are of significance to us since they are the prototypes for numerous other pseudo-trigonal bipyramidal molecules, such as several halogen fluorides and oxyfluorides. We have recorded the infrared and Raman spectra of the gas, liquid, and solid phases, and have determined ^{32}S-^{34}S isotopic shifts by a matrix isolation study. Force fields and mean square amplitudes of vibration were computed for the various possible assignments in collaboration with Dr. Curtis of Rocketdyne, Prof. Sawodny of the University Ulm (Germany), and Prof. Cyvin of the University of Trondheim (Norway). In view of the difficulty of this problem, the results have as yet not been summarized in manuscript form.

REFERENCES

1. R-9454, Annual Report, Inorganic Halogen Oxidizer Research, N00014-70-C-0294, Rocketdyne Division, Rockwell International, Canoga Park, California, 26 February 1974.
2. K. O. Christe, J. P. Guertin, and A. E. Pavlath, Inorg. Nucl. Chem. Lett., 2 83 (1966).
3. J. P. Guertin, K. O. Christe, and A. E. Pavlath, Inorg. Chem., 5, 1921 (1966).
4. W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Nucl. Chem. Lett., 2, 79 (1966)
5. W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Chem., 6, 1156 (1967).
6. C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner, and J. N. Wilson, Inorg. Chem., 11, 1696 (1972).
7. K. O. Christe, R. D. Wilson, and A. E. Axworthy, Inorg. Chem., 12, 2478 (1973).
8. K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, Inorg. Chem., 6, 533 (1967).
9. K. O. Christe and D. Pilipovich, Inorg. Chem., 10, 2803 (1971).
10. S. M. Sinel'nikov and V. Ya. Rosolovskii, Doklady Akad. Nauk. SSSR, 194, 1341 (1970).
11. V. Ya. Rosolovskii, V. I. Nefedov, and S. M. Sinel'nikov, Izvest. Akad. Nauk. SSSR, Ser. Khim., 7, 1445 (1973).
12. V. Grakauskas, A. H. Remanick, and K. Baum, J. Amer. Chem. Soc., 90, 3839 (1968).
13. V. Grakauskas, J. Inorg. Nucl. Chem., 35, 3034 (1973).
14. Reported as early as 13th Century.
15. K. O. Christe, J. P. Guertin, and A. E. Pavlath, U.S. Pat., 3,503,719 (1970).
16. Rocketdyne BC71-72, "Solid-Propellant Fluorine Generator," presented by D. Pilipovich to E. Gerry at ARPA, 28 October 1971.

17. *Fluorine Generator Solid Ingredient Development*, Air Force Contract F04611-74-C-0035, Rocketdyne.

18. J. E. Sicre and H. J. Schumacher, Z. Anorg. Allg. Chem., 385, 131 (1971).

19. K. O. Christe, C. J. Schack, R. D. Wilson, and D. Pilipovich, J. Fluor. Chem., 4, 423 (1974).

20. N. Aminadav, H. Selig, and S. Abramowitz, J. Chem. Phys., 60, 325 (1974).

21. R. J. Gillespie, and G. J. Schrobilgen, Inorg. Chem., 13, 1230 (1974).

22. D. E. McKee, C. J. Adams, A. Zalkin, and N. Bartlett, J.C.S. Chem. Comm., 26 (1973).

23. K. Züchner and O. Glemser, Angew. Chem., 84, 1147 (1972).

24. A. Engelbrecht and H. Atzwanger, J. Inorg. Nucl. Chem., 2, 348 (1956).

25. J. P. Faust, A. W. Jache, and A. J. Klanica, U.S. Pat., 3,545,924 (1970).

26. T. J. Richardson and N. Bartlett, J.C.S. Chem. Comm., 427 (1974).

CHLORINE OXYFLUORIDES

K. O. CHRISTE AND C. J. SCHACK

Rocketdyne, a Division of Rockwell rnational,

Canoga Park, California 9

- I. Introduction
- II. General Aspects
  - A. Geometry
  - B. Ligand Distribution
  - C. Relative Bond Strengths
  - D. Amphoteric Nature, Tendency to form Adducts, and Reactivity
- III. Particular Compounds
  - A. $FClO$
  - B. ClF_3O
  - C. ClF_2O^+
  - D. ClF_4O^-
  - E. ClF_5O
  - F. $FClO_2$
  - G. ClO_2^+
  - H. $ClO_2F_2^-$
  - I. ClF_3O_2
  - J. $ClF_2O_2^+$
  - K. $FClO_3$
  - L. Chlorine Fluoride Oxide Radicals
  - M. Miscellaneous

1. Introduction

This review is limited to compounds containing both oxygen and fluorine atoms bonded directly to a common chlorine central atom. Therefore, compounds, such as fluorine perchlorate, O_3ClOF, have not been included. Data on O_3ClOF were summarized in a recent review on inorganic hypofluorites (180).

The subject of chlorine oxyfluorides* has been reviewed in 1963 by Schmeisser and Braendle (253) and in 1969 in Gmelins Handbuch der Anorganischen Chemie (122). However, both reviews deal only with chloryl fluoride, $FClO_2$, and perchloryl fluoride, $FClO_3$. Since the writing of these reviews, three of the four possible remaining chlorine oxyfluorides, i.e., FClO, F_3ClO, and F_3ClO_2, have been characterized, and claims have been made for the synthesis of the fourth one, ClF_5O. Additional information on chlorine oxyfluorides can be found in various monographs and textbooks (32, 75, 77, 95, 156, 169, 244) and in particular in Comprehensive Inorganic Chemistry in the chapter on the halogens written by Downs and Adams (84). A second area of significant recent progress comprises ions derived from chlorine oxyfluorides. Therefore, these will also be discussed in detail.

For the present review, the literature cited in Chemical Abstracts (Jan. 1965 until Dec. 1973) was used in addition to more recent work published during 1973 and 1974. For literature predating 1965, we have relied mainly on Schmeisser's review (253) and Gmelins handbook (122).

In addition to a discussion of the individual compounds an introductory chapter was added correlating the physical and chemical properties of the chlorine oxyfluorides with their structure. In the Appendix, full tables of thermodynamic properties are given for each compound, where known.

II. General Aspects

Since most of the physical and chemical properties of the chlorine oxyfluorides can be readily correlated with their molecular structure, we shall briefly discuss some of the more general aspects.

A. Geometry

As can be seen from Figure 1, the structures of all the chlorine oxyfluoride molecules and ions can be derived from those of the corresponding binary chlorine fluorides (49) by replacing a free chlorine valence electron pair by a doubly bonded oxygen atom without significant rearrangement of the rest of the molecule.

The only possible exception to this rule could be the yet unknown (68) $ClF_4O_2^-$ anion. By comparison with the known structures of the pseudo-isoelectronic $IF_4O_2^-$ (45, 93) and $TeF_4O_2^{--}$ (260), anions, the two oxygens in $ClF_4O_2^-$ should also be in cis and not in trans position. In these and similar oxyfluoride anions, such as SF_5O^- (65) or CF_3O^- (58), the negative charge is located mainly on the most electronegative ligands, i.e., fluorine. Furthermore, in pseudo-octahedral species not containing a free valence electron pair on the central atom, such as XF_5O^-, the fluorine trans to the less electronegative ligand appears to be more weakly bonded than the remaining fluorines. This is plausible from molecular orbital arguments. Therefore, for $XF_4O_2^-$ the structure with two oxygen atoms trans to two fluorines and cis with respect to each other, should favor the resonance structures having the negative charge located on the fluorine ligands.

Since the degree of mutual repulsion decreases in the order: free valence electron pair > double bonded oxygen > fluorine, the observed bond angles deviate somewhat from those expected for the ideal geometries. Typical examples are $FClO_2$ and $FClO_3$ (see Figure 1).

The structure of radicals and radical ions can also readily be predicted by treating an unpaired electron in the same manner as a free valence electron pair. Therefore, a chlorine oxyfluoride free radical should have the same geometry as the corresponding anion with identical fluorine and oxygen ligands (see Figure 2). Similarly, the structure of a radical cation should be analogous to that of the corresponding molecule having the same ligands. For a radical anion, however, the additional sterically active valence electron will increase the coordination number around the central atom by one. This should result in a geometry resembling that of the anion containing one F ligand more, but in which one F ligand is replaced by the sterically active free electron. The exact spin distribution would have to be determined experimentally and is not necessarily the same as shown in Figure 2.

B. Ligand Distribution

As can be seen from Figure 1, the structures are simple and can be logically predicted if one keeps in mind that free valence electron pairs on the central atom are sterically active and behave as a ligand. For 3, 4, 5, and 6 ligands always the sterically most favorable arrangements are observed, i. e., the triangular plane, tetrahedron, trigonal bipyramid, and the octahedron, respectively (118). Based on the information available for halogen oxyfluorides and related compounds such as xenon or chalcogen oxyfluorides the following conclusions concerning the ligand distribution can be reached. In a triangular plane and a tetrahedron all positions are equivalent. In a trigonal bipyramid the two axial positions are occupied by the most electronegative ligands, i. e., F atoms. In octahedrons of the type XF_5A only one arrangement is possible. For XF_4AB however, the A or B ligands are trans if A and B are either two free electron pairs or one free electron pair and one oxygen ligand. When A and B are two O atoms, the cis arrangement appears more favorable (see above). The case of the pentagonal bipyramid is not of practical interest since it appears that the coordination number around a high oxidation state chlorine central atom is limited to a maximum of six.

C. Relative Bond Strengths

Unfortunately, exact bond lengths are known only for $FClO_2$ (220) and $FClO_3$ (72). However, complete vibrational spectra have been published for essentially all of the chlorine oxyfluorides. These can be used for the evaluation of the corresponding force constants. Since the latter are a good measure for the relative strengths of these bonds, their comparison is interesting. As can be seen from Table I, the ClO bonds all possess more or less double bond character. The variation in the values of the ClO stretching force constants is mainly due to the combination of several effects. For example a formal positive charge (i.e., in cations), a high oxidation state of the central atom, and a high number of fluorine ligands tend to increase the ClO stretching force constant (57). In contrast to the ClO bonds, the ClF bond strengths are subject to much larger changes. These strong variations cannot be explained anymore by such effects as listed above for the ClO bonds or by the Gillespie-Nyholm valence shell electron pair repulsion (VSEPR) theory (118) alone. By analogy with the halogen fluorides (49) it is necessary to assume contributions from two different kinds of bonding. In addition to the normal covalent bonds possessing a bond order of about one, the occurrence of semi-ionic 3 center - 4 electron bonds (130, 232, 243) must be invoked. The principle of a semi-ionic 3c-4e bond is demonstrated in Figure 3. For simplicity, ClF_2^- (63) was chosen as an example. Ideally, the two F-ligands form two semi-ionic 3c-4e [p-p] σ^- bonds with one p electron pair of the chlorine central atom, while the free Cl valence electron pairs form an sp^2 hybrid.

Instead of using this semi-empirical molecular orbital model, the bonding in ClF_2^- can also adequately be described in the valence-bond representation (76) as a resonance hybrid of the following canonical forms: (F-Cl) F^- and F^-(Cl-F). This results in the same average charge distribution as in the molecular orbital model, i.e., $^{-1/2}F-Cl-F^{-1/2}$. A third and the most simple bond model, proposed by Bilham and Linnett (29) for XeF_2 which is pseudo-isoelectronic with ClF_2^-, assumes single electron bonds for each X-F bond. It is relatively immaterial, which of these three descriptions is preferred since all of them result in the same charge distribution and a Cl-F bond order of about 0.5.

As can be seen from Table I, these weak ClF bonds occur only when the central atom has a coordination number in excess of four and possesses at least one free Cl valence electron pair. In addition to Gillespie's simple VSEPR theory, the following general rule has been proposed by Christe (49), which permits the prediction of whether, and how many, semi-ionic bonds are to be formed:

"The free valence electron pairs on the central atom seek high s-character; i. e., sp^n hybridization. If the number of ligands is larger than 4 and one or more of them are free valence electron pairs, then as many F ligands form linear semi-ionic 3 center -4 electron bonds as are required to allow the free electron pairs to form an sp^n hybrid with the remaining F ligands. These semi-ionic 3c-4e bonds are considerably weaker and longer than the mainly "covalent" sp^n hybrid bonds."

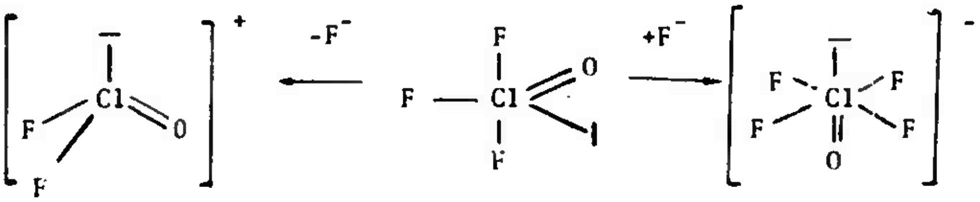
This rule also holds for the chlorine oxyfluorides as well as for the chlorine fluorides for which it was originally formulated.

An additional effect, however, must be invoked to be able to fully rationalize the experimental data. Inspection of Table 1 reveals that the ClF stretching force constants of $FClO_2$ and FClO are significantly lower than expected from the above discussion. In particular, if the known ClF stretching force constants and bond distances within the pseudo-tetrahedral series FCl, FClO, $FClO_2$, $FClO_3$ are compared (see Figure 1 and Table II), it becomes obvious that the ClF bonds in FClO and $FClO_2$ are abnormally long and weak. Application of the rules discussed above is of no help in explaining the observed trend. However, if a simple molecular orbital description, similar to that proposed by Spratley and Pimentel (274) for FNO and F_2O_2, is used, the data can be rationalized. The molecules FCl, FClO, $FClO_2$, and $FClO_3$ can be thought of as being derived from the combination of an F atom with the Cl, ClO, ClO_2, and ClO_3 radicals, respectively. This hypothetical bond formation involves a 2p electron of the fluorine atom and the unpaired electron of the Cl containing radical. If according to the example of $(NO)_2$ and $(CN)_2$, given by Spratley and Pimentel (274), the unpaired electron occupies an antibonding (π^*) orbital, the resulting bond is very weak. On the other hand, if the unpaired electron occupies a bonding orbital the resulting bond is strong. Since the unpaired electron in Cl and ClO_3 occupies a bonding orbital, the resulting Cl-F bond in FCl and $FClO_3$, respectively, should be strong, whereas those in FClO and $FClO_2$, derived from ClO and ClO_2, respectively, with an antibonding (π^*) electron (193), should be weak. These predictions are in excellent agreement with the data of Table II. As a consequence of the high electronegativity of fluorine, most of the electron density in the antibonding (π^*) orbital of ClO or ClO_2 is transferred to the F atom. For FClO and $FClO_2$, this results in a long and highly polar ClF bond with a significant negative charge located on F. Since at the same time electron density is removed from an antibonding orbital of the ClO_n part of the molecule, the bond strength of these ClO bonds is increased. As pointed out by Chi and Andrews (47) for ClClO, there is a marked difference in behavior between radicals with a first row element central atom and those with a second row element central atom. Owing to their larger size and polarizability, the second row elements facilitate a charge transfer and the XY_n stretching frequencies usually increase upon combination of XY_n with a halogen radical. For first row element central atoms, the corresponding frequencies usually show a slight decrease. It should be pointed out, however, that in both cases a highly polar and weak bond of the type $\overset{\delta^-}{F}\text{-}\overset{\delta^+}{XY_n}$ results provided the unpaired electron in the XY_n parent radical occupies an antibonding orbital. Supporting evidence for the above postulated charge transfer from XY_n to F was recently given by Parent and Gerry (220) for $FClO_2$.

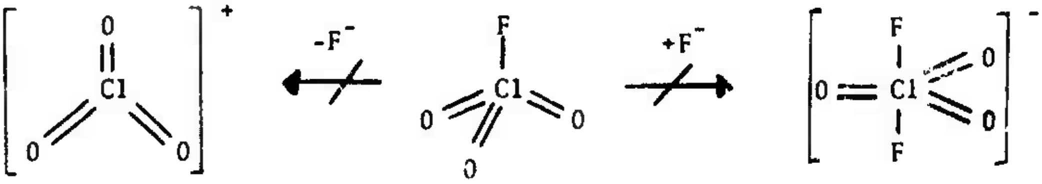
In summary, three types of bonding are invoked to rationalize the remarkable differences in Cl-F bonds encountered for chlorine fluoride oxides. These are: (i) conventional mainly covalent bonds, (ii) weak semi-ionic three center-four electron bonds, and (iii) weak highly polar $(p\text{-}\pi^*)\sigma$ bonds. It must be kept in mind, however, that all these bond descriptions are idealized extremes, used mainly for didactic reasons. The actual bonds can contain significant contributions from more than one kind of bonding and as a consequence, there is little black and white, but many shades of grey. Obviously, other bond models can also be used, as long as they adequately account for the experimental data. The steady increase in our knowledge about these compounds is bound to result in significant improvements of these rather empirical and intuitive bond models.

D. Amphoteric Nature, Tendency to form Adducts, and Reactivity

In many respects the chlorine oxyfluorides resemble the chlorine fluorides. For example, they exhibit little or no self-ionization, but are amphoteric. With strong Lewis acids or bases they can form stable adducts. The tendency to form adducts was found (64) not to be so much a function of the relative acidity of the parent chlorine oxyfluoride, but rather depends on the structure of the amphoteric molecule and of that of the anion or the cation formed. The preferred structures are the energetically favored tetrahedron and octahedron. Consequently, a trigonal bipyramidal molecule such as ClF_3O (64), exhibits a pronounced tendency to form either a stable pseudo-tetrahedral cation or a pseudo-octahedral anion according to:



On the other hand, tetrahedral $FClO_3$ does not form any adduct with either Lewis acids or bases (167, 209, 222):



Similarly, the chemical reactivity of these two chlorine oxyfluorides differs vastly. Whereas ClF_3O is extremely reactive and cannot be handled even in a well dried glass vacuum system, $FClO_3$ reacts only slowly with water.

III. Particular Compounds

A. Chlorine Monoxide Monofluoride, FClO

According to Ruff and Krug (242) FClO is formed during hydrolysis of ClF_3 as a solid melting at -70° to a red liquid which was unstable in the gas phase. However, no conclusive proof for the existence of FClO was given and it appears that the red color observed may have been due to the presence of chlorine oxides. Heras and coworkers (137) have proposed the formation of FClO as an intermediate in the thermal decomposition of $FClO_2$. More recent studies by Bougon and coworkers on the hydrolysis of ClF_3 (9, 36), by Christe on the reaction of ClF_3 with $HONO_3$ (53) and on the reaction of ClF_3O with SF_4 (60), by Pilipovich et al. on the photo-chemical synthesis of ClF_3O (228), and by Schack et al. on the reaction chemistry of ClF_3O (246), all pointed to the formation of FClO as an intermediate, unstable with respect to disproportionation according to:

$$2FClO \longrightarrow FClO_2 + ClF$$

Attempts to stabilize the intermediately formed FClO by complexing with a strong Lewis acid, such as AsF_5 to give $ClO^+AsF_6^-$, were also unsuccessful. Thus the controlled hydrolysis of $ClF_2^+AsF_6^-$ with stoichiometric amounts of H_2O in HF solution resulted only in the formation of $ClO_2^+AsF_6^-$ (53). This is not surprising since Lewis acids are known to catalize such disproportionation reactions.

Recently, Cooper and coworkers succeeded in obtaining direct evidence for the existence of free FClO in the gas phase (74). During a study of the hydrolysis of excess ClF_3 in a flow reactor, a novel species was observed in the infrared spectrum showing a PQR band centered at 1032 cm^{-1}. The species causing this band was found to decompose at ambient temperature with a half life of about 25 seconds into $FClO_2$ and ClF. If an excess of H_2O was used in the hydrolysis, no FClO but the expected (9, 36) ClO_2 was observed as the main product.

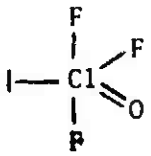
The results of Cooper, et al. were confirmed by a matrix isolation study by Andrews and associates (5). The latter authors observed the same species during the photolysis (2200-3600Å) of argon matrix isolated ClF and O_3 in the temperature range 4-15°K. All three fundamentals expected for a bent FClO molecule were observed and their assignment to FClO was confirmed by the measurement of the ^{18}O and ^{37}Cl isotopic shifts (see Table III) and by force field computations (see Table IV). For the force field computation an FClO bond angle of 120° was assumed, however, on the basis of the increased repulsion from the chlorine free valence electron pairs (see Section II, A) we would expect this angle to be less than the tetrahedral angle of 109°, but larger than that found for ClF_2^+ (103.17° in $ClF_2^+AsF_6^-$ (181) and 95.9° in ClF_2^+ SbF_6^- (88)). The small size of the molecule, its high dipole moment, the naturally occurring ^{37}Cl isotope, and its half life at ambient temperature make it ideally suited for a structure determination by micro-wave spectroscopy in a flow system.

The force field reported (5) for FClO allows some conclusions concerning the strength of the bonds in this molecule. Comparison of the ClO stretching force constant of FClO with those of the higher oxidation state species listed in Table I makes the FClO value appear surprisingly low. However, when compared to species of similar oxidation state and geometry (see Table V), FClO exhibits a value very much in line with our expectations for a ClO double bond. The ClF bond is relatively weak indicating that contributions from resonance structures such as II are significant as is also the case in the related $FClO_2$ molecule.

I II

The high ionicity of the Cl-F bond in these two chlorine fluoride oxides has been discussed above (Section II, C) in terms of a (p-π*)σ bond.

B. Chlorine Trifluoride Oxide, ClF_3O



Chlorine trifluoride oxide was discovered in 1965 at Rocketdyne by Pilipovich et. al. (226, 231). However, these results were not published until 1972 owing to classification. The same compound was independently discovered in 1970 by Bougon and coworkers (37, 39). A minor modification of Bougon's synthesis by Züchner and Glemser also produced (300) ClF_3O. All the data on ClF_3O, except for the short note by Züchner et al., were obtained either at Rocketdyne or at the Centre d'Études Nucléaires de Saclay.

Owing to its pseudo-trigonal bipyramidal structure with two highly polar Cl-F bonds, ClF_3O possesses only low kinetic stability. This renders it a powerful fluorinating and oxygenating agent requiring the use of metal or Teflon or Kel-F equipment for its handling.

1. Synthesis

Several synthetic routes to ClF_3O were developed at Rocketdyne (226, 228-231, 240). One of these involves the fluorination of Cl_2O at -78° according to:

$$2F_2 + Cl_2O \longrightarrow ClF_3O + ClF$$

$$3F_2 + Cl_2O \longrightarrow ClF_3O + ClF_3$$

When no catalyst is used or if KF and NaF are present as catalysts, ClF is the main by-product. When the more basic alkali metal fluorides, RbF and CsF, are used, ClF_3 is the favored coproduct. The formation of ClF_3 rather than ClF is presumably associated with the more ready formation of ClF_2^- intermediates with RbF and CsF. Yields of ClF_3O from Cl_2O are rather variable and may be affected by the particular alkali fluoride present. Yields of over 40% have been consistently obtained and have reached over 80% using either NaF or CsF. Since NaF does not form (64) an adduct with ClF_3O, stabilization of the product by complex formation does not seem to strongly influence the ClF_3O yields.

Owing to unpredictable explosions experienced with liquid Cl_2O, attempts were made to circumvent the Cl_2O isolation step. For this purpose, the crude Cl_2O, still absorbed on the mercuric salts, was directly fluorinated. Again, ClF_3O was formed, but its yield was too low to make this synthetic route attractive.

The fluorination of solid Cl_2O to ClF_3O proceeded at temperatures as low as -196° provided the fluorine was suitably activated by methods such as glow discharge. Unactivated fluorine did not interact with Cl_2O at -196°. The relatively low yield of ClF_3O (1 to 2%) makes this modification impractical.

The low-temperature fluorination of $NaClO_2$ produced ClF_3O in low yields (175, 226). However, the low yields and poor reproducibility make this route unattractive.

The method (176, 226, 229) most suitable for the preparation of ClF_3O on a larger scale involves the fluorination of chlorine nitrate at -35° according to:

$$2F_2 + ClONO_2 \longrightarrow ClF_3O + FNO_2$$

The main advantages of this process are: (1) less fluorine is required than in the fluorination reactions of Cl_2O yielding ClF_3 as a coproduct, (2) the great difference in the volatilities of the products FNO_2 and ClF_3O ($\Delta T_{bp} \sim 100°$) permits an easy separation by fractional condensation and (3) chlorine nitrate can be made more conveniently and, most importantly, does not appear to be hazardous in its handling. The yields of ClF_3O using $ClONO_2$ as a starting material are somewhat higher than those from Cl_2O.

In the fluorination of both Cl_2O and $ClONO_2$, side reactions compete with the actual fluorination step. These are caused by the thermal decomposition of the starting materials due to inefficient removal of the heat of reaction. Hence, the rate of the competing reactions is markedly affected by the reaction temperature. At reaction temperatures near or above ambient, the decomposition of the hypochlorite appears to be favored and little or no ClF_3O is formed, resulting in rapid, rather uncontrolled reactions. Apparently, thermal decomposition preceding the fluorination step yields only intermediates incapable of producing ClF_3O. Thus, in order to maximize the desired fluorination reaction, long reaction times at low temperature ($T<0°$) are indicated.

A convenient laboratory method for the synthesis of ClF_3O involves the uv photolysis of systems containing Cl, F, and oxygen containing starting materials. At Rocketdyne (228, 230, 240) ClF_3O was prepared from seven different systems, including a direct synthesis from the elements Cl_2, F_2, and O_2. Bougon et al. (37, 39) obtained ClF_3O in high yield from $ClF_3 + OF_2$. The latter synthesis was modified by Züchner et al. (300) by replacing ClF_3 with ClF_5.

In small scale operations, ClF_3O can conveniently be purified by complexing it with KF at room temperature. Impurities such as $FClO_2$, which do not form an adduct under these conditions can be pumped off. Pure ClF_3O can be obtained by vacuum pyrolysis at 50-70°, whereas compounds, such as ClF_3, which form a more stable KF adduct remain complexed (226).

A detailed kinetic study of the photolyses of the ClF_3-O_2 and of the Cl_2-F_2-O_2 system was carried out by Axworthy et al. (10). Contrary to the original report (228), the rate of ClF_3O formation was demonstrated to be the same for both systems, to increase with O_2 concentration, and to be independent of the irradiation time (see Figure 4). Furthermore, the rate of ClF_3O formation was shown to be proportional to the intensity of the 1847Å band of the Hg spectrum indicating that the dissociation of O_2 to two ground-state, ^3p, oxygen atoms is the primary photochemical process. The following mechanism was proposed which requires the photochemical dissociation of ClF_3 as well:

$$O_2 \xrightarrow{h\nu(1847\text{Å})} O + O$$

$$ClF_3 \xrightarrow{h\nu(2000\text{-}3500\text{Å})} ClF_2 + F$$

$$O + ClF_2 \longrightarrow ClF_2O$$

$$ClF_2O + F_2 \longrightarrow ClF_3O + F$$

The photolysis of ClF_3 was investigated under similar conditions. A photochemical steady state was quickly achieved where $[F_2] = [ClF] = \alpha[ClF_3]$ and α has a value of about 1 at low and of about 3 at high pressures. These results together with the known photochemical decomposition of OF_2 (113) explain why ClF_3O can be readily generated by the photolysis of so many different starting materials.

2. Molecular Structure

Although the exact geometry of ClF_3O has not yet been established, its approximate structure is known from vibrational and ^{19}F nmr spectroscopy.

Its uv spectrum has also been reported (228).

The ^{19}F nmr spectrum of ClF_3O was studied by several groups. A single signal at ϕ = -262 (226) or -253 (300) ppm was reported for liquid ClF_3O. For the gas, a singlet at ϕ = -327 ppm was observed (226). From nuclear relaxation time measurements, Alexandre and Rigny (3) were able to determine the chemical shift difference between the equatorial and the two axial fluorine atoms as 50 ± 2 ppm. They also obtained a value of 195 Hz for the mean Cl-F coupling constant and values for the exchange time between the fluorine atoms.

Vibrational spectroscopy (39, 55, 300) provided the best evidence for ClF_3O possessing a pseudo-trigonal bipyramidal structure of symmetry C_s, in which two fluorines occupy the axial and one fluorine, one oxygen, and a sterically active free valence electron pair occupy the equatorial positions (for a drawing of the structure see above). At Rocketdyne (55), a thorough spectroscopic study was carried out including the infrared spectra of gaseous, solid, and matrix isolated ClF_3O and the Raman spectra of the gas and the liquid. The observed spectra agree well with those reported by the other groups (39, 300), although the latter were incorrectly assigned. The best assignment (55) is given in Table VI. A normal coordinate analysis was also carried out for ClF_3O and a modified valence force field was computed (55) using the observed ^{35}Cl - ^{37}Cl isotopic shifts. Table VII summarizes the internal force constants thus obtained. The geometry of ClF_3O assumed for this computation was $D(ClO) = 1.42$, $R(ClF_{eq}) = 1.62$, and $r(ClF_{ax}) = 1.72$Å based on the known geometry of ClF_3 and Robinson's correlation between bond length and stretching frequency (236, 237). In the absence of exact structural data, the following ideal bond angle values were assumed: $\alpha\ (OClF') = 120$ and $\beta\ (OClF) = \gamma(FClF') = 90°$. However, increased repulsion from the free valence electron pair on chlorine and the double bonded oxygen should cause some deviations from this ideal structure (see Section II, A).

The force constants of greatest interest are the stretching force constants. The value of 9.37 mdyn/Å obtained for $f_{Cl=O}$ is similar to those computed for $FClO_2$ and ClO_2^+ (see Table I) indicating double bond character. The value of 2.34 mdyn/Å computed for the axial Cl-F stretching force constant f_r is almost identical with that of 2.34 mdyn/Å, previously calculated (63) for ClF_2^-. The corresponding interaction constant, $f_{rr'}$, is also very similar for both species. The relatively low value of f_r in ClF_2^- has previously been interpreted (63) in terms of semiionic three-center four-electron bonds. The same reasoning holds for the axial ClF bonds of ClF_3O. It should be pointed out, however, that in ClF_3O, enhancement of the ionic character of the axial ClF bonds is due to oxygen substitution, whereas in ClF_2^- it is due to the formal negative charge. The value of 3.16 mdyn/Å computed for the equatorial ClF bond of ClF_3O is considerably larger than that of the axial bonds indicating predominantly covalent bonding. These results are in excellent agreement with a generalized bonding scheme discussed in Section II, C and suggest that the overall bonding in ClF_3O might be described by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand and ignoring the second bond of the Cl=O double bond) is mainly due to a sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center four-electron pσ bond.

3. Physical Properties

Chlorine trifluoride oxide is colorless as a gas or liquid and white in the solid state. Some of its properties are summarized in Table VIII. The vapor pressure of the liquid can be described according to the Rocketdyne study (226) by the equation.

$$\log P_{(mm)} = 8.433 - \frac{1680}{T(^\circ K)}$$

or according to Bougon et al. (39) by the equation

$$\log P_{(mm)} = 8.394 - \frac{1655}{T(^\circ K)}$$

Vapor density measurements (39, 226) and mass spectroscopy (226, 300) were used to show that ClF_3O is monomeric in the gas phase. The relatively high boiling point and Trouton constant of ClF_3O imply its association in the liquid phase. More specific evidence about the nature of this association was obtained from the vibrational spectra recorded for the liquid and the solid and from a controlled diffusion experiment carried out for matrix isolated ClF_3O. It was concluded (55) that association appears to involve exclusively the axial fluorine atoms. This finding agrees with the association proposed (102) by Frey, et al. for the structurally related, trigonal-bipyramidal molecules SF_4 and ClF_3.

The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation. These properties are given for the range 0-2000°K in the Appendix.

4. Chemical Properties

Chlorine trifluoride oxide is stable at ambient temperature and can be stored and handled in well passivated metal, Teflon, or Kel-F containers without decomposition. Its thermal stability is intermediate between that of ClF_3 and ClF_5. When heated to 280-300° in a Monel cylinder (39, 226), or to 200° in a stainless steel cylinder, or to 350° in a flow system (226), ClF_3O decomposes according to

$$ClF_3O \longrightarrow ClF_3 + 1/2\ O_2.$$

It reacts rapidly with glass or quartz and, therefore, cannot be handled in standard glass vacuum systems (226). It reacts with numerous materials causing oxidation through both fluorination and oxygenation. With hydrogen-containing species, these reactions may occur at quite low temperature and with hydrocarbon-type compounds are generally explosive. However, many chlorine, fluorine, or oxygen substituted compounds, even with lower valent central atoms, react only slowly at ambient temperature, or not at all. Thus, no reaction was observed at room temperature between ClF_3O and chlorine, chlorine fluorides, chlorine oxyfluorides, and the nitrogen fluorides, FNO, FNO_2, NF_3, and N_2F_4 (246). However, elevated temperatures or uv photolysis have resulted in appreciable reaction of all compounds examined. With Cl_2 no interaction was detected at 25°, but at 200° the following reaction occurred

$$ClF_3O + Cl_2 \longrightarrow 3ClF + 0.5O_2$$

Chlorine monoxide and ClF_3O reacted slowly at room temperature (246) according to:

$$ClF_3O + Cl_2O \longrightarrow 2ClF + FClO_2$$

Similarly, $ClOSO_2F$ interacts with ClF_3O (246) according to:

$$ClF_3O + 2ClOSO_2F \longrightarrow S_2O_5F_2 + FClO_2 + 2ClF$$

$$\text{and} \quad ClF_3O + ClOSO_2F \longrightarrow SO_2F_2 + FClO_2 + ClF$$

All these reactions can be rationalized in terms of a reduction of ClF_3O to the unstable FClO (see Section III, A) which readily decomposes to $FClO_2$ and ClF. At elevated temperature $FClO_2$ can decompose further to ClF + O_2 (24, 137, 183).

Several reaction systems were discovered in which, in addition to fluorination, oxygenation also occurred. These include SF_4 (60); N_2F_4, HNF_2, and F_2NCFO (246, 248); and MoF_5 (35). In the following equations, the end products observed for the SF_4-ClF_3O reaction are underlined:

$$ClF_3O + SF_4 \xrightarrow[25°]{CsF} \underline{SF_6} + FClO$$

$$2FClO \longrightarrow \underline{FClO_2} + ClF$$

$$SF_4 + ClF \xrightarrow{CsF} \underline{SF_5Cl}$$

$$SF_4 + ClF_3O \longrightarrow \underline{SF_4O} + ClF_3$$

$$SF_4 + ClF_3 \longrightarrow \underline{SF_6} + ClF$$

In the MoF_5-ClF_3O system, both MoF_6 and MoF_4O were formed followed by adduct formation. With N_2F_4, an appreciable reaction rate was observed only above 100° according to:

$$ClF_3O + 2N_2F_4 \longrightarrow 3NF_3 + FNO + ClF$$

In addition to these products, small amounts of NF_3O were obtained. The yield of NF_3O from this reaction system could be increased to about 5% when uv irradiation was used. Higher yields of NF_3O (∿70%) could be obtained at low temperature from HNF_2 and ClF_3O according to:

$$ClF_3O + 2HNF_2 \longrightarrow [FClO] + 2HF + 2NF_2^{\cdot}$$

$$2NF_2^{\cdot} + [FClO] \longrightarrow \underline{NF_2Cl} + \underline{NF_3O}$$

with the side reactions: $2NF_2^{\cdot} \longrightarrow \underline{N_2F_4}$

$$2[FClO] \longrightarrow \underline{ClO_2F} + ClF$$

$$ClF + HNF_2 \longrightarrow \underline{HF} + \underline{NF_2Cl}$$

The reaction between difluoraminocarbonyl fluoride, F_2NCFO, and ClF_3O yielded again NF_3O and $ClNF_2$ in nearly equimolar amounts. However, the yields were much lower (20% based on ClF_3O consumed) with N_2F_4 being the main N-F containing product.

One reaction was discovered (246) in which ClF_3O did not act as an oxidizing but as a reducing agent. With the powerful oxidizer PtF_6 it reacted according to

$$ClF_3O + PtF_6 \longrightarrow ClF_2O^+PtF_6^- + 0.5F_2$$

The interaction of ClF_3O with HF, resulting in a fluoride ion abstraction to give the ClF_2O^+ cation (38) will be discussed below. With H_2O an excess of chlorine trifluoride oxide hydrolyzes (226) according to:

$$ClF_3O + H_2O \longrightarrow FClO_2 + 2HF$$

Mixtures of ClF_3O and ClF_5 (225) hold promise as an oxidizer in rocket propulsion.

As discussed in Section II, D, ClF_3O has an energetically unfavorable pseudo-trigonal bipyramidal structure. Consequently, it exhibits a pronounced tendency to form adducts with both strong Lewis acids and bases. Adducts containing the ClF_2O^+ cation (see Section III, C) were obtained (33-35, 38, 59, 64, 246, 300) with the following Lewis acids: BiF_5, SbF_5, AsF_5, PF_5, TaF_5, NbF_5, VF_5, PtF_5, UF_5, MoF_4O, SiF_4, BF_3, and HF. With WF_4O and UF_4O, no stable ionic products were formed (35) in spite of the fact that WF_4O is a stronger Lewis acid than MoF_4O. This is caused by the increased tendency of WF_4O to enter the following oxygen-fluorine exchange reaction:

$$ClF_3O + MF_4O \longrightarrow FClO_2 + MF_6 \text{ (M=W or U)}$$

Adducts containing the ClF_4O^- anion (see Section III, D) were prepared (56, 64, 300) by reaction of ClF_3O with the Lewis bases CsF, RbF and KF. With the weaker bases FNO and FNO_2 it does not interact even at -95° (64).

C. The Difluorooxychloronium (V) Cation, ClF_2O^+

Compounds containing the ClF_2O^+ cation with the following counterions are known: BiF_6^-, SbF_6^-, $Sb_2F_{11}^-$, AsF_6^-, PF_6^-, TaF_6^-, NbF_6^-, VF_6^-, PtF_6^-, UF_6^-, SiF_6^{--}, BF_4^-, HF_2^-, MoF_5O^-, and $Mo_2F_9O_2^-$ (33-35, 38, 59, 64, 246, 300).

1. Synthesis

With the exception of the PtF_6^- salt which was prepared from ClF_3O and PtF_6 (246 and Section III, B, 4), all the other salts were prepared by direct combination of ClF_3O with the corresponding Lewis acid. When the Lewis acid is a solid at the reaction temperature, or nonvolatile, it is advisable to either use a large excess of ClF_3O or anhydrous HF as a solvent to avoid polyanion formation (33-35, 64).

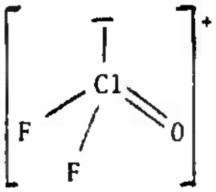
2. Molecular Structure

The ionic nature of ClF_3O·Lewis acid adducts was established by vibrational (33-35, 38, 59, 300) and ^{19}F nmr (61) spectroscopy.

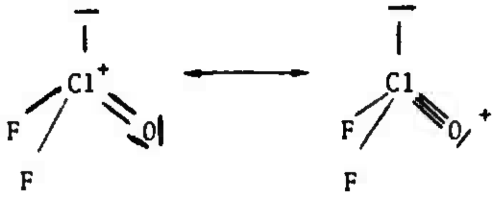
The nmr spectrum of $ClF_2O^+AsF_6^-$ in anhydrous HF showed (61) the characteristic quadruplet of AsF_6^- at $\phi = 67.5$ ppm in addition to a single signal due to rapidly exchanging HF and ClF_2O^+. Upon acidification of the HF solvent with AsF_5, a separate signal at $\phi = -272$ ppm was observed for ClF_2O^+ in addition to a single signal due to HF, AsF_6^-, and AsF_5. For $ClF_2O^+PtF_6^-$ in HF the ClF_2O^+ signal was also found at $\phi = -272$ ppm. The observation of a singlet for ClF_2O^+ shows the magnetic equivalence of the two fluorine atoms.

The vibrational spectra were reported (33-35, 38, 59, 300) for all of the above listed ClF_2O^+ salts. In addition to the bands characteristic of the anions, all spectra exhibited bands with frequencies and relative intensities similar to those shown in Table IX. These are characteristic for the ClF_2O^+ cation. The vibrational spectrum of ClF_2O^+ closely resembles that of isoelectronic SF_2O and therefore could be readily assigned. The only ambiguity in the assignment existed (34, 59) for the two deformation modes occurring in the 380-400 cm^{-1} region. Recent Raman polarization measurements (34) have shown that the 400 cm^{-1} band belongs most likely to ν_4 (A') and the 380 cm^{-1} band to ν_6 (A").

The spectroscopic evidence is consistent with the following structure of symmetry C_s for ClF_2O^+



A normal coordinate analysis was carried out (59) for ClF_2O^+ assuming the following geometry: $R_{ClO} = 1.41Å$, $r_{ClF} = 1.62Å$, $\beta(OClF) = 108°$, and $\alpha(FClF) = 93°$. A modified valence force field was computed and the results are given in Table X. As can be seen from Table 1, the ClO stretching force constant of ClF_2O^+ exhibits a high value, implying that the positive charge in ClF_2O^+ is partially located on the oxygen atom and that contributions from resonance structures such as (11) are significant.



(I) (II)

The ClF stretching force constant of ClF_2O^+ is within the range expected for a predominantly covalent ClF bond (see Table 1 and discussion in Section 11, C).

3. Properties

Except for the following salts, the above listed ClF_2O^+ salts are stable, white, crystalline solids. The UF_6^- salt is blue green and of marginal stability at ambient temperature. In HF solution or during exposure of the solid to a laser beam the UF_6^- anion is slowly oxidized by ClF_2O^+ to UF_6 (33). For MoF_5 this instability of the pentavalent metal towards oxidation to the hexavalent state is even more pronounced. When ClF_3O and MoF_5 are combined no stable MoF_6^- salt is formed, but MoF_6 and MoF_4O are the products with the latter being capable of forming stable adducts (35). The $ClF_2O^+PtF_6^-$ salt is a canary yellow solid (246). The VF_5 and PF_5 adducts exhibit dissociation pressures of 2.5 and 3.5 mm, respectively, at room temperature (33, 34). The $(ClF_2O^+)_2\ SiF_6^{--}$ salt is unstable at room temperature. It reaches a dissociation pressure of 760 mm at 31° and its dissociation pressure can be represented (64) by the equation

$$\log P_{mm} = 11.8018 - \frac{2712.3}{T(°K)}$$

From these data, the heat of dissociation, $\Delta H_d^\circ = 37.24$ kcal mol^{-1}, and the heat of formation of the solid adduct, $\Delta H^\circ_{f\ 298} = -495.7$ kcal mol^{-1} were obtained. For the latter the literature value was corrected by using the more precise value of -35.9 kcal mol^{-1} for the heat of formation of gaseous ClF_3O (see Table VIII). The adduct melts under its own vapor pressure at 50.5° (300).

The Raman spectrum of a solution of ClF_3O in anhydrous HF shows no bands due to ClF_3O but only those of ClF_2O^+ in agreement with the following ionization scheme (38):

$$ClF_3O + HF \longrightarrow ClF_2O^+ + HF_2^-$$

However, no attempts were reported to isolate the neat solid at low temperature and to examine its thermal stability.

The thermal stability of the adducts depends on the strength of the Lewis acids and decreases for the ClF_2O^+ salts in the following order: $SbF_5 > AsF_5 > BF_3 > VF_5 > PF_5 > SiF_4 > HF$ (33-35, 38, 64). The $ClF_2O^+MoF_5O^-$ salt, when heated in vacuum to 75-80° or when dissolved in anhydrous HF, is converted to ClF_2O^+ $Mo_2F_9O_2^-$ and ClF_3O. It was shown by Raman spectroscopy that this reaction is reversible. Heating of these compounds to higher temperatures results in decomposition to MoF_4O and ClO_2^+ salts of MoF_4O (35).

The x-ray powder patterns were reported for the XF_6^- type (34, 64, 246) and the BF_4^- (64) adduct and were tentatively indexed in the orthorhombic system.

D. The Tetrafluorooxychlorate (V) Anion, ClF_4O^-

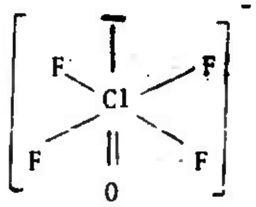
The existence of adducts between ClF_3O and CsF (56, 64, 300), RbF (64), and KF (64) has been reported. It was shown (56, 300) by vibrational spectroscopy that these adducts are ionic and contain the ClF_4O^- anion.

1. Synthesis and Properties

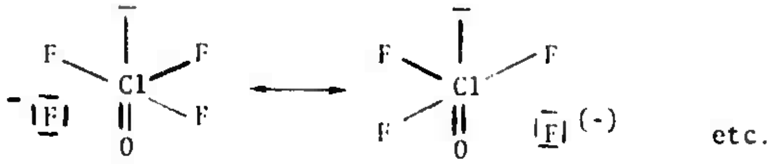
Chlorine trifluoride oxide was found (64) to readily combine with the alkali metal fluorides, CsF, RbF or KF, at room temperature to form white stable adducts. High conversion to the 1:1 adduct appears to be easiest for CsF. The use of a large excess of ClF_3O, agitation, and extended contact times are conducive to near complete conversions. These alkali metal ClF_4O^- salts have found use in the purification of ClF_3O (226). The thermal stability of the adducts decreases in the order CsF>RbF>KF. For example, the $KClF_4O$ salt can be decomposed by vacuum pyrolysis at 50-70° (226), whereas a much higher temperature is required for the pyrolysis of $CsClF_4O$.

2. Molecular Structure

The ionic nature of these adducts and the structure of the ClF_4O^- anion were established by vibrational spectroscopy (56, 300). It was shown (56) that the observed vibrational spectrum (see Table XI) is consistent with the following structure of symmetry C_{4v}:



A normal coordinate analysis was carried out (56) for ClF_4O^- assuming the following geometry: D(ClO) = 1.42Å, r(ClF) = 1.75Å, and all bond angles being 90°. The internal force constants obtained are listed in Table XII. Comparison with the stretching force constants of other chlorine fluorides oxides (see Table I) shows that the ClO bond in ClF_4O^- has full double bond character, but that the ClF bond is a rather weak semi-ionic 3 center-4 electron bond. This implies that the formal negative charge in ClF_4O^- is distributed almost exclusively over the four fluorine ligands. Resonance structures of the following type can be used to describe this effect:



E. Chlorine Pentafluoride Oxide, ClF_5O

The synthesis of ClF_5O was claimed in 1972 by Züchner and Glemser (300) by uv-photolysis of a mixture of ClF_5 and OF_2 in a nickel vessel fitted with a sapphire window. Although the authors failed to isolate a pure product, they "identified" ClF_5O in the product mixture by negative ion mass spectroscopy and ^{19}F nmr spectroscopy. However, the following properties attributed to ClF_5O do not agree with the general trends observed for the remaining chlorine fluorides and oxyfluorides: (i) low volatility at -78°C, (ii) a ^{19}F nmr resonance between -146 and -103 ppm relative to $CFCl_3$, and (iii) exchange broadening in the nmr spectrum even at -76°C. For ClF_5O, we would expect (i) a volatility comparable to those of ClF_5 (227) or SF_6 (279), (ii) an averaged ^{19}F nmr chemical shift of about -390 ppm (61), and (iii) the absence of intramolecular exchange owing to chlorine having its maximum coordination number and no free valence electron pair and owing to the lack of a plausible exchange mechanism.

Attempts to duplicate Züchner and Glemser's experiment (300) at Rocketdyne and the Centre d'Etudes Nucléaires de Saclay did not result in any evidence for ClF_5O. In the Rocketdyne study, the progress of the ClF_5-OF_2

photolysis in the temperature range -78° to 30°, using both unfiltered and Pyrex filtered uv radiation, was continuously monitored by gas chromatography. At the end of an experiment, the products were also separated by fractional condensation, in a Teflon-stainless steel vacuum system and were characterized by vibrational spectroscopy. It was shown that in the ClF_5-OF_2 system, when exposed to unfiltered uv radiation, ClF_5 rapidly decomposes to ClF_3 and F_2 and, therefore, yields only the same products obtainable from the photolysis of ClF_3-OF_2 mixtures, i.e., mainly ClF_3O.

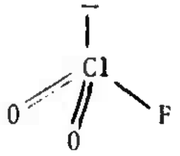
The ^{19}F nmr spectrum observed by Züchner and Glemser (300) might be rationalized in terms of a rapidly exchanging mixture of ClF_3 and ClF_3O as was pointed out to us by Dr. Bougon. To verify this, we have recorded the nmr spectra of ClF_3-ClF_3O mixtures over the temperature range 40 to -102°. It was found that mixtures of pure ClF_3 and ClF_3O yield separate signals for ClF_3 (at about ϕ = -118 and -10 ppm) and ClF_3O (at about -269 ppm) over the whole temperature range studied. However, upon addition of about 5 mole percent of HF, one single signal is observed for all three species with a chemical shift corresponding to the averaged chemical shifts of the three components. The temperature dependence of these spectra is similar to that reported by Züchner and Glemser (300). At 40° the signal was rather broad, became narrower with decreasing temperature, but broadened below -60° and shifted to higher field. At -102° a new and relatively narrow signal appeared significantly shifted upfield. The observed shifts and temperature dependence of these spectra are strongly dependent on the exact composition of the mixture.

The only remaining piece of evidence presented (300) for ClF_5O was the presence of a low intensity fragment due to ClF_4O^- in the negative ion mass spectrum of the crude reaction product. However, this fragment might be attributed to a recombination process in the mass spectrometer since a 52%

peak was also reported for F_2^- which can form only by recombination. Furthermore, negative ion spectra frequently show species of higher mass than that of the parent molecule due to attachment of other atoms or groups (28) as was recently also demonstrated for BrF_5, the negative ion spectrum of which shows a rather intense BrF_6^- fragment (194). In agreement with the above nmr interpretation, the observed (300) negative ion mass spectrum is best ascribed to a mixture of ClF_3O, ClF_3, $FClO_3$, and some ClF_5 with several higher mass peaks and F_2^- being due to recombination in the spectrometer.

Based on the cited evidence it appears unlikely that Züchner and Glemser (300) had indeed observed ClF_5O.

F. Chloryl Fluoride, $FClO_2$



Chloryl fluoride was first obtained in 1942 by Schmitz and Schumacher (256) by the low-temperature fluorination of ClO_2 with F_2. The compound itself has not been studied very intensively although it is the most frequently encountered reaction product in systems involving reactions of chlorine mono-, tri-, or pentafluorides with oxides or hydroxides. Its structure can be derived from a tetrahedron with a free valence electron pair of chlorine occupying one of the four corners. Compared to $FClO_3$, this structure is less symmetric, kinetically less stable, and contains a highly polar, long $(p-\pi^*)\sigma$ (see Section II, C) bond. Therefore at moderate temperatures, $FClO_2$ is far more reactive than $FClO_3$ in spite of its lower oxidation state.

1. Synthesis

In our experience (70), $FClO_2$ is most conveniently prepared by combining

$NaClO_3$ with an about equimolar amount of ClF_3 at -196° in a stainless steel cylinder and holding the mixture at room temperature for a day. Chloryl fluoride (bp = -6°) is thus obtained in high yield and can be separated from the by-products O_2, Cl_2 (bp=-33.8°) and unreacted ClF_3 (bp - 11.75°) either by fractional distillation or by repeated fractional condensation through a series of traps maintained at -95°, -112°, and -126°. This procedure is safe and does not involve the handling of any shock sensitive materials. This method is based on the previous reports by Engelbrecht and Atzwanger (92) and Smith and coworkers (270) that gaseous ClF_3 reacts with $KClO_3$ to give $FClO_2$ in high yield. The substitution of $KClO_3$ by $NaClO_3$ is significant since the product NaF does not form an adduct with ClF_3, whereas KF does. This decreases the amount of ClF_3 required for the reaction by 60 percent. By analogy with the known $KClO_3+BrF_3$ reaction (296) the idealized stoichiometry of the above reaction is:

$$6NaClO_3 + 4ClF_3 \longrightarrow 6NaF + 2Cl_2 + 3O_2 + 6FClO_2$$

The use of larger than stoichiometric amounts of ClF_3 is advisable to avoid the possible formation of shock sensitive chlorine oxides.

Woolf's original method (296) involved the use of $KClO_3$ and BrF_3 according to:

$$6KClO_3 + 10BrF_3 \longrightarrow 6KBrF_4 + 2Br_2 + 3O_2 + 6FClO_2$$

Although the yield of $FClO_2$ is high, it is very difficult to obtain pure colorless $FClO_2$ by this method. When $KClO_3$ is replaced by $KClO_4$ (285), $FClO_2$ was obtained in 97% yield according to:

$$3KClO_4 + 5BrF_3 \longrightarrow 3KBrF_4 + Br_2 + 3O_2 + 3FClO_2$$

The product purification problem for this system is analogous to that encountered for the $KClO_3$-BrF_3 system. The direct fluorination of $KClO_3$ with F_2 (30, 90, 92, 264) is not synthetically useful for preparing $FClO_2$, since the main product is always $FClO_3$. The interaction of $HOSO_2F$ with $KClO_3$ was reported (99) to produce $FClO_2$ in 30% yield. However, a study of this system carried out at Monsanto (198) failed to produce $FClO_2$, probably owing to formation of chloryl fluorosulfate.

An alternate route to $FClO_2$ involves the fluorination of chlorine oxides. The resulting $FClO_2$ is usually very pure but the handling of the shock sensitive chlorine oxides renders these methods unattractive, particularly for the production of larger amounts of material. The original synthesis of $FClO_2$ by Schmitz and Schumacher in 1942 (256) involved the direct fluorination of ClO_2. When F_2 was added at -80° to a quartz vessel containing ClO_2, followed hy slow warm up to 20°, $FClO_2$ was formed in a moderate reaction. The most favorable conditions were a reaction time of two minutes, a reaction temperature of 0°, and the use of a mixture consisting of 25.6 mm ClO_2, 54.0 mm F_2, and 540.7 mm air. The reaction was found to be homogenous and bimolecular (12). Modifications of this reaction involve passing gaseous F_2 through liquid ClO_2 at -50 to -55° (265) or, preferably, using $CFCl_3$ as a solvent at -78° (162, 254). Chlorine dioxide can also be fluorinated to $FClO_2$ by passing ClO_2 diluted with N_2 at room temperature over AgF_2 or CoF_3 or by passing ClO_2 through liquid BrF_3 at 30° (255).

The fluorination of chlorine oxides other than ClO_2 also produces $FClO_2$. Thus, $FClO_2$ was obtained in yields of up to 75% by fluorination of Cl_2O_6 with F_2 between 22 and 48°(7, 8). The high yield of $FClO_2$ coupled with the absence of $FClO_3$ indicates that the primary step is the decomposition of Cl_2O_6 to $2ClO_2+O_2$ followed hy the fluorination of ClO_2 to $FClO_2$. Similarly, the reaction between Cl_2O_6 and FNO_2, when carried out in $CFCl_3$ solution at 0°, produces $FClO_2$ in addition to $NO_2^+ClO_4^-$ (255). $FClO_2$ is also formed during the fluorination of Cl_2O_6 at -40° with BrF_3 or BrF_5 (294) or with HF (252). During the thermal decomposition of Cl_2O_7 in the presence of F_2 at 100-120° in quartz or Pyrex, $FClO_2$ if formed in addition to $FClO_3$ and ClF (98). The risk of explosions is somewhat reduced when in the ClO_2-AgF_2 reaction the ClO_2 is replaced by the less dangerous Cl_2O. The yield of $FClO_2$ was 35% (117, 182). Similarly, Cl_2O can be fluorinated at -78° with either ClF (53)

$$2Cl_2O + ClF \longrightarrow FClO_2 + 2Cl_2$$

or ClF_3O (246)

$$Cl_2O + ClF_3O \longrightarrow FClO_2 + 2ClF$$

Oxygenation of a chlorine fluoride, if possible, would be more attractive than fluorination of the shock sensitive chlorine oxides. A process for $FClO_2$ has been claimed by Faust et al. (97) furnishing $FClO_2$ in about 50% yield by simply heating a mixture of ClF and O_2 to 80-90°. However, attempts in our laboratory (70) to verify this synthesis failed. It appears, that the $FClO_2$ observed by Faust et al. (97) in their experiments was due to hydrolysis of ClF (9, 36, 70).

Numerous reactions have been reported in which $FClO_2$ is formed as a product. Most of these involve the interaction between a chlorine fluoride or oxyfluoride with an oxide or hydroxide. The oxidation state of the chlorine fluoride is not important since +I, +III, and +V compounds all yield $FClO_2$ owing to the tendency of the lower oxyfluorides, such as FClO, to disproportionate. The presence of excess chlorine fluoride is important to avoid formation of chlorine oxides. The following equations are typical examples for these types of reactions:

$$5ClF + 2H_2O \longrightarrow 4HF + FClO_2 + 2Cl_2 \qquad (9, 36)$$

$$2ClF_3 + 2H_2O \longrightarrow 4HF + FClO_2 + ClF \qquad (9, 36)$$

$$ClF_5 + 2H_2O \longrightarrow 4HF + FClO_2 \qquad (227)$$

$$ClF_3O + H_2O \longrightarrow 2HF + FClO_2 \qquad (226)$$

$$2ClF_3 + 2HONO_2 \longrightarrow 2HF + FClO_2 + ClF + 2FNO_2 \qquad (53)$$

$$ClF_5 + 2HONO_2 \longrightarrow 2HF + FClO_2 + 2FNO_2 \qquad (53)$$

$$\left.\begin{array}{l} ClF_3O + 2ClOSO_2F \longrightarrow S_2O_5F_2 + FClO_2 + 2ClF \\ ClF_3O + ClOSO_2F \longrightarrow SO_2F_2 + FClO_2 + ClF \end{array}\right\} \qquad (246)$$

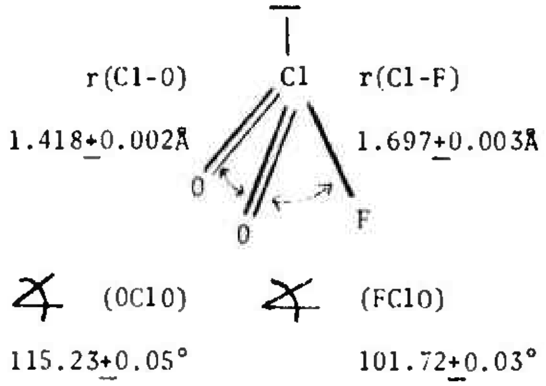
$$2ClF_3 + 3COF_2 \longrightarrow 2CF_4 + FClO_2 + CF_3OCl \qquad (288)$$

$$2ClF_3 + UO_2F_2 \longrightarrow UF_6 + FClO_2 + ClF \qquad (178, 179, 263)$$

$$6ClF + TeO_2 \longrightarrow TeF_5Cl + FClO_2 + 2Cl_2 \qquad (168)$$

2. Molecular Structure

The exact structure of $FClO_2$ was determined by Parent and Gerry (219, 220) using microwave spectroscopy. The molecule was shown to have C_s symmetry with the following internuclear parameters:



Values were also reported for the rotational constants, centrifugal distortion constants, and the chlorine nuclear quadrupole coupling constants of the three isotopic species $^{19}F\ ^{35}Cl\ ^{16}O_2$, $^{19}F\ ^{37}Cl\ ^{16}O_2$, and $^{19}F\ ^{35}Cl\ ^{16}O\ ^{18}O$. The molecular dipole moment was found to be 1.722± 0.03D.

The pyramidal structure of symmetry C_s for $FClO_2$ was also confirmed by vibrational spectroscopy. E. A. Smith, et al. (271) and Arvia and Aymonino (6) reported the infrared spectrum of the gas. D. F. Smith, et al. (270) studied the infrared spectrum of the gas, measured the ^{35}Cl-^{37}Cl and ^{16}O-^{18}O

isotopic shifts, recorded the Raman spectrum of the liquid, and carried out a normal coordinate analysis. The observed frequencies and their assignment are summarized in Table XIII.

Andrews and coworkers have recently reported (5) ^{35}Cl-^{37}Cl and ^{16}O-^{18}O isotopic shifts for the infrared spectrum of argon matrix isolated $FClO_2$. Tantot has studied in his thesis work (282) the infrared and Raman spectra of the gas, the Raman spectrum of the neat liquid and of HF solutions, and the infrared and Raman spectra of the solid.

Force fields for $FClO_2$ were computed by D. F. Smith et al. (270), Robinson et al. (238), So and Chau (272), and Tantot (282). The force fields computed by Smith et al. (270), So and Chau (272), and Tantot (292) agree relatively well for the two stretching force constants suggesting values of about 9.0 and 2.5 mdyn/Å for f_{ClO} and f_{ClF}, respectively. Except for Tantot's computation (282) which did not give plausible values for the deformation constants ($f_\alpha > f_\beta$), estimates were used for the geometry of $FClO_2$ which significantly deviate from the actual (220) geometry of $FClO_2$. Since the deformation constants are more likely to be angle dependent, a recomputation using the exact geometry and the observed (270) isotopic shifts is desirable.

Mean square amplitudes of vibration were calculated by Baran (14) based upon the frequencies and estimated geometry reported by Smith et al. (270). The uv absorption spectrum of $FClO_2$ was studied by Sicre and Schumacher (265) and Pilipovich et al. (228). From a mass spectroscopic study of $FClO_3$ (82) and using a value of 57 kcal mol^{-1} for the Cl-O bond energy, the electron affinity of $FClO_2$ was estimated to be $\geq$ 2.7 ev.

The ^{19}F nmr spectrum of liquid $FClO_2$ at -80° was recorded by Carter et al. (43) and Christe et al. (61) and consisted of a single peak at

ϕ = -328 or -315 ppm, respectively. A signal at ϕ = -332 ppm was tentatively assigned by Alexakos and Cornwell (2) to gaseous $FClO_2$.

The weak and highly polar Cl-F bond in FClO can be rationalized in terms of either a $(p-\pi^*)\sigma$ bond (see Section II, C) or a simple valence bond model (66) resulting in a resonance hybrid of the following canonical forms $FClO_2 \longleftrightarrow F^- + ClO_2^+$. It has been discussed in detail by Parent and Gerry (220), by Carter et al. (45), and in Section II, C of this review.

5. Physical Properties

Chloryl fluoride is colorless as a gas and liquid, and white as a solid. It is stable under normal conditions and some of its physical properties are summarized in Table XIV. Although precise measurements of some of its spectroscopic properties have recently been undertaken (220, 282), most of its physical properties are either still unknown or were determined (256) at a time when corrosion resistant metal - Teflon vacuum systems were not yet available. It was shown by vibrational spectroscopy (282) that solid $FClO_2$ between -263° and its melting point exists only in one phase. Neutron diffraction data obtained for this phase at -196° (282), were tentatively indexed based on a monoclinic unit cell with a = 8.7, b = 6.2, c = 4.7Å, α = 96°, and Z = 4, similar to that of ClF_3. Tantot et al. also studied (190, 282, 283) association effects in the liquid phase using vibrational spectroscopy, pulse ^{19}F nmr spectroscopy, and conductometric measurements. They suggest a dipolar dynamic interaction resulting in short-lived associated forms, and possibly a short-ranged local order observable on a vibrational, but not on an nmr time scale. The specific conductivity of $FClO_2$ in the temperature range -120 to 25°C varies according to Martin and Tantot (190) from 1.2 to 3.12μS cm^{-1} (= 10^{-6} ohm^{-1} cm^{-1}). The observed conductivity was taken as evidence for self ionization according to:

$$2FClO_2 \rightleftharpoons ClO_2^+ + ClO_2F_2^-$$

However, more conclusive evidence is required in view of the reluctance of

$FClO_2$ to form $ClO_2F_2^-$ anions (see Section III, F, 4) and of its known reactivity which renders the preparation and handling of very pure $FClO_2$ quite difficult. The vapor pressure of $FClO_2$ as a function of the temperature was measured by Schumacher et al. (256, 8) and is listed in Table XV. It can be described by the equation $\log P_{(mm)} = 8.23 - \frac{1412}{T(°K)}$. Several thermodynamic properties of $FClO_2$ have been estimated by Rips et al. (235) by means of correlation increments using only the boiling point of the substance. Whereas the correct boiling point of $FClO_2$ was used, its structure was erroniously assumed to be that of the hypofluorite F-O-Cl=O.

4. Chemical Properties

Chloryl fluoride is stable at ambient temperature in well passivated and dry containers. Its thermal decomposition in Quartz was studied by Schumacher et al. (24, 137). It reaches a measurable rate only above 300°. The decomposition reaction is monomolecular and its rate is pressure dependent. The activation energy was calculated to be 45 ± 2 kcal mol^{-1} and the rate constant was determined as $k_\infty = 2.3 \times 10^{13} \times 10^{-\frac{45000}{4.5T}}$ sec^{-1}. The following decomposition mechanism was proposed:

$$FClO_2 \longrightarrow FClO + O$$

$$O + FClO_2 \longrightarrow FClO + O_2$$

$$2FClO \longrightarrow 2ClF + O_2$$

However, based on our present knowledge about FClO (see Section III, A), a more likely decomposition mode for FClO in the above mechanism would be:

$$2FClO \longrightarrow ClF + FClO_2$$

The thermal decomposition of $FClO_2$ in Monel was studied (183) by Macheteau and Gillardeau. Decomposition to ClF and O_2 was observed at 100° (2.5% in 144h) and 200° (10% in 235h), but temperature ≥250° was required for rate measurements.

It was found that the decomposition is of first order and monomolecular at temperatures up to 285°. At 300° the reaction becomes second order. The calculated rate constants and half life times are summarized in Table XVI. The average activation energy between 250 and 285° was found to be 23.7 kcal mol^{-1}. The results at temperatures >300° agree with those reported by Schumacher et al. (137) for the quartz reactor. Glass is only slowly attacked by $FClO_2$ at room temperature, but traces of HF or H_2O catalyze the reaction (265, 90). Chloryl fluoride reacts with water (9, 36) and anhydrous nitric acid (53) according to:

$$2FClO_2 + H_2O \longrightarrow 2HF + 2ClO_2 + 1/2O_2$$

and

$$2FClO_2 + 2HONO_2 \longrightarrow 2HF + 2ClO_2 + N_2O_5 + 1/2O_2$$

Both reactions are relatively slow and do not go to completion in several hours at room temperature (9, 36, 53). In addition, some of the ClO_2 formed can decompose to Cl_2 and O_2 and the nascent oxygen can oxidize $FClO_2$ to $FClO_3$ which is resistant to hydrolysis:

$$FClO_2 + O \longrightarrow FClO_3$$

These results differ from the previous report by Schmeisser and Fink (255) that the reaction between $FClO_2$ and $HONO_2$ proceeds at -30° according to (46):

$$2FClO_2 + 2HONO_2 \longrightarrow NO_2ClO_4 + ClO_2 + NO_2 + 2HF$$

The statement made in Gmelin (122) and attributed to Bode and Klesper (30) that $FClO_2$ hydrolyzes to $FClO_3$ and H_2, is obviously incorrect. Hydrolysis of $FClO_2$ with base (253, 265, 296) proceeds according to:

$$FClO_2 + 2OH^- \longrightarrow ClO_3^- + F^- + H_2O$$

Traces of H_2O in $FClO_2$ generate a red brown color (256) which is probably due to ClO_2. With NH_3 it ignites at -78° and the end products are NH_4Cl and NH_4F (99). The observation of a weak band at 1052 cm^{-1} in the Raman spectra of

$FClO_2$ in dilute HF solutions in addition to strong bands due to $FClO_2$, was interpreted (283) in terms of the equilibrium:

$$HF + FClO_2 \rightleftharpoons ClO_2^+ + HF_2^-$$

With HCl, chloryl fluoride reacts (255) at -110° according to:

$$HCl + FClO_2 \longrightarrow HF + ClO_2 + 1/2Cl_2$$

With the stronger reducing agent HBr, it reacts explosively at -110° (99). With $HOSO_2F$, it forms at -78° (99) the stable ClO_2OSO_2F

$$FClO_2 + HOSO_3F \longrightarrow HF + ClO_2OSO_2F$$

but with $HOSO_2Cl$ at -90° only the decomposition products of the analogous ClO_2OSO_2Cl, i.e., SO_3, ClO_2, and Cl_2, are obtained. With anhydrous $HOClO_3$, the following reaction occurs (87, 252):

$$FClO_2 + HOClO_3 \longrightarrow HF + ClO_2OClO_3$$

Sulfur trioxide undergoes at -10° in $CFCl_3$ solution an insertion reaction to yield the orange solid (mp 27°) ClO_2OSO_2F (254). The same compound was also obtained (296) in the absence of a solvent:

$$FClO_2 + SO_3 \longrightarrow ClO_2OSO_2F$$

With the strong reducing agent SO_2, chloryl fluoride reacts explosively at -40° (99). When $FClO_2$ and I_2O_5 are combined at -196°, then warmed to -50 to -20°, I_2O_5 is dissolved with formation of O_2, IF_5, ClO_2, Cl_2O_6, and Cl_2O_7 (294).

Chloryl fluoride is a fluorinating agent and a moderately strong oxidizer. Thus it can fluorinate AsF_3 to the pentafluoride (294) according to:

$$3FClO_2 + AsF_3 \longrightarrow ClO_2^+AsF_6^- + 2ClO_2$$

Sulfur tetrafluoride is oxidized by $FClO_2$ at 50 to 300° to yield a mixture of SF_6, SF_4O, and SF_2O_2 (4). Similarly, N_2F_4 is fluorinated at 50° to give a mixture of NF_3, FNO_2, and FNO (223). Uranium tetrafluoride can be oxidized by $FClO_2$ to UF_5 and UF_6, the latter step requiring a reaction temperature between 50 and 150° (27). Metal chlorides are converted by $FClO_2$ into metal fluorides, most of which can form ClO_2^+ containing salts when an excess of $FClO_2$ is used. Typical examples are $SbCl_5$, $SnCl_4$, and $TiCl_4$ which are converted to $ClO_2^+SbF_6^-$, $(ClO_2^+)_2SnF_6^{--}$, and $(ClO_2^+)_2TiF_6^{--}$, respectively. Aluminum trichloride is coverted to AlF_3 (99, 255). Oxides, such as I_2O_5 (see above), SiO_2, Sb_2O_5, and B_2O_3 can be converted by $FClO_2$ at -10° to SiF_4, $ClO_2^+SbF_6^-$, and $ClO_2^+BF_4^-$, respectively (87). At 50-100°, UO_2F_2 reacts only slowly with $FClO_2$, but at 150° with contact times of 30 min, UF_6, Cl_2, and O_2 are formed (178, 179) according to:

$$4FClO_2 + UO_2F_2 \longrightarrow UF_6 + 2Cl_2 + 5O_2$$

Only one reaction was reported in which $FClO_2$ was oxidized from the penta- to the heptavalent state (50, 51, 69). The powerful oxidizer PtF_6 was required to obtain the following reaction:

$$2FClO_2 + 2PtF_6 \longrightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^-$$

Chloryl fluoride was converted to ClF_3O by uv-photolysis of systems containing mixtures such as $FClO_2$-F_2, $FClO_2$-ClF, $FClO_2$-ClF_3, and $FClO_2$-ClF_5 (228, 240). These reactions probably do not involve a direct oxygen-fluorine exchange in $FClO_2$, since ClF_3O can be synthesized by the same technique either directly from the three elements or from ClF_3 and oxygen (228).

Chloryl fluoride, like most of the other known chlorine fluorides and oxyfluorides, possesses amphoteric character. Owing to its weak and polar $(p\text{-}\pi^*)\sigma$ Cl-F bond (see Section II, C), it exhibits a much stronger tendency to form adducts with Lewis acids than with Lewis bases. The adducts with Lewis acids result in salts containing ClO_2^+ cations, and those with bases result in

$ClO_2F_2^-$ salts. Both ions are discussed in detail in Section G and H, respectively, of this review.

G. The Chloryl Cation, ClO_2^+

Although the chloryl cation does not contain a ClF bond and therefore, in a strict sense, does not belong to the family of the chlorine fluoride oxides, it was included in this review since it is a true derivative of $FClO_2$.

The existence of $FClO_2$ adducts with BF_3, AsF_5, PF_5, SbF_5, SiF_4, SO_3, and TaF_5 was first reported in 1954 by Schmeisser and Ebenhöch (87, 254) and Woolf (296). In 1957 Schmeisser and Fink obtained (99, 255) adducts with TiF_4 and SnF_4. In 1958 Clark and Emeleus described (73) the existence of a VF_5 adduct, and more recently Christe (50) obtained a PtF_5 and IrF_5 adduct.

In a previous review (253) the adducts of $FClO_2$ with the stronger Lewis acids, such as AsF_5 or SbF_5, were considered to be ionic and to contain ClO_2^+ cations. However, the corresponding BF_3 and PF_5 adducts were assumed to be molecular adducts. In 1968 Carter et al. (44) reported evidence for the existence of solvated ClO_2^+ ions in HSO_3F solution. Since then, vibrational spectroscopy has successfully been used to establish the ionic nature of solid $ClO_2^+AsF_6^-$ (43, 66), $ClO_2^+BF_4^-$ (66, 155, 157), $ClO_2^+SbF_6^- \cdot xSbF_5$ (42, 43, 155, 157), $ClO_2^+ClO_4^-$ (221), $ClO_2^+PtF_6^-$, and $ClO_2^+IrF_6^-$ (50).

1. Syntheses and Properties

Salts containing the ClO_2^+ cation can be prepared either by direct combination of $FClO_2$ with the corresponding perfluorinated Lewis acid with (254) or without a solvent (43, 66, 73, 155, 209, 296), by the interaction of $FClO_2$ with oxides (87), chlorides (99, 255), and lower (294) or higher (50) oxidation state fluorides, or by interaction of the perfluorinated Lewis acid with chlorine oxides (210, 247). The latter reactions, however, produce nonvolatile XF_3O as a by-product according to:

$$5Cl_2O + 3XF_5 \longrightarrow 2ClO_2^+XF_6^- + XF_3O + 4Cl_2 \quad (X = As, Sb)$$

$$5Cl_2O + 7SbF_5 \longrightarrow 2ClO_2^+Sb_3F_{16}^- + SbF_3O + 4Cl_2$$

$$5ClO_2 + 6SbF_5 \longrightarrow 4ClO_2^+SbF_6^- + 2SbF_3O + 0.5Cl_2$$

$$5ClO_2 + 14SbF_5 \longrightarrow 4ClO_2^+Sb_3F_{16}^- + 2SbF_3O + 0.5Cl_2$$

$$Cl_2O_6 + 2SbF_5 \longrightarrow ClO_2^+SbF_6^- + SbF_3O + FClO_3$$

Of the above approaches, the direct combination of $FClO_2$ with the corresponding Lewis acid is generally the most convenient. It yields well defined products, except for cases, such as SbF_5 (210) or TaF_5 (296), where polyanion formation is possible. From the $FClO_2$-SbF_5 system, depending on the ratio of the starting materials and the reaction conditions, only $ClO_2^+SbF_6^-$, $ClO_2^+Sb_3F_{16}^-$, or a mixture of the two but no $ClO_2^+Sb_2F_{11}^-$, were obtained (210).

The $FClO_2$ adducts are generally white solids, except for the yellow PtF_6^- and IrF_6^- salts (50) and for $FClO_2 \cdot SO_3$ which was reported to be a red-to-pale yellow low-melting solid (296). The properties of the latter compound indicate that in the liquid phase it may exist, by analogy with Cl_2O_6 (221), in its covalent form, i.e., O_2ClOSO_2F. The ionicity of chloryl fluorosulfate was also discussed (297) in a paper dealing with the liquid range of fluorosulfates. The literature reports on the thermal stability of the ClO_2^+ salts are rather sketchy. In addition to the data given in Table IV of Schmeisser's review (253), stability data were published only for the BF_3 and the SbF_5 adducts. The $FClO_2 \cdot BF_3$ adduct reaches a dissociation pressure of 1 atm. at 44.1° (66), whereas $ClO_2^+SbF_6^-$ (mp 220-225°) and $ClO_2^+Sb_3F_{16}^-$ (mp 50-53°) are stable up to 300 and 200°, respectively (209). The PtF_6^- and IrF_6^- salts of ClO_2^+ are stable at room temperature (50). It should be pointed out that Table IV of (253) implies that the thermal stability of the PF_6^- salt is higher than that of the BF_4^-. However, for related cations the reverse is true and it appears that the data cited might be inaccurate.

X-ray powder diffraction data have been reported for $ClO_2^+AsF_6^-$ (66) and $ClO_2^+SbF_6^-$ and $ClO_2^+Sb_3F_{16}^-$ (209). All the ClO_2^+ salts react violently with organic compounds and water. With stronger Lewis bases, such as NO, NO_2, $ClNO_2$ (99, 255), FNO, and FNO_2 (53, 68) the following type of displacement reactions can be carried out:

$$ClO_2^+AsF_6^- + NO_x \longrightarrow NO_x^+AsF_6^- + ClO_2$$

$$ClO_2^+AsF_6^- + ClNO_2 \longrightarrow NO_2^+AsF_6^- + ClO_2 + 1/2Cl_2$$

$$ClO_2^+PtF_6^- + FNO_x \longrightarrow NO_x^+PtF_6^- + FClO_2$$

2. Molecular Structure

The exact crystal structure of a ClO_2^+ salt has as yet not been published. However, the ClO_2^+ cation has been well characterized by vibrational spectroscopy (42, 43, 66, 155, 157). Characteristic frequencies and intensities for ClO_2^+ are summarized in Table XVII. The observed $^{35}Cl-^{37}Cl$ isotopic shifts were used to calculate the bond angle of ClO_2^+. It was shown that the cation is sharply bent and that the bond angle approximates 120° (66, 155). Force constants were computed as a function of the ClO_2^+ bond angle (66, 155) and the preferred set of constants is included in Table XVII. The value of 8.96 mdyn/Å obtained (66) for the ClO stretching force constant of ClO_2^+ demonstrates that the ClO bond has double bond character (see Table I).

H. The Difluorochlorate (V) Anion, $ClF_2O_2^-$

The existence of difluorochlorates of sodium, potassium, and barium was reported in 1965 by Mitra (195). However, this claim was met by skepticism since the reported synthesis involved the use of 40% aqueous hydrofluoric acid. In a subsequent paper (196), Mitra withdrew his claim. In 1969, Huggins and Fox reported (141, 142) the synthesis of $CsClF_2O_2$ from CsF and $FClO_2$, and a subsequent spectroscopic study by Christe and Curtis showed (54) that the vibrational spectrum of the adduct is consistent with a $ClF_2O_2^-$ anion of symmetry C_{2v}.

1. Synthesis and Properties

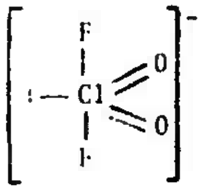
The synthesis of $CsClF_2O_2$ can be readily achieved by the interaction of dry CsF with excess $FClO_2$ at room temperature (141, 142). In the original work (141, 142), activated CsF was used which was obtained by vacuum pyrolysis of the CsF- hexafluoroacetone complex. The conversion of CsF to $CsClF_2O_2$ was 87%. When ordinary CsF (dried by fusion in a platinum crucible and powdered) was used (54) the conversion of CsF to $CsClF_2O_2$ was 73%.

The $CsClF_2O_2$ adduct is a white solid, stable at 25°. Vacuum pyrolysis at 80-100° yields CsF and $FClO_2$ (141) demonstrating that the formation reaction is reversible. It fumes in moist air and reacts explosively with water (141). Controlled hydrolysis (54) proceeds according to:

$$ClF_2O_2^- + H_2O \longrightarrow ClO_3^- + 2HF$$

2. Structure

The nature of the $CsClF_2O_2$ adduct was established (54) by vibrational spectroscopy. The observed spectra were consistent with a $ClF_2O_2^-$ anion possessing the following structure of symmetry C_{2v}



The observed bands and their assignments are summarized in Table XVIII. A normal coordinate analysis was carried out (54) for $ClF_2O_2^-$ assuming the following geometry: R(ClO) = 1.43Å, r(ClF) = 1.79Å, α(<OClO) = 120°, β(<OClF) = 90°, and (<FClF) = 180°. The actual bond angles are expected to deviate slightly from this ideal geometry owing to increased repulsion from

the free valence electron pair on Cl (see Section II, A). The internal force constants of $ClF_2O_2^-$ are summarized in Table XIX. As can be seen from Table 1 and the general discussion in Section II, C, the ClO bonds in $ClF_2O_2^-$ have double bond character and the ClF bonds are as expected, semi-ionic 3 center-4 electron bonds. The polarity of the latter is increased further by the formal negative charge and the high degree of oxygen substitution. The combination of these effects results in the lowest ClF stretching force constant value found to date for any ClF bond. As demonstrated for several other oxyfluoride anions (see Section III, D), the negative charge in $ClF_2O_2^-$ resides mainly on the ligands having the highest electronegativity, i.e., on the fluorine, and not on the oxygen atoms.

I. Chlorine Trifluoride Dioxide, ClF_3O_2

A compound having the empirical composition $(ClF_3O_2)_n$ was reported in 1962 by Streng and Grosse (128, 277, 278). It was obtained by the interaction of either Cl_2, ClF, or HCl with O_2F_2 between -154° and -143° or by uv photolysis of ClF_3 and O_2 mixtures at -78°. Both methods produced the same product, a violet unstable solid, which irreversibly decomposed above -78°. In a subsequent study of the infrared and visible spectra of these products Gardiner and Turner (108, 109) proposed the structure F_2ClOOF for the violet compound. However, both the synthetic and the spectroscopic study are not convincing and further work is required to establish the composition and structure of this violet species.

A well defined and characterized compound having the composition ClF_3O_2 and showing no resemblance to Streng and Grosse's violet compound, was reported in 1972 by Christe (52). This work is an excellent example for the perfection of handling techniques for extremely reactive oxidizers. Thus the physical, chemical, and spectroscopic properties of ClF_3O_2 and of its $ClF_2O_2^+$ adducts were determined from a total of 2.2 mmol of material. The fact that ClF_3O_2 as a powerful oxidizer is readily reduced to $FClO_2$ which cannot be removed from ClF_3O_2 by simple fractionation (see below), rendered the handling of this compound particularly difficult.

1. Synthesis and Properties

The synthesis of ClF_3O_2 is best described by the following reaction sequence:

$$2FClO_2 + 2PtF_6 \longrightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^-$$

Several side reactions compete with this reaction and the yield of $ClF_2O_2^+$ varies greatly with slight changes in the reaction conditions (50, 68). The ClF_3O_2 is then displaced from its $ClF_2O_2^+$ salt according to:

$$ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- + 2FNO_2 \longrightarrow 2NO_2^+PtF_6^- + ClF_3O_2 + FClO_2$$

Chloryl fluoride is slightly less volatile than ClF_3O_2. Therefore, most of it can be removed from ClF_3O_2 by fractional condensation in a -112° trap. The remaining $FClO_2$, however, has to be removed by complexing with BF_3:

$$ClF_3O_2 + FClO_2 + 2BF_3 \longrightarrow ClF_2O_2^+BF_4^- + ClO_2^+BF_4^-$$

Since $ClF_2O_2^+BF_4^-$ is stable (69) at 20°, whereas $ClO_2^+BF_4^-$ is not (66) the latter can be pumped away at 20°. The resulting pure $ClF_2O_2^+BF_4^-$ is then treated with an excess of FNO_2 and the evolved ClF_3O_2 and unreacted FNO_2 are readily separated by fractional condensation through a series of -126 and -196° traps:

$$ClF_2O_2^+BF_4^- + FNO_2 \longrightarrow NO_2^+BF_4^- + ClF_3O_2$$

The overall yield of pure ClF_3O_2 based on the PtF_6 used in step 1 was found to be about 10 mol %.

Pure ClF_3O_2 is colorless as a gas or liquid and white as a solid. Some of its measured (68) physical properties are summarized in Table XX. Near its melting point the vapor pressure above liquid ClF_3O_2 was found to be reproducibly lower than expected from the vapor pressure curve given in Table XX. This indicates that close to the melting point some ordering effect occurs in the liquid.

The measured vapor density of ClF_3O_2 indicates that no appreciable association occurs in the gas phase. Its relatively low boiling point and Trouton constant imply little association in the liquid phase. This prediction is confirmed by the vibrational spectra of the liquid and the neat solid which exhibit only minor frequency shifts when compared to the spectra of the gas and the matrix-isolated solid. This finding is somewhat surprising since both ClF_3 (102) and ClF_3O (55, 226) show a pronounced tendency to associate in the liquid and solid state through bridges involving the axial fluorine atoms.

The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given below assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation. These properties are given for the range 0-2000°K in the Appendix.

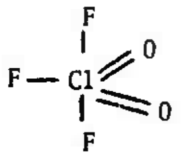
Chlorine trifluoride dioxide resembles chlorine fluorides and oxyfluorides in its corrosive and oxidizing properties. It must be handled in systems consisting of corrosion resistant metals, Teflon, or sapphire. It appears to be marginally stable in a well passivated system at ambient temperature. It is a strong oxidative fluorinator as evidenced by its tendency to fluorinate metal surfaces to metal fluorides with $FClO_2$ formation. It reacts explosively with organic materials and care must be taken to avoid such combinations. The hydrolysis of ClF_3O_2 was not quantitatively studied; however, on one occasion a slight leak in an infrared gas cell containing ClF_3O_2 resulted in the formation of $FClO_3$ and HF indicating the following reaction.

$$ClF_3O_2 + H_2O \longrightarrow FClO_3 + 2HF$$

Chlorine trifluoride dioxide forms stable adducts with strong Lewis acids, such as BF_3, AsF_5, or PtF_5 (51, 68, 69). These adducts have ionic structures containing the $ClF_2O_2^+$ cation (see Section III, I, 2). The high stability of these adducts can be explained by the change from the energetically unfavorable trigonal-bipyramidal structure of ClF_3O_2 to the more favorable tetrahedral $ClF_2O_2^+$ configuration (see Section II, D). Contrary to ClF_3 (295), but by analogy with ClF_3O (64), it does not form stable adducts with FNO or FNO_2 at temperatures as low as -78°. This was demonstrated by the various displacement reactions where ClF_3O_2 and unreacted FNO or FNO_2 could be readily removed from the reactor at -78°. With the stronger base, CsF, it did not form a stable adduct but decomposed to $FClO_2$ and F_2. However, only relatively small amounts of ClF_3O_2 were available for the complex formation study with CsF and the possibility of preparing salts such as $Cs^+ClF_4O_2^-$ under more favorable reaction conditions cannot entirely be ruled out.

2. Molecular Structure

Vibrational (57) and ^{19}F nmr (68) spectroscopy were used to establish for ClF_3O_2 the following structure of symmetry C_{2v}, which according to semi-empirical LCAO MO SCF calculations (239) is most stable:



The ^{19}F nmr spectrum of liquid ClF_3O_2 was measured in the temperature range -20 to -80°. It showed at all temperatures one partially resolved signal centered at -413 ppm below the external standard $CFCl_3$. The observed signal is in excellent agreement with an AB_2 pattern with $J/\nu_0\delta = 1.0$ and $J_{FF} = 443$ Hz. The low chemical shift of -413 ppm for ClF_3O_2 is in excellent agreement with a heptavalent chlorine fluoride and the fluorine-fluorine coupling constant of 443 Hz observed for ClF_3O_2 is similar to that of 421 Hz observed for the structurally related ClF_3 (61). Additional support for the above structure was derived from the fact that the B_2 part of the AB_2 pattern occurs downfield from the A part as expected for the axial fluorine atoms in a trigonal-bipyramidal arrangement (120, 203).

The infrared spectra of gaseous, solid, and matrix-isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 were reported (57) and are summarized in Table XXI. The observed data are in excellent agreement with the above model of symmetry C_{2v}. A normal coordinate analysis was carried out for ClF_3O_2 assuming the following geometry: $D(ClO) = 1.40$ Å, $R(ClF_{eq}) = 1.62$ Å, $r(ClF_{ax}) = 1.72$ Å, $\alpha(OClO) = 130°$, $\beta(F_{eq}ClF_{ax}) = \delta(OClF_{ax}) = 90°$, and $\gamma(OClF_{eq}) = 115°$, based on the observed geometries of ClF_3 and $FClO_3$ and a correlation between ClO bond length and stretching frequency. The deviation of the OClO bond angle from the ideal 120° was estimated by comparison with the known geometries of SF_4O and $FClO_3$. The force constants thus obtained are summarized in Table XXII. The value of the ClO stretching force constant (9.23 mdyn/Å) is in excellent agreement with that of 9.37 mdyn/Å found for ClF_3O (55) and the general valence force field values of 9.07 and 8.96 mdyn/Å reported for $FClO_2$ (270) and ClO_2^+, (66) respectively. The values of the ClF stretching force constants are comparable to those previously reported for the related pseudo-trigonal-bipyramidal molecules ClF_3 (102) and ClF_3O (55) and are summarized in Table XXIII. In all three molecules, the stretching force constant of the equatorial ClF bond is significantly higher than that of the two axial bonds, although their relative difference decreases with increasing oxidation state of the central atom. The difference in bond strength between equatorial and axial bonds implies significant contributions from semi-ionic 3-center 4-electron bonds to the axial ClF bonds. This bonding scheme has been discussed in detail for the related pseudo-trigonal-bipyramidal ClF_2^- anion in Section II, C.

Inspection of Table XXIII also reveals that the value of f_r does not depend exclusively on the oxidation state of the central atom. Obviously, formal negative charges (as in the anions) and increasing oxygen substitution facilitate the formation of semi-ionic bonds and, hence, counteract the influence of the oxidation state of the central atom. It is interesting to note that the relative contribution from semi-ionic bonding (see Section II, C) to the axial ClF bonds $[=(f_R - f_r)/f_R]$ decreases from ClF_3 to ClF_3O and ClF_3O_2 (see Table XXIII). This can be attributed to the decreasing electron density around the central atom with increasing oxidation state, thus making it more difficult to release electron density to the axial fluorine ligands as required for the formation of semi-ionic bonds.

The bonding in ClF_3O_2 might be described by the following approximation (49). The bonding of the three equatorial ligands, ignoring the second bond of the Cl=O double bond, is mainly due to an sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic 3-center 4-electron pσ bond.

J. The Difluoroperchloryl Cation, $ClO_2F_2^+$

The existence of the $ClO_2F_2^+$ cation in the form of its PtF_6^- salt was reported in 1972 by Christe (51). In a subsequent paper (69) a full account was given of the synthesis and properties of the PtF_6^-, AsF_6^-, and BF_4^- salts of $ClO_2F_2^+$.

1. Synthesis and Properties

It was found (50) that PtF_6 and $FClO_2$, when combined at -196° and allowed to warm up slowly to 25°, interacted according to

$$2FClO_2 + 2PtF_6 \longrightarrow ClO_2F_2^+PtF_6^- + ClO_2^+PtF_6^-$$

The yield of $ClO_2F_2^+$ was not 50% as expected from the above equation, but generally about 25% owing to the competing reaction

$$2FClO_2 + 2PtF_6 \longrightarrow 2ClO_2^+PtF_6^- + F_2$$

In some of the experiments, small amounts of $ClF_6^+PtF_6^-$ or ClF_5 and $FClO_3$ were observed, depending on the exact reaction conditions. The formation of some $FClO_3$ is not surprising since it is known that $FClO_2$ readily interacts with nascent oxygen to yield $FClO_3$ (9, 36, 53).

Attempts to suppress the competing reaction by changing the reaction conditions (rapid warm-up from -196 to -78° and completion of the reaction at -78°) resulted on one occasion in an entirely different course for the reaction

$$6FClO_2 + 6PtF_6 \longrightarrow 5ClO_2^+PtF_6^- + ClF_6^+PtF_6^- + O_2$$

Further modification of the reaction conditions (rapid warm-up of the $FClO_2$-PtF_6 mixture from -196 to either -78 or 25° and completion of the reaction at 25°) did not produce detectable amounts of either $ClO_2F_2^+$ or $ClF_6^+PtF_6^-$, but only $ClO_2^+PtF_6^-$ and ClF_5, F_2, and O_2. This indicates that the nature of the reaction products is more influenced by the warm-up rate of the starting materials from -196 to about -78° than by the final reaction temperature. Slow warm-up favors the formation of $ClO_2F_2^+$, whereas rapid warm-up yields ClF_6^+ or ClF_5 and F_2 (50).

The BF_4^- and AsF_6^- salts were prepared (69) according to:

$$ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^- + FNO_2 \longrightarrow FClO_2 + ClF_3O_2 + 2NO_2^+PtF_6^-$$

Unreacted FNO_2 and some of the $FClO_2$ could be separated from ClF_3O_2 by fractional condensation. The remaining $FClO_2$ was separated from ClF_3O_2 by complexing with BF_3. Since the resulting $ClO_2^+BF_4^-$ has a dissociation pressure (66) of 182 mm at 22.1° while $ClO_2F_2^+BF_4^-$ is stable, the former salt could be readily removed by pumping at 20°. Conversion of $ClO_2F_2^+BF_4^-$ to the corresponding AsF_6^- salt was accomplished through displacement of BF_4^- by the stronger Lewis acid AsF_5:

$$ClO_2F_2^+BF_4^- + AsF_5 \longrightarrow ClO_2F_2^+AsF_6^- + BF_3$$

All three salts, $ClO_2F_2^+PtF_6^-$, $ClO_2F_2^+AsF_6^-$, and $ClO_2F_2^+BF_4^-$, are solids, stable at 25°, and react violently with water or organic materials. The PtF_6^- compound is canary yellow, while those of AsF_6^- and BF_4^- are white. The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state and the X-ray powder diffraction patterns of $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ have been reported (69). The pattern of the former was tentatively indexed on the basis of an orthorhombic unit cell with $a = 5.45$, $b = 7.23$, and $c = 13.00$ Å. Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume, a plausible average volume of 16 Å^3 per F or O atom was obtained.

The thermal stability of $ClO_2F_2^+BF_4^-$ is higher than that of $ClO_2^+BF_4^-$ (66), $ClF_2^+BF_4^-$ (259) or other similar salts. The pronounced tendency of ClF_3O_2 to form stable adducts with Lewis acids is in good agreement with the correlations between the stability of an adduct and the structure of the parent molecule and its ions (see Section II, D). Thus, tetrahedral $ClO_2F_2^+$ (see below) should be energetically much more favorable than trigonal-bipyramidal ClF_3O_2.

2. Molecular Structure.

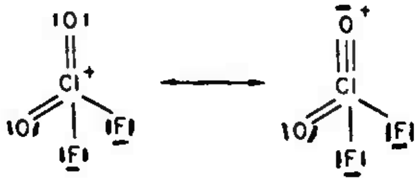
The structure of $ClO_2F_2^+$ salts was established by ^{19}F nmr and vibrational spectroscopy (69).

In the ^{19}F nmr spectrum of $ClF_2O_2^+PtF_6^-$ in anhydrous HF a broad singlet at -310 ppm relative to external $CFCl_3$ was tentatively assigned (61) to $ClF_2O_2^+$. Subsequent studies (69) of $ClF_2O_2^+BF_4^-$ and $ClF_2O_2^+AsF_6^-$ confirmed the original assignment. The spectrum of $ClF_2O_2^+BF_4^-$ in HF showed a strong temperature dependence. At 30° it consisted of a single peak at 185 ppm relative to external $CFCl_3$. With decreasing temperature the peak at first became broader and then separated at about 0° into three signals at -301 ($ClO_2F_2^+$), 146 (BF_4^-), and 194 ppm (HF) which became narrower with further decrease in temperature. The observed peak area ratio of approximately 2:1 for the 146 and -301 ppm signals confirmed their assignment to BF_4^- and $ClO_2F_2^+$, respectively, and proved the ionic nature of the $ClF_3O_2 \cdot BF_3$ adduct in HF solution.

The spectrum of $ClF_2O_2^+AsF_6^-$ in HF (which was acidified with AsF_5) consisted of two resonances at -307 ($ClO_2F_2^+$) and 105 ppm (HF, AsF_5, AsF_6^-), respectively. Rapid exchange among HF, AsF_5, and AsF_6^- preempted the measurement of the $ClO_2F_2^+$ to AsF_6^- peak area ratio (69).

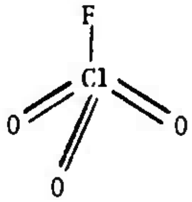
The vibrational spectra of the BF_4^-, AsF_6^-, and PtF_6^- salts of $ClO_2F_2^+$ were recorded for both the solids and HF solutions (69). It was shown that all three salts are ionic containing in addition to the anions, a common cation. The vibrational spectrum of this cation closely resembled that of SO_2F_2 indicating a pseudo-tetrahedral structure of symmetry C_{2v}. The observed frequencies together with the stretching force constants obtained from Cl isotopic shifts are listed in Table XXIV. Inspection of Table I shows that $ClO_2F_2^+$ possesses the highest value known for a ClO stretching force constant. This is not surprising, since the central atom in $ClO_2F_2^+$ has a high oxidation state (+VII), highly electronegative ligands, and a formal positive charge (cation). The influence of these factors on f_{ClO} has been discussed in Section II, C.

By analogy with ClF_2O^+ (59), the only other known species exhibiting a f_{ClO} value of similar magnitude, contributions from the resonance structure



might be invoked to explain the high f_{ClO} value. The value of the ClF stretching force constant (4.46 mdyn/Å) falls within the range expected for a predominantly covalent ClF bond in a cation having a central atom with a +VII oxidation state.

K. Perchloryl Fluoride, $FClO_3$



Perchloryl fluoride, the acyl fluoride of perchloric acid, was first obtained (31) by Bode and Klesper in 1951 by the action of F_2 on $KClO_3$ at -40°, but believed to be ClO_2OF. In 1952 it was prepared by Engelbrecht and Atzwanger (91) by electrolysis of $NaClO_4$ in anhydrous HF and was correctly identified. In the mid-fifties it became commercially available from Pennsalt Chemical Corporation and can be purchased in research quantities from Ozark Mahoning Company. Owing to its remarkably low reactivity and high specific impulse (see Section III, K, 5) it received considerable interest as a rocket propellant oxidizer, resulting in a rather thorough study of its properties. Unfortunately, its high vapor pressure (53 atm at Tc = 95°) and coefficient of expansion rendered it inferior to other oxidizer candidates. Owing to its relative inertness (it hydrolyzes only slowly in water) it has found use as a fluorinating agent in organic chemistry. In addition to the general reviews, listed in the Introduction and brief reviews in Japanese (205) and Chinese (48), reviews have been published by Pennsalt (224), Gall (105), and Khutoretskii et al. (158) which are devoted exclusively to $FClO_3$. The inertness of $FClO_3$ is due to its energetically favorable pseudo-tetrahedral configuration, its highly covalent and strong Cl-F bond (see Section II, C), and its extremely small dipole moment of 0.023 D. Combined, these properties give it a high kinetic stability in spite of its low thermodynamic stability ($\Delta H^{\circ}_{f298} = -5.7$ kcal mol^{-1}).

1. Synthesis

Perchloryl fluoride can be prepared by electrolysis of a saturated solution of $NaClO_4$ in anhydrous HF with a current efficiency of 10% (91, 92).

Fluorination of solid $KClO_3$ by F_2 (30, 31) produces $FClO_3$, $FClO_2$, ClF, Cl_2O_6, Cl_2, and O_2 (90, 92). The yields of $FClO_3$ were about 45% based on the F_2 used (92). When the fluorination was carried out below -20°, yields of $FClO_3$ as high as 60% were obtained (264). The fluorination of $NaClO_3$ with F_2 can also be carried out in aqueous solution at 25 - 75° resulting in a 50% yield of $FClO_3$ (299, see also 125). Replacement of F_2 by other fluorinating agents, such as ClF_3, BrF_3, or SbF_5, gives mainly $FClO_2$ and Cl_2 and only low yields of $FClO_3$ (92). Purification of crude $FClO_3$ by washing of the products condensible at -196° with an alkaline $Na_2S_2O_3$ solution produces material containing less than 1.5% of impurities (92).

The thermal decomposition of Cl_2O_7 at 100° in the presence of F_2 produces a mixture of $FClO_3$ and $FClO_2$ in a yield of about 75% (98). Similarly, the fluorination of either Cl_2O_6 or Cl_2O_7 with SbF_5 produces $FClO_3$ in high yield (210) according to:

$$Cl_2O_6 + 2SbF_5 \longrightarrow ClO_2^+SbF_6^- + SbF_3O + FClO_3$$

and

$$Cl_2O_7 + nSbF_5 \longrightarrow SbF_3O\cdot(SbF_5)_{n-1} + 2FClO_3$$

The fluorination of NO_2ClO_4 by ClF_3 at room temperature results in the formation of $FClO_3$ and smaller amounts of $FClO_2$, ClO_2 and $ClNO_2$ (25). Perchloryl fluoride is also formed by the interaction of $FClO_2$ with nascent oxygen (9, 36, 53) and in the reaction of gaseous ClF_3 with UO_2, U_3O_8 and UO_3 (149) and with UO_2F_2 (263), or by the reaction of $ClF_2^+BiF_6^-$ with metal oxides (78). Xenon dioxide tetrafluoride, XeO_2F_4, is capable of oxidizing either ClF_3 or ClF_5 to $FClO_3$ (143). Almost quantitative yields of $FClO_3$ and $R_fC\genfrac{}{}{0pt}{}{=O}{-F}$ can be obtained by the alkali metal fluoride catalyzed decomposition of the corresponding $R_fCF_2OClO_3$ at slightly elevated temperatures (249).

The most convenient and commercially attractive methods for preparing $FClO_3$ involve the fluorination of perchlorates. Heating of $KClO_4$ to 70-120° in an excess of SbF_5 produces $FClO_3$ in 50% yield (89). The yield of $FClO_3$ can be increased to 90% and the reaction temperature can be lowered to 20-50°, when a mixture of HF-SbF_5 is used (292, 293). Slightly lower yields were obtained when the HF solvent was replaced by AsF_3, IF_5, or BrF_5.

Most of the commercial processes are based on the use of $HOSO_2F$. This method was proposed in 1956 by Barth-Wehrenalp (21). Evolution of $FClO_3$ starts at 50° and goes to completion at 85-110°. The yields of $FClO_3$ vary from 50-80% (21, 22, 162, 163) and, if necessary, the $HOSO_2F$ can be regenerated (22). If desired, the reaction can be carried out in glass apparatus. The influence of certain additives on the yield of $FClO_3$ was studied (81). The addition of 5-25% of SbF_3 to the $HOSO_2F$ increases the yield of $FClO_3$ to 90% and higher, but hinders the regeneration of $HOSO_2F$. The addition of HF-BF_3 increases the $FClO_3$ yield to 85%, but requires elevated pressure. Zinc, aluminum, silver, and lead fluorides were found to decrease the yield of $FClO_3$.

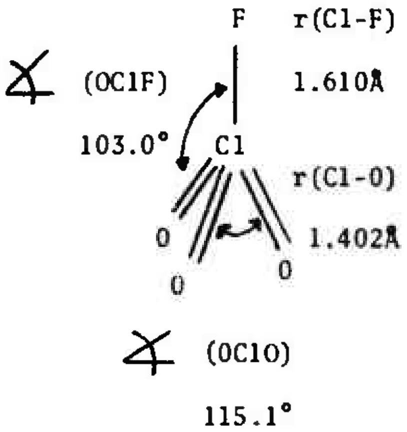
The highest yield of perchloryl fluoride (97%) was achieved with a mixture of fluorosulphonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction. Commercial reagents are used and their additional purification is not necessary; unlike all the previous methods the preparation of perchloryl fluoride by this method can be carried out at room temperature. At high temperature (100-135°) the reaction time is 1-10 min in all, which allows the process to be carried out continuously in a packed column. The purity of product obtained after the usual purification reaches 98% and over, air and carbon dioxide being present as trace impurities (23).

The exact mechanism of the reaction between ClO_4^- and superacids has as yet not been established, although numerous comments on it were published (19, 20, 167, 253, 292, 298). Based on our present understanding of superacid chemistry (67, 119, 216) and of the complex formation of $FClO_3$ (see Section III, K, 4) a mechanism involving ClO_3^+ as an intermediate is very unlikely. Furthermore, the high yields of $FClO_3$ (up to 97%) would be surprising in view of the expected instability of ClO_3^+. In our opinion, other mechanisms, such as the one shown, involving protonated perchloric acid (166) are more plausible:

$$\begin{array}{lcl}
2HF + 2SbF_5 & \longrightarrow & 2H_2F^+ + 2SbF_6^- \\
2H_2F^+ + ClO_4^- & \longrightarrow & H_2OClO_3^+ + 2HF \\
H_2OClO_3^+ + HF & \longrightarrow & FClO_3 + H_3O^+ \\
\hline
ClO_4^- + 3HF + 2SbF_5 & \longrightarrow & FClO_3 + H_3O^+ + 2SbF_6^-
\end{array}$$

2. Molecular Structure

The structural parameters of $FClO_3$ were determined by Clark, Beagley, and Cruickshank (72) by gas phase electron diffraction. The molecule has symmetry C_{3v} and the following bond angles and distances:



Owing to its small dipole moment, $FClO_3$ exhibits only a very weak microwave spectrum (171, 173). Since only the J = 4 → 5, K = 3 and the J = 6→7, K = 3 and K = 6 transitions were observed, a complete structure determination was not possible. However, the estimated geometry and dipole moment are in good agreement with the exact values measured by other methods. The following frequency (MHz) values and constants were obtained:

	$F\,^{35}ClO_3$	$F\,^{37}ClO_3$
J = 4 ← 5, K = 3	52585.97 ± 0.05	52560.4 ± 0.3
J = 6 ← 7, K = 3	73619.40 ± 0.05	73583.94 ± 0.05
J = 6 ← 7, K = 6	73618.72 ± 0.05	
B_o	5258.682 ± 0.005	5256.149 ± 0.005
D_J	0.0014 ± 0.0002	
D_{JK}	0.0018 ± 0.0003	
eqQ	-19.2 ± 0.5	-15.4 ± 1.5

The rotational constants, B_o, are in good agreement with the values obtained from the high resolution infrared spectrum (184) of the 549 and 589 cm^{-1} fundamentals.

The dipole moment of $FClO_3$ was determined by dielectric-relaxation measurements (192) as 0.023 ± 0.003 D and from the $J_{11} \rightarrow 12$ transition in a resonant cavity at 126196 MHz (101) as 0.025 ± 0.003 D. This low dipole moment indicates that the electronegativity of F and the ClO_3 group are comparable, thus resulting in a high degree of covalency for the Cl-F bond.

The ^{19}F nmr spectrum of $FClO_3$, according to Brownstein (41) consists of a partially resolved quartet ($J_{ClF} \sim 310$Hz) of equal intensity at $\phi = -241.5$ ppm. The lack of rapid quadrupole relaxation indicates a highly symmetric electric field around the central atom in good agreement with the small dipole moment observed for $FClO_3$ (see above). The temperature dependence of the ^{19}F nmr spectrum of $FClO_3$ was studied by Bacon et al. (13). An expression for the line broadening was derived, and a value of 1.0 kcal mol^{-1} was obtained for the activation energy of molecular reorientation. A value of 278 ± 5 Hz was calculated for $J35_{ClF}$. According to Agahigian et al. (1), the ^{19}F resonance of $FClO_3$ occurs at $\phi = -287$ ppm. The ^{35}Cl and ^{19}F nmr spin-lattice relaxation times and rotational diffusion in liquid $FClO_3$ were measured by Maryott et al. (96, 191) using pulse techniques.

The mass spectrum of $FClO_3$ was measured (82, 138, 234). The vertical ionization potential and the $F-ClO_3$ bond dissociation energy were found to be 13.6 ± 0.2 eV and $\sim$ 60 kcal mol^{-1}, respectively. The average ClO bond dissociation energy and the heat of formation were estimated (82) to be 60 and -5.3 kcal mol^{-1}, respectively.

The uv absorption spectrum of $FClO_3$ was reported by Sicre and Schumacher (265) and Pilipovich et al. (228).

The vibrational spectrum of $FClO_3$ has been well characterized. The infrared spectrum was thoroughly analyzed by Lide and Mann (174) and two of the fundamentals (ν_3 and ν_5) were studied at high resolution by Madden and Benedict (184). The Raman spectra of the liquid and of the gas were reported by Powell et al. (233) and Dunlap et al. (85) and by Claassen and Appelman (71), respectively. The observed fundamentals together with their assignment are summarized in Table XXV and are in excellent agreement with a molecule of symmetry C_{3v}. The infrared spectrum of $FClO_3$ has also been reported by Engelbrecht et al. (92), Pennsalt (224), Smith et al. (271), and Karelin et al. (154). A correlation of ClO stretching frequencies (236) and force constants with bond lengths and bond orders was given by Robinson (237), however his plots and assumptions must be thoroughly updated before being used. Absolute infrared intensities were reported for $FClO_3$ by Kharitonov et al. (157). Quantum Mechanical studies of the atomic, bond, and molecular polarizabilities were carried out by Nagarajan and Redmon (204). Numerous force fields (107, 140, 154, 157, 200, 204, 245, 273) were computed for $FClO_3$, but owing to the lack of sufficient experimental data, no unique solution was obtained. Values of about 9.4 and 3.9 mdyn/Å for the ClO and the ClF stretching force constant, respectively, appear to us most reasonable. Mean square amplitudes of vibration of $FClO_3$ were calculated by Müller et al. (200-202) and Nagarajan and Redmon (204). Müller et al. (200) have also computed the Coriolis zeta constants for $FClO_3$, however their values differ significantly from those given by Hoskins (140).

The high resolution photoelectron spectrum of $FClO_3$ was studied by DeKock et al. (80). The results from this study, including ab initio self-consistent field molecular orbital calculations of the electronic structures, are summarized in Tables XXVI and XXVII. These calculations indicate considerable participation by 3d orbitals of the Cl atom, although they tend to overestimate the importance of 3d orbitals in bonding by correcting for some inadequacy in the s and p basis. Results of molecular orbital calculations were also reported by Hillier et al. (129, 139) and Ionov and Ionova (146). The latter authors calculated the electron density distribution in $FClO_3$ as $Q_{Cl} = +0.83$, $Q_O = -0.23$, and $Q_F = -0.14$ using the geometry, the ionization potential of the molecule and of the free atoms, and the orbital exponents of the Slater functions as input data.

X-ray diffraction data were reported by Tallman et al. (280, 281) for solid $FClO_3$ at liquid air temperature. The data were indexed in terms of a tetragonal unit cell with a = 7.66 and c = 5.31Å, Z = 4, and d = 2.18 g/cm^3. Barberi (16, 17) has shown that solid $FClO_3$ exists between its melting point and -196°

in only one solid phase. Based on entropy calculations, Koehler and Giauque (160) suggested that there is a high degree of disorder in the arrangement of the F and O atoms in crystallinic $FClO_3$.

3. Physical Properties

Some of the physical properties of $FClO_3$ are summarized in Table XXVIII. In the Appendix the temperature dependence of some of the thermodynamic properties is given (147). In addition to these data, the viscosity of gaseous $FClO_3$ between 50° and 150° was reported (218). Some thermodynamic properties of $FClO_3$ were calculated (235) using only the boiling point of the compound and correlation increments.

$FClO_3$ is white as a solid and colorless as a liquid and gas. It possesses a characteristic sweetish odor (92). Its toxicity is moderate and comparable to that of CH_2CHCN or Cl_2. Tests on mice showed an acute vapor toxicity (LD/50) of 630 ppm at 4 hr exposure time. Exposure of monkeys to 40 ppm $FClO_3$ in air for three months resulted in enlarged spleens and lungs together with some evidence of red cell destruction (224).

The dielectric strength of $FClO_3$ is outstanding and over a broad pressure range is about 30% higher than that of SF_6. During irradiation with ^{60}Co γ-rays the dielectric strength decreases only by 5% (46). The correlation between negative ion formation and electric breakdown of $FClO_3$ was studied by Hickam and Berg (138) by mass spectroscopy. Perchloryl fluoride has been used as an insulator in high-voltage systems.

Perchloryl fluoride was reported (195, 185, 205, 206, 224) to be sparingly soluble (1-3g/l at 1 atm and 25°) in a wide variety of polar and nonpolar solvents, such as aqueous solutions, alcohols, ketones, esters, ethers, and aromatic and halogenated solvents. However, more recent measurements by Golub et al. (124) show that these solubilities are substantially (severalfold) higher. When working with larger amounts of $FClO_3$ in organic solvents, all necessary precautions should be taken since mixtures of this kind are potentially explosive. Hammond et al. (132-134) have extensively studied the extremely weak electron acceptor-donor (ball-plane) interactions between $FClO_3$ and aromatic hydro-and fluorocarbons. Several inorganic acid halides, $HOSO_2F$, PCl_3, $POCl_3$, SO_2Cl_2, $SOCl_2$, $TiCl_4$, and $SiCl_4$ dissolve gaseous $FClO_3$ to the extent of 20-30g/l at 25° and 1 atm pressure (105).

Liquid perchloryl fluoride is a typical nonpolar solvent. Most inorganic and organic salts are insoluble in it. Conversely, most covalent, essentially nonpolar substances, boiling within about 50°C of perchloryl fluoride, are completely miscible, eg, chlorine, boron trifluoride, sulfur hexafluoride, silicon tetrafluoride, phosgene, nitrous oxide, chlorine trifluoride, chlorofluorocarbons, silicon tetrachloride, sulfuryl chloride, dinitrogen tetroxide, and thionyl chloride (105)

Blends of perchloryl fluoride with halogen fluorides are homogeneous and stable. When these are used as storable liquid oxidizers for rocket propulsion, the halogen fluoride usually confers hypergolicity, increased density, and lowered vapor pressure; while the perchloryl fluoride provides oxygen needed for efficient combustion of carbon in the fuel or of certain metal additives. The mixtures are thermally stable and their compatibility with container materials is determined mainly by the halogen fluoride. The density and vapor pressure of perchloryl fluoride-chlorine trifluoride blends have been summarized in tables by Gall (105). The miscibility and compatibility of $FClO_3$ at low temperatures was studied by Streng (276) for O_2, O_3, O_2F_2, ClF, ClF_3, SF_4, SF_6, CF_3Cl, and C_4H_{10}.

4. Chemical Properties

Owing to its pseudo-tetrahedral configuration, its highly covalent strong

Cl-F bond, and low dipole moment, $FClO_3$ possesses high kinetic stability in spite of ΔH_f° being only -5.7 and ΔG_f° being positive (11.5 kcal mol^{-1}). This is reflected in its high thermal stability and its reluctance to hydrolyze. It is not shock sensitive and at room temperature is relatively inert. At elevated temperature, however, or in conditions supplying a sufficient amount of activation energy, it is a powerful oxidizer (211).

Perchloryl fluoride is thermally stable up to about 400°. The thermal decomposition of $FClO_3$ in quartz at pressures between 5 and 930 mm and temperatures between 465 and 495° was studied by Gatti et al. (112). They found that the decomposition reaction

$$2FClO_3 \longrightarrow 2ClF + 3O_2$$

is unimolecular and homogeneous with an activation energy of 58.4 ± 2 kcal mol^{-1}. The rate constant at 495.4° was found to be $k = 9.25 \times 10^{-4}$ sec^{-1} and the following decomposition mechanism was suggested:

$$FClO_3 \longrightarrow FClO_2 + O$$

$$O + FClO_3 \longrightarrow FClO_2 + O_2$$

$$FClO_2 \longrightarrow ClF + O_2$$

The decomposition kinetics were also calculated by Usmanov and Magarra (287) using a dimensionless molecular transfer equation. Perchloryl fluoride can be heated almost to the softening point of glass without explosion (92).

Hydrolysis of $FClO_3$ is very slow even at 250-300° (92). For quantitative hydrolysis, heating of $FClO_3$ with concentrated aqueous hydroxide solution to 300° in a sealed tube is required.

$$FClO_3 + 2NaOH \longrightarrow NaClO_4 + NaF + H_2O$$

For quantitative analysis, $FClO_3$ can conveniently be reduced at 25° by an alcoholic solution of KOH resulting in dissolved KF and a precipitate of $KClO_4$ (224).

The reaction of $FClO_3$ with metallic sodium or potassium starts only at ∿300°, although it proceeds vigorously (92). At room temperature $FClO_3$ is unreactive with a considerable number of gases, liquids, and solids. Again, however, if sufficient activation energy, such as heating to 100-300°, is supplied, violent reactions usually occur. With reducing agents, oxides, fluorides, and chlorides are formed. Typical examples are H_2, N_2O, H_2S, SO_2, SCl_2, PCl_3, CaC_2, KCN, NaI, KSCN, $CH_2=CCl_2$, and hydrocarbons (122, 158, 224). Using dilute mixtures, the H_2S - $FClO_3$ reaction can be controlled and the following products are obtained (224):

$$3FClO_3 + 4H_2S \longrightarrow 4SO_2 + 3HF + 3HCl + H_2O$$

In the spectra of H_2S - $FClO_3$ and H_2 - $FClO_3$ flames, bands due to S_2, SO_2, OH and to ClO, OH, respectively, were observed (177). With HCl at 200-300°, the following gas phase reaction occurs:

$$FClO_3 + 7HCl \longrightarrow HF + 4Cl_2 + 3H_2O$$

Many inorganic ions are oxidized by $FClO_3$ in aqueous solution (224). The oxidation rate often depends on the pH of the solution and the temperature. For example, the oxidation of KI in the presence of $NaHCO_3$ is barely detectable, in caustic soda a slow oxidation occurs, and in 0.1 molar mineral acid one observes quantitative reaction within four hours according to (92):

$$FClO_3 + 8I^- + 6H^+ \longrightarrow Cl^- + F^- + 4I_2 + 3H_2O$$

Other ions oxidized by $FClO_3$ include NO_2^-, SO_3^{--}, and CN^- which are converted to NO_3^-, SO_4^{--}, and NCO^-, respectively (105, 122, 224).

Whereas $FClO_3$ is rather inert towards most compounds, including gaseous NH_3, at room temperature, it reacts (92, 186, 187) easily with liquid NH_3 at -78° or its aqueous solutions according to:

$$FClO_3 + 3NH_3 \longrightarrow NH_4F + NH_4NHClO_3$$

The reaction is complete in several hours and in liquid NH_3 it is greatly accelerated by $NaNH_2$ (186, 187). From the ammonium perchloryl amide, which could not be isolated in pure form, the corresponding Ag^+, Cs^+, and K^+ salts and K_2NClO_3 and Cs_2NClO_3 have been obtained. These salts, especially when dry, are impact and friction sensitive.

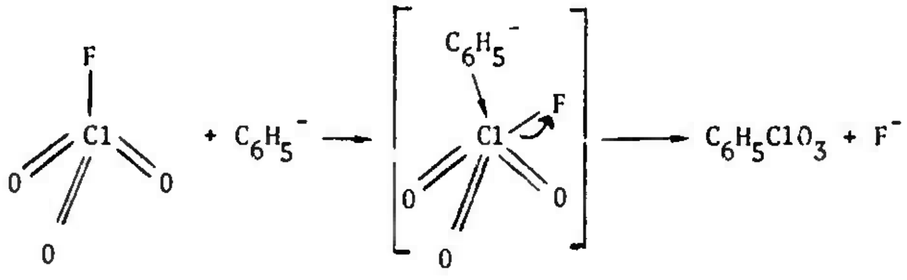
Perchloryl fluoride does not attack glass at moderate temperatures, but decomposes at 25° on contact with activated SiO_2 or Al_2O_3, particularly in the presence of small amounts of H_2O. With other surface active materials, such as charcoal, ignition may take place. However, there is no reaction at room temperature with synthetic zeolites. It passes freely through a 4Å molecular sieve, but is completely absorbed by a 5Å molecular sieve (188). Most combustible substances in contact with liquid $FClO_3$ form shock sensitive explosive compositions. Generally, metal oxides, fluorides, or chlorides do not react with $FClO_3$ at temperatures up to 400° (186). Lalande reported (164) that $FClO_3$ oxidizes UF_4 to UF_6. However, a subsequent study by Rude et al. (241) showed that an intermediate uranium oxyfluoride is formed which disproportionates to UF_6 and UO_2F_2. Photolysis of mixtures of $FClO_3$ with F_2 or ClF_5 produces ClF_3O (228, 240).

Perchloryl fluoride shows no tendency to form adducts with either strong Lewis acids or bases. This behavior has been rationalized in Section II. D. The binary systems of $FClO_3$ with BF_3, PF_5, AsF_5, SbF_5, or SO_3 were studied by Lang (167), at Pennsalt (222), and by Nikitina and Rosolovskii (209). Similarly, at Pennsalt (222) no evidence was found for complexing of $FClO_3$ with either CsF or FNO_2.

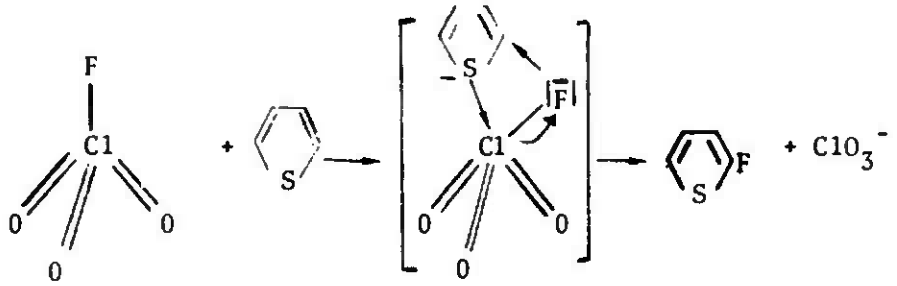
Anhydrous $FClO_3$ does not corrode most of the common metals, but in the presence of moisture slow hydrolysis may occur causing corrosion (40, 122, 127, 224). The compatibility of various elastomers with 1:1 mixtures of $FClO_3$ and N_2F_4 was studied by Green et al. (126) and Grigger et al. (127).

In reactions with organic compounds, $FClO_3$ behaves as either an oxident or a one or two-centre electrophile which, depending on the reaction conditions, can be used for the introduction of either fluorine, a ClO_3 group, or both fluorine and oxygen. A large number of publications have appeared on this subject and have been extensively reviewed by Khutoretskii et al. (158). Additional general information can be found in references (105, 122, 169, 262, 284). Since a systematic coverage of this subject is beyond the scope of this review, we will only give examples of the most important type of reactions, in addition to references to some of the more recent publications not covered in the previous reviews.

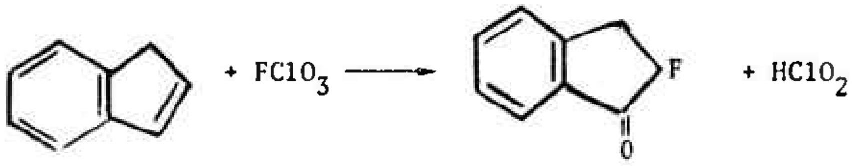
Since $FClO_3$ is highly susceptible to nucleophilic attack at the chlorine atom, it reacts readily with anions. These reactions are relatively well understood and Sheppard has proposed (261) a general mechanism for these reactions, by which the most nucleophilic center in the anion (oxygen or other hetero atom related to carbon) always attacks the chlorine and never the more electronegative fluorine. For localized nucleophiles (like alkoxides), simple fluoride ion displacement occurs, but for the mesomeric ions (ambient electrophiles) an intramolecular (cyclic) transfer of F^- can occur in the intermediate to give a C-F bond. The high energy gained by the formation of the C-F bond provides a strong driving force for this fluoride transfer and fluorine never has to achieve a highly unfavorable energy state with positive charge. This mechanism explains why penyllithium reacts with $FClO_3$ to give perchloryl-benzene, whereas 2 lithiothiophene gives 2-fluorothiophene in high yield (257):



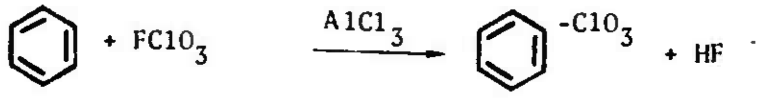
and



Compounds having a cyclic double bond conjugated with an aromatic ring are capable of reacting with $FClO_3$ to give α-fluoroketones. This type of reaction was named oxofluorination and in it $FClO_3$ acts as a two-centre electrophile as shown for indene (207):



In the presence of Friedel Crafts catalysts, such as $AlCl_3$, $FClO_3$ can be used for introducing a ClO_3 group (perchlorylation) into an aromatic ring (145) according to:



Hydrogenolysis (258) of perchloryl aromatic compounds yields ArH and not ArOH, thus confirming the presence of a C-Cl bond. Another useful reaction of $FClO_3$ involves the replacement of the active hydrogens of methylene compounds by fluorine (144, 262, 284). A typical example is the fluorination of malonic esters:

$$CH_2(COOR)_2 \xrightarrow{+FClO_3} CF_2\,(COOR)_2$$

Since $FClO_3$ is a very mild fluorinating agent, it has found widespread use for the selective fluorination of compounds, such as steroids.

The reaction of cyclic amines with $FClO_3$ is similar to that of $FClO_3$ with NH_3 (see above). For example, the following reaction takes place with piperidine (110):

For additional recent publications dealing with the use of $FClO_3$ as a reagent for the synthesis of organic compounds see references (94, 103, 111, 114-116, 153, 159, 212, 213, 217, 250, 286, 289, 290).

5. Uses

The most thoroughly studied application of $FClO_3$ is its use as an oxidant. The spectra of fuel - $FClO_3$ flames were studied (177) and the flame speed in mixtures of CH_4 with air and $FClO_3$ was measured (131). The H_2 - $FClO_3$ flame was found (251) to be readily controllable with a low background and useful as an excitation source for flame photometry. For rocket propulsion, the performance of either neat $FClO_3$ or combinations with other oxidizers, such as halogen fluorides (11, 26), was studied and typical performance data (105) are given in Table XXIX. Small amounts of ClF_3 can be added to neat $FClO_3$ to provide self-ignition. The performance of $FClO_3$ as an oxidizer is similar to that of N_2O_4 (105, 136) and the burning rate of solid propellants is increased by $FClO_3$ (267). It has also been proposed to use an acetylene - $FClO_3$ torch for cutting and welding of metals. in the Sterling cycle engine, in high-pressure gas generation for turbine drive, in fuel cells, and in explosives similar to

Sprengel liquid O_2 - carbon powder combinations (106), and as a deodorant in aerosol sprays (170). However, the latter application appears very doubtful in view of the substantial toxicity of $FClO_3$ (see above).

The use of $FClO_3$ as a chemical reagent for the introduction of fluorine or a ClO_3 group has been discussed in detail in Section III, K, 4 and is of special value for the synthesis of fluorine containing steroids. The polymerization of ethylene under a pressure of hundreds of atm and a temperature of about 200° in the presence of $FClO_3$ has been patented (135).

There are patents on the use of $FClO_3$ as a heat transfer medium in refrigeration (165) and as an insecticide-fungicide (123). Thanks to its ability to intensively absorb slow electrons (138), $FClO_3$ can be used as a gaseous insulator. Its dielectric properties are superior to those of SF_6 and it hardly deteriorates on exposure to γ-irradiation (104).

General information on shipping, handling, safety, etc. of $FClO_3$ can be found in Gall's review (105).

L. Chlorine Fluoride Oxide Radicals

Very little is known about chlorine fluoride oxide radicals. Although the formation of the $FClO_3^-$ radical anion in the reaction of $FClO_3$ with nucleophilic agents has been postulated (286), it has not been isolated and characterized.

The only well known species is the $FClO^+$ radical cation. The esr spectrum of this species was first reported by Olah and Comisarow (214, 215) for both the ClF_3-SbF_5 and the ClF_5-SbF_5 system. However, the spectrum was incorrectly interpreted in terms of a ClF^+ radical cation. Eachus, Slight, and Symons suggested that the observed spectrum is due to $FClO^+$ and not to ClF^+ (86). This conclusion was supported by Christe and Muirhead (62) who showed that in the pure ClF_3-SbF_5 and ClF_5-SbF_5 systems, this species could not be observed, but was generated by impurities in the starting materials. Additional evidence for this species containing oxygen was obtained by Gillespie and Morton (121) who investigated the reaction of ClF and of Cl_2-ClF with the superacid medium HSO_3F-SbF_5-SO_3. It was shown that the addition of H_2O to solutions of $ClF_2^+SbF_6^-$ in SbF_5 strongly enhanced the esr signal attributed by Olah and Comisarow to ClF^+. They suggested that the species was due either to $FClO^+$ or $FClO_2^+$, although their attempts to detect ^{17}O hyperfine splitting in a sample treated with enriched water were unsuccessful. The conclusive identification of this species was recently reported by Morton and Preston (199). Using ^{17}O substitution techniques they succeeded in proving that the species contains one oxygen atom and is best described as $FClO^+$. This radical cation is characterized by its g value of 2.0059 and the following hyperfine interactions $a_{17} = 18.0$, $a_{19} = 20.4$, and $a_{35} = 12.9G$.

During a matrix isolation infrared study of the F_2-Cl_2O and ClF-O_3 systems, a new species was observed by Andrews et al. (5) at 733.8 cm^{-1} which was tentatively assigned to the $ClF_2O\cdot$ radical. However, more data are needed for the positive identification of this species.

M. Miscellaneous

The ClO_3F^{--} anion has been reported by Mitra and Ray (197). However, in our opinion their claim is almost certainly incorrect.

A compound of the empirical composition FCl_2O_6 was claimed by DeGuevara (79). The following self explanatory abstract of this patent was found in Chemical Abstracts and, we are confident, will be enjoyed by the more knowledgeable readers:

"The title compd. which is claimed to be novel is prepd. by reacting in a hermetically sealed flask 500 ml. 55° Be H_2SO_4, $Ca(OCl)_2$ 5-10, $KClO_2$ 9-20, $KClO_3$ 10-20, and $Mg(ClO_4)_2$ 10-20g. Cl and a Cl oxide are given off, washed, and collected as a stabilized aq. soln. Simultaneously, F is produced from CaF_2 and H_2SO_4 and washed and dried. The F is passed into the stabilized aq. soln. of

FCl_2O_6, which is suitable for use as an antiseptic, preservative, and purifier in the food, wine, perfume, and water industries and as a humectant and bleach for textiles."

Acknowledgement

The authors are indebted to the Office of Naval Research, Power Branch, for their continued interest in and funding of halogen oxidizer research at Rocketdyne and to Dr. L. R. Grant for helpful discussions, and to Mrs. C. Mirras for typing the manuscript.

References

1. Agahigian, H., Gray, A. P., and Vickers, G. D., Canad. J. Chem. 40, 157 (1962).

2. Alexakos, L. G., and Cornwell, C. D., J. Chem. Phys. 41, 2098 (1964).

3. Alexandre, M., and Rigny, P., Canad. J. Chem. in press.

4. Allied Chemical Corporation, Unpublished Results on Contract No. DA-30-069-ORD-2638 (Sept. 1959-Sept. 1964).

5. Andrews, L., Chi, F. K., and Arkell, A., J. Amer. Chem. Soc. 96, 1997 (1974).

6. Arvia, A. J., and Aymonino, P. J., Spectrochim. Acta 19, 1449 (1963).

7. Arvia, A. J., Basualdo, W. H., and Schumacher, H. J., Angew. Chem. 67, 616 (1955).

8. Arvia, A. J., Basualdo, W. H., and Schumacher, H. J., Z. Anorg. Allgem. Chem. 286, 58 (1956).

9. Aubert, J., Bougon, R., and Carles, M., Commis. Energ. At. Fr., Rapp. CEA-R-3282 (1967).

10. Axworthy, A. E., Mueller, K. H., and Wilson, R. D., "Photochemistry of Interest as Rocket Propellants", Final Report on Contract No. AFOSR-TR-73-2183 (1973).

11. Ayers, O. E., and Huskins, C. W., U. S. 3,717,997 (1973).

12. Aymonino, P. J., Sicre, J. E., and Schumacher, H. J., J. Chem. Phys. 22, 756 (1954).

13. Bacon, J., Gillespie, R. J., and Quail, J. W., Canad. J. Chem. 41, 3063 (1963).

14. Baran, E. J., Z. Chem. 13, 391 (1973).

15. Barberi, P., Bull. d'Inform. Scient. Techn. CEA, No. 180, 55 (1973)

16. Barberi, P., Ph. D. Thesis, University of Provence Aix Marseille, France (1974).

17. Barberi, P., Paper I-7, presented at the 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland (1974).
18. Barberi, P., and Carre, J., Paper I-4, presented at the 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland (1974).
19. Barr, J., Gillespie, R. J., and Thompson, R. C., Inorg. Chem. 3, 1149 (1964).
20. Barth-Wehrenalp, G., J. Inorg. Nucl. Chem. 4, 374 (1957).
21. Barth-Wehrenalp, G., J. Inorg. Nucl. Chem. 2, 266 (1956).
22. Barth-Wehrenalp, G., U. S. 2,942,948 (1960).
23. Barth-Wehrenalp, G., and Mandell, H., U. S. 2,942,949 (1960) and G. P. 1,076,640 (1960).
24. Basualdo, W. H., and Schumacher, H. J., Angew. Chem. 67, 231 (1955).
25. Beardell, A. W., and Grelecki, C. J., U. S. 3,404,958 (1968).
26. Beighley, C. M., Missiles Rockets, 30 (1960).
27. Benoit, R., Besnard, G., Hartmanshenn, O., Luce, M., Mougin, J., and Pelisse, J., Commis. Energ. At. Fr., Rapp. CEA-R-3963 (1970).
28. Biemann, K., "Mass Spectrometry." McGraw-Hill, New York, p 161 (1962).
29. Bilham, J., and Linnett, J. W., Nature 301, 1323 (1964).
30. Bode, H., and Klesper, E., Angew. Chem. 66, 605 (1954).
31. Bode, H., and Klesper, E., Z. Anorg. Allgem. Chem. 266, 275 (1951).
32. Bougon, R., Bull. d'Inform. Scient. Techn. CEA, No. 161, 9 (1971).
33. Bougon, R., C. R. Acad. Sci. Paris, C274, 696 (1972).
34. Bougon, R., Bui Huy, T., Cadet, A., Charpin, P., and Rousson, R., Inorg. Chem. 13, 690 (1974).
35. Bougon, R., Bui Huy, T., and Charpin, P., Inorg. Chem. in press.
36. Bougon, R., Carles, M., and Aubert, J., C. R. Acad. Sci. Paris, C 265, 179 (1967).
37. Bougon, R., Isabey, J., and Plurien, P., Fr. P. 2,110,555 (1972).

38. Bougon, R., Isabey, J., and Plurien, P., C. R. Acad. Sci. Paris, C 273, 415 (1971).

39. Bougon, R., Isabey, J., and Plurien, P., C. R. Acad. Sci. Paris, C 271, 1366 (1970).

40. Boyd, W. K., Berry, W. E., and White, E. L., Rept. No. AD 613553 (1965), NASA Accession No. N65-24361

41. Brownstein, S., Canad. J. Chem. 38, 1597 (1960).

42. Carter, H. A., and Aubke, F., Canad. J. Chem. 48, 3456 (1970).

43. Carter, H. A., Johnson, W. M., and Aubke, F., Canad. J. Chem. 47, 4619 (1969).

44. Carter, H. A., Qureshi, A. M., and Aubke, F., Chem. Commun. 1461 (1968).

45. Carter, H. A., Ruddick, J. N., Sams, J. R., and Aubke, F., Inorg. Nucl. Chem. Letters, in press.

46. Chapman, J. J., and Frisco, L. J., paper presented at 111th Meeting of the Electrochem. Soc., Washington, D. C. (1957).

47. Chi, F. K., and Andrews, L., J. Phys. Chem. 77, 3062 (1973).

48. Ching-Yung Tao, Hua Hsueh Tung Pao No 5, 44 (1962).

49. Christe, K. O., Pure and Applied Chemistry, XXIVth International Congress of Pure and Applied Chemistry, Vol. 4, 115 (1974).

50. Christe, K. O., Inorg. Chem. 12, 1580 (1973).

51. Christe, K. O., Inorg. Nucl. Chem. Letters 8, 453 (1972).

52. Christe, K. O., Inorg. Nucl. Chem. Letters 8, 457 (1972).

53. Christe, K. O., Inorg. Chem. 11, 1220 (1972).

54. Christe, K. O., and Curtis, E. C., Inorg. Chem. 11, 35 (1972).

55. Christe, K. O., and Curtis, E. C., Inorg. Chem. 11, 2196 (1972).

56. Christe, K. O., and Curtis, E. C., Inorg. Chem. 11, 2209 (1972).

57. Christe, K. O., and Curtis, E. C., Inorg. Chem. 12, 2245 (1973).

58. Christe, K. O., Curtis, E. C., and Schack, C. J., Spectrochim. Acta, Part A, in press.

59. Christe, K. O., Curtis, E. C., and Schack, C. J., Inorg. Chem. 11, 2212 (1972).

60. Christe, K. O., Curtis, E. C., and Wilson, R. D., Paper I-25, presented at the 7th International Symposium on Fluorine Chemistry, Santa Cruz, Cal. (1973).

61. Christe, K. O., Hon, J. F., and Pilipovich, D., Inorg. Chem. 12, 84 (1973).

62. Christe, K. O., and Muirhead, J. S., J. Amer. Chem. Soc. 91, 7777 (1969).

63. Christe, K. O., Sawodny, W., and Guertin, J. P., Inorg. Chem. 6, 1159 (1967).

64. Christe, K. O., Schack, C. J., and Pilipovich, D., Inorg. Chem. 11, 2205 (1972).

65. Christe, K. O., Schack, C. J., Pilipovich, D., Curtis, E. C., and Sawodny, W., Inorg. Chem. 12, 620 (1973).

66. Christe, K. O., Schack, C. J., Pilipovich, D., and Sawodny, W., Inorg. Chem. 8, 2489 (1969).

67. Christe, K. O., Schack, C. J., and Wilson, R. D., unpublished data on $H_3O^+SbF_6^-$ and $H_3O^+AsF_6^-$.

68. Christe, K. O., and Wilson, R. D., Inorg. Chem. 12, 1356 (1973).

69. Christe, K. O., Wilson, R. D., and Curtis, E. C., Inorg. Chem. 12, 1358 (1973).

70. Christe, K. O., Wilson, R. D., and Schack, C. J., Inorg. Nucl. Chem. Letters, in press.

71. Claassen, H. H., and Appelman, E. H., Inorg. Chem. 9, 622 (1970).

72. Clark, A. H., Beagley, B., and Cruickshank, D. W. J., Chem. Commun. 14 (1968).

73. Clark, H. C., and Emeleus, H. J., J. Chem. Soc. 190 (1958).

74. Cooper, T. D., Dost, F. N., and Wang, C. H., J. Inorg. Nucl. Chem. 34, 3364 (1972).

75. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry", 3rd ed., John Wiley, New York (1972).

76. Coulson, C. A., J. Chem. Soc. 1442 (1964).

77. Dadieu, A., Damm, R., and Schmidt, E. W., "Raketentreibstoffe", Springer-Verlag, Wien (1968).

78. Dale, J. W., U. S. 3,663,183 (1972).

79. DeGuevara, M. L., Fr. P. 1,583,711 (1966).

80. DeKock, R. L., Lloyd, D. R., Hillier, I. H., and Saunders, V. R., Proc. R. Soc. Lond. A 328, 401 (1972).

81. Dess, H., U. S. 2,982,618 (1961).

82. Dibeler, V. H., Reese, R. M., and Mann, D. E., J. Chem. Phys. 27, 176 (1957).

83. Dow Chemical Co., Report Nr. T-0009-4Q-68, Quarterly Technical Report No. 4 under Contract F04611-67-C-0009 (Jan. 1969).

84. Downs, A. J., and Adams, C. J., in "Comprehensive Inorganic Chemistry" (J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman - Dickenson, eds.), Vol. II, pp. 1386-1396 Pergamon (1973).

85. Dunlap, J. L., and Jones, E. A., Spectroscopia Mol. 9, 32 (1960).

86. Eachus, R. S., Sleight, T. P., and Symons, M. C. R., Nature 222, 769 (1969).

87. Ebenhöch, F. L., Ph.D. Thesis, University of Munich, Germany, (1954).

88. Edwards, A. J., and Sills, R. J. C., J. Chem. Soc. A 2697 (1970).

89. Engelbrecht, A., U. S. 2,942,947 (1960).

90. Engelbrecht, A., Angew. Chem. 66, 442 (1954).

91. Engelbrecht, A., and Atzwanger, H., Monatsh. Chem. 83, 1087 (1952).

92. Engelbrecht, A., and Atzwanger, H., J. Inorg. Nucl. Chem. 2, 348 (1956).

93. Engelbrecht, A., Mayr, O., Ziller, G., and Schandara, E., Monatsh. Chem. 105, 796 (1974).

94\. Erashko, V. I., Sankov, B. G., Shevelev, S. A., and Fainzilberg, A. A., *Izv. Akad. Nauk. SSSR, Ser. Khim.* 344 (1973).

95\. Farrar, Jr., R. L., Report No. K-1416, Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (1960).

96\. Farrar, T. C., Maryott, A. A., and Malmherg, M. S., *Ber. Bunsenges Phys. Chem.* *75*, 246 (1971).

97\. Faust, J. P., Jache, A. W., and Klanica, A. J., *U. S.* 3,545,924 (1970), and *Fr.* 1,497,123 (1967).

98\. Figini, R. V., Goloccia, E., and Schumacher, H. J., *Z. Phys. Chem. (Frankfurt) 14*, 32 (1958).

99\. Fink, W., *Ph.D. Thesis*, University of Munich, Germany (1956).

100\. Francis, A. W., *Chem. Eng. Sci.* *10*, 37 (1959).

101\. Frenkel, L., Smith, W., and Gallagher, J. J., *J. Chem. Phys.* *45*, 2251 (1966).

102\. Frey, R. A. Redington, R. L., and Aljibury, A. L. K., *J. Chem. Phys.*, *54*, 344 (1971).

103\. Fridland, S. V., Dmitrieva, N. V., Vigalok, I. V., Zykova, T. V., and Salakhutdinov, R. A., *Zh. Obshch. Khim.* *43*, 572 (1973).

104\. Gall, J. F., *U. S.* 3,038,955 (1956).

105\. Gall, J. F., in Kirk Othmer "Encyclopedia of Chemical Technology", Vol. 9, 2nd edition (1966).

106\. Gall, J. F., *U. S.* 3,066,058 (1962).

107\. Gans, P., *J. Mol. Struct.* *12*, 411 (1972).

108\. Gardiner, D. J., *J. Fluor. Chem.* *3*, 226 (1973).

109\. Gardiner, D. J., and Turner, J. J., Paper C-13, presented at the *6th International Fluorine Symposium*, Durham, England (1971).

110. Gardner, D. M., Helitzer, R., and Mackley, C., J. Org. Chem. 29, 3738 (1964).

111. Gardner, D. M., Helitzer, R., and Rosenblatt, D. H., J. Org. Chem. 32, 1115 (1967).

112. Gatti, R., Sicre, J. E., and Schumacher, H. J., Z. Phys. Chem. (Frankfurt) 23, 164 (1960), and Angew. Chem. 69, 638 (1957).

113. Gatti, R., Staricco, E., Sicre, J. E., and Schumacher, H. J., Z. Phys. Chem. Neue Folge, 35, 343 (1962), see also Ghibaudi, E., Sicre, J. E., and Schumacher, H. J., Z. Phys. Chem. (Frankfurt) 90, 95 (1974).

114. Gensler, W. J., Ahmed, Q. A., and Leeding, M. V., J. Org. Chem. 33, 4279 (1968).

115. Gershon, H., Renwick, J. A. A., Wynn, W. K., and Ascoli, R. D., J. Org. Chem. 31, 916 (1966).

116. Gershon, H., Schulman, S. G., and Spevack, A. D., J. Med. Chem. 10, 536 (1967).

117. Gillardeau, J., and Macheteau, Y., Fr. P. 1,527,112 (1968).

118. Gillespie, R. J., "Molecular Geometry", Van Nostrand Reinhold Co., London (1972).

119. Gillespie, R. J., Acc. Chem. Res. 1, 202 (1968).

120. Gillespie, R. J., Landa, B., and Schrobilgen, G. J., Chem. Commun. 1543 (1971).

121. Gillespie, R. J., and Morton, M. J., Inorg. Chem. 11, 591 (1972).

122. Gmelins Handbuch der Anorganischen Chemie, System Nr. 6, Chlor, Ergänzungsband Teil B, Lieferung 2, Verlag Chemie, Weinheim, Germany (1969).

123. Goebel, M., U. S. 2,913, 366 (1959).

124. Colub, V. B., Khutoretskii V. M., Besprozvannyi, M. A., Temchenko, V. G., and Antipenko, G. L., Zh. Prikl. Khim. (Leningrad) 44, 679 (1971).

125. Grakauskas, V., Fr. P. 1,360,968 (1964).

126. Green J., Levine, N. B., and Sheehan, W., Rubber Chem. Techn. 39, 1222 (1966).

127. Grigger, J. C., and Miller, H. C., WADD Technical Report 61-54, U. S. Air Force, Wright-Patterson Air Force Base, Ohio, (1961).

128. Grosse, A. V., and Streng, A. G., U. S. 3,285,842 (1966).

129. Guest, M. F., and Hillier, I. H., Int. J. Quantum Chem. 6, 967 (1972).

130. Hach, R. J., and Rundle, R. E., J. Amer. Chem. Soc. 73, 4321 (1951).

131. Halpern, C., J. Res. Nat. Bur. Stand. 65A, 513 (1961).

132. Hammond, P. R., J. Chem. Soc. A, 3826 (1971).

133. Hammond, P. R., and Lake, R. R., Chem. Commun. 987 (1968).

134. Hammond, P. R., and Lake, R. R., J. Chem. Soc. A, 3819 (1971).

135. Hardwike, N., U. S. 2,947,738 (1960).

136. Hendel, F., and Cavecche, E., Chem. Eng. 67, 93 (1960).

137. Heras, M. J., Aymonino, P. J., and Schumacher, H. J., Z. Phys. Chem. (Frankfurt) 22, 161 (1959).

138. Hickam, W., and Berg, D., J. Chem. Phys. 29, 517 (1958).

139. Hillier, I. H., and Saunders, V. R., Chem. Commun. 1183 (1970).

140. Hoskins, L. C., J. Chem. Phys. 50, 1130 (1969).

141. Huggins, D. K., and Fox, W. B., Inorg. Nucl. Chem. Letters 6, 337 (1970).

142. Huggins, D. K., and Fox, W. B., U. S. 3,423,168 (1969).

143. Huston, J. L., J. Amer. Chem. Soc. 93, 5255 (1971).

144. Inman, C., Oesterling, R., and Tyczkowski, E., J. Amer. Chem. Soc. 80, 6533 (1958).

145. Inman, C., Oesterling, R., and Tyczkowski, F., J. Amer. Chem. Soc. 80, 5286 (1958).

146. Ionov, S. P., and Ionova, G. V., Russ. J. Inorg. Chem. 14, 886 (1969).

147. JANAF Thermochemical Tables, PB-168370 (1965).

148. Jarry, R. L., J. Phys. Chem. 61, 498 (1957).

149. Jarry, R. L., and Davis, W.,US At. Energy Comm. K-847 (1951).

150. Jarry, R. L., and Fritz, J. J., Chem. Eng. Data Ser. 3, 34 (1958).

151. Johnson, G. K., Smith, P. N., and Hubbard, W. N., J. Chem. Thermodyn. 5, 793 (1973).

152. Kalman, O. F., private communication (1967).

153. Kamlet, M. J., U. S. 3,624,129 (1971).

154. Karelin, A. J., Ionov, S. P., and Ionova, G. V., Zh. Strukt. Khim. 11, 454 (1970).

155. Karelin, A. I., Nikitina, Z. K., Kharitonov, Y. Y., and Rosolovskii, V. Y., Russ. J. Inorg. Chem. 15, 480 (1970).

156. Kemmit, R. D. W., and Sharp, D. W. A., Adv. Fluor. Chem. 4, 242 (1965).

157. Kharitanov, Y. Y., Karelin, A. I., and Rosolovskii, V. Ya., J. Mol. Struct. 19, 545 (1973).

158. Khutoretskii, V. M., Okhlobystina, L. V., and Fainzilberg, A. A., Usp. Khim. 36, 377 (1967).

159. Khutoretskii, V. M., Okhlobystina, L. V., and Fainzilberg, A. A., Izv. Akad. Nauk. SSSR, Ser. Khim. 387 (1970).

160. Koehler, J. K., and Giauque, W. F. J. Amer. Chem. Soc. 80, 2659 (1958).

161. Krishna Pillai, M. G., and Curl, Jr., R. F., J. Chem. Phys. 37, 2921 (1962).

162. Kwasnik, W. In "Handbook of Preparative Inorganic Chemistry" (G. Brauer, ed.), Vol. I, pp. 165-166, 2nd edit., Academic Press, New York, 1963.

163. Lalande, W., U. S. 2,982,617 (1961), and G. P. 1,026,285 (1958).

164. Lalande, W., U. S. 3,086,842 (1963).

165. Lalande, W., and Gall, J., U. S. 2,998,388 (1956).

166. Lang, K., Diploma Thesis, University of Munich, Germany, (1955).

167. Lang, K., Ph.D. Thesis, University of Munich, Germany, (1956).

168. Lau, C., and Passmore, J., Inorg. Chem. 13, 2278 (1974).

169. Lawless, E. W., and Smith, I. C., "Inorganic High-Energy Oxidizers", Marcel Decker, New York (1968).

170. Laycock, T. B., and Tucker, N. B., U. S. 3,328,312 (1967).

171. Lide, D. R., J. Chem. Phys. 43, 3767 (1965).

172. Lide, D. R., and Mann, D. E., Natl. Bur. Std. (U. S.), Rept. Nr. 4399 (1955).

173. Lide, D. R., and Mann, D. E., J. Chem. Phys. 25, 595 (1956).

174. Lide, D. R., and Mann, D. E., J. Chem. Phys. 25, 1128 (1956).

175. Lindahl, C. B., U. S. 3,709,982 (1973).

176. Lindahl, C. B., Schack, C. J., and Pilipovich, D., U. S. 3,701,630 (1972).

177. Lodwig, R. M., and Margrave, J. L., Combustion Flame, 3, 147 and 249 (1959).

178. Luce, M., and Hartmanshenn, O., J. Inorg. Nucl. Chem. 29, 2823 (1967).

179. Luce, M., and Hartmanshenn, O., Commis. Energ. At. Fr., Rapp. No. 3210 (1967).

180. Lustig, M., and Shreeve, J. M., Advances in Fluorine Chemistry 7, 175 (1973).

181. Lynton, H., and Passmore, J., Canad. J. Chem. 49, 2539 (1971).

182. Macheteau, Y., and Cillardeau, J., Bull. Soc. Chim. Fr. 4075 (1967).

183. Macheteau, Y., and Gillardeau, J., Bull. Soc. Chim. Fr. 1819 (1969).

184. Madden, R. P., and Benedict, W. S., J. Chem. Phys. 25, 594 (1956).

185. Magerlein, B., Pike, J., Jackson, R., Vandenberg, G., and Kagan, F., J. Org. Chem. 29, 2982 (1964).

186. Mandell, H. C., in Kirk Othmer "Encyclopedia of Chemical Technology", 2nd suppl., 1st ed. (1960).

187. Mandell, H., and Barth-Wehrenalp, G., J. Inorg. Nucl. Chem. 12, 90 (1959).

188. Mandell, H. C., and Barth-Wehrenalp, G., U. S. 3,140,934 (1964).

189. Margrave, J. L., and Wendt, R. P., J. Chem. Phys. 31, 857 (1959).

190. Martin, D., and Tantot, G., Paper I-12, presented at 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland (1974).

191. Maryott, A. A., and Farrar, T. C., J. Chem. Phys. 54, 64 (1971).

192. Maryott, A. A., and Kryder, S. J., J. Chem. Phys. 27, 1211 (1957).

193. McDowell, C. A., Raghunathan, P., and Tait, J. C., J. Chem. Phys. 59, 5858 (1973).

194. Meinert, H., and Gross, U., Z. Chem. 9, 455 (1969).

195. Mitra, G., Z. Anorg. Allgem. Chem. 340, 110 (1965).

196. Mitra, G., Z. Anorg. Allgem. Chem. 368, 336 (1969).

197. Mitra, G., and Ray, A., Sci. Cult. (Calcutta) 21, 179 (1956).

198. Monsanto Research Corporation, Quarterly Technical Summary Report No 2, MRB-2022-Q2, Contract No. AF 04(611)-8520 (1963).

199. Morton, J. R., and Preston, K. F., Inorg. Chem. 13, 1786 (1974).

200. Müller, A., Krebs, B., Fadini, A., Glemser, O., Cyvin, S. J., Brunvoll, J., Cyvin, B. N., Elvebredd, I., Hagen, G., and Vizi, B., Z. Naturforsch. A, 23, 1656 (1968).

201. Müller, A., and Nagarajan, G., Z. Anorg. Allgem. Chem. 349, 87 (1966).

202. Müller, A., Peacock, C. J., Schulze, H., and Heidborn, U., Mol. Struct. 3, 252 (1969).

203. Muetterties, E. L., Mahler, W., Packer, K. J., and Schmutzler, R., Inorg. Chem. 3, 1298 (1964).

204. Nagarajan, G., and Redmon, M. J., Monatsh. Chem. 103, 1406 (1972).

205. Nakanishi, S., J. Jap. Chem. 13, 864 (1959).

206. Nathan, A., Magerlein, B., and Hogg, J., J. Org. Chem. 24, 1517 (1959).

207. Neeman, M., and Osawa, Y., J. Amer. Chem. Soc. 85, 232 (1963).

208. Neugebauer, C. A., and Margrave, J. L., J. Amer. Chem. Soc. 79, 1338 (1957).

209. Nikitina, Z. K., and Rosolovskii, V. Ya., Izv. Akad. Nauk. SSSR, Ser. Khim. 750 (1972).

210. Nikitina, Z. K., and Rosolovskii, V. Ya., Izv. Akad. Nauk. SSSR, Ser. Khim. 273 (1973).

211. Oesterling, R. E., and Tyczkowski, E. A., J. Amer. Chem. Soc. 80, 5286 (1958).

212. Okhlobystina, L. V., and Khutoretskii, V. M., Izv. Akad. Nauk. SSSR, Ser. Khim. 1188 (1969).

213. Okhlobystina, L. V., Khutoretskii, V. M. and Fainzilberg, A. A., Izv. Akad. Nauk, SSSR, Ser. Khim. 1487 (1971).

214. Olah, G. A., and Comisarow, M. B., J. Amer. Chem. Soc. 90, 5033 (1968).

215. Olah, G. A., and Comisarow, M. B., J. Amer. Chem. Soc. 91, 2172 (1969).

216. Olah, G. A., White, A. M., and O'Brien, D. H., Chem. Rev. 70, 561 (1970).

217. Osawa, Y., and Neeman, M., J. Org. Chem. 32, 3055 (1967).

218. Ostero, J., Commis. Energ. At. Fr. Note, CEA-N-1293 (1970).

219. Parent, C. R.,, and Gerry, M. C. L., Chem. Commun. 285 (1972).

220. Parent, C. R., and Gerry, M. C. L., J. Mol. Spectrosc. 49, 343 (1974).

221. Pavia, A. C., Pascal, J. L., and Potier, A., C. R. Acad. Sci. Paris, Ser. C. 272, 1495 (1971).

222. Pennsalt Chemicals Corporation, Unpublished results on Contract No. AF 04 (611)-8518 (Nov. 1963 - Dec. 1964).

223. Pennsalt Chemicals Corporation, Unpublished results on Contract No. AF 33 (616)-6532 (April 1960 - March 1962).

224. Pennsalt Chemicals Corporation, "Perchloryl Fluoride", New Products Booklet No. DC-1819 (1957).

225. Pilipovich, D., U. S. 3,707,413 (1972).

226. Pilipovich, D., Lindahl, C. B., Schack, C. J., Wilson, R. D., and Christe, K. O., Inorg. Chem. 11, 2189 (1972).

227. Pilipovich, D., Maya, W., Lawton, E. A., Bauer, H. F., Sheehan, D. F., Ogimachi, N. N., Wilson, R. D., Gunderloy, F. C., and Bedwell, V. E., Inorg. Chem. 6, 1918 (1967).

228. Pilipovich, D., Rogers, H. H., and Wilson, R. D., Inorg. Chem. 11, 2192 (1972).

229. Pilipovich, D., and Schack, C. J., U. S. 3,692,476 (1972).

230. Pilipovich, D., and Wilson, R. D., U. S. 3,697,394 (1972) and Brit. 1,278,684 (1972).

231. Pilipovich, D., Wilson, R. D., and Bauer, H. F., U. S. 3,733,392 (1972) and Brit. 1,278,863 (1972).

232. Pimentel, G. C., J. Chem. Phys. 19, 446 (1951).

233. Powell F., and Lippincott, E. R., J. Chem. Phys. 32, 1883 (1960).

234. Reese, R., Dibeler, V., and Mohler, F., J. Res. Nat. Bur. Stand. 57, 367 (1957).

235. Rips, S. M., Zercheninov, A. N., and Pankratov, A. V., Russ. J. Phys. Chem. 43, 208 (1969).

236. Robinson, E. A., Canad. J. Chem. 41, 173 (1963).

237. Robinson, E. A., Canad. J. Chem. 41, 3021 (1963).

238. Robinson, E. A., Lavery, D. S., and Weller, S., Spectrochim. Acta, Part A 25, 151 (1968).

239. Rode, B. M., and Engelbrecht, A., Chem. Phys. Letters 16, 26 (1972).

240. Rogers, H. H., and Pilipovich, D., U. S. 3,718,557 (1973).

241. Rude, H., Benoit, R., and Hartmanshenn, O., Commis. Energ. At. Fr. Rapp. CEA-R-4205 (1971).

242. Ruff, O., and Krug, H., Z. Anorg. Allgem. Chem. 190, 270 (1930).

243. Rundle, R. E., J. Amer. Chem. Soc. 85, 112 (1963).

244. Ryss, I. G., "The Chemistry of Fluorine and Its Inorganic Compounds", State Publishing House for Scientific, Technical and Chemical Literature, Moscow (1956), translated by the U. S. Atomic Energy Comm. (AEC-tr-3927).

245. Sawodny, W., Fadini, A., and Ballein, K., Spectrochim. Acta 21, 995 (1965).

246. Schack, C. J., Lindahl, C. B., Pilipovich, D., and Christe, K. O., Inorg. Chem. 11, 2201 (1972).

247. Schack, C. J., and Pilipovich, D., Inorg. Chem. 9, 387 (1970).

248. Schack, C. J., and Pilipovich, D., U. S. 3,777,901 (1973).

249. Schack, C. J., Pilipovich, D., and Hon, J. F., Inorg. Chem. 12, 897 (1973).

250. Schlosser, M., and Heinz, G., Chem. Ber. 102, 1944 (1969).

251. Schmauch, G., and Servass, E., Appl. Spectrosc. 12, 98 (1958), and Anal. Chem. 30, 1160 (1958).

252. Schmeisser, M., Angew. Chem. 67, 493 (1955).

253. Schmeisser, M., and Brändle, K., Adv. Inorg. Chem. Radiochem. 5, 41 (1963).

254. Schmeisser, M., and Ebenhöch, F. L., Angew. Chem. 66, 230 (1954).

255. Schmeisser, M., and Fink, W., Angew. Chem. 69, 780 (1957).

256. Schmitz, H., and Schumacher, H. J., Z. Anorg. Allgem. Chem. 249, 238 (1942).

257. Schuetz, R. D., Taft, D. D., O'Brien, J. P., Shea, J. L., and Mork, H. M., J. Org. Chem. 28, 1420 (1963).

258. Scott, F. L., and Oesterling, R. E., J. Org. Chem. 25, 1688 (1960).

259. Selig, H., and Shamir, J., Inorg. Chem. 3, 294 (1964).

260. Seppelt, K., Z. Anorg. Allgem. Chem. 406, 287 (1974).

261. Sheppard, W. A., Tetrahedron Lett. 83 (1969).

262. Sheppard, W. A., and Sharts, C. M., "Organic Fluorine Chemistry", Benjamin, New York (1969).

263. Shrewsberry, R. C., and Williamson, E. L., J. Inorg. Nucl. Chem. 28, 2535 (1966).

264. Sicre, J. E., and Schumacher, H. J., Angew. Chem. 69, 266 (1957).

265. Sicre, J. E., and Schumacher, H. J., Z. Anorg. Allgem. Chem. 286, 232 (1956).

266. Siebert, H., "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer-Verlag, Berlin (1966).

267. Silla, H., Burwasser, H., and Calcote, H. F., U. S. Dept. Comm. Office Tech. Serv. AD-258390 (1960).

268. Simkin, J., and Jarry, R. L., J. Phys. Chem. 61, 503 (1957).

269. Sinke, G., private communication (1967).

270. Smith, D. F., Begun, G. M., and Fletcher, W. H., Spectrochim. Acta 20, 1763 (1964).

271. Smith, E. A., Steinbach, F. C., and Beu, K. E., US At. En. Comm. Report GAT T-687 (1959).

272. So, S. P., and Chau, F. T., Z. Phys. Chem. (Neue Folge) 84, 241 (1973).

273. So, S. P., and au, F. T., Z. Phys. Chem. (Neue Folge) 85, 69 (1973).

274. Spratley, R. D., and Pimentel, G. C., J. Amer. Chem. Soc. 88, 2394 (1966).

275. Streng, A. G., Chem. Rev. 63, 607 (1963).

276. Streng, A. G., J. Chem. Eng. Data 16, 357 (1971).

277. Streng, A. G., J. Amer. Chem. Soc. 85, 1380 (1963).

278. Streng, A. G., and Grosse, A. V., Adv. in Chem. 36, 159 (1962).

279. Stull, R. D., Ind. Eng. Chem. 39, 545 (1947).

280. Tallman, R., Ph.D. Thesis, University of Wisconsin (1960), Diss. Abs. 20, 4293 (1960).

281. Tallman, R., Wampler, D., and Margrave, J. L., J. Inorg. Nucl. Chem. 21, 38 (1961).

282. Tantot, G., Ph.D. Thesis, University of Paris, (1974).

283. Tantot, G., and Bougon, R., Paper 1 11 presented at 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland (1974).

284. Titov, Y. A., Reshotova, I. G., and Akhrem, A. A., Reakts. Methody. Issled. Org. Soedin. 15, 7 (1966).

285. Toeniskoetter, R. H., and Gortsema F. P., Union Carbide Corp., Final Report under Contract No. DA-31-124-ARO(D)-77 (1965).

286. Tyurikov, V. A., Okhlobystina, L. V., Shapiro, B. I., Khutoretskii, V. M., Fainzilberg, A. A., and Syrkin, Y. K., Izv. Akad. Nauk. SSSR, Ser. Khim. 2373 (1972).

287. Usmanov, A. G., and Magarra, R. I., Russ. J. Phys. Chem. 36, 1454 (1962).

288. Veyre, R., Quenault, M., and Eyraud, C., C. R. Acad. Sci. Paris, Ser. C, 268, 1480 (1969).

289. Vigalok, I. V., Il'yasov, A. V., and Levin,Ya. A., Zh. Obshch. Khim. 39, 715 (1969).

290. Vigalok, I. V., and Ostrovskaya, A. V., Zh. Obshch. Khim. 41, 1410 (1971).

291. Wagman, D. C., Evans, W. H., Halow, J., Parker, V. B., Bailey, S. M., and Schumm, R. H., U. S. Natl. Bur. Stand. Tech. Note 270-1 (1965).

292. Wamser, C. A., Fox, W. B., Gould, D., and Sukornick, B., Inorg. Chem. 7, 1933 (1968).

293. Wamser, C. A., Sukornick, B., Fox, W. B., and Gould, D., Inorg. Synth. 14, 29 (1973).

294. Weiss, R., Ph.D. Thesis, Techn. University Aachen, Germany (1959).

295. Whitney, E. D., MacLaren, R. O., Hurley, T. J., and Fogle, C. E., J. Amer. Chem. Soc. 86, 4340 (1964).

296. Woolf, A. A., J. Chem. Soc. 4113 (1954).

297. Woolf, A. A., J. Chem. Soc. A 401 (1967).

298. Woolf, A. A., J. Inorg. Nucl. Chem. 3, 250 (1956).

299. Yodis, A. W., and Cunningham, W. J., *U. S.* 3,375,072 (1968).

300. Züchner, K., and Glemser, O., *Angew. Chem.* *84*, 1147 (1972).

Table I. Stretching Force Constants (mdyn/Å) of Some Chlorine Oxyfluorides

Oxidation State	Compound	f_{ClO}	f_{ClF}			References
			I[a]	II[b]	III[c]	
+VII	$ClF_2O_2^+$	12.1	4.46			(69)
+V	ClF_2O^+	11.20	3.44			(59)
+VII	$FClO_3$	9.4	3.9			(174)
+V	ClF_3O	9.37	3.16	2.34		(55)
+VII	ClF_3O_2	9.23	3.35	2.70		(57)
+V	ClF_4O^-	9.13		1.79		(56)
+V	$FClO_2$	9.07			2.5	(270)
+V	ClO_2^+	8.96				(66)
+V	$ClF_2O_2^-$	8.3		1.6		(54)
+III	FClO	6.85			2.59	(5)

(a) mainly covalent bonds

(b) mainly semi-ionic 3c - 4e bonds

(c) special case of highly polar (p-π*) σ bonds

Table II. Comparison of ClF Stretching Force Constants (mdyn/Å) and Bond Lengths (Å) Within the Pseudo-tetrahedral Series FCl, FClO, $FClO_2$, $FClO_3$

Molecule	f_{ClF}	r_{ClF}	References	
FCl	4.56	1.628	(122)	(122)
FClO	2.59	-	(5)	-
$FClO_2$	2.5	1.697	(270)	(220)
$FClO_3$	3.9	1.610	(174)	(72)

Table III. Observed and Calculated Frequencies (cm^{-1}) for the FClO Species (5)

Isotope	Assignment	Obsd	Calcd
$F^{35}Cl^{16}O$	ν_1	1038.0	1038.3
	ν_2	593.5	593.9
	ν_3	315.2	316.0
$F^{37}Cl^{16}O$	ν_1	1029.0	1028.9
	ν_2	587.5	588.4
	ν_3	315.2	313.8
$F^{35}Cl^{18}O$	ν_1	999.2	999.5
	ν_2	593.5	592.6
	ν_3	307.0	308.3
$F^{37}Cl^{18}O$	ν_1	990.1	989.6
	ν_2	587.5	587.1
	ν_3	307.0	306.2

Table IV. Force Field of FClO Assuming a Bond Angle of 120° and All Interaction Constants to be Zero (5)

f_{ClO} = 6.85 mdyn/Å

f_{ClF} = 2.59 mdyn/Å

f_{α} = 0.92 mdyn Å/rad^2

Table V. Comparison of the ClO Stretching Force Constants (mdyn/Å) and Bond Orders of FClO with Those of Related Pseudo-tetrahedral Species Having a Comparable Oxidation State

Species	Oxidation State	f_{ClO}	Bond Order	References
ClO_2^-	+III	4.26	1.5	(266)
FClO	+III	6.85	2	(5)
ClO_2	+IV	7.02	2	(161)

Table VI. Vibrational Spectra of ClF_3O Gas and Liquid and Their Assignment In Point Group C_s (55)

Observed frequencies, cm⁻¹, and relative intensities					Approx description of mode
Gas		Solid	Liquid		
Ir	Raman	Matrix ir	Raman	Assignment	
1228					
1224	1222 (1.5) p	1223 s	1224 (1.0) p	$\nu_1(A')$	$\nu(^{35}Cl{=}O)$
1218 s					
1213	1211 (0.5) p	1212 m		$\nu_1(A')$	$\nu(^{37}Cl{=}O)$
701	694 (2.6) p	686 s	689 (2.7) p	$\nu_2(A')$	$\nu(^{35}Cl{-}F')$
684	686 sh, p	678 m		$\nu_2(A')$	$\nu(^{37}Cl{-}F')$
676 vs		652 vs		$\nu_7(A'')$	$\nu_{as}(F^{35}ClF)$
666		641 s		$\nu_7(A'')$	$\nu_{as}(F^{37}ClF)$
		499 m		$\nu_8(A'')$	$\delta_{rock}(O^{35}ClF')$
501	500 (1)		497 sh		
		498 sh		$\nu_8(A'')$	$\delta_{rock}(O^{37}ClF')$
491 ms	489 (1)	486 mw		$\nu_4(A')$	$\delta_{scis}(O^{35}ClF')$
		484 w		$\nu_4(A')$	$\delta_{scis}(O^{37}ClF')$
481	482 (10) p	478 mw	466 (10)	$\nu_3(A')$	$\nu_s FClF$
412 w	414 (0.2) dp	414 w	405 (0.5) sh	$\nu_9(A'')$	
323 313 m	319 (0.1)	323 mw	316 (0.3) p	$\nu_5(A')$	$\delta_s FClF$ out of FClF plane ≡ $\delta_{wag} OClF'$
230 mw	224 (0.4) p		227 (1.2) p?	$\nu_6(A')$	$\delta_s FClF$ in FClF plane

Table VII. Internal Force Constants of ClF_3O^a (55)

f_D	9.37	f_{rr}	0.26
f_R	3.16	$f_{\beta\beta}$	0.11
f_r	2.34	$f_{\gamma\gamma}$	0.13
f_α	1.84	$f_{r\beta} = -f_{r\beta'}$	0.25
f_β	1.69	$f_{\beta\gamma} = f_{\beta'\gamma'}$	0.22
f_γ	1.87		

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian², and stretch-bend interaction constants in mdyn/radian.

Table VIII. Some Properties of ClF_3O

Property	Value	References
Melting point	-42 to -44.2°	(16, 39, 226)
Boiling point	29 or 27°	(39, 226)
ΔH_{fusion}	1.975 kcal mol^{-1}	(16)
ΔS_{fusion}	8.63 e.u.	(16)
ΔH_{vap}	7.7 or 7.57 kcal mol^{-1}	(39, 226)
Trouton constant	25.4 or 25.2 e.u.	(39, 226)
Density (1, 20°)	1.865 g ml^{-1}	(226)
ΔH°_{f298} (g)	-36.5^a or -35.3^b kcal mol^{-1}	(15, 16, 269)
ΔH°_{f298} (1)	$-44.1^{a,c}$, $-42.9^{b,c}$, or -38.7^b kcal mol^{-1}	(16, 152, 269)

(a) corrected for $\Delta H^\circ_{f\ HF\ (g)} = -65.14$ kcal mol^{-1} (83)

(b) corrected for $\Delta H^\circ_{f\ HF\ sol\ (75H_2O)} = -77.04$ kcal mol^{-1} (151)

(c) using the $\Delta H^\circ_{f\ 298\ (g)}$ values of Barberi (16) and Sinke (269) for the gas and the above listed $\Delta H_{vap} = 7.6$ kcal mol^{-1}

Table IX. Vibrational Spectrum (cm^{-1}) of the ClF$_2$O$^+$ Cation

Ra (HF solution)	Ir (solid)	Assignment in Point Group C_s	Approximate Description of Mode
1333 (4) p	1334 s	ν_1 (A')	νClO
1322 sh	1323 m		
741 (10) p	734 m	ν_2 (A')	ν_sClF$_2$
715 (1)	694 s	ν_5 (A")	ν_{as} ClF$_2$
512 (2) p	512 s	ν_3 (A')	δ_s OClF$_2$
404 (2) p	405 m	ν_4 (A')	δ sciss ClF$_2$
383 (1)	383 m	ν_6 (A")	δ_{as} OClF$_2$

Table X. Vibrational Force Constants of ClF_2O^{+a} (59)

f_R	11.20
f_r	3.44
f_β	1.65
f_α	1.78
$f_{\beta\beta}$	0.21
f_{rr}	0.39

(a) Stretching constants in mdyn/Å and deformation constants in mdyn Å/radian^2.

Table XI. Vibrational Spectra of $Rb^+ClF_4O^-$ and $Cs^+ClF_4O^-$ and Their Assignment (56)

Observed frequencies, cm^{-1}, and relative intensities				Assignment for XZF_4 in point group C_{4v}		
$Rb^+ClF_4O^-$		$Cs^+ClF_4O^-$				
Ir	Raman	Ir	Raman			Type of vibration
1210 s	1211 (0.6)	1201 s	1203 (0.6)	A_1	ν_1	ν XZ
462 w	461 (10)	457 w	456 (10)		ν_2	ν_{sym} in-phase XF_4
339 s	[350]^c	339 s	[345]^c		ν_3	δ_{sym} out-of-plane XF_4
	350 (4.3)		345 (4)	B_1	ν_4	ν_{sym} out-of-phase XF_4
					ν_5	δ_{asym} out-of-plane XF_4
283 vw	285 (0.4)	280 vw	283 (0.4)	B_2	ν_6	δ_{sym} in-plane XF_4
600} vs	599 (0.1)	600} vs	593 (0.2)	E	ν_7	ν_{asym} XF_4
550}	557 (0.4)	560}	564 (0.3)			
415} s	416 (1.4)	415} s	416 (1.4)		ν_8	δ ZXF
394}	395 (0.1)	396}	397 (0.1)			
	213 (0.6)		204 (0.7)		ν_9	δ_{asym} in-plane XF_4

Table XII. Force Constants of ClF_4O^{-a} (56)

f_R	9.13		
f_r	1.79	$f'_{\beta\beta}$	0.29
f_β	1.33	$f'_{\alpha\alpha}$	0.08
f_α	0.61	$f_{r\beta}$	0.15
f_{rr}	0.25	$f''_{r\beta}$	−0.15
f'_{rr}	0.04		

[a] Stretching force constants in mdyn/Å and deformation force constants in mdyn Å/radian^2.

Table XIII. Fundamental Vibrational Frequencies (cm^{-1}) of $FClO_2$ (270)

		$F^{35}ClO_2$	$F^{37}ClO_2$	$F^{35}Cl^{18}O_2$	$F^{37}Cl^{18}O_2$	$F^{35}Cl^{16}O^{18}O$	$F^{37}Cl^{16}O^{18}O$
A'	ν_1 sym ClO_2 stretch	1105.8	1098.4	1060.4	1052.6	1080.7	1072.4
	ν_2 ClF stretch	630.2	621.6	624.7	616.0	628.6	618.6
	ν_3 ClO_2 scissor	546.5	543.0	529.0		537.8	534.0
	ν_4 FClO bend	401.6					
A"	ν_5 asym ClO_2 stretch	1271.4	1258.6	1229.6	1215.0	1253.6	
	ν_6 FClO bend	367.0					

Table XIV. Some Properties of $FClO_2$

Property	Value	References
Melting point	-115 or -123.0 ±0.4°C	(15, 16, 256)
Boiling point	∿ -6°C	(256)
ΔH_{fusion}	1.440 kcal mol^{-1}	(15, 16)
ΔS_{fusion}	9.60 e.u.	(15, 16)
ΔH_{vap}	6.2 kcal mol^{-1}	(256)
Trouton constant	23.2 e.u.	(256)
$\Delta H^{\circ}_{f298\ (g)}$	-8.1±2.5 kcal mol^{-1a}	(15, 16)
Dipole moment (g)	1.722±0.03 D	(220)

(a) corrected for $\Delta H^{\circ}_{f\ HF\ (g)} = -65.14$ kcal mol^{-1} (83)

Table XV. Vapor Pressures of Chloryl Fluoride

°C	-78	-65.5	-55	-45.5	-38	-30.2	-23.8	-17.2	-9.7	-6.3
mm of Hg	8.8	25.2	55.9	103.8	161.4	244	338	459	645	740

Table XVI. Thermal Decomposition of $FClO_2$ in Monel (183)

Temp. (°C)	Initial press. of $FClO_2$ (mm)	Average rate Constant (sec^{-1})	Half life
250	52	$6.8x10^{-6}$	20h
250	101	$8.5x10^{-6}$	22h 30m
270	52	$1.8x10^{-5}$	10h 30m
285	52	$2.8x10^{-5}$	6h 40m

Table XVII. Characteristic Frequencies[a] and Internal Force Constants[b] of ClO_2^+

obsd freq, cm^{-1}, int		assignment in point group C_{2v}		
Ir	Ra			
1296.4m	1296.4 (1)	$\nu_3(B_1)$	ν_{as}	$^{35}ClO_2$
1282.6mw		$\nu_3(B_1)$	ν_{as}	$^{37}ClO_2$
1043.7mw	1044.4 (10)	$\nu_1(A_1)$	ν_s	$^{35}ClO_2$
1038.3w	1039.1 (4)	$\nu_1(A_1)$	ν_s	$^{37}ClO_2$
521.0m	521.3 (3)	$\nu_2(A_1)$	δ	$^{35}ClO_2$
517 sh		$\nu_2(A_1)$	δ	$^{37}ClO_2$

$f_r = 8.96 \pm 0.06$

$f_{rr} = -0.45 \pm 0.13$

$f_{r\alpha} = 0.24 \pm 0.13$

$f_\alpha = 0.82 \pm 0.03$

(a) taken for $ClO_2^+AsF_6^-$ from (66)

(b) in mdyn/Å, calculated for ∡ OClO = 120°

Table XVIII. Vibrational Spectrum of $Cs^+ClF_2O_2^-$ and Its Assignment (54)

Obsd freq, cm^{-1}, and intens Ir	 Raman	Assignment for XO_2F_2 in point group C_{2v}	Approx description of vibration
1225 1191 } vs	1221 (0.8)	$\nu_8(B_2)$	$\nu_{as}(XO_2)$
1070 s	1076 (10) 1064 1055	$\nu_1(A_1)$	$\nu_s(XO_2)$
569 m	569 (1.2)	$\nu_2(A_1)$	$\delta_s(XO_2)$
510 vs, br		$\nu_6(B_1)$	$\nu_{as}(XF_2)$
	480 (1), br	$\nu_5(A_2)$?	τ
380–370 m	363 (10)	$\nu_3(A_1)$	$\nu_s(XF_2)$
	337 (8)	$\nu_7(B_1)$, $\nu_9(B_2)$	δ_{rock}, δ_{wag}
	198 (0.7)	$\nu_4(A_1)$	$\delta_s(XF_2)$

Table XIX. Force Constants[a] of $ClF_2O_2^-$ (54)

f_R	8.3	f_β	1.2
f_{RR}	0.1	$f_{\beta\beta'}$	0.57
f_r	1.6	$f_{\beta\beta}$	0.1
f_{rr}	-0.1	$f_{r\beta}-f_{r\beta'}$	0.3
f_α	1.95		

(a) Stretching force constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interactions in mdyn/radian

Table XX. Some Properties of ClF_3O_2 (68)

Property	Value
Melting point	-81.2°C
Boiling point	-21.58°C
ΔH_{vap}	5.57 kcal mol^{-1}
Trouton constant	22.13 eu
Vapor pressure	$\log P_{(mm)} = 7.719 - \frac{1217.2}{T\ (°K)}$

Table XXI. Vibrational Spectrum (cm^{-1}) of ClF_3O_2 and its Assignment in Point Group C_{2v} (57)

Ir	R	Assignment for ClF_3O_2 in point group C_{2v}	Approx description of mode
1093 s	1093 (4) p	A_1 ν_1	Sym ClO_2 str
683 m	683 (10) p	ν_2	ClF_{eq} str
519 w	520 (8) p	ν_3	ClO_2 scissor
487 vw	487 (6) p	ν_4	Sym $F_{ax}ClF_{ax}$ str
287 w	285 (1)	ν_5	$F_{ax}ClF_{ax}$ scissor in ClF_3 plane
(417)[a]	402 (0+)	A_2 ν_6	Torsion
695 vs		B_1 ν_7	Antisym $F_{ax}ClF_{ax}$ str
592 s	586 (0+)	ν_8	ClO_2 wag
372 w		ν_9	Antisym $F_{eq}ClF_{2ax}$ def in ClF_3 plane
1327 vs	1320 (0+)	B_2 ν_{10}	Antisym ClO_2 str
531 m	530 (1)	ν_{11}	ClO_2 rock
b	222 (1)	ν_{12}	$F_{ax}ClF_{ax}$ scissor out of ClF_3 plane

(a) Observed only for solid ClF_3O_2.

(b) Below frequency range of spectrometer used.

Table XXII. Internal Force Constants of ClF_3O_2[a] (57)

$f_D = 9.23$
$f_R = 3.35$
$f_r = 2.70$
$f_\alpha = 1.41$
$f_\beta = 1.40$
$f_\gamma = 1.33$
$f_\delta = 1.30$
$f_{DD} = -0.09$
$f_{rr} = -0.04$

$f_{\beta\beta} = 0.09$
$f_{r\beta} = -f_{r\beta'} = 0.10$
$f_{r\delta} = -f_{r\delta'} = 0.25$
$f_{D\alpha} = 0.61$
$f_{\beta\delta} = -f_{\beta\delta'} = -0.16$
$f_{\delta\delta} = -f_{\delta\delta'} = -0.34$
$f_{\delta\delta''} = -0.17$
$f_{\gamma\gamma} = -0.30$
$f_{R\alpha} = -0.37$

[a] Stretching constants in mdyn/A, deformation constants in mdyn A/radian^2, and stretch-bend interaction constants in mdyn/radian.

Table XXIII. ClF Stretching Force Constants (mdyn/Å) of ClF_3O_2 Compared to those of Pseudo-Trigonal-Bipyramidal ClF_3O, ClF_3, ClF_2^-, and $ClF_2O_2^-$

	f_R	f_r	f_{rr}	$(f_R - f_r)/f_R$	References
ClF_3	4.2	2.7	0.36	0.36	(102)
ClF_3O	3.2	2.3	0.26	0.26	(55)
ClF_3O_2	3.4	2.7	-0.04	0.19	(57)
ClF_2^-		2.4	0.17		(63)
$ClF_2O_2^-$		1.6	-0.1		(54)

Table XXIV. Observed Frequencies (cm^{-1}), Approximate Description of Modes, and Most Important Internal Force Constants (mdyn/Å) Computed to Fit the Observed ^{35}Cl and ^{37}Cl Isotopic Shifts and Assuming Two Different Bond Angles of $ClO_2F_2^+$ (69)

A_1	ν_1	1241	$\nu_{sym}(ClO_2)$
	ν_2	756	$\nu_{sym}(ClF_2)$
	ν_3	514	$\delta_{sym}(ClO_2)$
	ν_4	390	$\delta_{sym}(ClF_2)$
A_2	ν_5	390	τ
B_1	ν_6	1479	$\nu_{asym}(ClO_2)$
	ν_7	530	$\delta_{rock}(ClO_2)$
B_2	ν_8	830	$\nu_{asym}(ClF_2)$
	ν_9	514	$\delta_{rock}(ClF_2)$

		∠OClO, ∠FClF, deg	
		124, 96	114, 106
f_D	(ClO)	12.20	12.04
f_{DD}		−0.46	−0.66
f_R	(ClF	4.40	4.53
f_{RR}		−0.32	0.03

Table XXV. Vibrational Spectrum (cm^{-1}) of Gaseous $FClO_3$ and its Assignment for Point-Group C_{3v}

			Infrared (174)	Raman (71)
A_1	ν_1	sym ClO_3 stretch	1061s	1062.8, 1060.9[a] vs, p
	ν_2	ClF stretch	717s, 707m	716.8, 706.6 s, p
	ν_3	sym ClO_3 deform.	549w	548.8 m, p
E	ν_4	asym ClO_3 stretch	1315 vs	1314w
	ν_5	asym ClO_3 deform.	589m	573w
	$\nu 6$	rocking	405w	414w

(a) Splittings are due to ^{35}Cl and ^{37}Cl isotopes

Table XXVI. Ionization Data for Perchloryl Fluoride (80)

band number	adiabatic i.p./eV	vertical i.p./eV	vibrational spacing/cm^{-1}	vibrational assignment	orbital assignment
1	13.04(1)	—	370(40)	ν_2 or ν_4	6b$_2$
	13.57(2)	—	475(60)	ν_3	2a$_2$
2	14.65(1)	15.15[illegible] (6)	340(16)	ν_2	6b$_1$
	15.161(6)	15.307(6)	1025(30)	ν_1	11a$_1$
3	16.676(5)	16.676(5)	1135(16)	ν_1	5b$_2$
			605(30)	ν_2	
			510(20)	ν_2	
4	18.07(3)	16.31(2)	—	—	5b$_1$
5	19.175(7)	19.390(4)	850(30)	ν_2	4b$_2$
			465(40)	ν_2	
	19.699(7)	19.607(7)	855(30)	ν_2	9a$_1$
			500(20)	ν_3	
6	—	21.7(1)	—	—	4b$_1$
7	—	24.2(1)	—	—	6a$_1$
		ground state	1269	ν_1	
			646	ν_2	
			544	ν_3	
			384	ν_4	

Standard deviations are given in parentheses after each quantity. Sh, inflexion point of shoulders observed.

Table XXVII. Calculated Eigenvalues and Percentage Character of Valence Molecular Orbitals for $FClO_3$ (80)

		atomic character (%)						
		chlorine orbital			oxygen orbital		fluorine orbital	
orbital	eigenvalue eV	3d	3s	3p	2s	2p	2s	2p
$1a_2$	−12.9	—	—	—	—	100	—	—
$7e$	−14.1	10.5	—	—	—	78.0	—	11.0
$10a_1$	−15.4	12.6	—	1.9	1.1	44.3	—	39·8
$6e$	−16.0	16.5	—	—	5.3	74.0	—	3.9
$5e$	−18.6	9.2	—	1.8	1.3	18.7	—	68.9
$4e$	−21.5	4.3	—	24.8	19.1	38.0	—	13.3
$9a_1$	−23.3	1.1	1.1	34.1	16.8	29.4	2.6	11.4
$8a_1$	−26.2	—	18.2	10.0	34.2	12.3	7.6	17.2
$3e$	−40.6	2.9	—	24.5	66.7	5.0	—	—
$7a_1$	−43.0	2.4	3.9	8.1	14.0	1.9	68.7	—
$6a_1$	−47.6	—	44.7	—	29.2	6.5	17.5	1.6

Table XXVIII. Some Physical Properties of $FClO_3$

Property	Value	References[a]
Melting point	-147.75°C	(92, 160)
Boiling point	-46.67°C	(31, 92, 160)
T_{crit}	95.17°C	(92, 100, 148)
P_{crit}	53.0 atm	(148)
Crit. density	0.637 g cm^{-3}	(92, 100)
Crit. molar volume	161 cm^3	(92)
Vapor pressure (for T= -109 to -44°C)	log p(mm)= -1652.3/T(°K) -8.62625 log T +0.0046098T +28.44780	(92, 148, 160)
Density of solid (-190°C)	2.19 g cm^{-3}	(281)
Density of liquid (for T= -142 to -39°C)	ρ(g cm^{-3})= 2.266-1.603x10^{-3}T -4.080x$10^{-6}T^2$(°K)	(92, 100, 148, 224)
(for T= 29.9 and 53.8°C)	ρ(g cm^{-3})= 1.390 and 1.276	(268)
Viscosity of liquid (for T= -77 to 54°C)	log η = 299T^{-1}-1.755 (centipoise)	(224, 268)
Surface tension (for T= -75.2 to -55.6°C)	24.1 to 21.3 dyn cm^{-1}	(268)
ΔH_{fusion}	0.9163 kcal mol^{-1}	(16, 17, 160)
ΔS_{fusion}	7.12 e.u.	(16, 17)
ΔS_{vap} (-46.67°C)	4.619 kcal mol^{-1}	(31, 92, 148, 160)
Trouton constant	20.395 e.u.	(31, 92, 160)
$\Delta H^{\circ}_{f\ 298}$ (g)	-5.7 kcal mol^{-1}	(15-18, 8[illegible], 204, 291)
$\Delta G^{\circ}_{f\ 298}$ (g)	11.5 kcal mol^{-1}	(291)
S°_{298}	66.65 e.u.	(147, 148, 172, 208, 291)

$C_{p\ 298}$ (g)	15.517 e.u.	(147, 160, 204, 291)
$C_{p\ 298}$ (l)	27.19 e.u.	(150, 160)
Specific heat ratio, $C_p \div C_v$, gas at 25°C	1.12	(174, 189)

(a) reference from which the listed value is quoted is underlined.

Table XXIX. Performance of Selected Storable Liquid Oxidizers for Rocket Propulsion (105)

Oxidizer	Fuel	Specific impulse,[a] sec	Density impulse, g sec/cm³
ClO_3F	UDMH[b]	290	337
ClF_5	UDMH	279	382
65 ClF_3/35 ClO_3F	UDMH	288	386
ClO_3F	LiH solid[c]	273	337
ClF_5	LiH solid	288	436
88 ClF_3/12 ClO_3F	LiH solid	291	433
ClO_3F	N_2H_4	295	358
ClF_3	N_2H_4	292	436
N_2O_4	N_2H_4	291	354

[a] lb force × sec/lb mass; shifting equilibrium; pressure ratio 1000:14.7.

[b] Unsymmetrical dimethylhydrazine.

[c] 85% LiH, 15% organic binder.

APPENDIX

TABLE XXX. THERMODYNAMIC PROPERTIES FOR ClF_3O GAS (55)

T, °K	$C_p°$, cal/mol	$H° - H_0°$, kcal/mol	$-(F° - H_0°)/T$, cal/(mol deg)	$S°$, cal/(mol deg)
0	0	0	0	0
100	9.721	0.837	49.255	57.624
200	14.932	2.072	55.613	65.971
298.15	18.593	3.732	60.159	72.675
300	18.646	3.766	60.237	72.790
400	20.875	5.751	64.108	78.486
500	22.260	7.913	67.478	83.305
600	23.160	10.187	70.470	87.448
700	23.771	12.536	73.159	91.067
800	24.200	14.936	75.602	94.271
900	24.512	17.372	77.838	97.141
1000	24.744	19.835	79.900	99.736
1100	24.921	22.319	81.813	102.103
1200	25.059	24.818	83.595	104.277
1300	25.168	27.330	85.265	106.288
1400	25.256	29.851	86.834	108.156
1500	25.328	32.380	88.314	109.901
1600	25.387	34.916	89.715	111.538
1700	25.437	37.458	91.044	113.078
1800	25.479	40.003	92.309	114.533
1900	25.514	42.553	93.516	115.912
2000	25.545	45.106	94.668	117.221

TABLE XXXI. THERMODYNAMIC PROPERTIES FOR ClF_3O_2 GAS (57)

T, °K	$C_p°$, cal/mol	$H° - H°_0$, kcal/mol	$-(F° - H°_0)/T$, cal/(mol deg)	$S°$, cal/(mol deg)
0	0	0	0	0
100	10.127	0.847	48.967	57.437
200	16.511	2.179	55.516	66.411
298.15	21.256	4.049	60.375	73.956
300	21.327	4.089	60.459	74.088
400	24.384	6.386	64.711	80.675
500	26.362	8.930	68.484	86.344
600	27.685	11.636	71.881	91.275
700	28.599	14.453	74.968	95.615
800	29.251	17.347	77.795	99.479
900	29.727	20.298	80.400	102.953
1000	30.085	23.289	82.816	106.105
1100	30.360	26.312	85.066	108.985
1200	30.574	29.359	87.171	111.637
1300	30.745	32.425	89.148	114.091
1400	30.883	35.507	91.012	116.375
1500	30.995	38.601	92.775	118.509
1600	31.089	41.705	94.447	120.513
1700	31.167	44.818	96.036	122.400
1800	31.233	47.938	97.551	124.183
1900	31.289	51.064	98.997	125.873
2000	31.337	54.196	100.382	127.480

TABLE XXXII. THERMODYNAMIC PROPERTIES FOR $FClO_3$ GAS (147)

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.178	-3.034	-3.034	INFINITE
100	8.462	54.278	78.032	-2.375	-3.996	1.097	-2.397
200	12.073	61.160	67.968	-1.362	-4.715	6.493	-7.095
298	15.517	66.653	66.653	.000	-5.120	12.090	-8.861
300	15.573	66.749	66.653	.029	-5.125	12.196	-8.884
400	18.152	71.602	67.297	1.722	-5.298	18.002	-9.835
500	20.000	75.863	68.593	3.635	-5.312	23.831	-10.416
600	21.315	79.633	70.125	5.704	-5.226	29.653	-10.801
700	22.271	82.994	71.728	7.886	-5.076	35.455	-11.069
800	22.967	86.016	73.320	10.150	-4.884	41.231	-11.263
900	23.467	88.753	74.893	12.474	-4.665	46.983	-11.408
1000	23.883	91.249	76.405	14.843	-4.426	52.710	-11.519
1100	24.189	93.540	77.860	17.248	-4.175	58.410	-11.604
1200	24.430	95.655	79.256	19.679	-3.914	64.090	-11.672
1300	24.624	97.619	80.594	22.132	-3.649	69.746	-11.725
1400	24.789	99.449	81.876	24.602	-3.382	75.380	-11.767
1500	24.909	101.164	83.106	27.087	-3.112	80.998	-11.801
1600	25.016	102.775	84.285	29.584	-2.843	86.596	-11.828
1700	25.105	104.294	85.418	32.090	-2.574	92.179	-11.850
1800	25.181	105.731	86.507	34.604	-2.311	97.744	-11.867
1900	25.246	107.094	87.555	37.125	-2.051	103.297	-11.881
2000	25.301	108.391	88.564	39.653	-1.795	108.833	-11.892
2100	25.349	109.626	89.538	42.185	-1.544	114.359	-11.901
2200	25.391	110.807	90.478	44.723	-1.300	119.871	-11.908
2300	25.428	111.936	91.387	47.264	-1.060	125.374	-11.913
2400	25.461	113.019	92.266	49.808	-.828	130.868	-11.917
2500	25.489	114.059	93.117	52.356	-.605	136.347	-11.919
2600	25.515	115.059	93.942	54.906	-.386	141.823	-11.921
2700	25.538	116.023	94.742	57.458	-.176	147.289	-11.922
2800	25.558	116.952	95.518	60.013	.027	152.747	-11.922
2900	25.577	117.849	96.273	62.570	.223	158.199	-11.922
3000	25.593	118.716	97.007	65.129	.411	163.641	-11.921
3100	25.608	119.556	97.721	67.689	.593	169.082	-11.920
3200	25.622	120.369	98.416	70.250	.767	174.513	-11.918
3300	25.635	121.158	99.093	72.813	.935	179.937	-11.916
3400	25.646	121.923	99.752	75.377	1.095	185.360	-11.914
3500	25.657	122.667	100.398	77.942	1.249	190.776	-11.912
3600	25.666	123.390	101.026	80.508	1.396	196.192	-11.910
3700	25.675	124.093	101.640	83.075	1.537	201.600	-11.907
3800	25.683	124.778	102.240	85.643	1.673	207.009	-11.905
3900	25.691	125.445	102.827	88.212	1.803	212.404	-11.902
4000	25.698	126.096	103.400	90.782	1.926	217.803	-11.900
4100	25.704	126.730	103.961	93.352	2.043	223.200	-11.897
4200	25.711	127.350	104.511	95.922	2.156	228.592	-11.894
4300	25.716	127.955	105.049	98.494	2.264	233.986	-11.892
4400	25.721	128.546	105.577	101.066	2.366	239.370	-11.889
4500	25.726	129.124	106.093	103.638	2.464	244.755	-11.886
4600	25.731	129.690	106.600	106.211	2.558	250.143	-11.884
4700	25.735	130.243	107.097	108.784	2.646	255.525	-11.881
4800	25.739	130.785	107.585	111.358	2.731	260.904	-11.879
4900	25.743	131.316	108.064	113.932	2.812	266.277	-11.876
5000	25.747	131.836	108.534	116.507	2.889	271.652	-11.873
5100	25.750	132.346	108.996	119.082	2.961	277.029	-11.871
5200	25.753	132.846	109.450	121.657	3.030	282.399	-11.868
5300	25.756	133.336	109.896	124.232	3.097	287.779	-11.866
5400	25.759	133.818	110.335	126.808	3.158	293.140	-11.863
5500	25.762	134.290	110.766	129.384	3.220	298.518	-11.861
5600	25.765	134.755	111.190	131.960	3.274	303.881	-11.859
5700	25.767	135.211	111.608	134.537	3.327	309.248	-11.857
5800	25.769	135.659	112.019	137.114	3.378	314.621	-11.855
5900	25.771	136.099	112.423	139.691	3.425	319.982	-11.852
6000	25.[illegible]	[illegible]	112.821	142.268	3.470	325.347	-11.850

Diagram Captions

Figure 1. Geometries of the chlorine oxyfluoride molecules and their ions compared to those of the corresponding chlorine fluorides

(a) Since the Cl^+ cation would possess only an electron sextet it is stabilized by a ClF molecule to form the Cl_2F^+ cation.

(b) double brackets indicate yet unknown ions.

(c) see text for preference of cis model.

(d) these compounds with a coordination number of 7 are unlikely to exist.

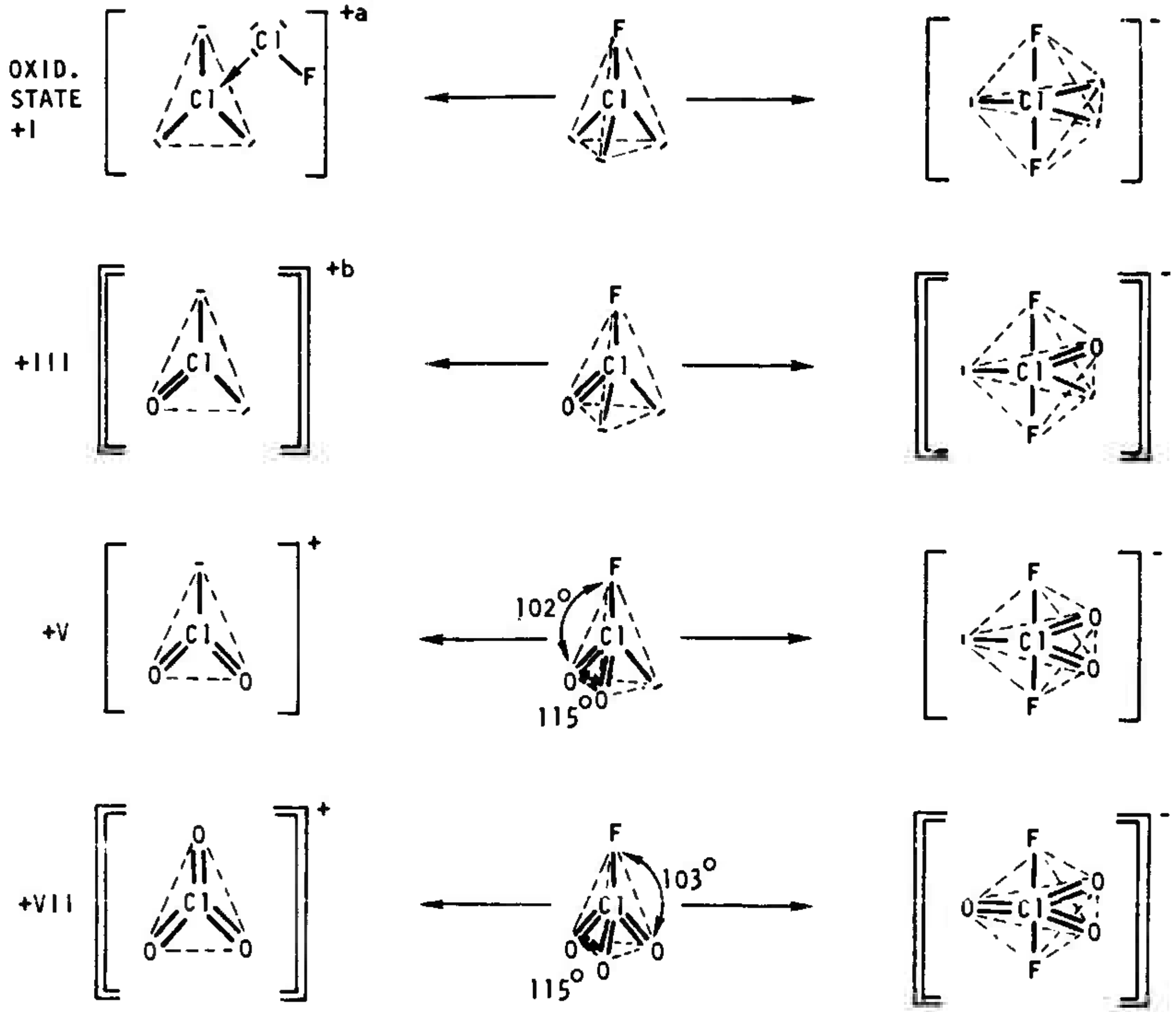
Figure 2. Structures of the yet unknown ClF_3O^+, ClF_4O, and ClF_3O^- radicals (upper row) predicted by comparison with the known structures (bottom row) of ClF_3O and ClF_4O^-.

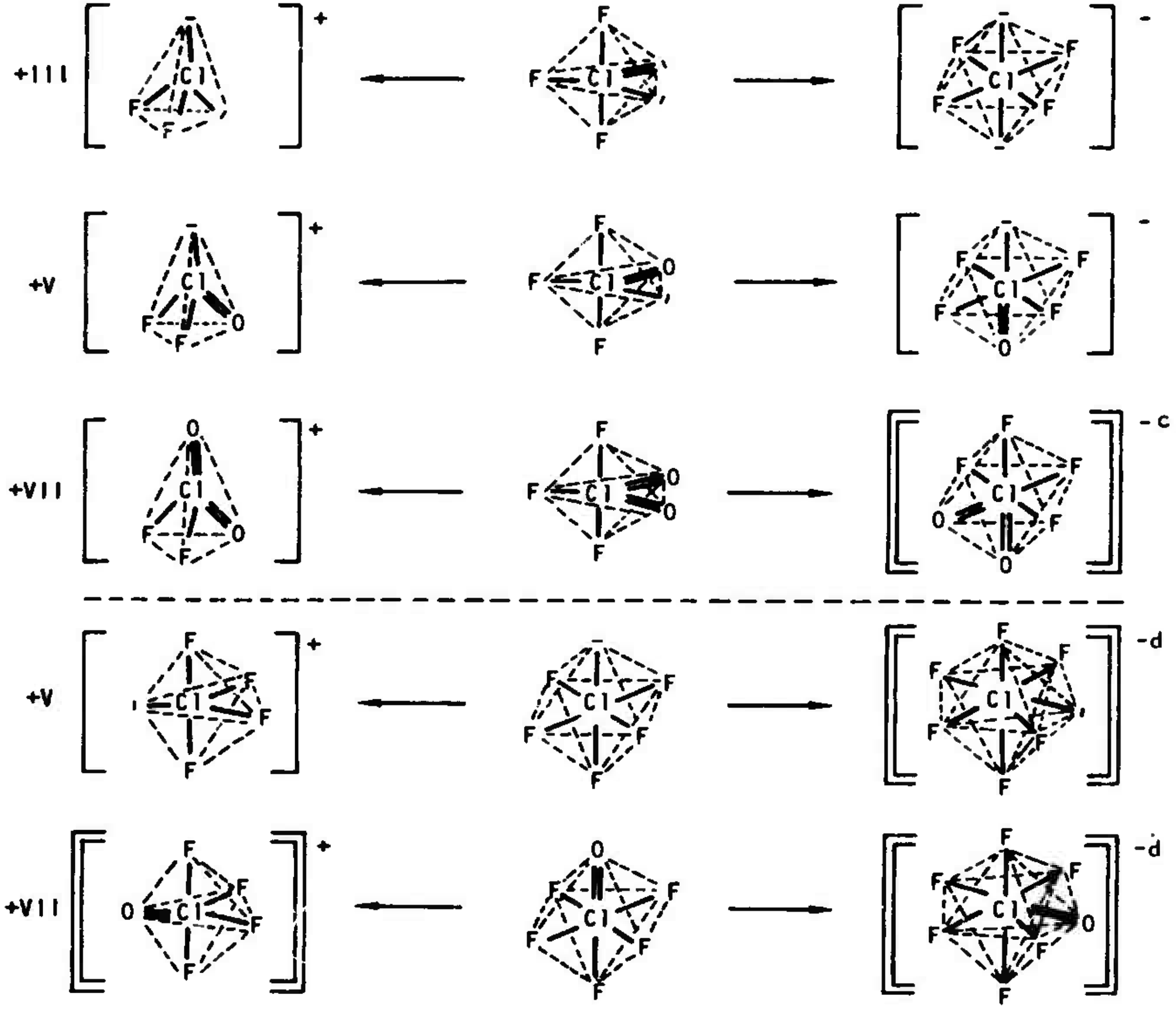
Figure 3. The schematic bonding in ClF_2^- as explained by a semi-ionic 3c-4e bond model.

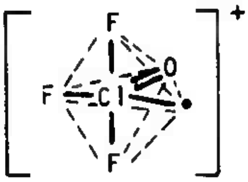
Figure 4. ClF_3O Formed as a Function of Time and Oxygen Partial Pressure (P_{ClF_3} = 10 Torr).

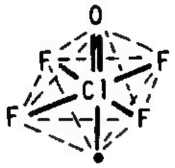
Footnotes

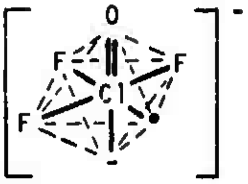
page 1: * For the sake of clarity, we have not followed a rigid system of nomenclature, such as starting formulas with the central atom followed by the ligands. If for example FClO is written as ClOF, an uninformed reader might be induced to think of the compound as a hypofluorite.


OXID.
STATE
+I
+a
Cl
F
Cl
F
Cl
F
Cl
F
-
+III
+b
Cl
O
F
Cl
O
F
Cl
O
F
-
+V
+
Cl
O
O
F
102°
Cl
O
115°
O
F
Cl
O
O
F
-
+VII
+
O
Cl
O
O
F
103°
Cl
O
115°
O
O
F
O
Cl
O
O
F
-

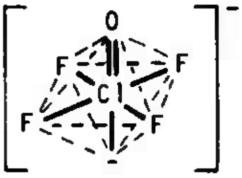

+III
+V
+VII
+V
+VII
+
-
-c
-d
F
O
Cl


F
O
F
Cl
F
+

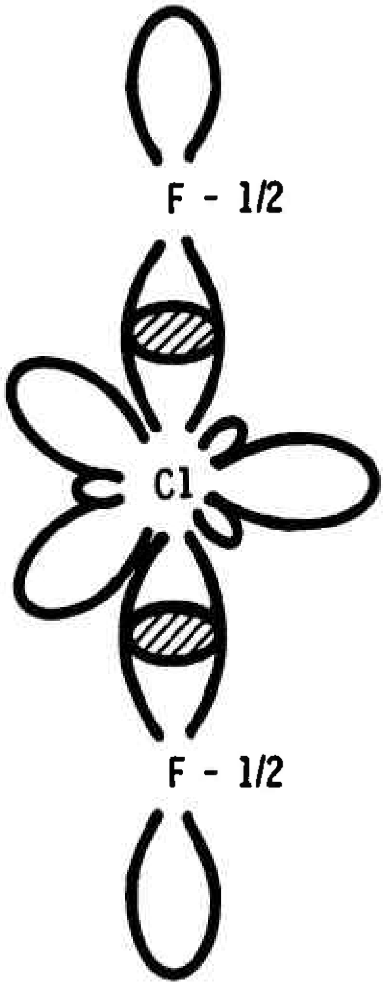

O
F
F
Cl
F
F

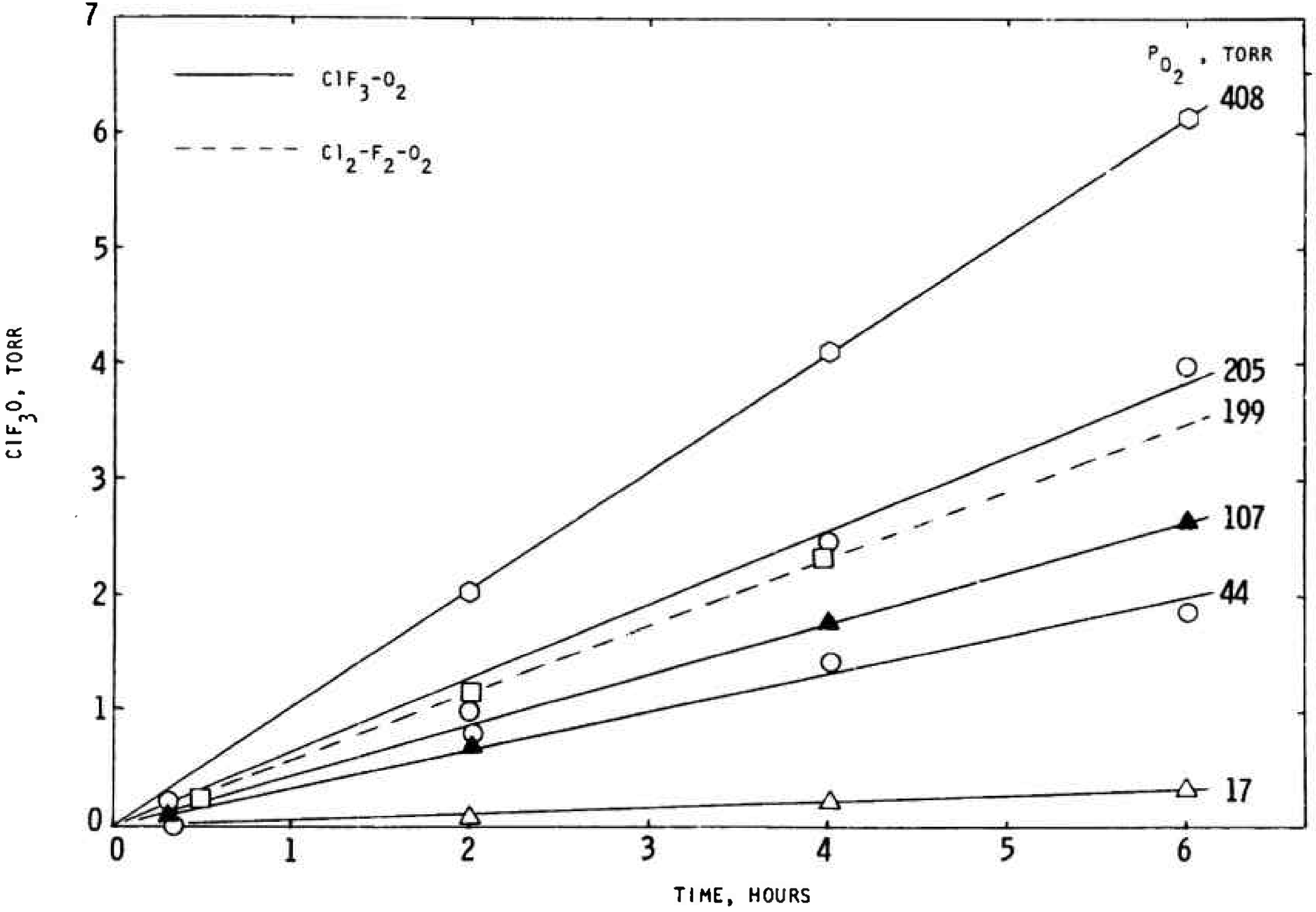

O
F
F
Cl
F
-


F
O
F
Cl
F


O
F
F
Cl
F
F
-


O
F
F
Cl
F
F
-


F - 1/2
Cl
F - 1/2


ClF_3-O_2
Cl_2-F_2-O_2
P_{O_2}, TORR
408
205
199
107
44
17
ClF_3O, TORR
0
1
2
3
4
5
6
7
TIME, HOURS

Contribution from the Department of Chemistry, The University,
Leicester LEI 7RH and Rocketdyne, a Division of Rockwell
International, Canoga Park, California 91304

The NF_3^+ Radical Cation. Electron Spin Resonance Studies of Radiation Effects in NF_4^+ Salts

S. P. Mishra, M. C. R. Symons, K. O. Christe,*
R. D. Wilson and R. I. Wagner

Received. . . August 9, 1974. . . .

Abstract

Exposure of $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^+\cdot 0.8SbF_5$ to ^{60}Co γ-rays at 77°K gave two paramagnetic centres, one of which is shown by esr spectroscopy to contain one nitrogen atom and three equivalent fluorine atoms. Based on its magnetic properties it is identified as pyramidal $\dot{N}F_3^+$, a novel radical cation. The other center exhibits strong interaction of the electron with two fluorine atoms, weaker interaction with the antimony or arsenic central atom, and small interaction with several other fluorine atoms. It is tentatively assigned to the electron-loss species $As\dot{F}_6$, $Sb\dot{F}_6$, or $Sb_2\dot{F}_{11}$ with the unpaired electron largely confined to two fluorine ligands. Irradiation of $NF_4^+BF_4^-$ did not result in well defined magnetic centers. An improved synthesis of $NF_4^+BF_4^-$ is reported.

Introduction

Although carbon readily forms tetrahedral molecules with electronegative ligands, such as the halogens, the synthesis of the isoelectronic nitrogen compounds has been achieved only recently.[1] Attempts to prepare NF_4^+ salts had been discouraged by theoretical computations[2,3] showing that these salts should be thermodynamically unstable, and by the nonexistence of the parent compound NF_5. Once the principle was recognized[1] that NF_4^+ salts can be prepared from NF_3, F_2 and a strong Lewis acid in the presence of a suitable activation energy source, a number of synthetic methods became available. These involve the use of different activation energy sources such as glow discharge,[4,5] elevated temperature and pressure,[6,7] γ-irradiation,[8] and uv photolysis.[9]

On exposure to high energy radiation, CF_4 undergoes the dissociative electron-capture process

$$CF_4 + e^- \rightarrow \dot{C}F_3 + F^- \qquad (1)$$

to give $\dot{C}F_3$ radicals which have been detected both in the liquid[10] and solid[10-12] phase. The fact that no evidence for the existence of the $\dot{C}F_4^-$ radical anion was observed is not surprising in view of the validity of the octet rule for first row elements of the periodic system. A study of the corresponding NF_4^+ system appeared interesting, particularly in view of the recent suggestion[9] that $\dot{N}F_3^+$ and the radicals derived from the Lewis acid-fluorine interaction, such as $\dot{As}F_6$, are the key intermediates in the formation mechanism of NF_4^+ salts. By analogy with CF_4, one might expect that $\dot{N}F_3^+$ might be prepared by γ-irradiation of NF_4^+ salts according to:

$$NF_4^+ + e^- \rightarrow \dot{N}F_3^+ + F^- \qquad (2)$$

In this paper we report esr spectroscopic evidence for the existence of the novel radicals $\dot{N}F_3^+$ and $\dot{M}F_6$, in addition to an improved synthesis of $NF_4^+BF_4^-$ by metathesis in HF solution.

Experimental

Syntheses of NF_4^+ Salts. A sample of $NF_4^+SbF_6^-\cdot0.8SbF_5$ was prepared as previously described[7] by heating a 1:1.2:1 molar mixture of NF_3, F_2, and SbF_5 in a Monel cylinder to 120° for two days under an autogenous pressure of 200 atm. The resulting white solid, having the composition $NF_4^+SbF_6^-\cdot1.9SbF_5$, was converted to $NF_4^+SbF_6^-\cdot0.8SbF_5$ by heating in a dynamic vacuum to 200° for three days. The compound was analyzed us previously described.[13] The only detectable impurities were small amounts of Ni(0.066 weight%) and Cu (0.03%) in form of their salts. The synthesis of $NF_4^+AsF_6^-$ has previously been described.[13] Again, the only detectable impurities were Ni(0.98%) and Cu(0.27%).

For the synthesis of $NF_4^+BF_4^-$ by metathesis, commercial HF was dried by shaking it overnight in a 1-liter Monel cylinder with fluorine (10 l/0.7 Kg HF) after which oxygen and residual fluorine (ca 210 psi) were removed under vacuum at -78°. The metathesis apparatus, fabricated entirely from Teflon and Kel-F, consisted of four identical 1-liter vessels connected in series through valves and filters with a fitting carrying a vacuum line connection, a 60 psi pressure relief valve, and a compound pressure-vacuum gage (Kel-F coated diaphragm) between the last two vessels. In addition, each vessel was stirred with a Teflon coated magnetic stirring bar and equipped with a valve which by-passed the filter for introduction or removal of gaseous or liquid materials. All manipulations of reagents and products were conducted either in an inert atmosphere glove box or by standard high vacuum techniques.

A 251.5g (1.94 moles) quantity of silver fluoride (Cationic, Inc.), which contained 2.1% HF insoluble impurities, was loaded into the first vessel and 284g HF was added. Into the second vessel were placed 400.5g (0.822 mole) $NF_4SbF_6 \cdot 0.8SbF_5$ and 148g HF. The $AgHF_2$ solution in the first vessel was pressurized to 30 psi with nitrogen and passed through a filter into the stirred NF_4^+ salt - HF solution under autogeneous pressure in the second vessel. The resulting NF_4HF_2 solution was separated from the $AgSbF_6$ precipitate by filtration into the evacuated third reaction vessel. After brief pumping to remove the nitrogen pressurizing gas, BF_3 (68g, 1.0 mole) was added to the third vessel until the total pressure above the liquid remained constant at 19-20 psi. The NF_4BF_4 solution was separated from the precipitated $AgBF_4$ by filtration into the evacuated fourth vessel. After removal of excess BF_3 and solvent HF the residual solid product (101.9g) was isolated. The composition of the solid in mole % was NF_4BF_4 (89), $NF_4\ Sb_2F_{11}$ (7.9) and $AgBF_4$ (3.1).

γ-Irradiation and esr Spectra. The NF_4^+ salts were transferred in the dry nitrogen atmosphere of a glove box into passivated, 4 mm o.d. quartz tubes which were flame sealed in vacuo. For the solution study, a 0.24 molar solution of $NF_4^+SbF_6^- \cdot 0.8SbF_5$ in anhydrous HF was heat sealed in a Teflon FEP tube.

The sample tubes were cooled to 77°K prior to exposure to ^{60}Co γ-rays in a Vickrad cell at a nominal dose rate of about 4 MRad h^{-1}. It was necessary to expose samples to high doses (about 10 MRad) before good esr signals were obtained.

The esr spectra were obtained with a Varian E3 spectrometer at 77°K. Samples were annealed by gradual warming to above 77°K and re-cooling whenever significant changes were observed in the continuously monitored esr signals. Signals were independent of sample-tube orientation indicating the absence of sample graining effects.

Results and Discussion

Synthesis. For the preparation of $NF_4^+SbF_6^- \cdot xSbF_5$ and $NF_4^+AsF_6^-$ the previously reported[7] elevated pressure-temperature method was chosen. For that of $NF_4^+BF_4^-$, a metathetical process similar to that of Tolberg et al.,[14] was selected which was significantly improved by substituting AgF for the originally used[14] CsF. The reaction sequence is best described by the following equations:

$$AgF + HF \xrightarrow{HF} Ag^+ HF_2^- \qquad (3)$$

$$Ag^+HF_2^- + NF_4^+SbF_6^- \xrightarrow{HF} AgSbF_6\downarrow + NF_4^+HF_2^- \qquad (4)$$

$$NF_4^+HF_2^- + BF_3 \xrightarrow{HF} NF_4^+BF_4^- + HF \qquad (5)$$

Since $Ag^+HF_2^-$ was used in excess for the precipitation of the fluoroantimonate, the rather insoluble $AgBF_4$ precipitated from the $NF_4^+HF_2^-$ solution upon BF_3 addition. This required an additional filtration step. The level of impurities ($NF_4Sb_2F_{11}$ and $AgBF_4$) in the final crude product is determined by the solubility products of $AgSbF_6$ and $AgBF_4$ in HF.

Since the $NF_4^+SbF_6^- \cdot xSbF_5$ starting material can readily be prepared on a large scale,[7] this metathetical process is well suited for the synthesis of larger amounts of $NF_4^+BF_4^-$. Its main drawback is the relatively low product purity. Using CsF the purity is quite low, but with AgF we have been able to obtain purities as high as 89 mole percent of $NF_4^+BF_4^-$. The main impurities could significantly be decreased by subsequent recrystallization[14] of the crude $NF_4^+BF_4^-$ from suitable solvents. Whereas the γ-irradiation[8] and uv-photolysis[9] processes yield purer products, they are at present much less amenable to scale up.

Electron Spin Resonance Spectra. The best defined spectra were obtained from $NF_4^+SbF_6^- \cdot 0.8SbF_5$ and typical spectra, obtained before and after annealing, are given in Figures 1 and 2, respectively. The $NF_4^+AsF_6^-$ salt gave very similar results, but $NF_4^+BF_4^-$ proved to be remarkably resistant to ^{60}Co γ-rays. Two radical species, A and B, can be detected in the initial spectra (Figure 1), but radical B decayed rapidly on annealing to about 150°K, leaving a well defined spectrum of A (Figure 2).

Radical A. Well defined wing (parallel) triplets characteristic of hyperfine coupling to $^{14}N[I(^{14}N) = 1]$ establish the presence of one strongly coupled ^{14}N nucleus. If the outer sets of triplets are described as the $M_I(^{19}F) = \pm 3/2$ "parallel" features for $\dot{N}F_3^+$ $[I(^{19}F) = 1/2]$ for the three equivalent fluorine atoms, then the ± 1/2 lines are predicted to fall close to the more intense set of six lines in the central region of the spectrum. However, the apparent A (^{14}N) coupling on these inner features has decreased by about 15 G relative to the outer lines, and hence we suggest that these inner lines contain dominant contributions arising from "anisotropic" features.

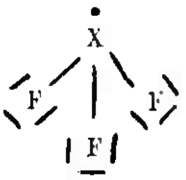
Interpretation of esr spectra for pyramidal radicals of this type is complicated by the fact that the principle values for the three ^{19}F hyperfine tensors lie along three different axes, two of which always differ from those for the ^{14}N hyperfine coupling. Also, there should be a relatively large second-order splitting (δ) of the $M_I(^{19}F) = \pm 1/2$ lines which can be approximately estimated[15] from $\delta_{\parallel} = 3/2 \frac{A_{\perp}(^{19}F)}{H_{\perp}}$ and $\delta_{\perp} = 3/4 \frac{(A_{\perp} + A_{\parallel})}{H_{\parallel}}$

From the initial approximate data, we find $\delta_{\parallel} \simeq 3$ G and $\delta_{\perp} \simeq 23$ G. Thus the former will be barely defined in our spectra, but the latter result is clearly significant. This problem has been discussed in depth by Coope,[11, 16] especially for the isoelectronic radical, $\dot{C}F_3$, and we have followed their procedure in arriving at the parameters listed in Table 1. The results for $\dot{C}F_3$ [10, 12] are included for comparison.

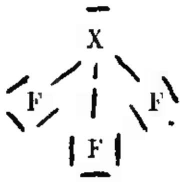
The results for ^{19}F of $\dot{N}F_3^+$ are in good agreement with those[12] of $\dot{C}F_3$, but indicate a small increase in spin-density on fluorine on going from $\dot{C}F_3$ to $\dot{N}F_3^+$.

Since these are not principle values, we make no attempt to estimate the actual spin-density on fluorine from these data. However, the data for ^{14}N can be taken as principle values and hence we can deduce approximate spin densities in the 2s and 2p atomic orbitals that nitrogen contributes to the total M.O. of the unpaired electron. This we do by dividing the A and 2B values by the values for A° (550 G) and 2B° (33G) estimated from recent accurate atomic wave functions.[17] (A and 2B are the experimental isotropic and traceless parts of the hyperfine tensor components, and A° and 2B° are the corresponding computed values for unit population of the 2S and 2p A. Os.) The results (Table 2) indicate that the total spin-density on nitrogen is about 69%, and the 2p:2s ratio is about 2.8. Only the isotropic ^{13}C datum is known[10] for $^{13}\dot{C}F_3$, and this gives about 24% spin-density in the 2s A.O. on carbon. The latter value might be somewhat high, since the anisotropic components of ^{19}F in $\dot{N}F_3^+$ and $\dot{C}F_3$ are quite similar (133 and 123G, respectively) implying that the spin-densities on F and hence also on the central atoms should be similar in both species. An alternate, although less plausible, explanation might be that the atomic orbitals of the central atom in $\dot{C}F_3$ have more s-character (i.e., a stronger contribution from sp^2 hybridization) than those in $\dot{N}F_3^+$. This would imply that $\dot{C}F_3$ is less pyramidal than $\dot{N}F_3^+$.

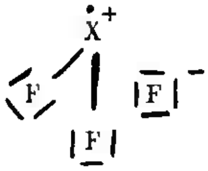
The implications from the esr data that in $\dot{N}F_3^+$ the spin-density on F is somewhat higher than in $\dot{C}F_3$ and that the atomic orbitals of the central atom in $\dot{C}F_3$ have more s-character than those in $\dot{N}F_3^+$ are in accord with arguments based on consideration of the following resonance structures.



I



II



III

In $\dot{N}F_3^+$ the formal positive charge and the higher oxidation state of the central atom should increase the effective electronegativity of the NF_2^+ group when compared to that of CF_2. Therefore, for $\dot{N}F_3^+$ the relative contribution from structure II should be higher than for CF_3 hereby increasing the spin-density on F in $\dot{N}F_3^+$. Since with an increasing electronegativity difference between X and F the XF bond becomes more ionic, the contribution from the sp^2 hybridized model III to the bonding should be more significant in $\dot{C}F_3$ than in $\dot{N}F_3^+$. In addition, model III for $\dot{N}F_3^+$ would require an unfavorable double positive charge on the NF_2 part of the molecule.

The failure to observe any evidence for the NF_4 radical is not surprising in view of the above mentioned strict validity of the octet rule for first row elements. This is in marked contrast with second row elements, such as phosphorous for which the corresponding PF_4 has been observed.[18,19] We have also studied the irradiation products from HF solutions of $NF_4^+SbF_6^- \cdot 0.8\ SbF_5$ since it is often found that dissociative reactions, such as the hypothetical process

$$NF_4 \rightarrow \dot{N}F_3^+ + F^- \qquad (6)$$

are solvent dependent. Unfortunately, solutions in HF, the only suitable solvent, gave, after irradiation, only very broad uninformative features.

<u>Radical B.</u> The other species (B), lost during mild annealing, is tentatively identified as $Sb\dot{F}_6$ (or $As\dot{F}_6$) or $Sb_2\dot{F}_{11}$ for the following reasons:

(1) $\dot{N}F_3^+$ is undoubtedly formed by electron capture, and the most reasonable initial electron-loss centre is $Sb\dot{F}_6$.

(2) The results indicate the presence of two (or less reasonably, one) strongly coupled ^{19}F nuclei with very weak coupling to magnetic isotopes of antimony or arsenic and possible further ^{19}F nuclei. Electron loss from SbF_6^- is from one of the non-bonding orbitals on fluorine, and a suitable distortion could well tend to isolate the unpaired electron on just two of the ligands. This model provides a reasonable explanation for the observed data.

(3) The broad similarity between the results for the arsenic and antimony salts requires a low spin-density on the central atom, in accord with the model.

(4) Lack of $\dot{N}F_3^+$ radicals in the BF_4^- salt accord with the apparent inability to form $\dot{B}F_4$ radicals from such salts.[18]

Based on the above arguments, we favor the spectral analysis indicated in Fig. 1 rather than the alternative of treating the B features as a doublet, on the basis of the relatively small anisotropy. For a distorted radical with the unpaired electron delocalized between two adjacent fluoride ligands, the apparent anisotropy deduced from the powder spectrum must be greatly reduced compared with the real anisotropy, or that to be expected from spin confined to just one ligand.

The super-hyperfine coupling present on the $M_I(^{19}F) = \pm 1$ lines must then arise from coupling to ^{121}Sb ($I = 5/2$; 57.25% abundance) and to a lesser extent from ^{123}Sb ($I = 7/2$; 42.75% abundance). This will not explain all the resolved features in Fig. 1 and hence extra ^{19}F coupling or interaction with the second antimony atom of Sb_2F_{11} must also be present.

It is interesting to compare these results with those for a species formed in irradiated sodium hexafluoroantimonate, originally thought to be SbF_5^- or SbF_6^{2-},[20] but later assigned to an impurity species, $\dot{O}\text{-}SbF_4$ or $\dot{O}SbF_5^-$.[21] This centre had only very weak coupling to ^{19}F (about 5G) and a near-isotropic coupling to ^{121}Sb in the 60 - 70 G region. Our present results indicate a coupling to ^{121}Sb of 30 or 60G. A reduction of the coupling in $Sb\dot{F}_6$ or $Sb_2\dot{F}_{11}$, when compared to that for $\dot{O}\text{-}SbF_5^-$, can be rationalized by electro-negativity arguments.[21, 22]

Although we have been unable to obtain well resolved esr spectra for radical B, we conclude that this center is probably $Sb\dot{F}_6$ or $Sb_2\dot{F}_{11}$, with the unpaired electron largely confined to two adjacent fluoride ligands. Other possible assignments that had occurred to us, have been rejected for various reasons. For example, the assignment to F_2^-, weakly interacting with neighbouring ions, can be ruled out since the observed hyperfine coupling is too small.

Summary. γ-Irradiation of NF_4^+ salts at 77°K produces the novel pyramidal cation $\dot{N}F_3^+$ in addition to a second less stable species which is tentatively assigned to the corresponding anion electron-loss species, $Sb\dot{F}_6$, $Sb_2\dot{F}_{11}$, and $As\dot{F}_6$, respectively. The experimental observation of these species lends further credibility to the reaction mechanism previously suggested[9] for the formation and thermal decomposition of NF_4^+ salts. In this mechanism, the $As\dot{F}_6$ radical was postulated to be the crucial intermediate capable of supplying the energy (ionization potential of NF_3 minus the energy released by the formation of the ion pair) required for the oxidation of NF_3 according to:

$$As\dot{F}_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6^- \qquad (7)$$

Acknowledgement. The group from Rocketdyne is grateful to the Office of Naval Research, Power Branch, for financial support and to Drs. L. R. Grant, C. J. Schack, and I. B. Goldberg for helpful discussions.

Table 1

ESR Data for Radical in γ-Irradiated NF_4^+ Salts, Together with Those for $\dot{\mathrm{C}}\mathrm{F}_3$

Radical	Hyperfine Tensor Components (G) [a, b]						g-Values		
	$^{14}\mathrm{N}/^{13}\mathrm{C}/^{121}\mathrm{Sb}$			$^{19}\mathrm{F}$					
	∥	⊥	iso	∥	⊥	iso	∥	⊥	av.
$\dot{\mathrm{N}}\mathrm{F}_3^{+}$ [i]	115	90	98.3	300	100	167	2.003	2.009	2.007
$\dot{\mathrm{C}}\mathrm{F}_3$ [d]				264	80	141.3			
[e]			272			143			
$\mathrm{SbF}_6^{\bullet}$	~ 30 or ~ 60 (see text)			630[f,g]	420[f,g]	490 + ~ 30 G[h]		~ 2.00	

a. G = 10^{-4} T.

b. Errors ~ ± 3 G.

c. Data relate to the C_{3v} axes and therefore are not principle values.

d. Reference 12.

e. Reference 10.

f. For two equivalent fluorine atoms.

g. Approximate since number of sub-components unknown.

h. Weak coupling to other fluoride ligands.

i. The NF_3^{+} signals derived from either $\mathrm{NF}_4\mathrm{SbF}_5$ or $\mathrm{NF}_4\mathrm{AsF}_6$ had experimentally undistinguishable parameters.

Table 2

Estimated Spin-Densities (%) for $\dot{N}F_3^+$ and $\dot{C}F_3$ on Central Atom

	a_s^2	a_p^2	Total	2p/2s
$\dot{N}F_3^+$	18	50.5	68.5	2.8
$\dot{C}F_3$	24			

Diagram Captions

Fig. 1

First derivative X-band esr spectrum for $NF_4^+SbF_6^- \cdot 0.8SbF_5$ after exposure to ^{60}Co γ-rays at 77°K, showing features assigned to species A and B. The intense central component stems in part from paramagnetic centers generated in the quartz tube.

Fig. 2

Sample of Fig. 1 but after annealing at about 140°K and recooling to 77°K, showing features assigned to radical A.

References

(1) K. O. Christe, J. P. Guertin, and A. E. Pavlath, U. S. Patent 3,503,719 (1970).

(2) W. C. Price, T. R. Passmore, and D. M. Roessler, Discussions Faraday Soc., 35, 201 (1963).

(3) J. N. Wilson, paper presented at the Symposium on Advanced Propellant Chemistry, American Chemical Society, Detroit, Mich., April 1965.

(4) K. O. Christe, J. P. Guertin, and A. E. Pavlath, Inorg. Nucl. Chem. Lett., 2, 83 (1966).

(5) J. P. Guertin, K. O. Christe, and A. E. Pavlath, Inorg. Chem., 5, 1921 (1966).

(6) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Nucl. Chem. Lett., 2, 79 (1966).

(7) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M E. Hill, Inorg. Chem., 6, 1156 (1967).

(8) C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner, and J. N. Wilson, Inorg. Chem., 11, 1696 (1972).

(9) K. O. Christe, R. D. Wilson, and A. E. Axworthy, Inorg. Chem., 12, 2478 (1973).

(10) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 43, 2704 (1965).

(11) J. Maruani, J.A.R. Coope, and C. A. McDowell, Mol. Phys., 18, 165 (1970).

(12) J. Maruani, C. A. McDowell, H. Nakajima and P. Raghunathan, Mol. Phys., 14, 349 (1968).

(13) K. O. Christe and D. Pilipovich, Inorg. Chem., 10, 2803 (1971).

(14) W. E. Tolberg, private communcation.

(15) R. W. Fessenden, J. Chem. Phys., 37, 747 (1962).

(16) J.A.R. Coope, Chem. Phys. Letts., 3, 589 (1969).

(17) Calculated from the data of C. Froese, J. Chem. Phys., 45, 1417 (1966).

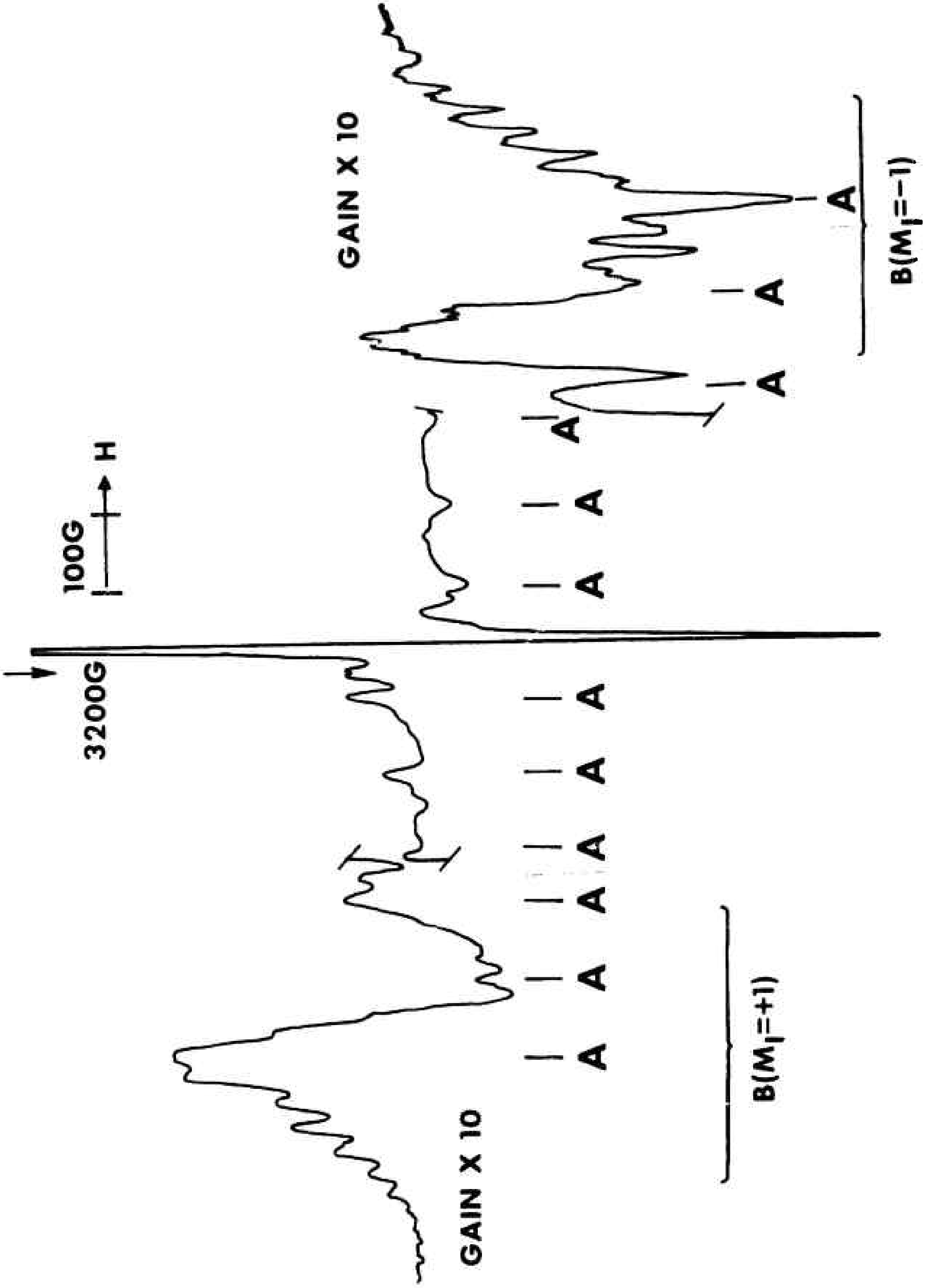
(18) S. P. Mishra and M.C.R. Symons, unpublished results.

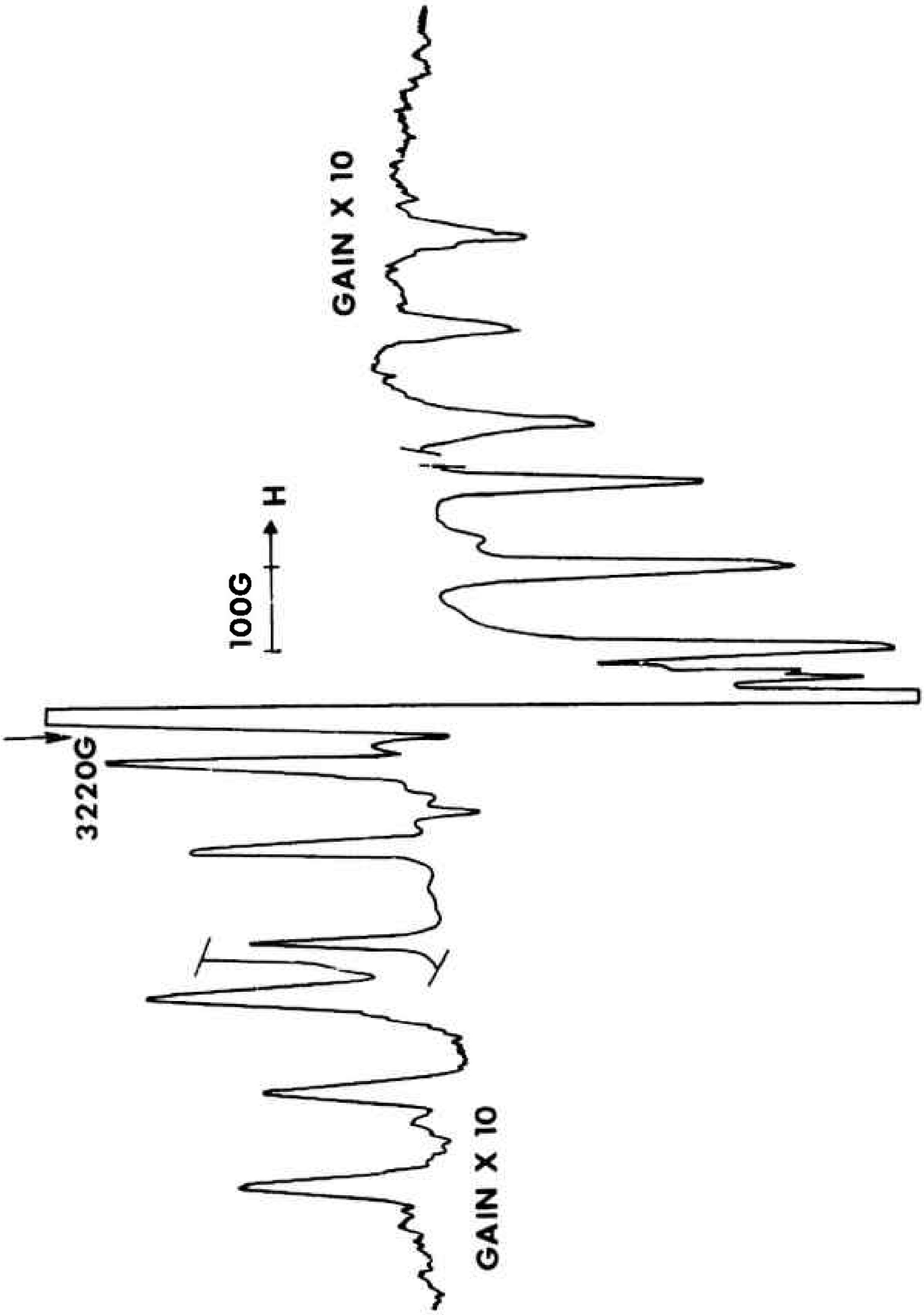
(19) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 45, 1845 (1966).

(20) F. G. Herring, J. H. Hwang and W. C. Lin, J. Phys. Chem., 71, 2086 (1967).

(21) M.C.R. Symons, J. Chem. Soc. (A), 2393 (1971).

(22) S. Subramanian, M.C.R. Symons and H. W. Wardale, J. Chem. Soc. (A), 1239 (1970).


3200G
100G
H
GAIN X 10
GAIN X 10
A
A
A
A
A
A
A
A
A
A
A
A
B(M$_I$=+1)
B(M$_I$=−1)


GAIN X 10
100G
H
3220G
GAIN X 10

[Reprinted from Inorganic Chemistry, 13, 2811 (1974).]

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

Halogen Nitrates

KARL O. CHRISTE,* CARL J. SCHACK, and R. D. WILSON

Received May 30, 1974 AIC40349+

The low-temperature infrared and Raman spectra of $I(NO_3)_3$ and the Raman spectra of liquid $ClONO_2$, $FONO_2$, FNO_2, and $ClNO_2$ have been recorded. Comparison of the vibrational spectra within the series NO_2, FNO_2, $ClNO_2$, $FONO_2$, and $ClONO_2$ allows unambiguous assignments for the halogen nitrate molecules. Raman polarization measurements show that in halogen nitrates the halogen atom is perpendicular to the ONO_2 plane contrary to previous assumptions and to the known planar structure of $HONO_2$ and CH_3ONO_2. The vibrational spectrum of $I(NO_3)_3$ is consistent with predominantly covalent nitrato ligands. However, the complexity of the spectrum suggests a polymeric structure with bridging nitrato groups. Experimental evidence was obtained for the formation of the new and thermally unstable compound $CF_3I(NO_3)_2$ in the CF_3I–$ClONO_2$ system. Attempts to convert this compound into CF_3ONO_2 were unsuccessful.

Introduction

Highly electronegative groups such as perchlorates, nitrates, fluorosulfates, or trifluoroacetates can be considered as pseudohalides. As such they either can form stable anions in the presence of suitable cations or can act as covalent ligands particularly when bonded to highly electronegative elements such as the halogens or oxygen. Whereas the vibrational spectra of the free anions are relatively well understood, those of the corresponding covalent ligands have only recently received more attention. Reliable spectra and assignments are now available for covalent perchlorates,[1-3] trifluoroacetates,[4] and fluorosulfates.[5-7] In spite of extensive infrared spectroscopic studies on halogen nitrates,[8-11] a recent paper, reporting the vibrational spectrum of CF_3OONO_2, demonstrates[12] how poorly understood these spectra are at present.

The question whether the halogen atom in $XONO_2$ is coplanar or perpendicular with respect to the ONO_2 plane added further interest to our study. The consensus[9-12] appears to favor coplanarity based on analogy with the planar structures established for the related molecules $HONO_2$[13] and CH_3ONO_2.[14] However, the assumption of a planar structure for the halogen nitrates is against our intuition. Similarly, Pauling and Brockway suggested[15] for $FONO_2$ a nonplanar structure based on low-precision electron diffraction data, although a planar structure could not be ruled out. Raman polarization measurements should clearly distinguish between a planar and a nonplanar structure provided that unambiguous assignments are available. For this purpose Raman data were also required for the closely related nitryl halides.

Another objective of this study was to characterize $I(NO_3)_3$. This interesting compound was first prepared by Schmeisser and Braendle.[16] It is unstable above 0° and no data concerning its structure have been published. Attempts were also made to synthesize the novel covalent nitrate CF_3ONO_2 which led to the synthesis of the novel compound $CF_3I(NO_3)_2$.

Experimental Section

Caution! Fluorine nitrate is shock sensitive.

Material and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitryl chloride,[17] $ClONO_2$,[18] and FNO_2[19] were prepared by literature methods. Fluorine nitrate was prepared by direct fluorination of KNO_3 in a stainless steel cylinder.[11] The purity of volatile materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The low-temperature spectrum of $I(NO_3)_3$ was obtained as a dry powder between CsI plates at −196° using a low-temperature transfer technique similar to one previously reported.[20] The instrument was calibrated by comparison with standard calibration points.[21]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-A exciting line and a Claassen filter[22] for the elimination of plasma lines. Sealed quartz tubes (3-mm o.d.) were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature Raman spectra were recorded using a device similar to one previously described.[23] Polarization measurements were carried out according to method VIII listed by Claassen, *et al.*[22]

Preparation of $I(NO_3)_3$. Resublimed I_2 (1.005 mmol) was placed into a Teflon FEP tube fitted with a stainless steel valve. Freshly fractionated $ClONO_2$ (8.20 mmol) was condensed into the tube at −196°. The mixture was kept at −45° for 1 week. The materials, volatile at −45°, were removed *in vacuo* and separated by fractional condensation. They consisted of unreacted $ClONO_2$ (2.20 mmol) and Cl_2 (3.01 mmol) in excellent agreement with the values calculated for a quantitative conversion of I_2 to $I(NO_3)_3$. The nonvolatile residue was a fluffy light yellow solid which decomposed above 0° under dynamic vacuum yielding N_2O_5 (2.05 mmol) and a tan solid residue. This residue gradually decomposed further as evidenced by the buildup of NO_2-colored fumes above the solid. An infrared spectrum of the solid after several weeks of storage at 25° did not show any absorptions characteristic for N=O double bonds.

The $ClONO_2$–CF_3I System. Chlorine nitrate (4.02 mmol) and CF_3I (1.75 mmol) were combined at −196° in a 30-ml stainless steel cylinder. The reactor was slowly warmed to −45° and kept at this temperature for 6 days. Recooling to −196° did not show any noncondensable material. Products volatile at −78° were removed *in vacuo* and separated by fractional condensation. They consisted of unreacted $ClONO_2$ (0.40 mmol) and Cl_2 (1.79 mmol) in good agreement with the amounts expected for a quantitative conversion of CF_3I to $CF_3I(NO_3)_2$. Warming of the solid residue to 25° yielded N_2O_5 (1.14 mmol), COF_2 (1.07 mmol), and CF_3I (0.65 mmol) in addition to 219 mg of a sticky solid residue of varied orange color.

Results and Discussion

Synthesis and Properties. The interaction between I_2 and excess $ClONO_2$ at −45° produced $I(NO_3)_3$ in quantitative yield according to

$$I_2 + 6ClONO_2 \rightarrow 2I(NO_3)_3 + 3Cl_2$$

Thus, this reaction offers an excellent route to high-purity $I(NO_3)_3$, contrary to a previous statement[16] that, although $I(NO_3)_3$ is formed in this system, it is not of synthetic usefulness.

The properties and thermal instability observed for $I(NO_3)_3$ are in good agreement with those previously reported[16] for the product obtained from the $ICl_3 + ClONO_2$ reaction. The evolution of 1 mol of N_2O_5/mol of $I(NO_3)_3$ in the initial stage of the thermal decomposition indicates the possible formation of $OINO_3$ as an intermediate of marginal stability at 0°

$$I(NO_3)_3 \rightarrow OINO_3 + N_2O_5$$

The subsequent slow decomposition of this intermediate involves a redox reaction in which the +V nitrogen is reduced to the +IV state (N_2O_4) with simultaneous oxidation of the +III iodine. This observation is in excellent agreement with the thermal decomposition of $I(OClO_3)_3$ which yields Cl_2O_7, lower chlorine oxides, and I_2O_5.[2]

---

(1) K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, 10, 1589 (1971).

(2) K. O. Christe and C. J. Schack, *Inorg. Chem.*, 11, 1682 (1972).

(3) C. J. Schack and K. O. Christe, *Inorg. Chem.*, 13, 2374 (1974).

(4) K. O. Christe and D. Naumann, *Spectrochim. Acta, Part A*, 29, 2017 (1973), and references cited therein.

(5) K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta, Part A*, 26, 2367 (1970).

(6) H. A. Carter, S. P. L. Jones, and F. Aubke, *Inorg. Chem.*, 9, 2485 (1970).

(7) A. M. Qureshi, L. E. Levchuk, and F. Aubke, *Can. J. Chem.*, 49, 2544 (1971).

(8) W. E. Sk[illegible]s and G. H. Cady, *J. Amer. Chem. Soc.*, 80, 5640 (1958).

(9) K. Braendle, M. Schmeisser, and W. Luettke, *Chem. Ber.*, 93, 2300 (1960).

(10) A. J. Arvia, L. F. R. Cafferat[illegible], and H. J. Schumacher, *Chem. Ber.*, 96, 1187 (1963).

(11) R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, 23, 223 (1967).

(12) F. A. Hohorst and D. D. DesMarteau, *Inorg. Chem.*, 13, 715 (1974).

(13) A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, 42, 3106 (1965).

(14) W. B. Dixon and E. B. Wilson, Jr., *J. Chem. Phys.*, 35, 191 (1961).

(15) L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, 59, 13 (1937).

(16) M. Schmeisser and K. Braendle, *Angew. Chem.*, 73, 388 (1961).

(17) M. Schmeisser, *Z. Anorg. Chem.*, 255, 33 (1948); G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. I, Academic Press, New York, N. Y., 1963, p 513.

(18) C. J. Schack, *Inorg. Chem.*, 6, 1938 (1967).

(19) K. O. Christe, R. D. Wilson, and E. C. Curtis, *Inorg. Chem.*, 12, 1358 (1973).

(20) K. R. Loos, V. A. Campanile, and C. T. Goetschel, *Spectrochim. Acta, Part A*, 26, 365 (1970).

(21) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand., Sect. A*, 64, 841 (1960).

(22) H. H. Claassen, H. Selig, and J. Shamir, *Appl. Spectrosc.*, 23, 8 (1969).

(23) F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, 24, 291 (1970).

In the CF_3I–$ClONO_2$ system, the observed material balance is in good agreement with the reaction

$$CF_3I + 2ClONO_2 \rightarrow CF_3I(NO_3)_2 + Cl_2$$

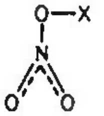
Again the observation of such an intermediate is in excellent agreement with the closely related $ClOClO_3$ reaction chemistry. Thus, the interaction of R_fI with $ClOClO_3$ produced $R_fI(ClO_4)_2$.[24] When R_f was $(CF_3)_2CF$ or n-C_7F_{15}, the $R_fI(ClO_4)_2$ intermediate was successfully isolated. At 40°, the n-$C_7F_{15}I(ClO_4)_2$ could be converted into R_fOClO_3 by vacuum pyrolysis. For $R_f = (CF_3)_2CF$, however, vacuum pyrolysis at 105° resulted exclusively in decomposition products. For $R_f = CF_3$, the $CF_3I(ClO_4)_2$ intermediate was not isolated; however, a quantitative yield of CF_3OClO_3 was obtainable at −45°.[24,25] Therefore, it appeared interesting to determine whether the novel compound CF_3ONO_2 could be prepared by controlled decomposition of $CF_3I(NO_3)_2$. No evidence for CF_3ONO_2 could be obtained, but CF_3I and about equimolar amounts of N_2O_5 and COF_2 were formed.

The observation of CF_3I as a decomposition product is interesting. A plausible explanation for its formation can be offered. For $R_fI(ClO_4)_2$, Raman spectra support[24] the ionic structure $[(R_f)_2I]^+[I(ClO_4)_4]^-$. If $CF_3I(NO_3)_2$ had the analogous ionic structure $[(CF_3)_2I]^+[I(NO_3)_4]^-$, as much as 50% of the originally used CF_3I might be recovered in the thermal decomposition of such an intermediate. The difficulty in obtaining CF_3ONO_2 indicates that this compound might be relatively unstable toward decomposition into COF_2. This is in good agreement with previous studies[12,26] aimed at the synthesis of R_fONO_2.

Vibrational Spectra. Figure 1 shows the Raman spectra of $ClNO_2$, FNO_2, $ClONO_2$, and $FONO_2$ and the infrared and the Raman spectrum of $I(NO_3)_3$. The observed frequencies are listed in Tables I and II.

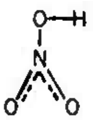
Before the assignment of the fundamentals of the halogen nitrate molecules can be discussed in more detail, it must be established whether $XONO_2$ has structure I or II, *i.e.*, whether X is perpendicular to or coplanar with the ONO_2 plane.

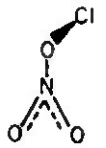
I



II

Whereas in $HONO_2$ intramolecular hydrogen bridging should favor planarity, in $HalONO_2$ the expected mutual repulsion between the halogen and the two oxygen atoms should favor the perpendicular model.





Raman spectroscopy should readily distinguish between models I and II. Both models possess symmetry C_s and nine fundamentals, but for model I three of the fundamentals are antisymmetric with respect to the symmetry plane, whereas for model II only two modes are antisymmetric.

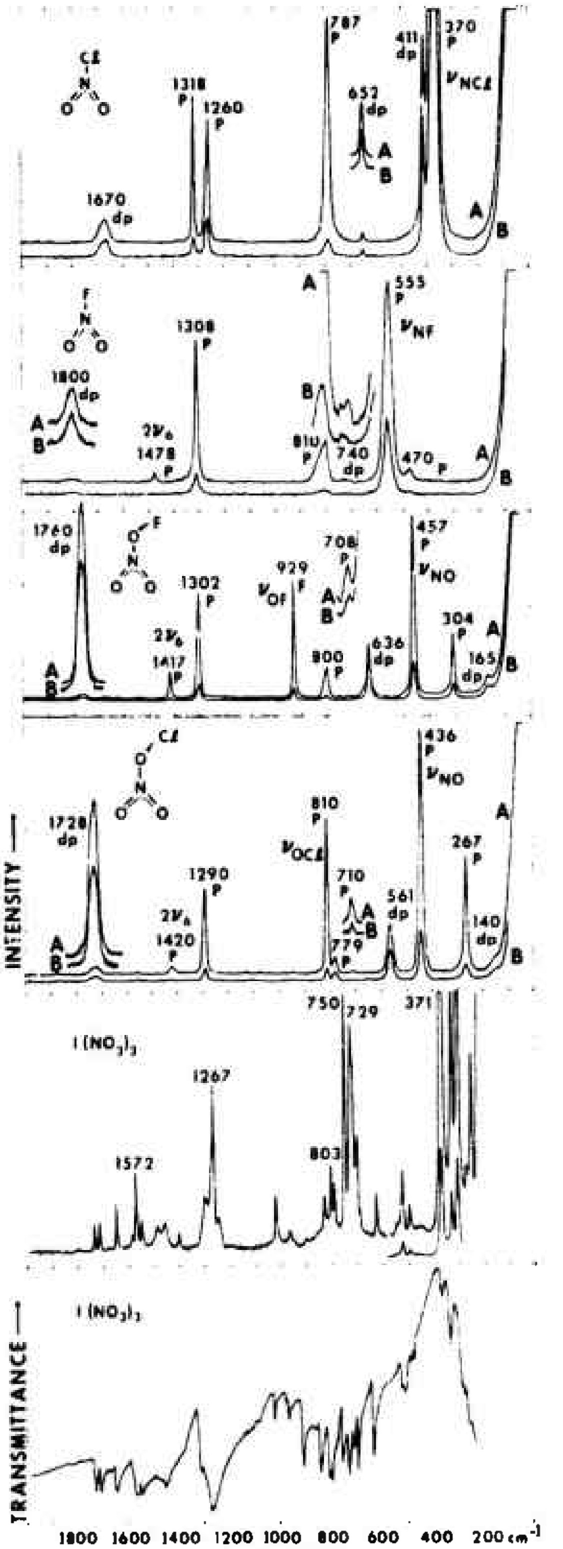


Figure 1. Raman spectra of liquid $ClNO_2$ (recorded at −110°), FNO_2 (−80°), $FONO_2$ (−100°), and $ClONO_2$ (−80°) and of solid $I(NO_3)_3$ (−90°) and infrared spectrum of solid $I(NO_3)_3$ (−196°). Spectral slit width used for the recording of the Raman spectra was 3 cm^{-1}. Traces A and B were recorded with parallel and perpendicular polarizations, respectively. The inserts represent the weaker bands recorded at higher sensitivity and larger slit width. Polarized and depolarized bands are marked by p and dp, respectively.

One mode which for model I belongs to species A″ and for model II belongs to species A′ is the antisymmetric NO_2 stretching vibration. Since no question exists concerning

[24] C. J. Schack, D. Pilipovich, and K. O. Christe, *Inorg. Chem.*, in press.

[25] C. J. Schack, D. Pilipovich, and K. O. Christe, *Inorg. Nucl. Chem. Lett.*, 10, 449 (1974).

[26] B. Tittle and G. H. Cady, *Inorg. Chem.*, 4, 259 (1965).

Table I. Fundamental Vibrations of NO_2, $ClNO_2$, FNO_2, $FONO_2$, and $ClONO_2$

Approx description of mode	Mode designation			Obsd freq, cm^{-1}								
	NO_2 C_{2v}	XNO_2 C_{2v}	$XONO_2$ C_s[a]	NO_2	$ClNO_2$		FNO_2		$FONO_2$		$ClONO_2$	
				Ir gas[b]	Ir gas[d]	Raman liq[e]	Ir gas[d]	Raman liq[e]	Ir gas[h]	Raman liq[e]	Ir gas[h]	Raman liq[e]
$\nu_{as}(NO_2)$	B_1 (ν_3)	B_1 (ν_4)	A″ (ν_7)	1618 [38][c] vs	1685 [38] vs	1670 (1),[f] 0.75[g]	1792 [41] vs	1800 (1), 0.75	1759 [39] vs	1760 (3), 0.75	1735 [41] vs	1728 (4) dp[i]
$\nu_s(NO_2)$	A_1 (ν_1)	A_1 (ν_1)	A′ (ν_1)	1318 [12] s	1286 [10] s	1318 (8), 0.15[j] 1260 (6), 0.32	1310 [12] s	1308 (7), 0.15	1301 [10] vs	1302 (59), 0.16	1292 [12] vs	1290 (30), 0.15
$\delta_{sciss}(NO_2)$	A_1 (ν_2)	A_1 (ν_2)	A′ (ν_3)	750 [10] s	793 [11] vs	787 (12), 0.07	822 [14] s	810 (21), 0.10	804 [12] s	800 (17), 0.10	780 [7] ms	779 (6), 0.45
$\nu(NX)$		A_1 (ν_3)	A′ (ν_4)		370 [2.2] vs	370 (100), 0.20	568 [1] ms	555 (100), 0.37	454 [0] ms	457 (100), 0.21	434 [2] m	436 (100), 0.21
$\delta(XNO_2)$ in-plane		B_1 (ν_5)	A″ (ν_8)		408 vw	411 (8), 0.75	560		633 [1] m	636 (31), 0.75	560 [3] s	561 (20) dp[i]
$\delta(XNO_2)$ out-of-plane		B_2 (ν_6)	A′ (ν_5)		652 [17] m	652 (0.3), 0.75	742 [20] mw	740 (1), 0.75	709 [18] m	708 (0.6), 0.40	711 [17] mw	710 (1), 0.40
$\nu(XY)$			A′ (ν_2)						928 [0] m	929 (67), 0.11	809 [5] s	810 (49), 0.07
$\delta(NXY)$ in-plane			A′ (ν_6)						303 [1] vw	304 (33), 0.24	270 vvw	267 (47), 0.10
$\tau(NX)$			A″ (ν_9)						152 vvw	165 (4), 0.75		140 (2) dp

[a] For model with *O*-Hal bond being perpendicular to ONO_2 plane. [b] E. T. Arakawa and A. H. Nielsen, *J. Mol. Spectrosc.*, **2**, 413 (1958). [c] Values listed in brackets behind infrared frequencies are observed $^{14}N-^{15}N$ isotopic shifts. [d] D. L. Bernitt, R. H. Miller, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, **23**, 237 (1967). [e] Data from this study. [f] Values listed in parentheses are uncorrected Raman intensities. [g] Measured depolarization ratios; depolarized bands 0.75. [h] R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, **23**, 223 (1967). [i] The experimentally observed depolarization ratios for these two bands were slightly less than 0.75. However, we believe that these two bands are depolarized and that the observed deviation is due to either experimental conditions or interference from a trace of Cl_2 which has a highly polarized Raman band at 560 cm^{-1} and from the combination band $\nu_s(NO_2) + \nu(NX)(A') = 1726$ cm^{-1}. [j] Splitting due to Fermi resonance between ν_1 and $2\nu_6$.

Table II. Low-Temperature Infrared (−196°) and Raman (−90°) Spectra (cm^{-1}) of Solid $I(NO_3)_3$

Ir	Raman	Ir	Raman
1734 m	1734 (6)	837 m	830 (10)
1715 m	1718 (7)	805 m	803 (18)
1649 m	1649 (11)	793 m	791 (13)
1587 w, sh	1588 (3)	780 w	
1568 m	1572 (18)	775 w	775 sh
1550 m	1551 (6)	754 mw	752 (57)
1485 sh	1489 (5)	729 m	729 (50)
1457 m	1459 (6)		720 sh
1400 sh, br	1402 (4)	710 w	
1313 w		702 w	702 (22)
1300 sh	1301 (10)	690 m	690 (4)
1270 vs	1267 (34)	629 ms	627 (9)
1250 w	1249 (5)		549 sh
1024 mw	1021 (11)	525 mw	524 (14)
1010 w, sh	1008 sh	512 mw	
979 vw			498 (7)
967 mw	966 (3)	490 w	
950 sh	950 sh	478 w	
906 m	902 (1)	370 mw	370 (100)
863 w		335 m	332 (60)
			310 (23)
		280 m	282 (4)
		255 m	255 (30)

the assignment of this mode, its Raman depolarization ratio should answer the planarity question. Figure 1 and Table I show that in $FONO_2$ the antisymmetric NO_2 stretch is clearly depolarized and, hence, the fluorine atom is not coplanar with the rest of the molecule.

Additional support in favor of model I can be derived from polarization data on the XNO_2 deformational modes. For model I the ONO_2 in-plane deformation should be depolarized, whereas for model II the depolarized band should be the ONO_2 out-of-plane deformation. Application of this criterion, however, requires reliable assignments for these modes which, as stated above, were not available owing to an almost complete lack of Raman data on these and related molecules. As can be seen from Figure 1 and Table I, the combination of previously reported infrared data (including $^{14}N-^{15}N$ isotopic shifts)[11,27,28] with the Raman spectra of this study allows unambiguous assignments for all fundamentals of $FONO_2$ and $ClONO_2$. These results convincingly show that the ONO_2 in-plane deformation is depolarized and that the corresponding out-of-plane mode is polarized in agreement only with model I.

Since the assignments for the halogen nitrates are self-evident from the data given in Table I, we can limit ourselves to a comparison with previously reported assignments and some specific comments. For $ClNO_2$ only one previous reference to a Raman study was found in which only one very wide diffuse line centered at about 360 cm^{-1} was observed.[29] The observation of a depolarized line at 411 cm^{-1} in the present study confirms the previous assignment of this frequency to $\nu_5(B_1)$ based on microwave data.[30]

Similarly, our Raman data for FNO_2 are in excellent agreement with the previous assignment[27] which had been confirmed by a microwave study.[31] The observed relative Raman intensities and depolarization ratios of ν_2 and ν_3, when compared to the remaining molecules of Table I, support the conclusion[27] reached by Bernitt, *et al.*, concerning the identity of ν_2 and ν_3. On the basis of the observed $^{14}N-$

---

(27) D. L. Bernitt, R. H. Miller, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, **23**, 237 (1967).

(28) E. T. Arakawa and A. H. Nielsen, *J. Mol. Spectrosc.*, **2**, 413 (1958).

(29) R. Ryason and M. K. Wilson, *J. Chem. Phys.*, **22**, 2000 (1954).

(30) Y. Morino and T. Tanaka, *J. Mol. Spectrosc.*, **16**, 179 (1965).

(31) T. Tanaka and Y. Morino, *J. Mol. Spectrosc.*, **32**, 430 (1969).

^{15}N isotopic shifts, they chose from the two possible force fields[27,32] the one which results in ν_2 being mainly the NO_2 scissoring and ν_3 being mainly the NF stretching mode. A Raman spectrum of liquid FNO_2 has previously been reported[33] and is in fair agreement with our data. Two weak features at 470 and 710 cm^{-1}, respectively, in our Raman spectrum of FNO_2 require some comment. Both were also observed previously,[33] but the 470-cm^{-1} line was subsequently ascribed,[27] together with a line at 926 cm^{-1}, to $FONO_2$ impurity. Since our spectrum does not show any line at about 930 cm^{-1}, a different explanation for the 470 cm^{-1} band is required. It could possibly be due to the difference band $\nu_1 - \nu_2$ which could have borrowed intensity from ν_3 through Fermi resonance. The very weak polarized feature at about 710 cm^{-1} might similarly be explained by Fermi resonance between ν_2 and $\nu_1 - \nu_3$.

For $ClONO_2$ an incomplete Raman spectrum has previously been reported.[11] The five frequencies listed are in good agreement with our results. However, no polarization data were given and the fundamentals were assigned on the basis of the incorrect planar model II. Both of the two most recent assignments reported[11,12] for $ClONO_2$ need revision. Hohorst and DesMarteau assigned three and Miller, *et al.*, two fundamentals incorrectly. Both corrections involve the mode of greatest interest, the N-O stretching mode. The data of Table I (in particular the ^{14}N-^{15}N isotopic shifts and the polarization data) indicate that the similar frequencies of the NO_2 scissoring and the O-Cl stretching modes cause a strong [illegible]ing of the corresponding symmetry coordinates. The fre[illegible]f 140 cm^{-1} observed for the N-OCl torsional mode results in a barrier to internal rotation of 10.40 kcal mol^{-1} in good agreement with previous estimates and the value of 10.[illegible]3 kcal mol^{-1} found for $FONO_2$.[11]

For $FONO_2$ no Raman data have been published except for the impurity bands[33] in the spectrum of FNO_2 which were attributed by others[11] to $FONO_2$. By analogy with $ClONO_2$ (see above), the previous assignments[11,12] need revision for three and two fundamentals, respectively.

Several general aspects deserve emphasis. (i) Whereas the XNO_2 out-of-plane deformation is of very low intensity in the Raman spectra and therefore difficult to detect, its first overtone was generally observed as a reasonably intense Raman band. This allows reliable identification of this fundamental. (ii) The symmetric NO_2 stretch and the NO_2 scissoring mode have very characteristic frequencies and occur in the ranges 1285-1300 and 780-820 cm^{-1}, respectively. Therefore, these two modes are useful for identifying XNO_2 groups. The XNO_2 out-of-plane deformation is moderately dependent and the corresponding in-plane deformation is strongly dependent on the mass of X. The large ^{14}N-^{15}N isotopic shifts (17-20 cm^{-1}) observed for the XNO_2 out-of-plane deformation indicates that in this mode mainly the N atom moves, *i.e.*, swings through the XO_2 plane. (iii) The NX stretching mode occurs for all compounds at a surprisingly low frequency, *i.e.*, 370-570 cm^{-1}. This is in agreement with the known thermal instability of these compounds. Contrary to the N-O stretching modes, the O-Hal stretching modes occur in their usual frequency range. They exhibit frequencies much higher than those of the N-O stretches indicating that the N-O single bond is by far the weakest bond in $ClONO_2$ and $FONO_2$.

The low-temperature spectra of $I(NO_3)_3$ (see Figure 1 and Table II) clearly show that the compound is not ionic. In the higher frequency range three clusters of bands centered at about 1570, 1270, and 800 cm^{-1}, respectively, occur, indicating the presence of covalent nitrato group. However, the number of individual bands within these clusters is too high and they are distributed over too wide a frequency range to be comfortably accounted for by a simple in-phase, out-of-phase coupling of the motions of monodentate or bidentate ligands.[3,34] It seems more reasonable to explain the complexity of the spectra by a polymeric structure involving bridging ligands as was previously suggested for the closely related compounds $I(ClO_4)_3$[2] and $I(SO_3F)_3$.[6] We suggest tentative assignments of the clusters to the following types of vibrations: 1750-1450 cm^{-1}, antisymmetric NO_2 stretches; 1300-1200 cm^{-1}, symmetric NO_2 stretches; 830-780 cm^{-1}, NO_2 scissoring; 750-690 cm^{-1}, IO stretches; 370-300 cm^{-1}, N-O stretches. The significant decrease in the N-O stretch frequencies, when compared to those in $FONO_2$ (457 cm^{-1}) and $ClONO_2$ (436 cm^{-1}), indicates increasing polarity of the Hal-O bonds within this series. This is generally true for related compounds and is caused by the increasing electronegativity difference between the halogen and the ligands with increasing atomic weight of the halogen.

Acknowledgment. We are indebted to Dr. L. R. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

Registry No. $ClNO_2$, 13444-90-1; FNO_2, 10022-50-1; $FONO_2$, 7789-26-6; $ClONO_2$, 14545-72-3; $I(NO_3)_3$, 52760-88-0; $CF_3I(NO_3)_2$, 52760-89-1.

---

(32) A. M. Mirri, G. Cazzoli, and L. Ferretti, *J. Chem. Phys.*, 49, 2775 (1968).

(33) R. E. Dodd, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, 52, 145 (1956).

(34) C. C. Addison, D. W. Amos, and D. Sutton, *J. Chem. Soc. A*, 808 (1967).

On the Existence of several new O,N,F-Compounds.

A critical Comment on the Paper by Sicre and Schumacher.

By Karl O. Christe

Abstract. It is shown that the infrared spectra previously attributed to the three novel compounds FONO, NO_2F_3, and an unknown are due to the known compounds $HONO_2$, $FONO_2$, and covalent N_2O_5, respectively. The observed chemical and physical properties agree well with this reinterpretation.

Über die Existenz einiger neuer O,N,F-Verbindungen.

Ein kritischer Kommentar zur Veröffentlichung von Sicre und Schumacher.

Inhaltsübersicht. Es wird gezeigt, dass die Infrarot Spcktren, die zuvor den drei neuen Verbindungen FONO, NO_2F_3 und einer nichtidentifizierten Substanz zugeschrieben wurden, vollständig den bekannten Verbindungen $HONO_2$, $FONO_2$ und kovalentes N_2O_5 zugeordnet werden können. Die beobachteten chemischen und physikalischen Eigenschaften stimmen mit der neuen Interpretation überein.

In the course of a spectroscopic study of halogen nitrates [1], it became obvious that the infrared spectrum reported by Sicre and Schumacher [2] for the new compound FONO was inconsistent with such a structure. In addition, these authors have given data for two more new N,O,F-compounds and suggested for one of these the composition NO_2F_3. In view of this inconsistency, we have critically reviewed the given experimental data and succeeded in positively identifying all three compounds as known substances. Sicre and Schumacher had chosen [2] the designations X_1, X_2, and X_3 for their new compounds which will be retained in the following discussion to facilitate comparison.

Compound X_1. This compound could be prepared from NO_2 and small amounts of F_2 only in an aluminum cylinder, the walls of which were coated with a thick layer of aluminum oxyfluoride or corrosion products.

---

[1] K. O. Christe, C. J. Schack, and R. D. Wilson, Inorg. Chem., in press.

[2] J. E. Sicre and H. J. Schumacher, Z. anorg. allg. Chem., 385, 131(1971).

Based on its infrared spectrum, apparent molecular weight of 64.5, and facile conversion to FNO_2, it was identified 2) as the FNO_2 isomer FONO. However. a closer inspection of the infrared spectrum attributed to FONO indicated a structure containing an XNO_2 group. 1) Comparison with known spectra revealed that the infrared band shapes and frequencies (in cm^{-1}) and relative intensities of X_1 (1713 vs, 1302 vs, 885 s) are in excellent agreement with those reported 3) for $HONO_2$ (1712 vs, 1311 vs, average of 895 and 879 branches = 887 s). Further support for its identification as $HONO_2$ can be derived from its chemical behavior. Thus it could not be separated by fractionation from compound X_3 which was identified (see below) as N_2O_5.

The following facts indicate that the original reaction product in the $NO_2 + F_2$ reaction was FNO_2 which was subsequently converted by hydrolysis into $HONO_2$. (i) The original product was volatile at -125°. (ii) Sometimes the infrared spectra showed FNO_2 which was attributed to an isomerization of FONO to FNO_2. However, a plausible explanation for this behavior can be offered. For example, lack of hydrolysis of FNO_2 or secondary reactions of $HONO_2$ with passivated surfaces or strong fluorinating agents such as compound X_2 (=$FONO_2$) could easily generate FNO_2. (iii) Clean reactors did not produce any X_1. Only in the presence of substantial amounts of aluminum corrosion products was X_1 formed. The likelihood of such corrosion products containing hydroxyl-groups supports our interpretation that X_1 is formed by hydrolysis of FNO_2 and is $HONO_2$. (iv) The molecular weight determination would not be expected to effectively discriminate between FNO_2 (65) and $HONO_2$ (63). However, from the fact that the determination was carried out at a pressure of 700mm. it can be concluded that the sample used at this point was still mainly FNO_2. The vapor pressure of $HONO_2$ at ambient temperature is considerably lower than 700mm.

Compound X_2. This compound is formed 2) when NO_2 is reacted with an excess of F_2. As has previously been found, 4) some $FONO_2$ is readily formed under

---

3) G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, J. Chem. Phys., 42, 237(1965).

4) D. L. Bernitt, R. H. Miller, and I. C. Hisatsune, Spectrochim. Acta, 23A, 237(1967).

these conditions. Comparison between the infrared spectrum of X_2 (1761 vs, 1294 vs, 927 m, 804 s) and that [5) 6)] of $FONO_2$ (1759 vs, 1301 vs, 928 m, 804 s) reveals that X_2 is indeed $FONO_2$. The minor frequency discrepancy for the 1300 cm^{-1} band is caused by the difficulty in estimating the true band center for X_2 due to overlap with an intense X_1 band. Again the observed band contours of X_2 are identical to those of $FONO_2$ and their chemical and physical properties agree.

When X_2 was allowed to interact with an excess of NO_2 the following reaction was observed:

$$X_2 + \text{excess } NO_2 \longrightarrow X_3 + X_1$$

If we substitute $FONO_2$ for X_2 and N_2O_5 for X_3 (see below), this observed reaction further confirms the identities of X_2 and X_3:

$$FONO_2 + 2NO_2 \longrightarrow FNO_2 + N_2O_5$$

The formation of X_1 (=$HONO_2$) can be explained by hydrolysis of FNO_2 according to:

$$FNO_2 + H_2O \longrightarrow HONO_2 + HF$$

Compound X_3. As discussed above, X_3 was formed by interaction of X_2 with an excess of NO_2 and, therefore, was suspected to be N_2O_5. Comparison of the infrared spectrum of X_3 (1720 vs, 1240 s) [2)] with that of covalent gaseous N_2O_5 (1728 vs, 1247 s) [7)] confirmed our suspicion. The minor discrepancy in the listed frequency values is due to the relative broadness of these bands making estimation of the exact band centers difficult. The observed low volatility of X_3 and its tendency to associate with $HONO_2$ agree with X_3 being N_2O_5.

---

5) A. J. Arvia, L. R. F. Cafferata, and H. J. Schumacher, Chem. Ber., 96, 1187(1963).

6) R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, Spectrochim. Acta, 23A, 223(1967).

7) I. C. Hisatsune, J. P. Devlin, and Y. Wada, Spectrochim. Acta, 18, 1641(1962).

Conclusion. Without doubt, compounds X_2 and X_3 of Sicre and Schumacher are $FONO_2$ and N_2O_5, respectively, since their spectra, physical and chemical properties all agree with those of the latter ones. There is also no doubt that the infrared spectrum of X_1 which was the only direct experimental proof for FONO, is due to $HONO_2$. Therefore, the existence of FONO has not been established since all the experimental data of Sicre and Schumacher might be explained by assuming FNO_2 which during transfer to or in the infrared cell hydrolyzed to $HONO_2$.

Recently, matrix isolation data have been presented as evidence for the existence of FON and FONO at cryogenic temperatures. 8) 9) Although the infrared bands attributed 8) to matrix isolated FONO are quite different from those of X_1, their frequencies are difficult to reconcile with the proposed FONO structure.

Acknowledgement. I am indebted to the Office of Naval Research, Power Branch, for financial support and to Drs. C. J. Schack and L. R. Grant for helpful discussions.

Anschr. d. Verf.: Dr. Karl O. Christe
Rockwell International Corporation
Rocketdyne Division
Canoga Park, California 91304 (U.S.A.)

---

8) R. R Smardzewski and W. B. Fox, J.C.S. Chem. Comm., 241(1974).

9) R. R. Smardzewski and W. B. Fox, J. Amer. Chem. Soc., 96, 304(1974).

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

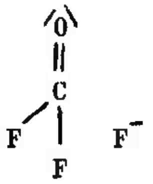
The CF_3O^- Anion: Vibrational Spectrum of an Unusual CF_3 Compound

Karl O. Christe*, E. C. Curtis, and Carl J. Schack

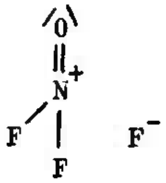
Received 9 August 1974

Abstract

The infrared and Raman spectra of solid $CsOCF_3$ and the Raman spectra of liquid and gaseous NF_3O have been recorded. The vibrational spectrum of CF_3O^- closely resembles that of isoelectronic NF_3O. For CF_3O^-, six fundamentals were observed and assigned consistent with a pseudo-tetrahedral structure of symmetry C_{3v}. It is shown that the unusual bonding in NF_3O is not unique but also occurs in CF_3O^-. In both isoelectronic XF_3O species, the XO bond possesses almost double bond character whereas the three XF bonds are highly polar implying very strong contributions from resonance structures such as



and



The occurrence of this type of bonding can be rationalized by the high electronegativity of fluorine and by the importance of the octet rule for first row elements limiting the sum of the bond orders to a maximum of four.

INTRODUCTION

When the NF_3O molecule was discovered,[1-4] the observed high frequency ($1690 cm^{-1}$)[5,6] of the NO stretching mode was very surprising since it implied a NO bond order of approximately two. This interpretation was confirmed by a subsequent electron diffraction study showing a short NO (1.158Å) and long NF (1.431Å) bonds.[7] For the theoreticians this posed an interesting problem since it raised the question whether the strict validity of the octet rule for first row elements also holds for NF_3O.[8] A systematic study[9] of the force constants and bond orders of a large number of simple inorganic fluorides showed that for the first row elements the sum of the bond orders does not tend to exceed the maximum allowed by the octet rule. This is in agreement with the results from recent Hartree-Fock computations[10] giving a possible origin for the non-expansion of the octet among first row elements. However, the severe shortcomings of molecular orbital, underdetermined force field, and approximate bond order computations must be kept in mind when interpreting such data.

It appeared interesting to determine whether the occurrence of abnormally strong XO bonds coupled with highly polar XF bonds is limited to X being N (i.e., NF_3O and the nitrosyl halides), or if it also extends to other first row elements. Of the possible truly isoelectronic[11] species, only two, CF_3O^- and BF_3O^{--}, have been reported to exist. However, the original reports on BF_3O^{--} salts by Ray and Mitra[12] were subsequently refuted by Clark and Lynton.[13]

The existence of the trifluoromethoxides of Cs, Rb, and K was first reported[14] by Redwood and Willis in 1965. Ionic structures containing the CF_3O^- anion were postulated for these salts based on X-ray powder diffraction patterns.[14] These patterns showed the trifluoromethoxides to be isomorphous with the corresponding tetrafluoroborates. In a subsequent paper,[15] the same authors reported incomplete infrared spectra for these trifluoromethoxides. However, these spectra showed more bands than expected for a simple CF_3O^- anion of symmetry C_{3v}. Furthermore, Dear and co-workers found[16] that the fluorinated higher alkoxides of Li and Na can be sublimed without decomposition and, therefore, must possess considerable covalent character. These conflicting data added further interest to our study.

There was also a question concerning the assignment of $\nu_3(A_1)$ and $\nu_5(E)$ of NF_3O. The original assignment [5,6] for these modes has recently been questioned. [17,18] Since Raman polarization data should readily distinguish between these two modes, we have also recorded the Raman spectra of liquid and gaseous NF_3O. After completion of our study, the Raman spectrum of gaseous NF_3O has been published. [19] It is in excellent agreement with our measurements and resulted in a reassignment of ν_3 and ν_5.

EXPERIMENTAL

Materials and Apparatus. Cesium trifluoromethoxide was prepared from CsF and COF_2 in dry CH_3CN as previously described. [14] The conversion of CsF to $CsOCF_3$ was 70 mole percent. Nitrogen trifluorideoxide (Allied Chemical) was purified by fractional condensation and showed no impurities detectable by infrared spectroscopy. Volatile materials used in this work were manipulated in a stainless steel-Teflon FEP vacuum line. Solid products were handled in the dry nitrogen atmosphere of a glove box.

Vibrational Spectra. The infrared spectra of the solids were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000-250cm^{-1} as dry powders pressed between thin AgCl windows. The pressing operation was carried out using a Wilks mini pellet press.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880Å exciting line of an Ar-ion laser and a Claassen filter [20] for the elimination of plasma lines. For the solids, glass melting point capillaries were used as sample containers in the transverse-viewing-transverse-excitation technique. The spectrum of gaseous NF_3O was recorded at a pressure of 15 atm using a stainless steel cell with three sapphire windows in a double pass mode. Liquid NF_3O was contained in a 4mm o.d. quartz tube. The spectra were recorded at -120° using a device similar to one previously described. [21] Polarization measurements were carried out according to method VIII listed by Claassen et al. [20]

RESULTS AND DISCUSSION

Observed Spectra. The infrared and Raman spectrum of solid $CsOCF_3$ and the Raman spectrum of liquid NF_3O are shown in Figure 1. The observed frequencies are listed in Table 1. The Raman spectrum of gaseous NF_3O was identical to that recently reported [19] and, hence, is not given. In addition to the fundamentals listed in Table I, two overtones were observed in the Raman spectra of NF_3O. Both of them are polarized and occur in the vicinity of A_1 fundamentals thus allowing an increase in their intensity by Fermi resonance. One of the bands is due to $2\nu_6$ and occurs at 799 cm^{-1} in the liquid and at 796 cm^{-1} in the gas. The other overtone is ascribed to $2\nu_4$ and was observed at 1735 cm^{-1} in the liquid and at 1775 cm^{-1} in the gas. The relatively large frequency shift of $2\nu_4$ between the gas and the liquid is caused by the corresponding shift of ν_4 which in the liquid became relatively broad and had its maximum at about 860 cm^{-1}. The remaining fundamentals of NF_3O show only minor frequency shifts when going from the gas phase to the liquid indicating little or no association in the liquid. The fact that ν_2 and ν_3 of NF_3O appear more weakly polarized in the gas than in the liquid is due to the sample cell used for the gas. This type of cell allows only qualitative polarization measurements owing to internal reflection from the metal surfaces and owing to the optical activity of the sapphire windows. Since the reassignment of ν_3 and ν_5 of NF_3O has recently been discussed in detail [19] no further comment is required.

For $CsOCF_3$, no Raman polarization measurements could be carried out owing to the lack of a suitable solvent. It hydrolyzes in water [14] and is insoluble in CH_3CN. [15] In the infrared spectrum, a medium to weak absorption at 1230 cm^{-1} and a shoulder at 1450 cm^{-1} varied in relative intensity compared to the rest of the spectrum. These bands are due to $CsHF_2$ and represented the only detectable impurity.

Assignments. An XY_3Z species of symmetry C_{3v}, such as possibly CF_3O^-, has six fundamentals classified as $3A_1 + 3E$. All six should be active in both the infrared and Raman spectrum. Inspection of Figure I and Table I reveals that indeed six bands, active in both the infrared and Raman spectrum, were observed for $CsOCF_3$. Their frequencies and relative infrared intensities are similar to

Table I

Vibrational Spectrum of $Cs^+ CF_3O^-$ Compared to That of Isoelectronic NF_3O

Obsd freq, cm^{-1}, and intens[a]					Assignment in point group C_{3v}	Approximate description of mode
$Cs^+ CF_3O^-$ solid		NF_3O				
		gas				
IR	Raman	IR[b]	Ra	Liquid Ra		
1560vs, br	1555(0.7)	1691vs	1692(0+)p	1680(0+)	A_1 ν_1	X-0 stretch
813s	812(10)	743s	743(10)p	738(10)p	ν_2	sym XF_3 stretch
595mw	597 (7.3)	558sh	542(6.1)p	541(9.3)p	ν_3	δ sym XF_3
960vs, br	960(0.8)br	883vs	884(0.9)dp	860-900(0.5)br, dp	E ν_4	asym XF_3 stretch
574ms	576(4.4)	528s	529(5)dp	528(5.3)dp	ν_5	OXF deformation
423w	422(7.9)	400w	400(0.7)dp	400(1.4)dp	ν_6	δ asym XF_3

(a) uncorrected Raman intensities

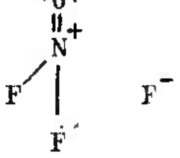
(b) data from ref. 5

those of isoelectronic NF_3O. This similarity, together with the fact that the CF_3O^- salts are isomorphous with the corresponding BF_4^- salts,[14] strongly supports the assumption of a pseudo-tetrahedral structure of symmetry C_{3v} for the CF_3O^- anion. Assignments of the six bands to the individual modes (see Table I) were made by analogy with those of NF_3O and are supported by the following arguments.

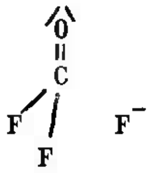
Of the six fundamentals, three are stretching and three are deformation vibrations. The three bands occurring above 800 cm^{-1} must be the stretches and those below 600 cm^{-1} must be the deformations. The strong infrared band at 1560 cm^{-1} has too high a frequency and is too far away from the other two frequencies to be a CF_3 mode. Consequently, it must be the CO stretch. The two remaining bands at 960 and 812 cm^{-1}, respectively, show about the right frequency separation expected for an antisymmetric and a symmetric CF_3 stretching vibration. Based on their relative band widths and Raman intensities, the 960 cm^{-1} band must be the antisymmetric and the 812 cm^{-1} band the symmetric CF_3 stretch.

Of the three deformation modes, the antisymmetric CF_3 deformation should have the lowest frequency and be relatively weak in the infrared and, therefore, is assigned to the 422 cm^{-1} band. The CF_3 rocking and CF_3 umbrella deformation modes were assigned to the 575 and the 596 cm^{-1} band, respectively, based on their relative intensities and by analogy with NF_3O for which these assignments are well established by polarization data.

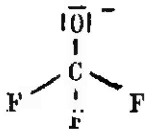
Conclusion. In spite of the lack of reliable force fields for NF_3O and CF_3O^-, some qualitative statements can be made about the nature of bonding in CF_3O^-. Since the exact bond distances in NF_3O are known from electron-diffraction data,[7] it is well established that the NO bond possesses almost double bond character and that the NF bonds are unusually long. This implies very strong contributions from resonance structures such as:



Inspection of Table 1 shows that the frequencies of CF_3O^- are comparable to those of NF_3O. Furthermore, when compared to conventional carbon oxyfluorides containing single bonded oxygen, the CO stretching frequency has increased by about 500 cm^{-1} and the CF_3 stretching frequencies have decreased by about 350 cm^{-1}. These enormous frequency shifts suggest that the bonding in NF_3O is not unique, but also extends to isoelectronic CF_3O^-. Thus, one must invoke also for CF_3O^- strong contributions from resonance structures such as:


(I)

in addition to some contribution from:


(II)

The predominance of I can be rationalized by the high electronegativity of fluorine favoring highly polar bonds and by the strict validity of the octet rule for first row elements. The latter is caused by the high energy required to promote electrons to the 3s level. If these assumptions are valid, an increase in the bond order of the XO bond must be accompanied by a simultaneous decrease in the bond order of the X-F bonds, since the sum of the bond orders cannot surpass four. For higher row elements, the next higher unoccupied electron levels lie much closer and, therefore, the octet can readily be exceeded.

Acknowledgement. This work was supported by the Office of Naval Research, Power Branch. We are indebted to Dr. L. R. Grant for helpful discussions.

REFERENCES

(1) W. Maya, U. S. Patent 3,320,147 (1967).

(2) W. B. Fox and J. S. MacKenzie, U. S. Patent 3,346,652 (1967).

(3) W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornick, C. A. Wamser, J. L. Holmes, R. E. Eilbeck, and B. B. Stewart, J. Amer. Chem. Soc., 88, 2604 (1966).

(4) N. Bartlett, J. Passmore, and E. J. Wells, Chem. Comm., 213 (1966).

(5) E. C. Curtis, D. Pilipovich, and W. H. Moberly, J. Chem. Phys., 46, 2904 (1967).

(6) R. P. Hirschmann, D. F. Harnish, J. R. Holmes, J. S. MacKenzie, and W. B. Fox, Appl. Spectry, 23, 333 (1969).

(7) V. Plato, W. D. Hartford, and K. Hedberg, J. Chem. Phys., 53, 3488 (1970).

(8) See for example D. C. Frost, F. C. Herring, K. A. R. Mitchell, and I. A. Stenhouse, J. Amer. Chem. Soc., 93, 1596 (1971).

(9) W. Sawodny, Habilitation Thesis, Techn. University, Stuttgart, Germany (1969).

(10) R. F. Stewart and B. C. Webster, J. Chem. Soc. (A), 2987 (1971).

(11) J. F. Liebman, J. Chem. Educ., 48, 189 (1971).

(12) A. Ray, J. Indian Chem. Soc., 35, 874 (1958) and preceding papers.

(13) M. J. R. Clark and H. Lynton, Canad. J. Chem., 47, 2943 (1969).

(14) M. E. Redwood and C. J. Willis, Canad. J. Chem., 43, 1893 (1965).

(15) M. E. Redwood and C. J. Willis, Canad. J. Chem., 45, 389 (1967).

(16) R. E. A. Dear, W. B. Fox, R. J. Fredericks, E. E. Gilbert and D. K. Huggins, Inorg. Chem., 9, 2590 (1970).

(17) S. Abramowitz and I. W. Levin, J. Chem. Phys., 51, 463 (1969).

(18) C. V. Berney and A. D. Cormier. J. Chem. Phys. 58, 4709 (1973).

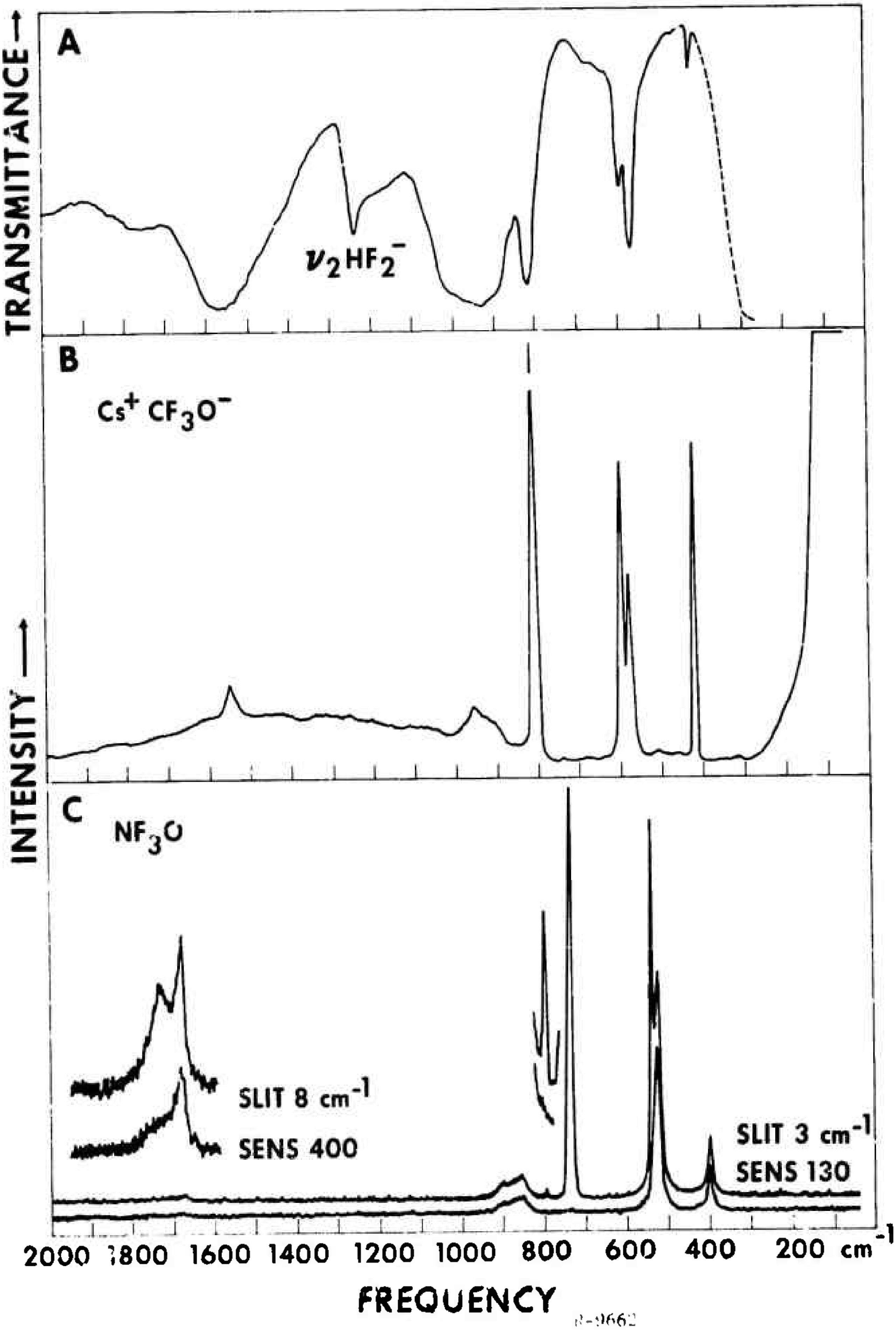
(19) N. Aminadav. H. Selig, and S. Abramowitz, J. Chem. Phys., 60, 325 (1974).

(20) H. H. Claassen, H. Selig, and J. Shamir, Appl. Spectroscop., 23, 8 (1969).

(21) F. A. Miller and B. M. Harney, Appl. Spectroscop., 24, 291 (1970).

DIAGRAM CAPTION

Figure 1. Trace A, infrared spectrum of solid $CsOCF_3$ as AgCl disk; trace B, Raman spectrum of solid $CsOCF_3$; trace C, Raman spectrum of liquid NF_3O with parallel (upper curve) and perpendicular (lower curve) polarization; the inserts show the weaker bands recorded with increased gain and slit width.


TRANSMITTANCE ⟶
A
$\nu_2 HF_2^-$
INTENSITY ⟶
B
$Cs^+ CF_3O^-$
C
NF_3O
SLIT 8 cm^{-1}
SENS 400
SLIT 3 cm^{-1}
SENS 130
2000 1800 1600 1400 1200 1000 800 600 400 200 cm^{-1}
FREQUENCY

AN IMPROVED SYNTHESIS OF $FClO_2$

K. O. Christe*, R. D. Wilson, and C. J. Schack
Rocketdyne, a Division of Rockwell International,
Canoga Park, California 91304

The literature methods reported (1) for the synthesis of $FClO_2$ are inconvenient, since they either involve the fluorination of shock sensitive chlorine oxides or, as in the case of the $KClO_3$ + BrF_3 reaction (2), result in product mixtures which are difficult to separate. In this note, we report an improved synthesis of $FClO_2$ from $NaClO_3$ and ClF_3 which, in our opinion, is more convenient than the literature methods. It is based on the previous observations (3,4) that gaseous ClF_3 reacts with $KClO_3$ to produce $FClO_2$ in high yield, but it reduces the ClF_3 requirement by 60 percent.

In our method, dry $NaClO_3$ is combined with approximately an equimolar amount of ClF_3 at -196° in a stainless steel cylinder. The mixture is kept at room temperature for about one day. Chloryl fluoride is thus obtained in high yield according to the idealized stoichiometry:

$$6NaClO_3 + 4ClF_3 \longrightarrow 6NaF + 2Cl_2 + 3O_2 + 6FClO_2$$

The products condensible at -196° can be separated either by fractional distillation (bp: Cl_2=-33.8, $FClO_2$=-6, ClF_3=11.75°) or by repeated fractional condensation through a series of U-traps kept at -95, -112, and -126°. The use of well passivated metal, Teflon, or KelF equipment is essential for handling $FClO_2$. The use of larger than stoichiometric amounts of ClF_3 in the above reaction is recommended to avoid the possible formation of chlorine oxides. The substitution of the previously used (3, 4) $KClO_3$ by $NaClO_3$ is significant since KF forms a 1:1 adduct with ClF_3, whereas NaF does not. Therefore, the use of $NaClO_3$ reduces the ClF_3 requirement for the reaction by 60 percent. In summary, the above process incorporates the following advantages: (1) safety, no shock sensitive materials must be handled, (2) better utilization of ClF_3, and (3) good product purity.

We have also examined the synthesis of $FClO_2$ according to Faust et al. (5). According to their claim, $FClO_2$ can be prepared in 50% yield by simply heating a mixture of ClF and O_2 for about one day to 80 - 90°. This process would be superior to any of the previously reported syntheses. However, duplication of the experiments of Faust et al. (5) in our laboratory failed to produce significant amounts of $FClO_2$. For example, heating mixtures of ClF and O_2 in a well passivated (with ClF_3) Monel cylinder to 80 - 90° for one day under an autogenous pressure of 1000 psi produced only a trace of $FClO_2$ (less than 0.1%). We believe that the observation of a trace of $FClO_2$ in the products is not due to $FClO_2$ formation from ClF and O_2 but due to the following well known (6) hydrolysis of ClF during the handling of the starting materials and products:

$$5\,ClF + 2H_2O \longrightarrow 4HF + FClO_2 + 2Cl_2$$

The failure to obtain $FClO_2$ from ClF and O_2 by simple heating agrees with the following observations: (i) chlorine oxyfluorides are extremely difficult to prepare by oxygenation of chlorine fluorides; (ii) thermodynamics favor the decomposition of $FClO_2$ to ClF and O_2 as was also demonstrated by kinetic studies of the thermal decomposition of $FClO_2$ (7, 8).

Acknowledgement: We are indebted to the Office of Naval Research, Power Branch for financial support of this work and to Dr. L. Grant for helpful discussions.

References

1. Gmelins Handbuch der Anorganischen Chemie, System Nummer 6, Chlor, Ergänzungsband Teil B-Lieferung 2, page 576, Verlag Chemie, GMBH, Weinheim, Germany (1969).
2. A. A. Woolf, J. Chem. Soc., 4113 (1954).
3. A. Engelbrecht and H. Atzwanger, J. Inorg. Nucl. Chem., 2, 348 (1956).
4. D. F. Smith, G. M. Begun, and W. H. Fletcher, Spectrochim. Acta, 20, 1763 (1964).
5. J. P. Faust, A. W. Jache, and A. J. Klanica, U. S. Pat., 3,545,924 (1970) and French Pat., 1,497,123 (1967).
6. R. Bougon, M. Carles, and J. Aubert, C. R. Acad. Sci., Ser. C, 265, 179 (1967).
7. M. J. Heras, P. J. Aymonino, and H. J. Schumacher, Z. phys. Chem., [Frankfurt], 22, 161 (1959).
8. Y. Macheteau and J. Gillardeau, Bull. Soc. Chim. France, 1819 (1969).

Contribution from the Science Center, Rockwell International, Thousand Oaks, California 91360,
and from the Rocketdyne Division, Rockwell International, Canoga Park, California 91304

Electron Spin Resonance Study of O_2^+ Salts. Influence of Crystal Field Effects and Relaxation

IRA B. GOLDBERG,* KARL O. CHRISTE, and RICHARD D. WILSON

Received June 14, 1974 AIC40379C

Electron spin resonance spectra of polycrystalline $O_2^+BF_4^-$, $O_2^+AsF_6^-$, $O_2^+SbF_6^-$, and $O_2^+Sb_2F_{11}^-$ were recorded over the temperature range −190 to +20° at 9.35 GHz. The *g* tensors calculated from simulated spectra of $O_2^+BF_4^-$, $O_2^+AsF_6^-$, and $O_2^+Sb_2F_{11}^-$ at −196° indicated the ions are in sites of orthorhombic or lower symmetry. Two of the components of the *g* tensor were between 1.96 and 2.00. The third component was between 1.73 and 1.76 in agreement with crystal field theory. The line shapes were lorentzian indicating that dipolar broadening is at least partially averaged by thermal motion. Above −196°, the line widths of the spectra increased rapidly indicating a relaxation process which has a small activation barrier. The spectrum of $O_2^+SbF_6^-$ was very broad at −196° and exhibited additional lines at magnetic fields in the region of 1000–1500 G. This may be due to strong exchange between nearest O_2^+ ions. An improved synthesis of $O_2^+BF_4^-$ was described involving low-temperature uv photolysis of a BF_3–F_2–O_2 mixture.

Introduction

The preparation of a variety of dioxygenyl salts has been reported.[1,2] Although electron spin resonance (esr) has been used to confirm the paramagnetic character of dioxygenyl tetrafluoroborate[3,4] and hexafluoroarsenate,[5] no interpretations of these spectra have been reported. An esr spectrum was reported for $O_2^+BF_4^-$ at −196° consisting of one asymmetric line with a peak to peak line width (ΔH_{pp}) between 400 and 500 G and a *g* factor between 1.94 and 1.97.[3,4] The spectrum reported for $O_2^+AsF_6^-$ was characterized by a *g* factor of 1.9880 ± 0.0002 and a temperature-dependent line width of 24 G at −50° and 66 G at 23°.[5] Both the BF_4^- and the AsF_6^- anions are large such that both materials would be expected to exhibit similar spectra. Recently, esr spectra of $O_2^+SbF_6^-$, $O_2^+AsF_6^-$, and $O_2^+Sb_2F_{11}^-$ at temperatures near liquid helium were studied. These spectra were interpreted in terms of near-axial symmetry.[6] Values of $g_\perp$ were about 1.97 and those of $g_\parallel$ were 1.73. In addition, the magnetic susceptibility of these salts and the ^{19}F nmr of $O_2^+AsF_6^-$ were reported.[6]

Esr spectra of concentrated paramagnetic samples generally exhibit a variety of relaxation processes. Dipolar broadening results from the various magnetic fields generated by the close magnetic dipoles acting on the central ion. Exchange processes, cross relaxation, or motion of the magnetic ion can also cause a modulation of the magnetic energy levels and therefore relax the spin states. The O_2^+ ion has the additional possibility of Jahn–Teller relaxation since it is in a nearly degenerate state. In a crystal field which is symmetric with respect to the internuclear axis, two states are separated only by the spin-orbit coupling energy (about 200 cm^{-1}). These effects have not been considered in the interpretation of the esr spectra of compounds of O_2^+.

Esr spectra have been observed for O_2^+ and the isoelectronic species N_2^- and NO in single crystals and adsorbed on surfaces. Detailed studies of O_2^+ on rutile surfaces,[7] N_2^- in single crystals of irradiated azides,[8] and nitric oxide adsorbed on various surfaces[9-11] and generated by irradiation in azides[12] have been reported. Nitric oxide in single crystals and on some surfaces exhibits spectra characteristic of a three-component *g* tensor when the line widths are sufficiently narrow so that all components can be resolved. On some surfaces NO exhibits a spectrum with a broad line characteristic of apparent axial symmetry; however, [illegible] assuming axial symmetry [illegible] reproduce the spectra.

Synthetic aspects add further interest to this study. Recent communications[13,14] indicate that the previously reported photochemical synthesis of $O_2^+SbF_6^-$ results in a product which contains appreciable amounts of the dimeric anion $Sb_2F_{11}^-$. In addition, no convenient synthesis has been reported for the preparation of $O_2^+BF_4^-$.

In view of the discrepancies in the esr spectra of O_2^+ and for the purpose of understanding the behavior of O_2^+ in a crystalline environment, we have investigated the esr spectra of this ion in the presence of several counterions. In addition, an improved synthesis is reported for O_2BF_4.

Experimental Section

Preparation of O_2^+ Salts. The $O_2^+AsF_6^-$ and $O_2^+SbF_6^-$ samples were prepared at 200° from O_2, F_2, and AsF_5 or SbF_5, respectively, in Monel cylinders according to the method of Beal, *et al.*[15] Material balances, vibrational spectra,[16] and elemental analyses (oxygen content was determined by displacement reaction with excess FNO at −78° and As or Sb were determined by conventional techniques) showed that the solid products had the compositions $O_2^+AsF_6^-$ and $O_2^+SbF_6^-\cdot 0.06SbF_5$, respectively. A sample having the composition $O_2^+SbF_6^-\cdot 0.73SbF_5$ was prepared by the above method but by heating the starting materials to 150° for 12 hr. A sample of $O_2^+Sb_2F_{11}^-$ was prepared by uv photolysis of a 1:$^1/_2$:2 mole ratio mixture of O_2–F_2–SbF_5 in a manner similar to that described by McKee and Bartlett.[14]

For the synthesis of $O_2^+BF_4^-$, a 1-l. Pyrex bulb containing equimolar amounts of O_2, F_2, and BF_3, at a total pressure of 800 mm, was exposed for 7 days to uv radiation from a high-pressure mercury lamp (Hanovia 616A, 100 W) equipped with a water filter. The condensing tip of the reactor was kept at −78°. The solid $O_2^+BF_4^-$ accumulated in the cold section of the reactor and was periodically removed at 0° from the walls to the bottom of the reactor by means of an ultrasonic cleaning bath. After completion of the photolysis, products volatile at −78° were removed *in vacuo*. The white solid residue was transferred, while cold, from the Pyrex container to a Teflon FEP ampoule in an inert-atmosphere glove box. Vibrational spectroscopy[17] and elemental analysis (see above) showed the product to be $O_2^+BF_4^-$. The yield was 51%.

Esr Spectra. Esr spectra were obtained on a modified Varian V-4502 dual-cavity esr spectrometer.[18] The magnetic field was monitored using a sample of Mn^{2+} in forsterite.[19] Each of the six lines from the Mn^{2+} were narrower than 1.5 G, and the splittings and the *g* factor were determined against DPPH (g = 2.00365) using a proton resonance probe to calibrate the magnetic field. The esr parameters for Mn^{2+} were g = 2.00095 ± 0.00006 and a = 86.75 ± 0.05 G. To calibrate the field difference from the field corresponding to $g_{Mn^{2+}}$ for each manganous line, the hyperfine Hamiltonian was expanded to second order.

The reference channel was operated at 100-kHz field modulation and the sample channel [illegible] [illegible] peak-to-peak modulation amplitude [illegible]. In all cases the modulation amplitude was [illegible] of the peak-to-peak [illegible] of the spectrum. Simulations of the powder spectra were carried out by the method of [illegible], Taylor, Ware, and Bray[21] on a CDC 6600 computer with a Calcomp plotter. Three components of a *g* tensor were required to simulate the spectra. Since two components were very close (g_1 and g_2) and one component

---

* To whom correspondence should be addressed at the Science Center.

Table I. Esr Parameters of Dioxygenyl Compounds at −196°

	g_x	g_y	g_z	ΔH_{pp},[a] G	Δ,[b] cm⁻¹	$10^2 E$,[b] cm⁻¹
O_2AsF_6	2.001	1.973	1.742	80	1480	1.00
O_2BF_4	2.00	1.98	1.78	260	1500	2.0
O_2SbF_6	1.75	Isotropic		2200		
$O_2Sb_2F_{11}$	1.970	1.958	1.729	120	1960	1.20

[a] Lorentzian line width used to simulate the powder spectrum. [b] Parameters derived from g factors assuming λ = 195 cm⁻¹.

(g_z) was at considerably higher fields, the dependence of magnetic field on the intensity was treated by the relationship

$$I \propto \left(\frac{g_x + g_y}{2}\right)^2 \left[\left(\frac{g_e}{g}\right)^2 + 1\right]$$

where I is the intensity and g is the apparent g factor given by $h\nu/\beta H$. This is analogous to the relationship derived by Bleaney.[22]

Samples of the dioxygenyl salt were placed in 4-mm Teflon FEP or quartz tubes and heat sealed. The Teflon FEP tubes exhibited a weak spectrum of two lines each about 1 G wide, at points very close to $g = 2$. Under the high powers and high modulation amplitudes used, these lines were broadened and weakened even further. At liquid nitrogen temperatures where large signals were observed, low gains and small modulation amplitudes were used and the Teflon FEP spectrum was too weak to be detected. Samples prepared in Monel vessels exhibited a weak line about 20 G wide at −196°. This is probably due to a copper or nickel ion impurity. This signal is similar to that previously reported for $O_2{}^+AsF_6{}^-$.[3] The samples of antimonates and the arsenates were stored for several weeks at room temperature with no noticeable decrease of signal intensity. The tetrafluoroborate salts were stored at −20° and were also stable for several weeks.

Results and Discussion

Syntheses of $O_2{}^+$ Salts. The previous reports on the photochemical synthesis[5] of $O_2{}^+AsF_6{}^-$ and the thermal synthesis[15] of $O_2{}^+SbF_6{}^-$ were confirmed. For the thermal synthesis of $O_2{}^+SbF_6{}^-$ it was found important to keep the reaction temperature sufficiently high, i.e., at about 200°, in order to suppress the formation of $O_2{}^+Sb_2F_{11}{}^-$. A reasonable explanation for this temperature requirement is the melting point of $O_2{}^+Sb_2F_{11}{}^-$ which was recently reported[12] to be 180–185°. Below 180°, $O_2{}^+Sb_2F_{11}{}^-$ can solidify thus escaping further interaction with O_2 and F_2.

The uv photolysis of O_2–F_2–SbF_5 mixtures yields mainly $O_2{}^+Sb_2F_{11}{}^-$ and not $O_2{}^+SbF_6{}^-$ as originally reported.[5] This finding is in excellent agreement with a recent study by McKee and Bartlett.[14] Since the esr spectra of $O_2{}^+SbF_6{}^-$ and $O_2{}^+Sb_2F_{11}{}^-$ (see below) strongly differ, they are useful for distinguishing the two compounds.

The previously reported syntheses[4] of $O_2{}^+BF_4{}^-$ required oxygen fluorides, such as O_2F_2 or O_4F_2, as starting materials. Since these oxygen fluorides are difficult to prepare (low-temperature glow discharge, γ irradiation, or photolysis) and, owing to their thermal instability, inconvenient to handle, a direct synthesis from O_2, F_2, and BF_3 appeared desirable. We have found that $O_2{}^+BF_4{}^-$ can easily be prepared by uv photolysis of O_2–F_2–BF_3 mixtures. During this photolysis part of the reactor must be kept at −78° to avoid thermal decomposition of the product which is of only marginal thermal stability at ambient temperature. Our yield (~50%) of $O_2{}^+BF_4{}^-$ and conversion rates could probably be significantly improved by choosing a reactor geometry more favorable than the cold-finger Pyrex bulb used in our experiment.

Observed Spectra. Parameters determined from the esr spectra of $O_2{}^+$ compounds are given in Table I. Although the spectra of $O_2{}^+Sb_2F_{11}{}^-$ and $O_2{}^+AsF_6{}^-$ at −196° appear characteristic of radicals with axial symmetry, the spectra cannot be accurately simulated unless three independent g factors are used. The experimental and computed spectra of $O_2{}^+AsF_6{}^-$ are shown in Figure 1. The spectrum of $O_2{}^+BF_4{}^-$ is similar to that described in the literature.[3,4] We observe an asymmetric line with a peak-to-peak width of 430 G. Parameters shown in Table I were determined assuming orthorhombic symmetry. Due to the low resolution of this spectrum, those parameters are not particularly accurate. The spectrum of $O_2{}^+SbF_6{}^-$ at −196° appears isotropic with a g factor of about 1.75 and a line width of 2200 G. This spectrum and the spectrum of $O_2{}^+SbF_6{}^-\cdot 0.73SbF_5$ are shown in Figure 2. Lines due to gaseous molecular oxygen are identified by an asterisk. The spectrum of $O_2{}^+SbF_6{}^-\cdot 0.73SbF_5$ exhibits two components: one component is very broad, and the second component is similar to the spectra of $O_2{}^+Sb_2F_{11}{}^-$ and $O_2{}^+AsF_6{}^-$. The broad component in the spectrum of $O_2{}^+SbF_6{}^-\cdot 0.73SbF_5$ is considerably different from the spectrum of $O_2{}^+SbF_6{}^-$. These samples were prepared in Monel which exhibits magnetic behavior. Esr spectra of scrapings from different parts of the bomb were recorded and the spectra showed considerable variation. The line widths varied between 700 and 1100 G and the field corresponding to the mean amplitude between maximum and minimum peaks of the derivative varied between 2100 and 2500 G. It is therefore likely that the low-field component in Figure 2b is due to Monel. Apparently the Monel contributes little to the spectrum shown in Figure 2a.

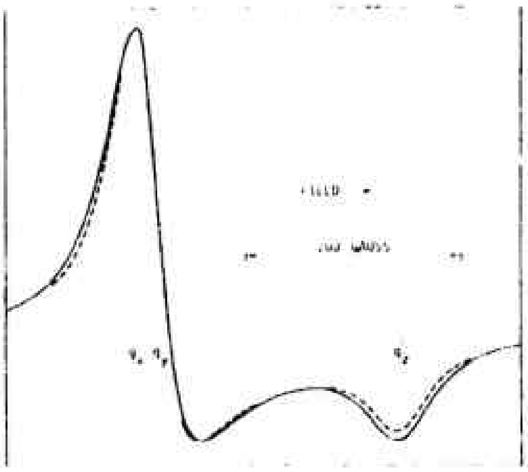


Figure 1. Esr spectrum of dioxygenyl hexafluoroarsenate at −196° (solid line) and computer simulation using the parameters g_x = 2.001, g_y = 1.973, g_z = 1.742, and ΔH_{pp} = 80 G (broken line).

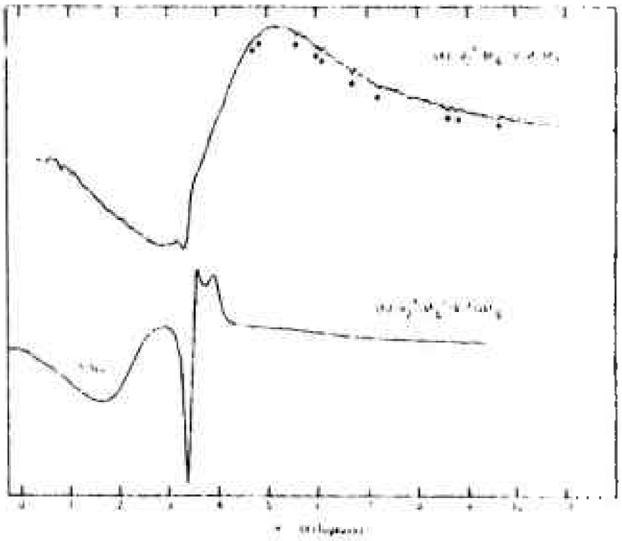


Figure 2. Esr spectra of dioxygenyl fluoroantimonates at −196° (frequency 9.317GHz): (a) sample of composition $O_2{}^+SbF_6{}^-\cdot$ 0.06SbF₅; (b) sample of composition $O_2{}^+SbF_6{}^-\cdot 0.73SbF_5$.

The line widths of the spectra of $O_2{}^+BF_4{}^-$, $O_2{}^+AsF_6{}^-$, and

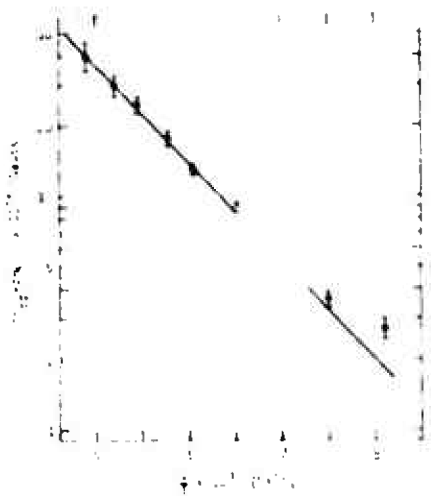


Figure 3. Temperature dependence of the line width of the esr spectrum of dioxygenyl hexafluoroarsenate.

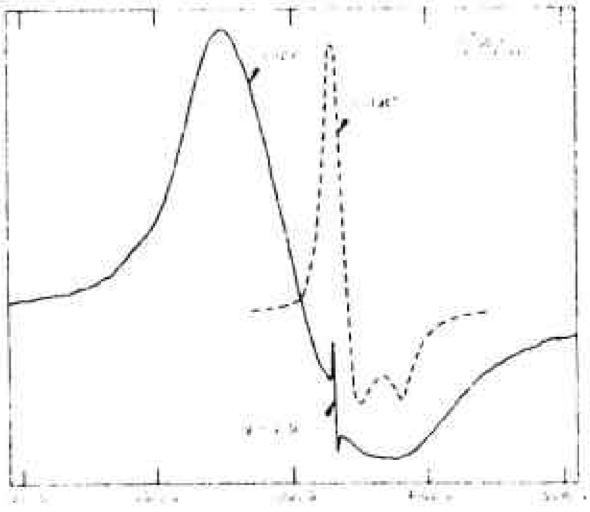


Figure 4. Comparison of esr spectra recorded at −196° (broken line) and −20° (solid line) of $O_2^+Sb_2F_{11}^-$ prepared in quartz. Signal at $g = 2$ is due to an undetermined impurity.

$O_2^+Sb_2F_{11}^-$ and the narrow component of the spectrum of $O_2^+SbF_6^- \cdot 0.73SbF_5$ increase rapidly at temperatures greater than −170°. The line width of $O_2^+AsF_6^-$ exhibits an exponential dependence on $1/T$ between −160 and −70° as shown in Figure 3. The spectrum of $O_2^+BF_4^-$ appears to behave in a similar way; however within a few degrees of −130° the spectrum disappears when warmed and reappears when cooled. This suggests that a crystal modification occurs at this temperature.

The compounds $O_2^+Sb_2F_{11}^-$, $O_2^+SbF_6^-$, and $O_2SbF_6 \cdot 0.73SbF_5$ exhibit different temperature dependences. At −165° the spectrum of $O_2^+Sb_2F_{11}^-$ is broadened and a low-field shoulder begins to appear. As the temperature is increased, the original component broadens out, and an asymmetric line with an apparent g factor of 2.3 emerges from the shoulder. Above −100°, only the "$g = 2.3$" line can be detected as shown in Figure 4. This sample was not prepared in Monel.

The spectrum of $O_2^+SbF_6^-$ at −196° is very broad with ΔH_{pp} about 2300 G and a g factor of 1.75. At higher temperatures this absorption shifts to higher fields and low-field shoulders emerge. These absorptions become defined at [illegible] with apparent g factors of 4.69 and 2.83 for the low-field absorptions and approximately 0.8 for the high-field absorption. The high-field absorption can be ascribed to the O_2^+ in which the angular momentum is virtually unquenched. The absorption at $g = 2.83$ is probably due to Monel. The absorption of $g = 4.69$ broadens with temperature. The spectrum of $O_2^+SbF_6^- \cdot 0.73SbF_5$ (Figure 2b) exhibits two components. At temperatures above −196° the sharper component is again broadened. At 20°, only an 800 G wide absorption at $g = 2.80$ can be seen which is probably due to Monel. All spectra described here are reversible as the temperature is increased or decreased.

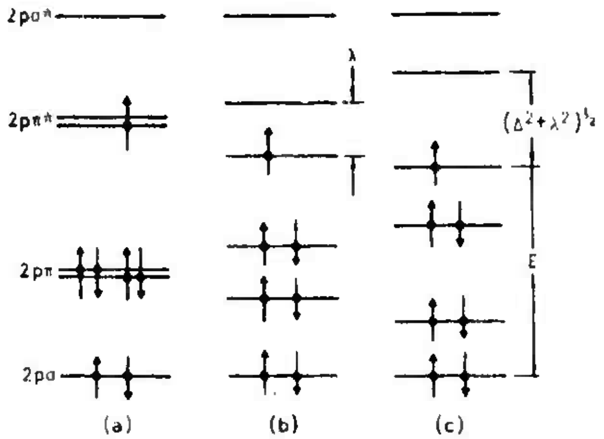


Figure 5. Energy level diagram of the dioxygenyl ion showing the σ- and π-bonding 2p orbitals: (a) energy levels in the absence of spin–orbit coupling and crystal field effects; (b) energy levels with spin–orbit splitting; (c) energy levels with spin–orbit and orthorhombic field splittings.

g Tensor. In the absence of spin–orbit coupling and crystal field effects, the dioxygenyl ion would be in a degenerate state, and the energy level diagram would be given by Figure 5a. Spin–orbit coupling splits the energy levels of the 2pπ and 2pπ* states (Figure 5b). The application of an orthorhombic crystal field further separates the energy levels and quenches the angular momentum (Figure 5c)). Crystal field calculations were carried out in a manner similar to that described by Mergerian and Marshall.[12] The matrix elements of the crystal field potential operator V_{cl} are given by eq 1 where Dirac

$$\langle M_l', M_s' | V_{cl} | M_s M_l \rangle = \Delta \delta_{M_s M_s'} \delta_{M_l \pm 1, M_l'} \quad (1)$$

notation is used, M_l and M_s are the azimuthal quantum numbers for the angular momentum and spin, δ is the Dirac δ function, and Δ is the magnitude of the crystal field energy. The π and π* levels consist of values of M_l which are equal to +1 or −1. The spin–orbit coupling operator only has diagonal elements equal to $\lambda M_l M_s$.

The solution of the secular determinant gives the energies of either the 2pπ or 2pπ* states relative to the energy of the unsplit levels. Each of the two states which result are degenerate in spin, and the energies are given in eq 2

$$E_1 = {}^1\!/_2(\Delta^2 + \lambda^2)^{1/2} \quad (2a)$$

$$E_2 = -{}^1\!/_2(\Delta^2 + \lambda^2)^{1/2} \quad (2b)$$

The wave functions which correspond to these energies are

$$\Psi_1^{\alpha} = N_1\left(|1,{}^1\!/_2\rangle - \left\{\frac{\lambda}{\Delta} - \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1,{}^1\!/_2\rangle\right) \quad (3a)$$

$$\Psi_1^{\beta} = N_2\left(|1,-{}^1\!/_2\rangle + \left\{\frac{\lambda}{\Delta} + \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1,-{}^1\!/_2\rangle\right) \quad (3b)$$

$$\Psi_2^{\alpha} = N_2\left(|1,{}^1\!/_2\rangle - \left\{\frac{\lambda}{\Delta} + \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1,{}^1\!/_2\rangle\right) \quad (3c)$$

$$\Psi_2^{\beta} = N_1\left(|1,-{}^1\!/_2\rangle - \left\{\frac{\lambda}{\Delta} - \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1,-{}^1\!/_2\rangle\right) \quad (3d)$$

where N_1 and N_2 are normalization constants given by

$$N_1 = \left(2\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\left\{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2} - \frac{\lambda}{\Delta}\right\}\right)^{1/2} \qquad (4a)$$

$$N_2 = \left(2\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\left\{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2} + \frac{\lambda}{\Delta}\right\}\right)^{1/2} \qquad (4b)$$

The O_2^- ion behaves in a similar way and exhibits the same crystal field splittings. The difference between O_2^- and O_2^+ is that the unpaired electron of O_2^- is considered to be in the state corresponding to energy E_1, while the unpaired electron of O_2^+ is considered to be in the state corresponding to energy E_2.

The *g* tensor for the dioxygenyl ion may be calculated by the method of Känzig, *et al.*[23] An additional term which contributes to the $2p\pi^*$ levels arises from interaction with the $2p\sigma$ levels. This results in a small admixture of $-^1/_2$ spin to wave functions which are predominantly of $+^1/_2$ spin, and a small admixture of $+^1/_2$ spin to the wave functions which are predominantly $-^1/_2$ spin. The additional term added to eq 3c is of the form $(\lambda/E)|0, -^1/_2\rangle$, and the term added to eq 3d is of the form $(\lambda/E)|0, ^1/_2\rangle$. Using second-order perturbation theory, the additional terms added to the basis wave functions are shown in eq 5.

$$\Psi_{2\alpha}' = \Psi_{2\alpha}^{\circ} - \frac{\lambda}{2E}\,\frac{\left\{\frac{\lambda}{\Delta} + \left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}^{1/2}}{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}}\,|0, -^1/_2\rangle \qquad (5a)$$

$$\Psi_{2\beta}' = \Psi_{2\beta}^{\circ} + \frac{\lambda}{2E}\,\frac{1}{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\left\{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2} - \frac{\lambda}{\Delta}\right\}}\,|0, ^1/_2\rangle \qquad (5b)$$

The *g* factors can now be calculated using the magnetic Hamiltonian. Fields are independently assumed along the *x*, *y*, or *z* axes of the dioxygenyl ion.

In the absence of the $M_l = 0$ functions, only the wave functions are coupled through $\hat{S}_+$ and $\hat{S}_-$. The addition of the $M_l = 0$ functions allows coupling through $\hat{L}_+$ and $\hat{L}_-$. The *g* factors are obtained by diagonalizing the 2 × 2 matrices formed by application of H_{mag}. This procedure is outlined in more detail by Wertz and Bolton.[24]

The results of these calculations are given in eq 6 which

$$g_z = g_e - 2\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} \qquad (6a)$$

$$g_x = g_e\left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\lambda}{E}\left[\left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} + \left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} + 1\right] \qquad (6b)$$

$$g_y = g_e\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} + \frac{\lambda}{E}\left[\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} \left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} - 1\right] \qquad (6c)$$

shows that the g tensor should be comprised of three different principal values provided that *E* is sufficiently small.

Crystal Field Effects. The esr parameters determined from the simulations, which are given in Table I, can be used to calculate the parameters Δ and *E* shown in Figure 5. The *g* factors of $O_2^+AsF_6^-$ and $O_2^+Sb_2F_{11}^-$ are believed accurate to ±0.002, and that of $O_2^+BF_4^-$ is believed accurate to ±0.02. There is some doubt of the spin–orbit coupling constant λ of O_2^+ in a crystal lattice. The values of λ are 195 cm^{-1} for the free ion[25] and 151 cm^{-1} for atomic oxygen. Since the crystal field probably reduces the value of λ from the free ion, the correct value is probably between 151 and 195 cm^{-1}. In principle, the value of λ can also be determined from the solutions of the simultaneous equations (6a)–(6c), but the precision of the *g* factors is not sufficiently accurate for this purpose. Arbitrarily, the free-ion value of λ was used. The values of Δ and *E* which are given in Table I must therefore be considered as upper limits of these energies.

These values can be compared with those determined from spectra of O_2^- and the isoelectronic NO. The comparison of the crystal field parameters of O_2^+ and O_2^- is valid since a similar mixing of orbitals takes place to give shifts of the *g* factor from g_e. In NaI where large negative ions and small positive ions surround the O_2^- ion, the angular momentum is unquenched.[23] However, in other halides[23] values of Δ range from 650 to 1200 cm^{-1} and values of *E* range from 6 × 10^4 to 15 × 10^4 cm^{-1}. The precise values depended upon the sizes of the ions and the symmetry of the lattice sites. The asymmetry was attributed to covalent interaction between the O_2^- and the alkali metal ions since the site of the O_2^- ion aligns in the 110 direction such that the crystal ions are axially symmetric with respect to the O_2^- internuclear axes. In other studies, alkali metal O_2^- compounds were trapped in an argon matrix at 4°K,[26,27] so that the principal interaction is with one alkali metal ion. In these cases Δ for O_2^- was considerably larger than in alkali metal halides.

Values of Δ and *E* obtained for NO adsorbed on various zeolites agree more closely with the values obtained here for O_2^+. Values of Δ range from 1050 to 1700 cm^{-1}, and values of *E* range between 1.2 × 10^4 and 3.7 × 10^4 and are consistent with a small interaction with the surface.[9] NO adsorbed on MgO and generated in various crystals exhibits larger values of Δ and *E*, and thus the elements of the **g** tensor are much closer to g_e.[10] Similarly, the N_2^- generated in KN_3[8] is also in sites with greater asymmetry and exhibits *g* factors closer to g_e.

The data of Table I suggest that in $O_2^+BF_4^-$, $O_2^+AsF_6^-$, and $O_2^+Sb_2F_{11}^-$, the O_2^+ cation is in the site of a small orthorhombic field. The origin of the field can be due either to covalent interaction with the fluorine in the complex anion, as suggested from neutron diffraction studies on $O_2^+PtF_6^-$,[28] or to an asymmetric arrangement of anions around O_2^+. Values of Δ were also estimated from magnetic susceptibility measurements.[6] If a value for λ of 195 cm^{-1} is assumed, then Δ would be about 1400 cm^{-1}.

Measurements of the spectrum of $O_2^+SbF_6^-$ at −250°[6] indicate that the spectrum is sharpened considerably when the temperature is below −195°, and the O_2^+ ion may also be in an orthorhombic environment.

Temperature Dependence. The spectra of each of the O_2^+ compounds exhibit a strong temperature dependence. In all samples studied, as the temperature is increased, the lines broaden. Only $O_2^+AsF_6^-$ exhibited a spectrum with a single component over a sufficiently large temperature range so that the line width can be investigated as a function of temperature. $O_2^+BF_4^-$ was assumed to be linear over a narrow range of temperature. If the slopes of ln ($\Delta H_{pp} - \Delta H_0$) vs $1/T$ for $O_2^+AsF_6^-$ and $O_2^+BF_4^-$ are considered to be related to activation energies in an Arrhenius plot, the energy for the relaxation of the spectrum of $O_2^+AsF_6^-$ is 1.92 kcal (690 cm^{-1}) and that of $O_2^+BF_4^-$ is 1.3 kcal (470 cm^{-1}). These values are considerably smaller than the crystal field energies calculated from the g factors and suggest that there may be several modes operating to cause relaxation.

Since cross relaxation and exchange interactions are possible modes of relaxations in concentrated paramagnetic samples, attempts were made to form dilute O_2^+ salts in an $NO^+AsF_6^-$ lattice. The simultaneous formation of $NO^+AsF_6^-$ was unsuccessful since the reaction of NO + F_2 + AsF_5 is much faster than that of O_2 + F_2 + AsF_5. The displacement of O_2^+ by NO^+ by exposing $O_2^+AsF_6^-$ to FNO at -77° did not produce the desired cation distribution.

The mechanism of the relaxation process cannot be determined from line width measurements alone since the components of spin-lattice and spin-spin relaxation times cannot be separated. At line widths in the order of 100 G an incident microwave power far in excess of the Klystron output would be required in order to use progressive saturation techniques. Based on other measurements we can speculate on the relaxation mechanism.

Calculations of the dipolar broadening based on the published crystal structure of the dioxygenyl compounds[14,29,30] were carried out according to the model of Van Vleck.[31] In all cases the second moment was about 10^4 G^2. If this is the dominant broadening mechanism, the powder spectrum should be simulated by convoluting the powder spectrum onto a gaussian line shape with a width of more than 100 G peak-to-peak. However, for O_2AsF_6 and $O_2^+Sb_2F_{11}^-$ lorentzian lines were required. This result indicates that at least some of the dipolar interactions are partially averaged in the lattice even at -196°.

Recent ^{19}F nmr studies of $O_2^+AsF_6^-$ indicate substantial cation motion in the lattice at temperatures above -240°.[6] A similar conclusion was derived from electron diffraction studies of $O_2^+PtF_6^-$.[28] These results suggest that modulation of the crystal field energy[32] is indeed one reasonable mechanism for relaxation of the electron spin. Although the spectrum of $O_2^+SbF_6^-$ is extremely broad at -196°, cooling further sharpens the line.[6] This further suggests that in this lattice there is more room for motion of the O_2^+ ion. $O_2^+BF_4^-$ is also somewhat broader than $O_2^+AsF_6^-$ and $O_2^+Sb_2F_{11}^-$ although the crystal field is stronger. In the $O_2^+BF_4^-$ lattice, the O_2^+ ions are closer, and it is more likely that exchange processes are more significant than in the other materials as a means of relaxation. This would also explain the apparently smaller activation energy.

In the three dioxygenyl antimonate compounds studied, different low-field absorptions appear at temperatures greater than -130°. This may be the result of strong exchange interactions between neighboring O_2^+ ions. This exchange process may also account for part of the more rapid relaxation of O_2^+ at -196°. One mechanism which may account for the enhanced exchange in the antimonates would be one wherein the SbF_6^- ion acts as a bridge between O_2^+ ions. This is more likely in antimonates than in any of the other materials studied since the antimonates are more polarizable. Figure 4 shows the spectrum of $O_2^+Sb_2F_{11}^-$ at -20°. An asymmetric line with an apparent *g* factor of 2.3 can be seen.

Although these processes are not completely understood, the different spectra of $O_2^+Sb_2F_{11}^-$ and $O_2^+SbF_6^-$ at -196° appear to be a simple, nondestructive qualitative method to detect the presence of $Sb_2F_{11}^-$ formed in $O_2^+SbF_6^-$ during synthesis. Figure 2a demonstrates that amounts of $Sb_2F_{11}^-$ as low as about 5% can be readily detected by esr.

Conclusions

1. *g* factors of $O_2^+AsF_6^-$, $O_2^+Sb_2F_{11}^-$, and $O_2^+BF_4^-$ indicate strong orthorhombic symmetry around the O_2^+ ion in the lattice.

2. Values for the orthorhombic crystal field and for the energy separation between σ and π^* states are in agreement with values of O_2^- and NO in single crystals and NO adsorbed on zeolites.

3. Several different relaxation processes to account for the temperature dependence of the line width of the esr spectra were proposed. Modulation of the crystal field by ion motion appears to be a dominant mechanism. The spectrum of $O_2^+SbF_6^-$ undergoes faster relaxation at -196° than each of the other salts.

4. Anomalous spectra for dioxygenyl antimonates above -140° were observed. Absorptions where $g > 2$ may indicate coupling between dioxygenyl ions.

5. Because of the difference between spectra of $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$ or $O_2^+SbF_6^-\cdot 0.73SbF_5$ at -196°, esr can be used to demonstrate the absence of excess SbF_5 in $O_2^+SbF_6^-$.

Acknowledgment. The portion of this work carried out at the Rocketdyne Division of Rockwell International was supported by the Office of Naval Research, Power Branch. We are indebted to Drs. D. Pilipovich, L. Grant, and C. J. Schack for helpful discussions and to Dr. W. E. Falconer for communicating his results to us prior to publication.

Registry No. O_2AsF_6, 12370-43-3; O_2BF_4, 12228-13-6; O_2SbF_6, 12361-66-9; $O_2Sb_2F_{11}$, 12592-38-0.

References and Notes

(1) I. V. Nikitin and V. Ya. Rosolovskii, *Russ. Chem. Rev.*, **40**, 889 (1971); *Usp. Khim.*, **40**, 1913 (1971), and ref cited therein.
(2) A. J. Edwards, W. E. Falconer, J. E. Griffiths, W. A. Sunder, and M. J. Vasile, *J. Chem. Soc., Dalton Trans.*, 1129 (1974).
(3) C. T. Goetschel, V. A. Campanile, C. D. Wagner, and J. N. Wilson, *J. Amer. Chem. Soc.*, **91**, 4702 (1969).
(4) I. J. Solomon, R. I. Brabets, R. K. Uenishi, J. N. Keith, and J. M. McDonough, *Inorg. Chem.*, **3**, 457 (1964).
(5) J. Shamir and J. Binenboym, *Inorg. Chim. Acta*, **2**, 37 (1968).
(6) F. J. DiSalvo, W. E. Falconer, R. S. Hutton, A. Rodriguez, and J. V. Waszcak, submitted for publication in *J. Chem. Phys.*
(7) R. D. Iyengar, M. Codell, J. S. Karra, and J. Turkevich, *J. Amer. Chem. Soc.*, **88**, 5055 (1966); R. D. Iyengar and R. Kellerman, *J. Colloid Interface Sci.*, **35**, 424 (1971).
(8) E. Gelerinter and R. H. Silsbee, *J. Chem. Phys.*, **45**, 1703 (1966); E. Gelerinter, *ibid.*, **53**, 2991 (1970); B. Ford and E. Gelerinter, *ibid.*, **55**, 3660 (1971).
(9) C. L. Gardiner and M. A. Weinberger, *Can. J. Chem.*, **48**, 1317 (1970).
(10) J. H. Lunsford, *J. Chem. Phys.*, **46**, 4347 (1967); *J. Phys. Chem.*, **72**, 4163 (1968); **74**, 1518 (1970); *J. Catal.*, **14**, 379 (1969); M. Primet, *J. Chim. Phys. Physicochim. Biol.*, **67**, 1629 (1970); C. Naccache, M. Che, and Y. Ben Taarit, *Chem. Phys. Lett.*, **13**, 109 (1972); B. M. Hoffman and N. J. Nelson, *J. Chem. Phys.*, **50**, 2598 (1969).
(11) M. Che, J. Vedrine, and C. Naccache, *Bull. Soc. Chim. Fr., Suppl.*, 121 (1970).
(12) D. Mergerian and S. A. Marshall, *Phys. Rev.*, **127**, 2015 (1962).
(13) Z. K. Nikitina and V. Ya. Rosolovskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **10**, 2048 (1970).
(14) D. E. McKee and N. Bartlett, *Inorg. Chem.*, **12**, 2738 (1973).
(15) J. B. Beal, Jr., C. Pupp, and W. E. White, *Inorg. Chem.*, **8**, 828 (1969).
(16) J. Shamir, J. Binenboym, and H. H. Claassen, *J. Amer. Chem. Soc.*, **90**, 6223 (1968).
(17) K. R. Loos, V. A. Campanile, and C. T. Goetschel, *Spectrochim. Acta, Part A*, **26**, 365 (1970).
(18) I. B. Goldberg and W. E. Goeppinger, *Inorg. Chem.*, **11**, 3129 (1972).
(19) G. K. Miner, T. P. Graham, and G. T. Johnston, *Rev. Sci. Instrum.*, **43**, 1297 (1972).
(20) I. B. Goldberg, A. J. Lewin, and H. R. Crandall, *Rev. Sci. Instrum.*, **45**, 555 (1974).
(21) D. L. Griscom, P. C. Taylor, D. A. Ware, and P. J. Bray, *J. Chem. Phys.*, **48**, 5158 (1968); P. C. Taylor and P. J. Bray, *J. Magn. Resonance*, **2**, 305 (1970).
(22) B. Bleaney, *Proc. Phys. Soc., London, Sect. A*, **63**, 407 (1950); *Proc. Phys. Soc., London*, **75**, 621 (1960); *Phil. Mag.*, **42**, 441 (1951).
(23) W. Kanzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959); H. R. Zeller and W. Kanzig, *Helv. Phys. Acta*, **40**, 845 (1967); H. R. Zeller, R. T. Shuey, and W. Kanzig, *J. Phys. (Paris), Suppl.*, **28**, C4 (1967).
(24) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972, Chapters 11 and 12.
(25) F. Ishiguro and M. Kotani, *J. Phys. Soc. Jap.*, **22**, 266 (1967).
(26) E. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **59**, [illegible] (1973).
(27) D. M. Lindsay, D. R. Herschbach, and A. L. Kwiram, *Chem. Phys. Lett.*, **25**, 175 (1974).
(28) J. A. Ibers and W. C. Hamilton, *J. Chem. Phys.*, **44**, 1748 (1966).
(29) J. N. Wilson, R. M. Curtis, and C. T. Goetschel, *J. Appl. Crystallogr.*, **4**, 260 (1971).
(30) A. R. Young, T. Hirata, and S. I. Morrow, *J. Amer. Chem. Soc.*, **86**, 20 (1964).
(31) C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., 1963, Chapter 3.
(32) J. Levy, *J. Phys. C*, **2**, 1371 (1969); *Phys. Rev. B*, **1**, 4261 (1970); **2**, 232 (1970).

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

The Hexafluorobromine (VII) Cation, BrF_6^+. Infrared Spectrum and Force Field

Karl O. Christe* and Richard D. Wilson

Received June 6, 1974

Introduction

The syntheses of $BrF_6^+AsF_6^-$ and $BrF_6^+Sb_2F_{11}^-$ from BrF_5 and the corresponding KrF_2·Lewis acid adducts have recently been reported by Gillespie and Schrobilgen.[1,2] These BrF_6^+ salts were characterized by ^{19}F nmr and Raman spectroscopy.[2] Since complete vibrational spectra and modified valence force fields are known for ClF_6^+ [3] and IF_6^+, [4-6] similar information on BrF_6^+ was desirable to obtain more quantitative data on the bonding in these unusual high oxidation state cations.

Experimental Section

Apparatus and Materials. The materials used in this work were manipulated in a well-passivated (with ClF_3 and BrF_5) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube type gage (0-1500mm ± 0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. The spectra of solids at room temperature were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation. The low-temperature spectra were recorded at -196° using a cell and transfer technique similar to one previously described.[7] The inner windows of the cell were AgCl, the outer ones CsI disks. The instrument was calibrated by comparison with standard calibration points.[8]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880Å exciting line and a Claassen filter[9] for the elimination of plasma lines. For low-temperature work a Miller Harney device[10] was used. Passivated quartz, Teflon FEP, or Kel-F capillaries were used as sample tubes in the transverse-viewing-transverse-excitation technique.

Debye-Scherrer powder patterns were taken using a G.E. Model XRD -6 diffractometer with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (~ 0.5mm o d.).

The purification of BrF_5 and AsF_5 and the preparation of $BrF_5 \cdot 2SbF_5$ have previously been described.[11] Krypton difluoride was prepared from Kr (Matheson, 99.995%) and F_2 using glow-discharge at -183°. Our method was similar to that[12] of Schreiner et al., except for the elimination of the gas circulation system. The KrF_2 was collected at the end of a run in a tared Teflon FEP U trap maintained at -78°. The only detectable impurity in the KrF_2 was a small amount of N_2O_5 which could be removed by treatment of the crude KrF_2 with BF_3 at -78° and -10°, which converted the N_2O_5 to nonvolatile $NO_2^+BF_4^-$.[13] Pure KrF_2 was obtained by pumping off the volatile material and trapping the KrF_2 at -78°.

Preparation of BrF_6^+ Salts. The $BrF_6^+AsF_6^-$ salt was prepared by the method of Gillespie and Schrobilgen[2] using a KrF_2:AsF_5 mole ratio of 2:1 and a large excess of BrF_5. Complete material balances were obtained for the experiments. The yields of $BrF_6^+AsF_6^-$ were found to range from 5.3 to 7.0 mol% based on KrF_2 and the correct amounts of Kr and F_2 were evolved.

For the synthesis of the [illegible] salt, weighed amounts of $BrF_4^+Sb_2F_{11}^-$ were dissolved in BrF_5 and KrF_2 was [illegible] at -196°. The mixture was kept at 25° until no further gas evolution was observed. Volatile materials were removed at room temperature. The Raman spectrum of the solid residue was identical to that previously reported.[2] Since in a separate experiment we had demonstrated that $BrF_4^+Sb_2F_{11}^-$ can be removed in a dynamic vacuum at 50°, this residue was warmed to 50° for one week in a dynamic vacuum. Starting originally with 1.62 mmol of $BrF_4^+Sb_2F_{11}^-$ and 7.63 mmol of KrF_2, 23.2 mg of a white solid residue was obtained which according to its infrared and Raman spectra was only $BrF_6^+SbF_6^- \cdot xSbF_5$ with x being less than 1.

Results and Discussion

Synthesis and Properties. The synthesis data are in excellent agreement with the reports[2] of Gillespie and Schrobilgen. The following observations deserve some comment. In the previous study[2] no material balances were obtained. In our study the yield of $BrF_6^+AsF_6^-$ was found to be about 6 mol% based on the assumption that 1 mol of KrF_2 could produce 1 mol of BrF_6^+ salt. In addition, it was established that $BrF_6^+SbF_6^- \cdot xSbF_5$ can be separated from $BrF_4^+Sb_2F_{11}^-$ by vacuum sublimation. However, the resulting product was not of sufficient quantity and purity to allow further characterization and to determine whether the anion was mainly SbF_6^- or $Sb_2F_{11}^-$. When samples of BrF_6^+ salts were placed in passivated quartz capillaries and flame sealed, Raman spectroscopy showed that at ambient temperature the BrF_6^+ salts attacked the quartz with formation of the corresponding O_2^+ salts. Similarly, the BrF_6^+ salts interacted at ambient temperature with AgCl. The attack of AgCl by $BrF_6^+AsF_6^-$ was much faster than that by the corresponding SbF_5 salt and preempted the recording of $BrF_6^+AsF_6^-$ infrared spectra at room temperature. In Teflon FEP containers the BrF_6^+ salts were stored at room-temperature for prolonged periods without noticeable decomposition.

X-Ray Powder Data. The observed and calculated X-ray powder diffraction data for $BrF_6^+AsF_6^-$ are listed in Table I. The pattern was corrected for lines[14] due to $NO_2^+AsF_6^-$ resulting from the interaction[13] between AsF_5 and some N_2O_5 which was present as an impurity in the KrF_2 starting material. The powder pattern of $BrF_6^+AsF_6^-$ very closely resembles that [4,15] of $IF_6^+AsF_6^-$ indicating that the two compounds are isomorphous. By analogy with $IF_6^+AsF_6^-$, it was indexed in the face-centered cubic system with $a = 9.394$ Å. As expected, the unit cell of $BrF_6^+AsF_6^-$ is slightly smaller than that of $IF_6^+AsF_6^-$ (9.49Å). [4,15] This relatively small change in the unit cell dimensions is not surprising because the small radii of the +VII halogen ions allow them to occupy interstices in the fluoride packing. Assuming four molecules per unit cell and neglecting contributions to the volume from the highly charged central atoms, a plausible average volume [16,17] of 17.27Å^3 per F and a calculated density of 3.068 g/cm^3 are obtained.

Weaker lines were observed having mixed, even and odd Miller indices. These are not expected for a simple NaCl structure, but can readily be explained [4,15] by scattering from the fluorine atoms grouped around the Br and As atoms with these central atoms occupying the positions of Na and Cl in the NaCl lattice. By analogy with $IF_6^+AsF_6^-$, [15] the space group of $BrF_6^+AsF_6^-$ is Pa3.

Vibrational Spectra. The infrared spectra of $BrF_6^+AsF_6^-$ and of $BrF_6^+SbF_6^-\cdot xSbF_5$ after the removal of $BrF_4^+Sb_2F_{11}^-$ are shown in Figure 1. The Raman spectra of $BrF_6^+AsF_6^-$ and of the SbF_5 adduct before the removal of $BrF_4^+Sb_2F_{11}^-$ were

Table I

X-Ray Powder Data for $BrF_6^+AsF_6^-$

d (obsd) Å	d (calcd) Å	Intens	h k l
4.69	4.69	vs	2 0 0
3.32	3.32	s	2 2 0
2.712	2.712	ms	2 2 2
2.509	2.511	w	3 2 1
2.102	2.100	m	4 2 0
2.002	2.003	w	3 3 2
1.916	1.918	ms	4 2 2
1.661	1.661	m	4 4 0
1.565	1.566	ms	4 4 2 6 0 0
1.486	1.486	mw	6 2 0
1.417	1.416	mw	6 2 2
1.356	1.356	w	4 4 4
1.302	1.303	m	6 4 0
1.278	1.279	vw	7 2 1 6 3 3 5 5 2
1.256	1.255	m	6 4 2
1.193	1.193	w	7 3 2 6 5 1
1.174	1.174		8 0 0
1.140	1.141	mw	8 2 0 6 4 4
1.107	1.107	mw	8 2 2 6 6 0
1.077	1.078	w	6 6 2
1.051	1.050	w	8 4 0
1.025	1.025	w	8 4 2
.940	.939	w	8 6 0 10 0 0
.922	.921	w	10 2 0

identical to those previously reported.[2] The Raman spectrum of the SbF_5 adduct after the removal of $BrF_4^+Sb_2F_{11}^-$ had its most intense band at 660 cm^{-1} (ν_1 of SbF_6^-) with two pronounced shoulders on its high frequency side. In addition to weak bands attributable to $Sb_2F_{11}^-$ stretching modes and to the SbF deformational modes in the 300-220 cm^{-1} frequency range, the BrF_6^+ deformation ν_5 (F_{2g}) was observed at 406 cm^{-1}.

In addition to the three previously reported[2] Raman active modes, octahedral BrF_6^+ is expected to exhibit two infrared active fundamentals. These are the antisymmetric stretch, $\nu_3(F_{1u})$, and the antisymmetric deformation, $\nu_4(F_{1u})$. By comparison with the known frequencies of the closely related ClF_6^+, IF_6^+, SF_6, SeF_6, and TcF_6 species, ν_3 and ν_4 of BrF_6^+ are expected to occur between 760-800 and 400-450 cm^{-1}, respectively. Inspection of Figure 1 reveals that in both the AsF_5 and the SbF_5 adduct bands were observed at 775 and 430 cm^{-1}. Furthermore, these bands disappeared when the $BrF_6^+AsF_6^-$ IR sample was allowed to warm to ambient temperature or when the IR sample of the SbF_5 adduct was kept at ambient temperature for several hours. The remaining bands in the infrared spectra changed only little, thus supporting the assignment of the 775 and 430 cm^{-1} bands to ν_3 and ν_4, respectively, of the powerful oxidizing species BrF_6^+. The ready interaction between BrF_6^+ and the silver halide window material can also account for the weakening of the intensity of the BrF_6^+ infrared bands in the room temperature spectrum of the SbF_5 adduct.

In $BrF_6^+AsF_6^-$, the 430 cm^{-1} band shows a splitting of 6 cm^{-1}. Since the two components are of similar intensity, splitting due to the ^{79}Br ^{81}Br isotopes must be considered. The following arguments augur against the splitting being caused by the bromine isotopes and favors its attribution to crystal field or site symmetry effects. (i) The SbF_5 adduct does not show a comparable splitting. (ii) The observed splitting of 6 cm^{-1} is much larger than that (~ 2 cm^{-1}) predicted for the Br isotopes. (iii) The NO_2^+ deformation in the same spectrum shows a comparable splitting. (iv) The site symmetry of BrF_6^+ in space group Pa3 is only C_{3i}.

<u>Force Constants.</u> Since both the infrared and the Raman active fundamentals are now known, it was interesting to compute a force field for BrF_6^+. This

allows a more quantitative comparison of the relative bond strength of BrF_6^+ with those of related species.

Except for the F_{1u} block, all the symmetry force constants of BrF_6^+ are unique. The F_{1u} block is underdetermined since only two frequency values are available for the determination of three force constants. Consequently, the usefulness of mathematical constraints, such as minimizing or maximizing the value of one of the symmetry force constants[18], was tested for the isoelectronic series SF_6, SeF_6, and TeF_6, for which general valence force fields have been reported.[19-21] As can be seen from Table II, the condition F_{44} = minimum very closely duplicates the GVFF values for the two heavier molecules SeF_6 and TeF_6. Therefore, it is also expected to be a very good approximation for the force field of BrF_6^+. The values so obtained for BrF_6^+ are listed in Table II and correlate well with the remaining species of Table II. The modified valence force fields, listed for the lightest isoelectronic series, i.e., PF_6^-, SF_6, ClF_6^+, are less reliable since the lighter central atoms cause stronger coupling of the stretching and bending mode.

The force constant of greatest interest is the stretching force constant f_r. For BrF_6^+ its value of 4.9 mdyn/Å is the highest found to date for any BrF bond.[23-25] This is not surprising since the covalency and therefore also the force constant of such a bond tends to increase with increasing oxidation state of the central atom and a formal positive charge.[22] Since the Br-F bonds in BrF_6^+ are stronger than those in other bromine fluorides, the reactivity of these salts must be due to the high oxidizing power of BrF_6^+.

Acknowledgement. We are indebted to Drs. C. J. Schack and L. R. Grant for helpful discussions. This work was supported by the Office of Naval Research, Power Branch.

Table II

Symmetry and Internal Force Constants (mdyn/Å) of BrF_6^+ Compared to Those of Related Octahedral Species[a]

		PF_6^-	AsF_6^-	SbF_6^-	SF_6		SeF_6		TeF_6		ClF_6^+		BrF_6^+	IF_6^+
		F_{44}=MIN	F_{44}=MIN	F_{44}=MIN	GVFF[b],	F_{44}=MIN	GVFF[c],	F_{44}=MIN	GVFF[d],	F_{44}=MIN	$f_{rr}'=0$	F_{44}=MIN	F_{44}=MIN	F_{44}=MIN
A_{1g}	$F_{11}=f_r+4f_{rr}+f_{rr}'$	6.23	5.21	4.77	6.70[c]		5.59[c]		5.41[c]		5.16		4.88	5.61
E_g	$F_{22}=f_r-2f_{rr}+f_{rr}'$	3.52	3.64	3.52	4.61[e]		4.86[e]		5.03[e]		4.44		5.02	6.00
F_{1u}	$F_{33}=f_r-f_{rr}'$	4.36	3.82	3.86	5.26	5.80	4.88	4.85	4.98	4.95	4.68	5.28	4.82	5.23
	$F_{34}=2(f_{r\alpha}-f_{r\alpha}'')$	0.91	0.33	0.14	0.89	1.10	0.44	0.42	0.24	0.19	0.73	0.96	0.41	0.21
	$F_{44}=f_\alpha+2f_{\alpha\alpha}-2f_{\alpha\alpha}''-f_{\alpha\alpha}'''$	0.83	0.55	0.30	1.04	1.02	0.64	0.65	0.40	0.41	0.96	0.93	0.63	0.45
F_{2g}	$F_{55}=f_\alpha-2f_{\alpha\alpha}'+f_{\alpha\alpha}'''$	0.63	0.38	0.21	0.77[e]		0.46[e]		0.28[e]		0.74		0.46	0.32
	f_r	4.39	3.98	3.90	5.28	5.55	4.99	4.98	5.07	5.06	4.68	4.98	4.90	5.42
	f_{rr}	0.45	0.27	0.21	0.35		0.12		0.07		0.12		–0.03	–0.07
	f_{rr}'	0.03	0.16	0.04	0.02	–0.25	0.11	0.13	0.09	0.11	0	–0.33	0.08	0.19

(a) Frequencies (cm^{-1}) of ν_1-ν_5 used for force field computations: PF_6^-, 746, 561, 817, 557, 475; AsF_6^-, 682, 568, 696, 385, 369; SbF_6^-, 653, 561, 667, 250, 273; SF_6, 773.5, 641.7, 947.9, 614.5, 525; SeF_6, 706.9, 658.7, 778.5, 436, 405; TeF_6, 697.1, 670.3, 751, 326.5, 314; ClF_6^+, 679, 630, 890, 582, 513; BrF_6^+, 660, 670, 775, 430, 405; IF_6^+, 708, 732, 790, 343, 340.

(b) Ref. 19

(c) Ref. 21

(d) Ref. 20

(e) using Raman frequencies from H. H. Claassen, G. L. Goodman, J. L. Holloway, and H. Selig, J. Chem. Phys., 53, 341(1970).

References

(1) R. J. Gillespie and G. J. Schrobilgen, J. Chem. Soc., Chem. Commun., 90(1974).

(2) R. J. Gillespie and G. J. Schrobilgen, Inorg. Chem., 13, 1230(1974).

(3) K. O. Christe, Inorg. Chem., 12, 1580(1973).

(4) K. O. Christe and W. Sawodny, Inorg. Chem., 6, 1783(1967).

(5) K. O. Christe and W. Sawodny, Inorg. Chem., 7, 1685(1968).

(6) K. O. Christe, Inorg. Chem., 9, 2801 (1970).

(7) K. R. Loos, V. A. Campanile, and C. F. Goetschel, Spectrochim. Acta, 26A, 365(1970).

(8) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, J. Res. Natl. Bur. Std., 64, 841(1960).

(9) H. H. Claassen, H. Selig, and J. Shamir, Appl. Spectrosc., 23, 8(1969).

(10) F. A. Miller and B. M. Harney, Appl. Spectrosc., 24, 291 (1970).

(11) K. O. Christe and W. Sawodny, Inorg. Chem., 12, 2879(1973).

(12) F. Schreiner, J. G. Malm, and J. C. Hindman, J. Amer. Chem. Soc., 87, 25(1965).

(13) A. B. Ray, Inorg. Chem., 6, 110(1967).

(14) D. Moy and A. R. Young, J. Amer. Chem. Soc., 87, 1889(1965).

(15) S. P. Beaton, Ph.D. Thesis, University of British Columbia, Canada (1966).

(16) W. H. Zachariasen, J. Amer. Chem. Soc., 70, 2147(1948).

(17) F. H. Ellinger and W. H. Zachariasen, J. Phys. Chem., 58, 405(1954).

(18) W. Sawodny, J. Mol. Spectrosc., 30, 56(1969).

(19) A. Ruoff, J. Mol. Struct., 4, 332(1969).

(20) S. Abramowitz and I. W. Levin, J. Chem. Phys., 44, 3353(1966).

(21) S. Abramowitz and I. W. Levin, Inorg. Chem., 6, 538(1967).

(22) K. O. Christe, Pure and Appl. Chem., in press.

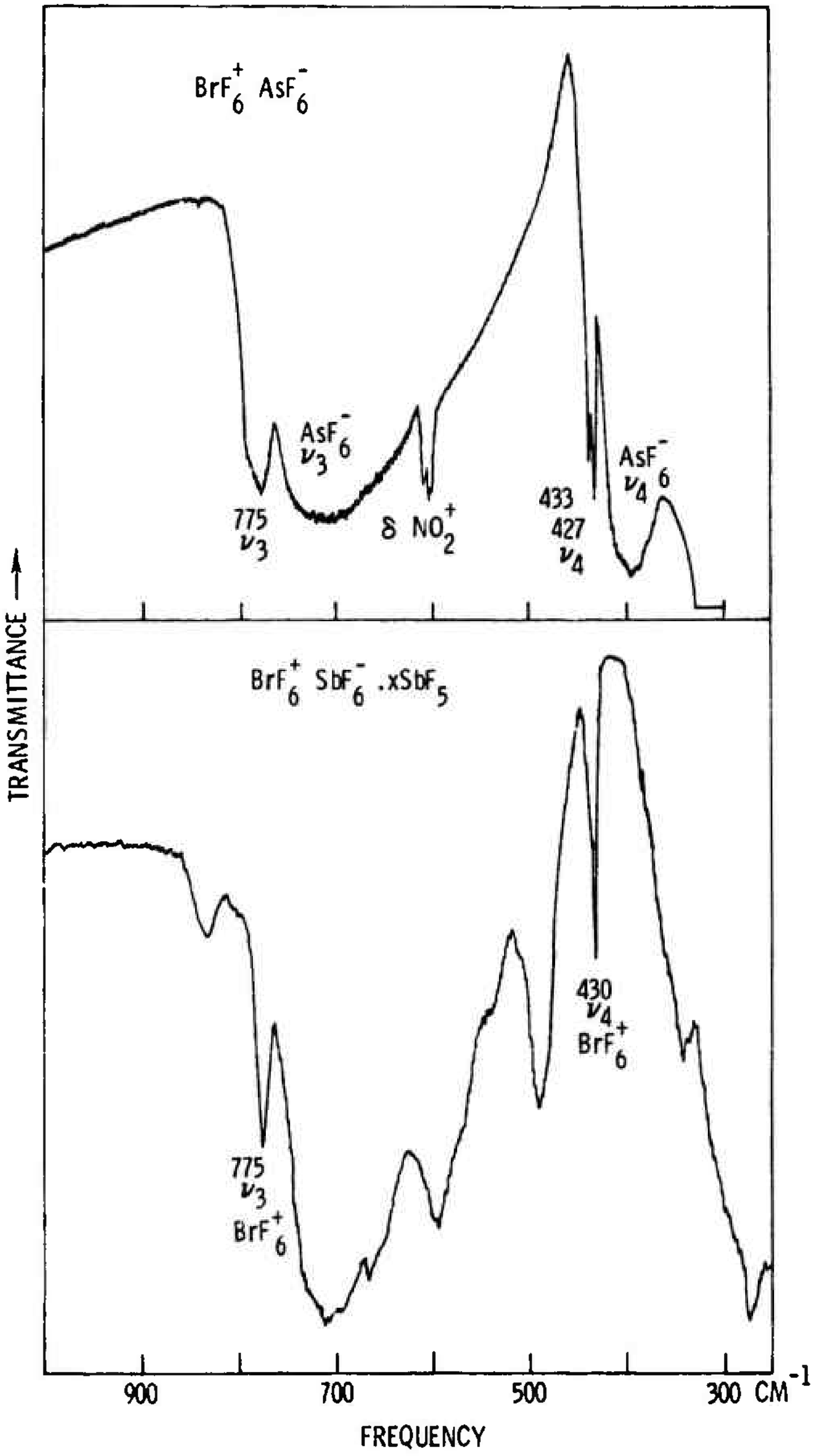
(23) K. O. Christe and C. J. Schack, Inorg. Chem., 9, 2296(1970).

(24) K. O. Christe, E. C. Curtis, and D. Pilipovich, Spectrochim. Acta, 27A, 931(1971).

(25) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, Inorg. Chem., 11, 1679(1972).

Diagram Caption

Figure 1. Infrared spectra of $BrF_6^+AsF_6^-$ recorded as a dry powder between AgCl plates at -196° and of $BrF_6^+SbF_6^- \cdot xSbF_5$ recorded as a AgBr disk at 25°. The increase in background at the low frequency end of the spectra is due to absorption by the windows.



$BrF_6^+ AsF_6^-$
AsF_6^- ν_3
775 ν_3
δ NO_2^+
433 427 ν_4
AsF_6^- ν_4
TRANSMITTANCE →
$BrF_6^+ SbF_6^- .xSbF_5$
430 ν_4 BrF_6^+
775 ν_3 BrF_6^+
900
700
500
300 CM^{-1}
FREQUENCY

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

Novel Onium Salts . Synthesis and Characterization of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$

Karl O. Christe, * Carl J. Schack, and Richard D. Wilson

Received..........

Abstract

The novel oxonium salts $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ were isolated as well defined crystalline solids from the H_2O-HF-SbF_5 and the H_2O-HF-AsF_5 system, respectively. These salts are the most stable oxonium salts presently known. It was shown by DSC studies that $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ decompose at about 357 and 193°, respectively. Their ionic nature in both the solid state and polar solvents was established by vibrational and ^{19}F and ^1H nmr spectroscopy. The infrared spectra of these adducts closely resemble those recently attributed to H_2F^+ salts, suggesting that the latter may have been incorrectly identified. Furthermore, the frequencies of the OH_3^+ fundamentals in these salts are very similar to those of isoelectronic NH_3, but significantly different from those previously observed for OH_3^+ in mineral acid monohydrates. This indicates that in the MF_6^- salts the hydrogen bridges are considerably weaker, although similar phenomena are observed for the low-temperature spectra suggesting rigidity of the lattice at low-temperature. The assignments for OH_3^+ were examined by force field computations. Based on its x-ray powder diffraction pattern, $OH_3^+AsF_6^-$ is cubic with a=8.015Å, Z=4. From the H_2O-HF-BF_3 system a solid adduct was isolated at low temperature, but was not further characterized owing to its thermal instability. A new method for drying HF based on oxonium salts is proposed.

INTRODUCTION

During a study of the controlled hydrolysis of $BrF_4^+Sb_2F_{11}^-$ in HF, a stable white solid was obtained in high yields. Elemental analysis of this solid showed that it did not contain detectable amounts of bromine. Its infrared spectrum closely resembled that recently reported [1] by Couzi et al. for H_2F^+. However, attempts to prepare a stable product from HF and SbF_5 alone failed. This agrees with a DTA study[2] of the $HF-SbF_5$ system which showed no evidence for any high melting adduct. Surprisingly, the addition of small amounts of water to $HF-SbF_5$ mixtures produced the same stable solid which, as shown in this paper, was identified as $OH_3^+SbF_6^-$.

A literature search did not reveal any reports on the isolation of $OH_3^+MF_6^-$ salts, in spite of many papers dealing with the relatively unstable mineral acid monohydrates and Commeyras and Olah's proton nmr (singlet at $\delta = 10.25$) evidence[3] for the existence of the oxonium ion in $SbF_5 - HOSO_2F$ solution. Recently, Bonnet and coworkers studied[4] solutions of SbF_5 in H_2O and HF by DTA and identified the crystalline phases $SbF_5 \cdot 2H_2O$, $4SbF_5 \cdot 5H_2O$, $SbF_5 \cdot H_2O$, $3SbF_5 \cdot 2H_2O$, and $SbF_5 \cdot HF \cdot 2H_2O$. Surprisingly, no evidence for $OH_3^+SbF_6^-$ was reported, although the infrared spectra attributed to $SbF_5 \cdot H_2O$ and $4SbF_5 \cdot 5H_2O$ closely resemble thos obtained by us for $OH_3^+SbF_6^-$.

The general interest in oxonium salts and super acid systems,[5,6] in which, unless rigorously dried, these salts are bound to be formed, prompted us to study these simple oxonium salts in more detail. Their unexpected high thermal stability also induced us to study the protonation of other compounds, such as H_2S, HCℓ, Xe, HNF_2, NF_3, etc. Details on novel salts containing the SH_3^+ and the $NH_2F_2^+$ cation will be reported elsewhere.[7]

Experimental

Materials and Apparatus. Volatile materials used in this work were manipulated in a well passivated (with $C\ell F_3$ and HF) Monel Teflon-FEP vacuum system. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Hydrogen fluoride (The Matheson Co.) was first electrolytically dried[8] followed by treatment with either fluorine or SbF_5. In the latter case, the HF was added to a Teflon-FEP ampoule containing SbF_5. Any water present formed nonvolatile $OH_3^+SbF_6^-$ and the anhydrous HF was pumped off at -40°. Antimony pentafluoride and AsF_5 (Ozark Mahoning Co.) and BF_3 (The Matheson Co.) were purified by distillation and fractional condensation, respectively, prior to their use.

of all volatile material in vacuo at 25° resulted in 2.116g of a white solid residue (weight calcd. for 8.30 mmol of $OH_3^+SbF_6^-$ = 2.115g). Anal. Calcd for OH_3SbF_6: H_2O, 7.07; Sb, 47.8. Found: H_2O, 6.93; Sb, 48.0.

Preparation of $OH_3^+AsF_6^-$. In a typical experiment, H_2O (5.421 mmol) and anhydrous HF (8ml liquid) were combined at -196° in a Teflon-FEP ampoule, followed by warm-up to 25°. Arsenic pentafluoride (5.427 mmol) was added to this mixture at -196° and the contents of the ampoule were allowed to warm slowly to room temperature. Removal of volatile material at 25° in vacuo resulted in 1.128g of a white solid residue (weight calcd. for 5.421 mmol of $OH_3^+AsF_6^-$ = 1.127g). Anal. Calcd for OH_3AsF_6: H_2O, 8.66; As, 36.0. Found: H_2O, 8.26; As, 35.7.

The H_2O-HF-BF_3 System. To a mixture of H_2O (3.66 mmol) and anhydrous HF (10 ml liquid), prepared as described above, BF_3 (7.4 mmol) was added at -196°. This mixture was kept at -78° for 10 minutes, then slowly warmed until a clear solution resulted. Removal of volatile material at -70° in vacuo produced a white solid residue melting at around 0° to a colorless liquid having a dissociation pressure of about 4mm at 22°. The weight of the adduct, after being pumped on at 0° for several minutes, was 376 mg (calcd for 3.66 mmol OH_3BF_4 = 387 mg).

Results and Discussion

Syntheses. Addition of water to mixtures of HF with the strong Lewis acids SbF_5 and AsF_5 produces stable 1:1:1 adducts in quantitative yield according to:

$$HF + H_2O + MF_5 \xrightarrow{HF} H_3O^+MF_6^-$$

The formation of these adducts is not surprising in view of the previous evidence[11-14] showing that in HF solution the following equilibrium exists

$$SbF_5 + 2HF \rightleftharpoons H_2F^+SbF_6^-$$

and that the stronger base H_2O can displace [3,1] H_2F^+ with formation of the OH_3^+ cation

$$H_2F^+ + SbF_6^- + H_2O \longrightarrow OH_3^+ + SbF_6^- + HF$$

However, in view of the several hundred recent publications dealing with super acid chemistry, the well known difficulties in obtaining completely anhydrous systems, and the general interest in oxonium salts, we were extremely surprised to find that these stable adducts had not previously been isolated.

It appears that the low-temperature infrared spectra of these adducts have been observed [1] previously by Couzi and coworkers in the course of their study of the binary HF-Lewis acid systems, but were mistaken for H_2F^+ salts. Although not impossible, it is highly unlikely that OH_3^+ amd H_2F^+ would show such similar vibrational spectra. Furthermore, comparison of the observed frequencies and computed force constants of "H_2F^+" with those of isolectronic H_2O show poor agreement (H_2O=f_r=8.45, f_α=0.76; "H_2F^+": f_r=5.71, f_α = 1.36 mdyn/Å)[1].

The failure of Bonnet et al. to isolate $OH_3^+SbF_6^-$ from the SbF_5-H_2O-HF system[4] may be explained by their unfortunate choice of reaction conditions. They combined H_2O with SbF_5 in the absence of a solvent. This can result in partial hydrolysis of SbF_5 with HF formation, thus making it very difficult to obtain well defined products.

We have established the 1:1:1 composition of the HF:H_2O:SbF_5 and the HF:H_2O:AsF_5 adduct by the observed material balances, elemental analyses, and vibrational and nmr spectroscopy. With the weaker Lewis acid BF_3, an unstable 1:1:1 adduct is formed at lower temperature. It melts at about 0° to a colorless liquid having a dissociation pressure of about 4 mm at 22°.

The quantitative formation of a stable nonvolatile OH_3^+ salt is an effective way to remove small amounts of water from HF by treating it with a strong Lewis acid. Bismuth pentafluoride, although not used in this study, should be the most convenient drying reagent, since it is nonvolatile at room temperature. Thus, its use would permit the removal of the dry HF from $OH_3^+BiF_6^-$ and the excess of BiF_5 at ambient temperature. This method appears more convenient than previously reported methods, such as pyrolysis of dried $NaHF_2$[16], electrolytic drying, [8]or fluorine treatment.[17] Furthermore, the stable solid $OH_3^+MF_6^-$ salts could find applications in systems requiring catalytic amounts of strong acids. Owing to their physical properties (see below), these solids should be easier to store, ship, and handle then highly corrosive liquids.

Properties. The $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ salts are white crystalline solids. They are highly soluble in HF and moderately soluble in polar solvents, such as $CH_3SO_2CH_3$. With stronger bases such as pyridine or acetonitrile, water is evolved and the nitrogen atom is protonated. The quantitative displacement of

The infrared spectra were recorded in the range 4000-250 cm^{-1} on a Perkin-Elmer Model 457 infrared spectrophotometer. The spectra of gases were obtained using Monel cells of 5-cm path length fitted with AgCℓ windows. Spectra of dry powders at room temperature were recorded as pressed (Wilks minipellet press) disks between AgCℓ windows. Low-temperature spectra were obtained as dry powders between CsI plates using a technique similar to one previously reported.[9]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880Å exciting line and a Claassen filter [10] for the elimination of plasma lines. Sealed quartz or Teflon-FEP tubes were used as sample containers in the transverse-viewing transverse-excitation technique. The low-temperature spectra were recorded using a previously described [11] device. Polarization measurements were carried out according to method VIII listed by Claassen et al. [10]

Debye-Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (∿ 0.5 mm o.d.)

The ^{19}F and ^{1}H nmr spectra were recorded at 56.4 and 60MHz, respectively, on a Varian Model DA60 spectrometer equipped with a variable temperature probe. Chemical shifts were determined by the side-band technique relative to external $CFCℓ_3$ and TMS, respectively.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used for the determination of the thermal stability of the compounds. The samples were sealed in aluminum pans, and heating rates of 2.5 and 10°/min in N_2 were used.

The H_2O content in the OH_3^+ salts was determined by dissolving a known amount of sample in pyridine and titrating the evolved H_2O with Karl Fischer reagent using a Labindustries Aquametry apparatus. Antimony and arsenic were determined by X-ray fluorescence spectroscopy of basic aqueous solutions.

Preparation of $OH_3^+SbF_6^-$. In a typical experiment, SbF_5 (8.305 mmol) was placed in a Teflon-FEP ampoule and 8 mℓ of liquid anhydrous HF was added at -196°. The mixture was warmed to 25° to give a homogenous solution. Distilled water (8.30 mmol) was added to the ampoule at -196° and the mixture was warmed to 25°. Removal

OH_3^+ by pyridine was successfully used for the determination of the H_2O content with Karl Fischer reagent. Evidence for the protonation of acetonitrile was obtained by proton nmr spectroscopy (see below). The oxonium ion is surprisingly inactive as a hydrolyzing agent. In addition to its compatibility with the SbF_6^- and AsF_6^- ions in HF solution, it does not hydrolyze to a significant extent BrF_5, BrF_4^+ salts,[7] and NF_4^+ salts.[18]

The thermal stability of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ was determined by DSC. The SbF_6^- salt exhibited reversible endotherms at 89 and 209°(probably phase changes), followed by some small irreproducible endotherms from about 230 to 357° and a large irreversible endotherm at 357°. The occurrence of complete decomposition at 357° was also confirmed by the observation of white fumes escaping from the sample cup at this temperature. Heating the salt to 150° in a static vacuum resulted in the build up of only a little pressure over a period of several hours. The $OH_3^+AsF_6^-$ salt exhibited no endo-or exotherms prior to the onset of its strongly endothermic decomposition at 193° indicating the absence of any phase change between 25 and 193°.

The thermal stability of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ is unusually high, when compared to the previously reported OH_3^+ salts. Most of these salts are stable only at low temperature, and the more stable $OH_3^+CF_3SO_3^-$, $OH_3^+ClO_4^-$, and $OH_3^+CH_3C_6H_4SO_3^-$ melt at 35, 50, and 105°, respectively.[19-21]

X-Ray Powder Diffraction Data. The powder diffraction patterns of $OH_3^+AsF_6^-$ and $OH_3^+SbF_6^-$ are listed in Tables I and II, respectively. The $OH_3^+AsF_6^-$ salt is cubic with a =8.015 Å and Z=4. As previously pointed out,[22] it is very difficult to distinguish from the powder pattern alone for this type of compound whether it has the face centered cubic $NaSbF_6$ or the primitive cubic $CsPF_6$ structure. The intensities observed for $OH_3^+AsF_6^-$ seem to agree somewhat better with the primitive cubic $CsPF_6$ type. Since the size of the OH_3^+ cation[23] is roughly comparable to that of K^+, Ag^+, or NH_4^+, it is not surprising that $OH_3^+AsF_6^-$ should be isotypic with $Ag^+AsF_6^-$ (a=7.74 Å) and $NH_4^+PF_6^-$ (a=7.90 Å).

The $OH_3^+SbF_6^-$ pattern was indexed for a tetragonal cell with a=11.48, c = 8.78A, and Z=8. By comparison with the known [22,24] structures of similar MXF_6 compounds, it might be considered as a tetragonally distorted cubic $KSbF_6$ structure. Tetragonal unit cells with Z=8 have previously been reported[25] for $KReF_6$, KWF_6, and $KMoF_6$, although their deviation from a cubic cell is much smaller. This might be explained by the fact that OH_3^+ is not spherical.[23] In addition to the cubic phase (Z=8), a high-temperature tetragonal phase (Z=2) has been reported[22,24] for $AgSbF_6$ and $KSbF_6$ containing one fourth of the cubic superlattice.

In summary, the structures observed for the $OH_3^+MF_6^-$ salts agree well with those reported[22,24] for related MF_6^- salts. This comparison also suggests the possibility of different phases as was indicated for $OH_3^+SbF_6^-$ by the DSC data (see above). Contrary to $OH_3^+SbF_6^-$, cubic $OH_3^+AsF_6^-$ did not exhibit a phase change between room temperature and its decomposition point. This is not surprising since $OH_3^+AsF_6^-$ appears to be isotypic with KPF_6 which has a rhombohedral low-temperature and a cubic high-temperature phase.[26]

<u>Nuclear Magnetic Resonance Spectra</u>. The nmr spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ were recorded in $CD_3SO_2CD_3$, CH_3CN, and CD_3CN solutions. The ^{19}F nmr spectra of $OH_3^+AsF_6^-$ in $CD_3SO_2CD_3$ and CH_3CN solution showed a quartet of equal intensity at ϕ=60.9 and 65.4 with J_{AsF}=915 and 930 Hz, respectively, in good agreement with the values previously reported[27], for octahedral AsF_6^-. Similarly, the $OH_3^+SbF_6^-$ samples showed a sextet ($J121_{SbF}$=1946 Hz) and octet ($J123_{SbF}$=1053 Hz) of equal intensities at ϕ=120.1, characteristic[27,28] of octahedral SbF_6^-. In agreement with the vibrational spectra (see below), no evidence was found for the presence of $MF_5 \cdot OH_2$[29] or $MF_5 \cdot NCCH_3$[30,31] molecular adducts in these systems.

The proton nmr spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ in $CD_3SO_2CD_3$ solution showed only a singlet at δ= -9.49 and -10.58, respectively. These values agree well with that of -10.2 previously attributed[3] to OH_3^+ in super acid solutions. In CH_3CN or CD_3CN solutions, however, the spectra were more complex. The strongest resonance for the SbF_6^- and AsF_6^- salts were observed at δ= -10.92 and -11.34, respectively. In addition, a very broad resonance at δ= -3.8 and a triplet of equal intensity (J_{NH}=53.5 Hz) at δ= -6.3 were observed. The latter is characteristic for NH_4^+.[32] The observation of NH_4^+ together with the fact that the proton resonance in CH_3CN solutions is significantly shifted to lower field, when compared to $CD_3SO_2CD_3$ solutions, indicate that this resonance is due to a $\geq NH^+$ type species and not to OH_3^+. The CH_3 resonance consisted of a single peak at δ= -2.21 indicating rapid exchange between CH_3CN and its protonated form. The ready protonation of CH_3CN in HSO_3F-SbF_5-SO_2 solution has previously been established.[33] The difference between the reported[33] and our spectrum can be explained by the fact that in one case small amounts of CH_3CN were dissolved in large amounts of acid, whereas in our case small amounts of $OH_3^+SbF_6^-$ were added to large amounts of CH_3CN. Since the nmr spectrum of OH_3^+ in super acids has previously been reported[3] and agrees with our data for the $CD_3SO_2CD_3$ solution we have not studied super acid or HF solutions.

Vibrational Spectra. Figures 1 and 2 show the vibrational spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$, respectively. The observed frequencies are listed in Table III. Whereas no difficulty was encountered in obtaining reproducible infrared spectra of $OH_3^+SbF_6^-$ as an AgCℓ disk at room temperature, for $OH_3^+AsF_6^-$ low-temperature conditions were required. At room temperature, the band centered at about 900 cm^{-1} would rapidly become broad and shift to higher frequency (~ 1020cm^{-1}). Similarly, the broad band centered at about 3200 cm^{-1} became less symmetric with its maximum being shifted to ∿3500 cm^{-1}, and the 1630 cm^{-1} band was shifted to about 1680 cm^{-1}. In the Raman spectra, except for that of $OH_3^+SbF_6^-$ in HF solution, the bands due to OH_3^+ were not observed owing to their very low intensity and broadness.

The anion bands, both in HF and $CD_3SO_2CD_3$ solution, were in excellent agreement with those previously observed for octahedral AsF_6^-[34-36] and SbF_6^-.[35-37] In the room temperature spectra of the solids, ν_2 (E_g) showed a splitting into two bands which is not uncommon for octahedral MF_6^- ions in solids.[35,37-40] For $OH_3^+SbF_6^-$, the intensities of the infrared bands at about 490 and 570 cm^{-1} varied from sample to sample (see Traces A and B of Figure 1). Although one might be tempted to attribute the 490 cm^{-1} band to the presence of some $Sb_2F_{11}^-$ polyanion[35,41-43] or to an OH_3^+ libration mode (see below), we prefer to assign it to SbF_6^- for the following reasons. The $OH_3^+AsF_6^-$ spectra show similar bands and AsF_6^- is unlikely to form stable polyanions,[34] the observed material balances and elemental analyses gave no indication of polyanion formation, and an OH_3^+ libration should be of very low Raman intensity. Whereas in the room temperature spectra of the solids, ν_3 (F_{1u}) and ν_1 (A_{1g}) appear as single bands, these bands become doublets in the low-temperature spectra. Furthermore, four relatively sharp bands were observed in the low-temperature infrared spectrum of $OH_3^+AsF_6^-$ (Trace B, Figure 2) in the region of ν_2 (E_g) of AsF_6^-.

The most plausible explanation for these additional low-temperature splittings is the assumption that at low temperature OH_3^+ and the lattice become rigid. This should result in site symmetry splittings[36] and in a large distortion of the MF_6^- octahedrons owing to cation-anion interaction (H...F bridging), particularly, since the MF_6^- ions are in a field of forces of nonoctahedral symmetry. Similar effects were observed for $OH_3^+ClO_4^-$ by broad line proton nmr[45,46] and vibrational spectroscopy.[47] However, some of the bands observed in the region of the MF_6^- fundamentals could be of different origin, as was shown[47] by Savoie and Giguere for $OH_3^+NO_3^-$, $OH_3^+ClO_4^-$, and $OH_3^+HSO_4^-$. They established that libration and translation modes of polar OH_3^+ are of relatively high frequency and infrared intensity. Since the OH_3^+ modes are only of very low intensity in the Raman spectrum, the observed Raman bands are very likely due to the anion. However, some of the infrared bands, which have no Raman counterpart, could be due to OH_3^+ libration or translation modes. Spectra of the deuterated species would be helpful to distinguish between these possibilities. In addition, extensive low-temperature vibrational and wide line nmr spectroscopic studies combined with x-ray and DTA data are desirable to correlate all the observed phenomena. However, this was beyond the scope of the present study.

Assignments for the fundamentals of the OH_3^+ cation were made by comparison with isoelectronic NH_3 (see Table III). Pyramidal XY_3 of symmetry C_{3v} has four fundamentals which are classified as $2A_1 + 2E$, all being active in both the infrared and Raman spectrum. Of these, each symmetry species contains one stretching and one bending mode. The frequencies of the two bending modes are sufficiently separated and present no assignment problem. Of the two stretching modes, the symmetric stretch ν_1 (A_1) is obviously represented by the polarized Raman band at 3300 cm^{-1} observed for $OH_3^+SbF_6^-$ in HF solution. This Raman band has an intense counterpart in the infrared spectrum of the solid. Assuming that no significant frequency shift occurred for ν_1 on going from the solution spectrum to that of the solid, the second intense infrared band in this region (~3150 cm^{-1}) should be due to the antisymmetric stretch ν_3 (E). These assignments are supported by the low-temperature infrared spectrum of $OH_3^+AsF_6^-$ which shows a strong band at about 3080 cm^{-1} with a strong shoulder at about 3250 cm^{-} in agreement with the higher ir intensity expected[48] for ν_3 in an ideal, rather oblique XY_3 pyramid. The agreement between the frequencies of isoelectronic NH_3 and OH_3^+ is excellent. The only difference in their assignments results from a reversal of ν_3 and ν_4 for OH_3^+. Whereas force field arguments (see below) augur against such a reversal, it must be kept in mind that we are comparing a free molecule with a poorly understood solid exhibiting relatively strong anion-cation coupling.

In our spectra two relatively weak broad infrared bands were frequently observed at about 1950 and 1350 cm^{-1}, respectively. Their relative intensity varied and they cannot readily be assigned to an overtone or combination band. Their origin is at the present not fully understood.

In summary, the vibrational spectra unambiguously establish that the $HF \cdot H_2O \cdot MF_5$ adducts are ionic in both the solid state and solution, and contain octahedral MF_6^- anions and pyramidal OH_3^+ cations, although some of the details of the spectra are still poorly understood. The fundamentals of OH_3^+ in its MF_6^- salts significantly differ from those found for OH_3^+ in mineral acid monohydrates,[21] such as OH_3^+ $C\ell O_4^-$, and resemble more closely those of isoelectronic NH_3. The fact that in $OH_3^+MF_6^-$ the OH stretches have higher and the deformations have lower frequencies than in the mineral acid hydrates, strongly indicates that the hydrogen bridging in $OH_3^+MF_6^-$ is significantly weaker, i.e., that these compounds are more ionic.

Force Constants. To support the above assignments, force fields were computed for OH_3^+ (see Table IV) using the vibrational frequency values from this study and the geometry ($\measuredangle$ = 110°, r = 1.01 Å) previously established[23] for the $OH_3^+CH_3C_6H_4SO_3^-$ salt. The force constants were computed by trial and error with the help of a computer to obtain an exact fit between observed and calculated frequencies. Three different force fields were computed to demonstrate that the choice of the force field has little influence on its values for a vibrationally weakly coupled species, such as OH_3^+, in which the central atom is much heavier than the ligands. To demonstrate the small variation in the force constant values, four decimals are listed in Table IV, in spite of the rather large uncertainties in the given force constant values.

These are caused by the broadness of the bands and the unknown bond angle of OH_3^+ in its MF_6^- salts. Two of the three force fields used, the diagonal force field and the force field requiring the deformation symmetry force constants to have minimal values, were selected owing to their established[49] usefulness for weakly coupled systems. For the third force field, the off-diagonal symmetry force constants were borrowed from the known[50] general valence force field of isoelectronic NH_3. Since the antisymmetric OH_3^+ stretch has a significantly lower frequency than the symmetric one and since their frequency separation is a function of the bond angle,[51] this might be taken as some evidence for the OH_3^+ bond angle being smaller than that in isoelectronic NH_3. Consequently, we have also computed the three force fields for OH_3^+ assuming a bond angle of 100°. Whereas the stretching force constants show little angle dependence, F_{22} becomes unreasonably small for $\alpha = 100°$, thus arguing against such a small bond angle for OH_3^+. As expected for a weakly coupled species containing only one stretching and one deformation vibration of very different frequency in each symmetry block, the potential energy distribution showed all fundamentals to be highly characteristic. The two high frequency fundamentals were in all cases pure stretches and the two low frequency fundamentals were 95-100% deformation modes depending upon the values of the chosen off-diagonal symmetry force constants.

Comparison of the OH_3^+ force fields with that[50] of isolectronic NH_3 shows good agreement. The only major divergence is found for the stretch-stretch interaction constant f_{rr} which is caused by $\nu_3(E)$ of OH_3^+ having a lower frequency value than $\nu_1(A_1)$. This discrepancy could be eliminated either by reversing their assignment (see Table IV) or by assuming very similar frequency values for them and explaining the observed splitting of the broad band at $\sim$3300 cm^{-1} in the infrared spectrum of $OH_3^+SbF_6^-$ by Fermi resonance between $2\nu_4(A_1 + E + F_2)$ and $\nu_1(A_1)$ or ν_3 (E). Clearly, the force field computations for OH_3^+ and comparison with those for NH_3,[50] PH_3,[50] and SH_3^+[7] favor $\nu_3 > \nu_1$. However, the experimental data (see above) seem to suggest $\nu_1 > \nu_3$. Obviously, additional experimental data are required to resolve this remaining ambiguity.

Several papers[20,21,52,53] have previously been published dealing with force fields of OH_3^+. Owing to the great variance of the frequencies used, the values reported, for example, for f_r range from 7.93 to 6.31 mdyn/Å. The variance of the frequencies is due partially to the different degree of hydrogen bridging in the different OH_3^+ salts studied[21] and partially to the broadness of the bands rendering their assignments extremely difficult and uncertain.

Conclusion. The novel oxonium salts $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ were synthesized and partially characterized. They possess unusual thermal stability, are easy to prepare, are well defined, appear to be highly ionic and, therefore, should be ideally suited for the study of the oxonium cation.

Acknowledgment. We thank Dr. L. Grant for helpful discussion, Dr. E. C. Curtis for the use of his computer program for the computation of the force constants, and the Office of Naval Research, Power Branch, for financial support.

References

(1) M. Couzi, J. C. Cornut, and P. Van Huong, J. Chem. Phys., 56, 426 (1972).

(2) V. K. Ezhov, Russ. J. Inorg. Chem., 17, 345 (1972).

(3) A. Commeyras and G. A. Olah, J. Amer. Chem. Soc., 91, 2929 (1969).

(4) B. Bonnet, J. Roziere, R. Fourcade, and G. Mascherpa, Canad. J. Chem., 52, 2077 (1974).

(5) G. A. Olah, A. M. White, and D. O'Brien, Chem. Rev., 70, 561 (1970).

(6) R. J. Gillespie, Acc. Chem. Res., 1, 202 (1968).

(7) K. O. Christe, unpublished data.

(8) H. H. Rogers, S. Evans, and J. H. Johnson, J. Electrochem. Soc., 6, 1937 (1967).

(9) K. R. Loos, V. A. Campanile, and C. T.Goetschel, Spectrochim. Acta, Part A, 26, 365 (1970).

(10) H. H. Claassen, H. Selig, and J. Shamir, Appl. Spectrosc., 23, 8 (1969).

(11) F. A. Miller and B. M. Harney, Appl. Spectrosc., 24, 291 (1970).

(12) M. Kilpatrick and T. J. Lewis, J. Amer. Chem. Soc., 78, 5186 (1956).

(13) H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, J. Phys. Chem., 65, 123 (1961).

(14) R. J. Gillespie and K. C. Moss, J. Chem. Soc., A, 1170 (1966).

(15) H. H. Hyman. T. J. Lane, and J. A. O'Donnell, 145th Meeting Amer. Chem. Soc., Abstracts, p. 63J.

(16) M. E. Runner, G. Balog, and M. Kilpatrick, J. Amer. Chem. Soc., 78, 51B3 (1956).

(17) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Chem., 6, 1156 (1967).

(18) R. I. Wagner, private communication.

(19) J. B. Spencer and J. O. Lundgren, Acta Cryst. Part B, 29, 1923 (1973).

(20) R. C. Taylor and G. L. Vidale, J. Amer. Chem. Soc., 78, 5999 (1956).

(21) L. J. Basile, P. LaBonville, J. R. Ferraro, and J. M. Williams, J. Chem. Phys., 60, 19B1 (1974).

(22) R. D. W. Kemmitt, D. R. Russell, and D. W. A. Sharp, J. Chem. Soc., 440B (1963).

(23) J. O. Lundgren and J. M. Williams, J. Chem. Phys., 58, 7B8 (1973).

(24) C. Hebecker, Z. Anorg. Allgem. Chem., 384, 12 (1971).

(25) G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 4212 (1957).

(26) H. Bode and H. Clausen, Z. Anorg. Chem., 265, 229 (1951).

(27) E. L. Muetterties and W. D. Phillips, J. Amer. Chem. Soc., 81 1084,(1959); K. J. Packer and E. L. Muetterties, Proc. Chem. Soc., 147 (1964).

(28) R. G. Kidd and R. W. Matthews, Inorg. Chem., 11, 1156 (1972).

(29) P. A. W. Dean and R. J. Gillespie, J. Amer. Chem. Soc., 91, 7264 (1969).

(30) F. N. Tebbe and E. L. Muetterties, Inorg. Chem., 6, 129 (1967).

(31) D. M. Byler and D. F. Shriver, Inorg. Chem., 12, 1412 (1973).

(32) M. T. Emerson, E. Grunwald, and R. A. Kromhout, J. Chem. Phys, 33, 547 (1960).

(33) G. A. Olah and T. E. Kiovsky, J. Amer. Chem. Soc., 90, 4666 (1968).

(34) K. O. Christe and W. Sawodny, Inorg. Chem., 6, 1783 (1967); K. O. Christe, Inorg. Chem., 9, 2801 (1970).

(35) A. M. Qureshi and F. Aubke, Canad. J. Chem., 48, 3117 (1970).

(36) G. M. Begun and A. C. Rutenberg, Inorg. Chem., 6, 2212 (1967).

(37) K. O. Christe and C. J. Schack, Inorg. Chem., 9, 2296 (1970).

(38) K. O. Christe, E. C. Curtis, and R. O. Wilson, J. Inorg. Nucl. Chem., in press.

(39) R. J. Gillespie and B. Landa, Inorg. Chem., 12, 1383 (1973).

(40) R. J. Gillespie and M. J. Morton, Inorg. Chem., 9, 811 (1970).

(41) J. K. Ruff, Inorg. Chem., 5, 1791 (1966).

(42) R. O. Peacock and I. L. Wilson, J. Chem. Soc. A, 2030 (1969).

(43) K. O. Christe and W. Sawodny, Inorg. Chem., 12, 2879 (1973).

(44) P. A. W. Dean, R. J. Gillespie, R. Hulme, and D. A. Humphreys, J. Chem. Soc. A, 341 (1971).

(45) O. E. O'Reilly, E. M. Peterson, and J. M. Williams, J. Chem. Phys., 54, 96 (1971).

(46) M. H. Cance and A. Potier, J. Chim. Phys. Physicochim. Biol., 68, 941 (1971).

(47) R. Savoie and P. A. Giguère, J. Chem. Phys., 41, 2698 (1964).

(48) W. M. A. Smit, J. Mol. Structure, 19, 789 (1973).

(49) W. Sawodny, J. Mol. Spectrosc., 30, 56 (1969).

(50) T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishii, J. Mol. Spectrosc., 19, 78 (1966).

(51) A. T. Kozulin, Opt. Spektrosk., 25, 353 (1968).

(52) J. R. Ferraro, J. M. Williams, and P. LaBonville, Appl. Spectrosc., 28, 379 (1974).

(53) M. Fournier and J. Roziere, C. R. Acad. Sci. C, 270, 729 (1970).

Table I. X-Ray Powder Data for $OH_3^+AsF_6^-$ [a]

d obsd.	d calcd.	Int.	h	k	ℓ
4.64	4.62	vs	1	1	1
4.01	4.00	vs	2	0	0
2.82	2.83	s	2	2	0
2.420	2.414	w	3	1	1
2.315	2.312	w	2	2	2
1.999	2.002	w	4	0	0
1.833	1.837	w	3	3	1
1.785	1.791	mw	4	2	0
1.636	1.634	m	4	2	2
1.542	1.541	mw	5 3	1 3	1 3
1.414	1.416	vw	4	4	0
1.355	1.353	w	5	3	1
1.336	1.335	w	6 4	0 4	0 2
1.267	1.266	vw	6	2	0

(a) cubic, a=8.015 Å, V=514.9 $Å^3$, Z = 4,

d_c = 2.890 g cm^{-3}, Cu K_α radiation Ni filter.

Table II. X-Ray Powder Data for $OH_3^+SbF_6^-$ [a]

d obsd	d calcd	Int.	h	k	ℓ
8.75	8.77	m	0	0	1
4.78	4.80	m	2	0	1
4.38	4.39	s	0	0	2
3.47	3.49	m	2	0	2
3.32	3.34	vs	2	1	2
2.868	2.869	mw	4	0	0
2.785	2.784	m	4	1	0
2.241	2.251	m	5	1	0
2.199	2.194	s	0	0	4
2.053	2.049	mw	4	0	3, 2 0 4
2.021	2.017	m	2	1	4
1.901	1.903	mw	3	0	4
1.877	1.877	m	3	1	4
1.779	1.777	mw	6	2	1
1.760	1.756	m	5	4	1
1.680	1.679	mw	6	3	1
1.663		m			
1.595		mw			
1.578		m			
1.515		vw			
1.505		w			
1.401		mw			
1.392		m			
1.347		mw			
1.341		m			
1.258		mw			
1.220		m			
1.187		mw			
1.155		mw			
1.100		mw			
1.075		mw			
1.052		mw			
1.030		mw			

Table II. X-Ray Powder Data for $H_3O^+SbF_6^-$ (Continued)

d obsd	d calcd	Int.	h	k	ℓ
1.010		m			
0.990		m			
0.972		w			
0.963		vw			
0.937		m			
0.922		m			
0.9072		mw			
0.8925		m			
0.8793		m			
0.8663		m			
0.8538		m			
0.8365		vw			
0.8306		m			
0.8251		w			
0.8195		m			
0.8144		w			
0.8091		w			
0.8037		w			
0.7988		m			
0.7890		m			
0.7880		w			
0.7794		m			
0.7786		w			

(a) tetragonal, a=11.48, c=8.78 Å, V=1157.1 $Å^3$, Z=8, d_c=2.93 g cm^{-3}; Cu K_α radiation, Ni filter.

TABLE III. Vibrational Spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ and Their Assignments Compared to that of NH_3[a]

Obsd freq (cm^{-1}) and rel intens[b]											Assignment (point group)	
NH_3	$OH_3^+SbF_6^-$					$OH_3^+AsF_6^-$					XH_3	MF_6
	IR	Raman				IR		Raman			(C_{3v})	(O_h)
	Solid	Solid		Solution		Solid		Solid		Solution		
	25°	25°	-120°	$CD_3SO_2CD_3$	HF	25°	-196°	25°	-120°	$CD_3SO_2CD_3$		
3336	3330 vs,br				3300(0.2) br,p	3600- vs	3250 sh				ν_1 (A_1)	
3444	3100 vs,br					2800 vbr	3080 vs				ν_3 (E)	
1626	1615 s				1630(0.1)br,dp	1630 s,br	1615 s				ν_4 (E)	
950	900 s,br					800-1050 s,br	912 s				ν_2 (A_1)	
	670 vs,br		674(10)			720 vs,br	715 vs		715(10)			$\nu_3(F_{1u})$
		663(10)						698(10)				
			640(5.3)	650(10)	658(10)p		676 s		677(7.4)	680(10)		$\nu_1(A_{1g})$
	588 sh	590 sh,br	590(0.3)				586 s					
	(551)[c]	558(0.8)	559(1.2)					580(1)br	566(4.1)			
				568(1)	568(0.9)dp	550 s,br	560 s			573(0.5)		$\nu_2(E_g)$
	(484)[c]	490(0.6)br	498(0.6)				511 s					
								500(1)br	480(1)			
		450 sh	450 (0+)				467 s					
						392 s br	392 vs					
		287 s	288(0.5)				371 w					$\nu_4(F_{1u})$
		280(4.1)	280(3.4)	274(3)	278(2.8)dp		367 w	378(4)	369(8)	368(1.8)		$\nu_5(F_{2g})$
		265 sh	263(0.4)				361 vw					
							255 s				Lattice vibration or XH...FM stretch	

(a) W. S. Benedict and E. K. Plyler, Canad. J. Phys., 35, 1235 (1957).
(b) Uncorrected Raman intensities.
(c) These infrared bands were of variable intensity from sample to sample (see Traces A and B of Figure 1), but the relative intensitites of their Raman counterparts were similar.

TABLE IV. Symmetry and Internal Force Constants [a] of OH_3^+ compared to those [b] of NH_3

		OH_3^+					NH_3
	Bond Angle (deg)	110				100	107
	Force Field	DFF	F_{22} and F_{44} $\equiv$ MIN	NH_3 TR	$\nu_3 > \nu_1$ F_{22} and F_{44} $\equiv$ MIN	F_{22} and F_{44} $\equiv$ MIN	GVFF
A_1	$F_{11} = f_r + 2\ f_{rr}$	6.3369	6.3398	6.3565	5.7783	6.2128	6.4540
	$F_{22} = f_\alpha + 2\ f_{\alpha\alpha}$	0.4296	0.4295	0.4448	0.4295	0.1942	0.4049
	$F_{12} = 2f_{r\alpha} + f_{r\alpha'}$	0	0.02395	0.3244	0.02395	0.0183	0.3244
E	$F_{33} = f_r - f_{rr}$	5.4213	5.4398	5.4542	5.9696	5.4908	6.4732
	$F_{44} = f_\alpha - f_{\alpha\alpha}$	0.5826	0.5817	0.5840	0.5817	0.6752	0.6161
	$F_{34} = -f_{r\alpha} + f_{r\alpha'}$	0	-0.0648	-0.1622	-0.0648	-0.0554	-0.1622
	f_r	5.7265	5.7398	5.7550	5.9058	5.7315	6.4668
	f_{rr}	0.3050	0.3000	0.3008	-0.0638	0.2407	-0.0064
	f_α	0.5316	0.5310	0.5376	0.5310	0.5149	0.5457
	$f_{\alpha\alpha}$	-0.0510	-0.0507	-0.0464	-0.0507	-0.1603	-0.0704
	$f_{r\alpha}$	0	0.0296	0.1622	0.0296	0.0246	0.1622
	$f_{r\alpha'}$	0	-0.0352	0	-0.0352	-0.0308	0

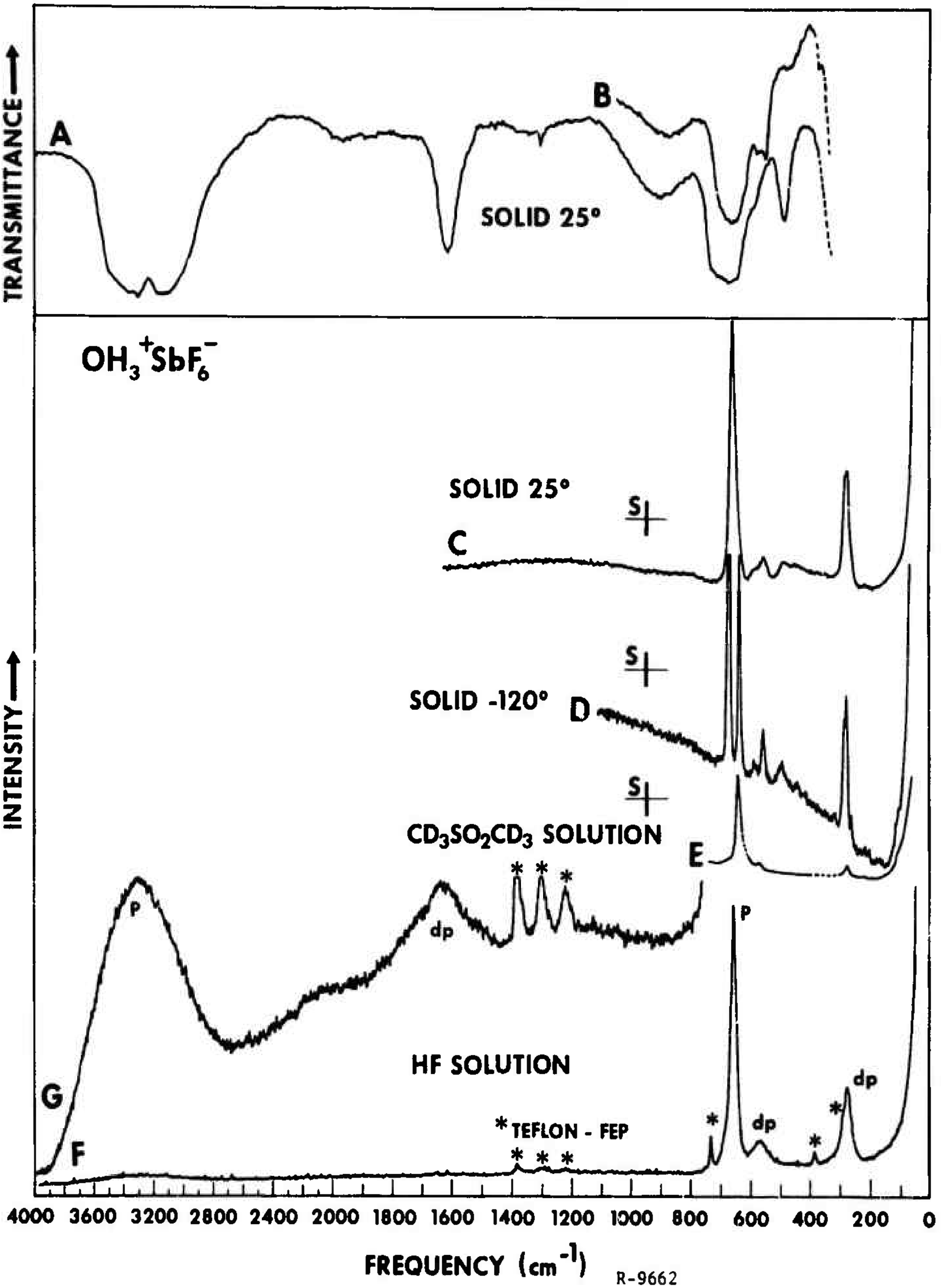
(a) All force constants have units of mdyn/Å; frequency values used: $\nu_1 = 3300$, $\nu_2 = 900$, $\nu_3 = 3150$, $\nu_4 = 1620\ cm^{-1}$, except for column 4 where the frequencies of ν_1 and ν_3 were exchanged.

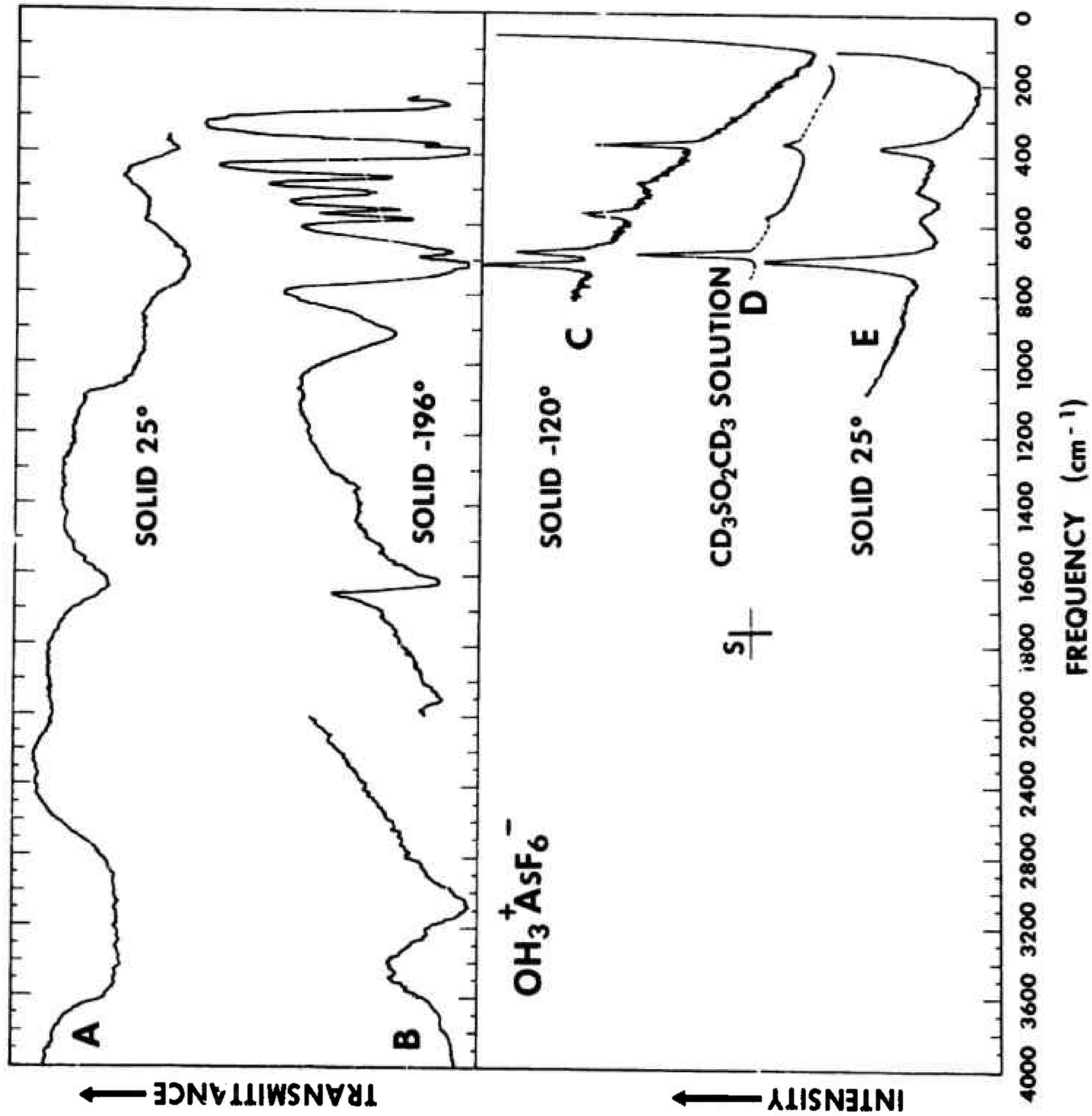
(b) Values from ref 50

Diagram Captions

Figure 1. Vibrational spectrum of $OH_3^+SbF_6^-$. Traces A and B: Infrared spectra of two different samples as dry powder between AgCl disks. Traces C and D: Raman spectra of the solid contained in a quartz tube at 25 and -120°, respectively. Trace E: Raman spectrum of a $CD_3SO_2CD_3$ solution; the broken lines indicate regions obscured by solvent bands. Traces F and G: Raman spectra of an HF solution contained in a Teflon -FEP tube at two different recorder voltages. P and dp indicate polarized and depolarized bands, respectively, and S indicates the spectral slit width.

Figure 2. Vibrational spectrum of $OH_3^+AsF_6^-$. Trace A: Infrared spectrum of the solid as a dry powder between AgCl disks at 25°. Trace B: Infrared spectrum of the solid as a dry powder between CsI disks at -196°. Traces C and E: Raman spectra of the solid in a quartz tube recorded at 25 and -120°, respectively. Trace D: Raman spectrum of a $CD_3SO_2CD_3$ solution; S indicates the spectral slit width.

TRANSMITTANCE
A
B
SOLID 25°
$OH_3^+SbF_6^-$
INTENSITY
SOLID 25°
C
S
SOLID -120°
D
S
S
$CD_3SO_2CD_3$ SOLUTION
E
* * *
P
dp
P
HF SOLUTION
G
* TEFLON - FEP
* * *
F
*
dp
*
*
dp
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
0
FREQUENCY (cm^{-1})


$OH_3^+AsF_6^-$
A
SOLID 25°
B
SOLID -196°
SOLID -120°
C
$CD_3SO_2CD_3$ SOLUTION
D
S
SOLID 25°
E
TRANSMITTANCE
INTENSITY
FREQUENCY (cm⁻¹)
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400 200 0

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

Novel Onium Salts. Synthesis and Characterization of $SH_3^+SbF_6^-$

Karl O. Christe

Received . . . .

Abstract

The synthesis and properties of $SH_3^+SbF_6^-$, the first known example of a stable salt containing the sulfonium cation, are reported. The SH_3^+ cation was characterized by vibrational spectroscopy and a normal coordinate analysis was carried out. Attempts to prepare $SH_3^+AsF_6^-$ resulted in the formation of As_2S_5. Protonation of HCl in $HF-SbF_5$ solution yields an unstable white solid, but no evidence was obtained for adduct formation in the $HF-SbF_5-Xe$ system at temperatures as low as -78^0.

INTRODUCTION

Recent studies[1] in our laboratory showed that the protonation of H_2O in HF-MF_5 (M=Sb and As) solutions produces the surprisingly stable oxonium salts $OH_3^+MF_6^-$. This prompted us to investigate the synthesis of other onium salts. In this paper we report on the protonation of H_2S, HCl, and Xe. Results on the protonation of HNF_2 and NF_3 will be given elsewhere.[2]

Whereas a huge number of alkyl or aryl substituted sulfonium salts are known, we could not find any literature reports on the isolation of a salt containing the SH_3^+ cation, although Olah and coworkers had observed[3] the SH_3^+ cation at low temperature in HSO_3F-SbF_5-SO_2 solution by proton nmr spectroscopy (singlet at δ =-6.60). In addition, the formation of gaseous SH_3^+ was studied[5-7] in mass spectrometers (ion-molecule and electron impact studies). Similarly, the protonation of HCl has been studied only in HSO_3F-SbF_5 solution at low temperature by nmr spectroscopy, but no direct evidence for the formation of a ClH_2^+ cation was reported.[8] For xenon, protonation in HF-SbF_5 solution was postulated[9] based on its ability to suppress isotopic hydrogen-deuterium exchange; protonation in ion-molecule reactions has been also reported.[10,11]

EXPERIMENTAL

The experimental techniques used in this study were essentially the same as those previously described.[1]

Preparation of $SH_3^+SbF_6^-$. In a typical experiment, SbF_5 (5.38 mmol) and anhydrous HF (10 ml liquid) were combined at -196° in a Teflon FEP ampoule. The mixture was warmed to 25° to give a homogenous solution. Hydrogen sulfide (7.10 mmol) was added to the ampoule at -196°. The mixture was warmed first to -78°, then slowly to 25°. During warm up a white solid formed, which was only partially soluble in the excess of HF. Volatile products were removed at 25° in vacuo, leaving behind 1.452g of a white, stable solid (weight calcd for 5.38 mmol of $SH_3^+SbF_6^-$=1.457g). Anal. Calcd for SH_3SbF_6: Sb, 44.95; S, 11.84. Found: Sb 44.8; S 11.9. The $SH_3^+SbF_6$ product can be stored at 25° without noticeable decomposition in Teflon or Kel-F containers, but it attacks quartz.

The HF-AsF_5-H_2S System. Anhydrous HF (10 ml liquid) and AsF_5 (3.54 mmol) were combined at -196° in a Teflon FEP ampoule. The mixture was warmed to 25°, then recooled to -196°. Hydrogen sulfide (3.54 mmol) was added to the ampoule at -196°. During slow warm up of the mixture to 0° a white to yellow solid formed. The ampoule was recooled to -78° and volatile material was pumped off during warm up to 25° leaving behind 221 mg of a stable yellow solid (weight calcd for 0.708 mmol As_2S_5=220 mg). Vibrational spectroscopy showed that the solid did not contain bands characteristic for either SH_3^+ (see below) or AsF_6^-. It was insoluble in water, but slowly dissolved in boiling conc. HNO_3. Anal. Calcd for As_2S_5: As, 48.3; S, 51.7. Found: As, 48.5; S, 51.6.

The HF-SbF_5-HCl System. To a homogenized mixture (see above) of SbF_5 (2.57 mmol) and anhydrous HF (5 ml liquid) in a Teflon FEP ampoule, HCl (6.81 mmol) was added at -196°. The mixture was warmed to -78°, then cycled several times between -78 and 0°. A white solid was formed upon melting of the starting materials. Volatile material was pumped off at -45°, resulting in 711 mg of an unstable, white solid melting below room temperature to a pale yellow, clear liquid (weight calcd for 2.57 mmol $ClH_2^+SbF_6^-$=702 mg). The vapor phase above the liquid at 26° was shown by infrared spectroscopy to consist essentially of HF and HCl. The Raman spectrum of the HF solution showed the bands characteristic of SbF_6^- (see below).

The HF-SbF_5-Xe System. To a homogenized (see above) mixture of SbF_5 (3.07 mmol) and anhydrous HF (10 ml liquid) in a Teflon FEP ampoule, Xe (7.04 mmol) was added at -196°. The mixture was slowly warmed to 0° and then kept at -78° for 16 hours. No evidence for adduct formation between Xe and HF-SbF_5 at -78° was detected, and the xenon starting material was quantitatively recovered from the reaction mixture at -78°.

RESULTS AND DISCUSSION

Synthesis and Properties of SH_3^+ Salts. Protonation of H_2S in HF-SbF_5 solution produces the white, stable solid $SH_3^+SbF_6^-$ in quantitative yield according to:

$$H_2S + HF + SbF_5 \longrightarrow SH_3^+SbF_6^-$$

To our knowledge this is the first reported example of a stable salt containing the sulfonium cation.

According to the DSC data, $SH_3^+SbF_6^-$ starts to decompose at 90° with the onset of an exotherm which rapidly changes into a large endotherm. The salt is moderately soluble in anhydrous HF. Attempts were unsuccessful to dissolve it in organic solvents, such as $CH_3SO_2CH_3$, which were found[1] suitable for $OH_3^+SbF_6^-$. When the solvent was added, gas evolution and the formation of a cinnabar solid (probably Sb_2S_5) and a yellow solution were observed. Attempts to dissolve the sulfonium salt in SbF_5 caused oxidation of SH_3^+ as indicated by gas evolution and the appearance of a strong blue color, similar to that previously reported[12] for polysulfur radical cations. When exposed to atmospheric moisture, the solid turns yellow first, then cinnabar accompanied by the evolution of H_2S. Obviously, H_2S is displaced from its salt by the more basic water. This displacement reaction might be used as a convenient way to generate gaseous H_2S from the storable solid, $SH_3^+SbF_6^-$, by the simple addition of water. Vibrational spectroscopy (see below) showed that some samples contained some sulfur in the form of S_8, as was also indicated by their faint yellow color.

The x-ray powder pattern of $SH_3^+SbF_6^-$ is listed in Table 1. The tetragonal unit cell with a=11.89, c=10.51Å, and Z=8 is in good agreement with those found for $OH_3^+SbF_6^-$[1] and the related $M^+XF_6^-$ salts.[13-15] As expected, $SH_3^+SbF_6^-$ has a larger unit cell and a lower density than $OH_3^+SbF_6^-$ owing to SH_3^+ having a significantly larger radius than OH_3^+.

Attempts to synthesize $SH_3^+AsF_6^-$ from the HF-AsF_5-H_2S system were unsuccessful and resulted in the quantitative conversion of AsF_5 to As_2S_5 according to:

$$2AsF_5 + 5H_2S \longrightarrow As_2S_5\downarrow + 10\ HF$$

This difference in behavior between SbF_5 and AsF_5 is not surprising since it is well known[16] that in the presence of fluoride ions H_2S will precipitate on[illegible] [illegible]nate, but not antimonate, as the corresponding pentasulfide.

Protonation of HCl and Xe. Since the protonation of H_2O and of the more acidic H_2S had resulted in the formation of novel stable MF_6^- salts, we decided to examine the protonation of the even more acidic species HCl and of Xe. For both, previous studies[8,9] had indicated protonation in solution.

The protonation of HCl in HF-SbF_5 solution produced a white solid product stable at -45°, but melting below room temperature with decomposition. From the observed material balance, the composition of the adduct was found to be approximately 1:1:1 and the more volatile decomposition products were shown to be HCl and HF. By analogy with the OH_3^+ and SH_3^+ salts, and based on the Raman spectrum of an HF solution showing the presence of SbF_6^-, this adduct is likely to be $ClH_2^+SbF_6^-$. For xenon, no evidence for the formation of a stable adduct was found at temperatures as low as -78°.

Our studies indicate that compounds less acidic than HCl stand a good chance of forming a reasonably stable protonated SbF_6^- salt. Nmr evidence for the existence of such protonated species in super acid solutions at low temperature has already been reported[17] for several species, and the isolation of these and other novel simple protonated cations in form of their stable MF_6^- salts can be predicted. Obviously, the parent species are not limited to nonmetal hydrides, but can include many other moieties.

Vibrational Spectrum of $SH_3^+SbF_6^-$. Since $SH_3^+SbF_6^-$ decomposes in organic solvents, such as $CH_3SO_2CH_3$, and its proton nmr spectrum in HSO_3F-SbF_5-SO_2 solution (singlet at $\delta = 6.60$)[3] yields little structural information, we have used vibrational spectroscopy to characterize the SH_3^+ cation. The vibrational spectrum of solid $SH_3^+SbF_6^-$ is shown in Figure 1. Attempts to record the Raman spectrum of an HF solution were unsuccessful owing to the moderate solubility of the salt in HF. When exposed to the blue 4880Å line of an Ar ion laser, the sample tended to rapidly decompose even at -120°. However, this problem could be overcome by defocusing the laser beam. In general, the Raman spectra showed bands[18,19] due to varying amounts of sulfur (S_8) as was also indicated by the yellowish color of these samples. In addition, the spectra showed a band at 760 cm^{-1} (marked in Figure 1 by an asterisk) which based on the literature data[18,19] does not belong to S_8. Decomposition studies showed that, contrary to the $SH_3^+SbF_6^-$ bands, this band was stable towards decomposition in the focused laser beam and, therefore, cannot belong to $SH_3^+SbF_6^-$ (see trace D, Figure 1).

The Raman spectrum contains also a weak band at about 500 cm^{-1} (marked by a diamond) which is definitely due to a decomposition product. This band becomes the most intense band in the spectrum, when most of the $SH_3^+SbF_6^-$ has decomposed. The remainder of the spectrum (see Table II) is in excellent agreement with our expectations for ionic $SH_3^+SbF_6^-$ and is discussed below.

The general appearance of the vibrational spectrum of $SH_3^+SbF_6^-$ (see Figure 1) strongly deviates from that[1] of $OH_3^+SbF_6^-$ recorded at room temperature. Contrary to $OH_3^+SbF_6^-$, the bands due to $SH_3^+SbF_6^-$ are sharp and narrow and show little or no splittings indicating for SbF_6^- and SH_3^+ no appreciable deviation from symmetry O_h and C_{3v}, respectively. In particular, the Raman bands due to SbF_6^- are very narrow and exhibit the frequencies and relative intensities expected[20-22] for octahedral SbF_6^-. This indicates that, contrary to $OH_3^+SbF_6^-$, the cation-anion coupling in $SH_3^+SbF_6^-$ is relatively weak. Since $OH_3^+SbF_6^-$ and $SH_3^+SbF_6^-$ have similar tetragonal unit cells with Z=8 (see above), it is unlikely that crystal effects are the main reason for this pronounced difference. A better explanation for the observed difference is the lower electronegativity of sulfur when compared to oxygen. This should markedly decrease the polarity of the X-H bond and thereby decrease the positive charge on the hydrogen ligands. This in turn should result in a much weaker Coulombic interaction between the positively polarized hydrogen ligands of the cation and the negatively polarized fluorine ligands of the anion, hence substantially reducing the cation-anion coupling.

The assignments for the SH_3^+ cation in point group C_{3v} were made by comparison with those [23] of isoelectronic PH_3 (see Table I1). Pyramidal XY_3 of symmetry C_{3v} has four fundamentals which are classified as $2A_1 + 2E$, all being active in both the infrared and the Raman spectrum. Of these, each symmetry species contains one stretching and one bending mode. By comparison with PH_3, the two stretching modes of SH_3^+ are expected to have very similar frequencies and indeed, only one intense band is observed in the S-H stretching region at 2520 cm^{-1}. Since the symmetric SH_3 stretch should be of much higher Raman intensity than the antisymmetric one, the maximum of the Raman band at 2520 must be due to $\nu_1(A_1)$. This band shows a shoulder at 2490 cm^{-1}, which might represent the antisymmetric stretch $\nu_3(E)$. However, we prefer to assume a complete coincidence of ν_1 and ν_3, since ν_3 should be more intense in the infrared spectrum[24] and the infrared band has its maximum at about 2520 cm^{-1}. The weak shoulder observed at 2360 cm^{-1} in the infrared spectrum is due to the overtone $2\nu_4(A_1 + E + F_2)$ in Fermi resonance with ν_1 and ν_3.

Of the two deformation modes of SH_3^+, one obviously is represented by the 1028 cm^{-1} infrared band. For the other deformation, we had originally considered the 760 cm^{-1} infrared band. However, a normal coordinate analysis, carried out with this assignment, resulted in unreasonable force constants. Whereas the stretching force constant in SH_3^+ was larger than in PH_3, the deformation constant was significantly lower. This is not plausible since any H· · ·F bridging possible in such a solid should decrease the value of the stretching and increase the value of the deformation force constant. A careful reexamination of the spectra established that the 760 cm^{-1} band is not part of the $SH_3^+ ShF_6^-$ spectrum and that the

Raman spectrum exhibits a band of moderate intensity at 1180 cm^{-1}, a frequency value quite reasonable for the missing SH_3^+ deformation. The assignment of this band to $\nu_4(E)$ of SH_3^+ is further supported by the observation of its overtone in the infrared spectrum (see above) and the results from a normal coordinate analysis (see below). Direct observation of ν_4 in the infrared spectrum is complicated by its relatively low infrared intensity and interference by SbF_6^- combination bands. This leaves the 1028 cm^{-1} infrared band for assignment to $\nu_2(A_1)$, in excellent agreement with the frequencies[23] of PH_3.

Normal Coordinate Analysis. To support the above assignments for SH_3^+, a normal coordinate analysis was carried out, the results of which are given in Table III. Since the geometry of SH_3^+ is unknown, we have computed force fields for different bond angles ranging from 90 to 110° (the bond angle in isoelectronic PH_3 is 93.345°)[25]. For the bond length in SH_3^+ an estimated value of 1.33Å was used. The force constants were computed by trial and error with the help of a computer to obtain an exact fit between observed and calculated frequencies. Three different force fields were used to show that for a vibrationally weakly coupled (heavy central atom, light ligands) species, such as SH_3^+, the choice of a particular force field is less important than other variables, such as the bond angle. To demonstrate the small variation in the computed force fields, insignificant decimals are carried in Table III. Of the three different force fields used, the diagonal force field (DFF) and the force field requiring the deformation symmetry force constants to have minimal values, were selected for their established[26] usefulness for vibrationally weakly coupled species. The third forcefield (PH_3 tr) was computed by using the general valence force field (GVFF) off-diagonal symmetry force constants of isoelectronic PH_3 for SH_3^+. As can be seen from Table III, all three force fields yield very similar force constants. Therefore, the given force fields are likely to be good approximations of a GVFF. By comparison with the known bond angles of H_2O, CH_3^+, NH_3, H_2S, and PH_3, a bond angle of about 95° appears to be most likely for SH_3^+, although the choice of the bond angle is not very critical as can be seen from the small variation of the force constants within the most probable bond angle range of 90-100°. As expected for a vibrationally weakly coupled species containing only one stretching and one deformation vibration of very different frequency in each symmetry block, the potential energy distribution showed all fundamentals to be highly characteristic. Thus, ν_1 and ν_3 were 100% pure stretching modes and ν_2 and ν_4 were 97-99% pure deformations. Comparison of the force constants of SH_3^+ with those[23] of PH_3 shows excellent agreement thus supporting the above given assignments for SH_3^+.

Acknowledgement. The author thanks Drs. L. Grant, C. Schack, and R. Wilson for their help, Dr. E. C. Curtis for the use of his computer program for the computation of force constants, and the Office of Naval Research, Power Branch, for financial support.

REFERENCES

(1) K. O. Christe, C. J. Schack, and R. D. Wilson, Inorg. Chem., in press.

(2) K. O. Christe, to be published.

(3) G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., J. Amer. Chem. Soc., 89, 2996, (1967).

(4) J. L. Beauchamp and S. E. Butrill, Jr., J. Chem. Phys., 48, 1783 (1968).

(5) A. G. Harrison and J. C. Thynne, Trans. Faraday Soc., 62, 3345 (1966).

(6) R. W. Kiser, "Introduction to Mass Spectroscopy and Applications", Prentice-Hall, Inc., Princeton, J. J., 1965.

(7) M. A. Haney and J. L. Franklin, J. Chem. Phys., 50, 2028 (1969).

(8) A. Commeyras and G. A. Olah, J. Amer. Chem. Soc., 91, 2929 (1969).

(9) G. A. Olah and J. Shen, J. Amer. Chem. Soc., 95, 3582 (1973).

(10) References 1-4 cited by D. Holtz and J. L. Beauchamp, Science, 173, 1237 (1971).

(11) J. A. Burt, J. L. Dunn, J. J. McEwen, M. M. Sutton, A. E. Roche, and H. I. Schiff, J. Chem. Phys., 52, 6062 (1970).

(12) R. J. Gillespie and J. Passmore, Chem. in Britain, 8, 475 (1972); R. J. Gillespie, J. Passmore. P. K. Ummat, and O. C. Vaidya, Inorg. Chem., 10, 1327 (1971).

(13) R. D. W. Kemmit, D. R. Russell, and D. W. A. Sharp, J. Chem. Soc., 4408 (1963).

(14) C. Hebecker, Z. Anorg. Allgem. Chem., 384, 12 (1971).

(15) G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 4212 (1957).

(16) G. Jander and H. Wendt, "Lehrbuch der Analytischen und Präparativen Anorganischen Chemie," Hirzel Verlag, Stuttgart, Germany, 1954.

(17). G. A. Olah, A. M. White, and D. O'Brien, Chem. Rev., 70, 561, (1970).

(18) A. F. Ward, J. Phys. Chem., 72, 4133 (1968).

(19) A. Anderson and Y. T. Loh, Canad. J. Chem., 47, 879 (1969).

(20) K. O. Christe and C. J. Schack, Inorg. Chem., 9, 2296 (1970).

(21) A. M. Qureshi and F. Aubke, Canad. J. Chem., 48,3117 (1970).

(22) G. M. Begun and A. C. Rutenberg, Inorg.Chem., 6, 2212 (1967).

(23) T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishii, J. Mol. Spectrosc., 19, 78 (1966).

(24) W. M. A. Smit, J. Mol. Structure, 19, 789 (1973).

(25) A. G. Maki, R. L. Sams, and W. 8. Olson, J. Chem. Phys., 58, 4502 (1973).

(26) W. Sawodny, J. Mol. Spectrosc., 30, 56 (1969).

TABLE 1 - X-RAY POWDER DATA FOR $H_3S^+SbF_6^-$[a]

d obsd.	d calcd	Int.	hkl
5.96	5.94	vw	200
5.26	5.26	vs	002
3.94	3.94	vs	202,300
3.56	3.54	vs	311
3.16	3.16	m	302
2.619	2.623	mw	303,004
2.456	2.471	w	332
2.257	2.265	m	403
2.176	2.165	ms	502
2.069	2.068	w	105
1.963	1.966	w	503,404
1.839	1.833	w	315
1.769	1.771	w	630
1.750	1.750	w	006
1.720		w	
1.616		mw	
1.572		w	
1.535		w	
1.484		mw	
1.461		mw	
1.401		w	
1.308		w	
1.251		w	
1.239		w	
1.212		w	

(a) tetragonal a = 11.89, c=10.51Å, V=1484.0Å^3, Z=8, d_c=2.43 g cm^{-3}; CuK_α radiation, Ni filter.

TABLE 11. VIBRATIONAL SPECTRUM OF $SH_3^+SbF_6^-$ AND ITS ASSIGNMENT COMPARED TO THAT OF PH_3[a]

Obsd. freq. (cm^{-1}) and rel. intens.[b]			Assignment (point group)	
PH_3	$SH_3^+SbF_6^-$ solid		XH_3	SbF_6^-
	infrared	Raman	(C_{3v})	(O_h)
2328		2520(1.3)	$\nu_3(E)$	
	2520vs			
2323		2490sh	$\nu_1(A_1)$	
	2360sh		$2\nu_4(A_1 + E + F_2)$	
	1308w			$\nu_1 + \nu_3(F_{1u})$
	1222w			$\nu_1 + \nu_2(E_g)$
1122	1180vw	1180(0.4)	$\nu_4(E)$	
992	1028mw	1025(0.3)	$\nu_2(A_1)$	
	848vw			$\nu_1 + \nu_6(F_{2u})$
	660vs			$\nu_3(F_{1u})$
		650(10)		$\nu_1(A_{1g})$
	569m	556(1.6)		$\nu_2(E_g)$
		282(2.8)		$\nu_5(F_{2g})$
		275sh		
	270s			$\nu_4(F_{1u})$

(a) ref 23

(b) Uncorrected Raman intensities; bands due to decomposition products have not been listed.

TABLE III. SYMMETRY AND INTERNAL FORCE CONSTANTS[a] OF SH_3^+ COMPARED TO THOSE OF ISOELECTRONIC PH_3

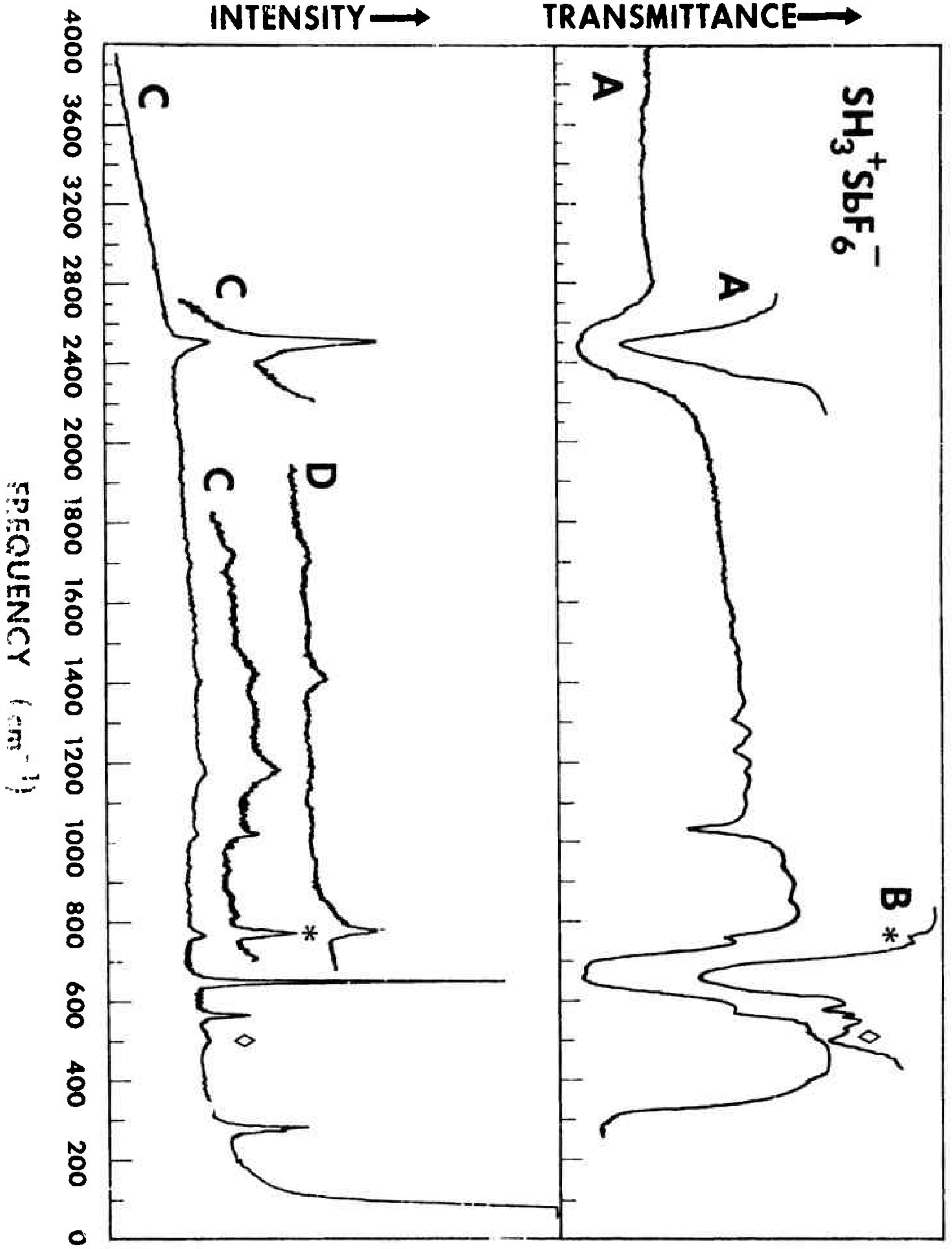
		SH_3^+							PH_3[b]
	Bond Angle (deg)	90	95			100	105	110	93
	Force Field	DFF	DFF, F_{22} and F_{44} = MIN, PH_3 tr.			DFF			GVFF
A_1	$F_{11}=f_r+2f_{rr}$	3.6535	3.67[illegible]0	3.6764	3.6797	3.6930	3.7130	3.7320	3.1222
	$F_{22}=f_\alpha+2f_{\alpha\alpha}$	0.2958	0.3252	0.3252	0.3263	0.3705	0.4472	0.6030	0.2938
	$F_{12}=2f_{r\alpha}+f_{r\alpha}'$	0	0	0.0180	0.0784	0	0	0	0.0784
E	$F_{33}=f_r-f_{rr}$	3.6543	3.6445	3.6467	3.6469	3.6350	3.625	3.6158	3.1087
	$F_{44}=f_\alpha-f_{\alpha\alpha}$	0.4071	0.3872	0.3873	0.3874	0.3658	0.3426	0.3178	0.3548
	$F_{34}=-f_{r\alpha}+f_{r\alpha}'$	0	0	-0.0140	-0.0392	0	0	0	-0.0392
	f_r	3.6540	3.6540	3.6566	3.6578	3.6543	3.6543	3.6545	3.1132
	f_{rr}	-0.0003	0.0095	0.0099	0.0109	0.0193	0.0293	0.0387	0.0045
	f_α	0.3700	0.3665	0.3666	0.3670	0.3674	0.3775	0.4129	0.3345
	$f_{\alpha\alpha}$	-0.0371	-0.0207	-0.0207	-0.0204	0.0016	0.0349	0.0951	-0.0203
	$f_{r\alpha}$			0.0107	0.0392				0.0392
	$f_{r\alpha}'$			-0.0033	0				0

(a) all force constants have units of mdyn/Å; frequency values used: $\nu_1=\nu_3=2520$, $\nu_2 = 1028$, $\nu_4 = 1180\ cm^{-1}$

(b) values from ref. 23.

DIAGRAM CAPTION

Figure 1: Vibrational Spectrum of $SH_3^+SbF_6^-$. For clarity, bands due to sulfur (S_8) were deleted. Trace A: Infrared spectra of the solid as dry powders between AgBr disks at two different concentrations. Part of the intensity of the 270 cm^{-1} band is due to absorption by the thin AgBr windows. Trace B: Spectrum of a different sample shown to demonstrate the variable relative intensities of the impurity bands marked by an asterisk and a diamond (see text). Traces C: Raman spectra of solid $SH_3^+SbF_6^-$ recorded at two different recorder volatges and a spectral slit widths of 4 (lower) and 8 cm^{-1} (upper traces). Sample container was a quartz tube. Trace D: Background spectrum recorded after complete decomposition of $SH_3^+SbF_6^-$ had occurred.


$SH_3^+SbF_6^-$
TRANSMITTANCE ⟶
INTENSITY ⟶
A
A
B
*
◇
C
C
C
D
*
◇
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400 200 0
FREQUENCY (cm⁻¹)

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

Novel Onium Salts. Synthesis and Characterization of the Difluroammonium Cation, $NH_2F_2^+$

Karl O. Christe

Received ....

Abstract

The syntheses and properties of $NH_2F_2^+SbF_6^-$ and $NH_2F_2^+AsF_6^-$, the first known examples of difluoroammonium salts, are reported. The $NH_2F_2^+$ cation was characterized by ^{19}F and ^1H nmr and vibrational spectroscopy. At room temperature the $NH_2F_2^+$ salts are metastable and undergo spontaneous exothermic decomposition by HF elimination. Attempts were unsuccessful to prepare either NHF_3^+ salts by protonation of NF_3 at temperatures as low as -78° or fluorine substituted ammonium salts by direct fluorination of $NH_4^+AsF_6^-$ in HF solution in the temperature range -78 to 25°.

INTRODUCTION

Recent studies in our laboratory demonstrated that several novel onium salts can be prepared by protonation of less acidic compounds in $HF\text{-}MF_5$ (M = Sb and As) solutions. Thus, protonation of H_2O and H_2S produced[1,2] the surprisingly stable $OH_3^+MF_6^-$ and $SH_3^+SbF_6^-$ salts, respectively. In this paper, we report on the protonation of HNF_2 and NF_3.

Whereas salts containing the NH_4^+ ion have been described already in the early part of the fourteenth century[3], fluorine substituted salts were unknown until 1965. Disproving earlier theoretical computations[4,5] that NF_4^+ salts should be thermodynamically unstable, these salts were synthesized[6,7] in 1965 and shown to be of high thermal stability. Since then, numerous papers dealing with NF_4^+ salts[8-18] and the thermally unstable NF_3^+ radical cation[17] have appeared. Of the mixed $NH_nF_{4-n}^+$ cations, the NH_3F^+ cation has previously been described[19,20], but no data on the remaining two members in this series, i.e., $NH_2F_2^+$ and NHF_3^+, have been published. This is not surprising, since from comparison with the highly shock sensitive HNF_2 molecule and its CsF adduct[21], one might expect these more highly fluorinated mixed ammonium salts to be very susceptible to HF elimination. The adduct formation of HNF_2 with the Lewis acids BF_3, BCl_3, PF_5, and SO_2 has been studied[22] at -196° by infrared spectroscopy, but no evidence was found for ion formation. The thermal stability of these adducts was rather low with (in some cases irreversible) decomposition occurring at about -80°.

EXPERIMENTAL

Caution! Difluoramine is highly explosive[21] and protective shielding should be used during handling operations. The compound was always condensed at -142° and the use of a -196° bath should be avoided[23]. In the course of the present study five explosions of both $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$ in HF solution occurred, when these solutions were kept between -80 and 25° for extended periods of time. However, the appearance of the ruptured Kel-F or Teflon-FEP containers indicated pressure explosions (probably caused by HF elimination with N_2 formation and by the small ullage above the liquid phase) rather than rapid explosive decomposition. The rate of decomposition of these $NH_2F_2^+$ salt solutions varied strongly from sample to sample, indicating catalysis by trace impurities. The exothermic irreversible decomposition of solid $NH_2F_2^+$ salts appeared to proceed without explosion on a mmol scale, provided the volume of the container was large enough to avoid overpressurization. When working with such solutions in containers with small ullage, we, therefore, recommend removing the volatile decomposition products by quick pumping at -78° every time before handling the sample.

The experimental techniques used in this study have previously been described[1]. Difluoramine was prepared from difluorourea[24]. Nitrogen trifluoride (99.9%, Rocketdyne) and $NH_4^+HF_2^-$ (Braun Chemical Co.) were used without further purification. Difluoramine was handled in a Pyrex, the other reactants in a Monel Teflon-FEP, vacuum system.

Preparation of $NH_2F_2^+AsF_6^-$. In a typical experiment, dry HF (50 mmol) and AsF_5 (1.74 mmol) were combined at -196° in a passivated (with ClF_3) thin walled Kel-F capillary. The mixture was shortly warmed to room temperature to obtain a homogenous solution. Difluoramine (2.0 mmol) was added to the ampoule at -142°. The mixture was warmed to -78° and a white solid was formed which was completely soluble in the HF solvent at 20°. Unreacted NHF_2 and HF solvent were removed in a dynamic vacuum between -78 and 0°, leaving behind 420 mg of a white solid. This weight is in excellent agreement with that (423 mg) expected for 1.74 mmol of $NH_2F_2^+AsF_6^-$.

For the preparation of the nmr samples, an excess of AsF_5 was used and not pumped off to suppress exchange between the cation and the HF solvent.

Decomposition of $NH_2F_2^+AsF_6^-$. A sample of solid $NH_2F_2^+AsF_6^-$, contained in a Teflon-FEP ampoule, was allowed to slowly warm from -78 to 20°. After about 20 minutes at 20°, the solid started to melt and spontaneously decomposed with gas and heat evolution (*caution!*). The decomposition products were separated by fractional condensation and identified by infrared spectroscopy or mass spectroscopy. The main constituents were AsF_5, HF, and N_2, in addition to some NF_3 and trans-N_2F_2.

Preparation of $NH_2F_2^+SbF_6^-$. In a typical experiment, SbF_5 (1.70 mmol) and dry HF (150 mmol) were combined at -196° in a passivated Teflon-FEP ampoule. The mixture was warmed to 25° to obtain a homogenous solution. Difluoramine (2.02 mmol) was added to the ampoule at -142° and the mixture was warmed to -78°. A white solid formed when the starting materials melted. On warm up towards 0°, the solid completely dissolved in the excess HF. The unreacted NHF_2 and the HF solvent were pumped off between -45° and 0° leaving behind a white solid residue (499 mg). This weight agrees well with that (493 mg) expected for 1.70 mmol of $NH_2F_2^+SbF_6^-$.

Decomposition of $NH_2F_2^+SbF_6^-$. A sample of $NH_2F_2^+SbF_6^-$ (1.70 mmol), when kept at 25° for about one hour, underwent spontaneous exothermic decomposition with melting and gas evolution. The decomposition products, volatile at -78°, consisted of N_2 (0.56 mmol) and NF_3 containing a small amount of trans-N_2F_2 (0.58 mmol total). The residue (~410 mg; weight calcd. for 1.70 mmol of $HF \cdot SbF_5$ = 402 mg) was warmed to 25° in a dynamic vacuum. A small amount of white solid, stable at 25° was obtained which, based on its infrared spectrum, contained some $N_2F_3^+SbF_6^-$.

The NF_3-HF-SbF_5 System. To a homogenized (see above) mixture of SbF_5 (1.93 mmol) and HF (150 mmol) in a Teflon-FEP ampoule, NF_3 (3.52 mmol) was added at -196°. The mixture was kept at -78° for 16 hours. No evidence for adduct formation between NF_3 and HF-SbF_5 at -78° was detected, and the NF_3 starting material was recovered from the mixture at -78°.

The $NH_4^+AsF_6^-$-HF-F_2 System. Ammonium bifluoride (2.79 mmol) was placed in a Teflon-FEP ampoule and 20 ml of liquid anhydrous HF was added at -78°. To the clear solution, AsF_5 (3.0 mmol) was added resulting in the formation of while solid $NH_4^+AsF_6^-$. This solid was only sparingly soluble in HF, even at 25°. The ampoule was pressurized with one atmosphere of F_2 at -78° and the contents of the ampoule were agitated for one hour at -78°. No pressure decrease (expected for F_2 consumption with HF formation) was observed. The ampoule was kept at each of the following temperatures, -45, -23, 0, 25°, for one hour with agitation, but again no F_2 uptake was observed.

RESULTS AND DISCUSSION

Synthesis and Properties. The observed material balances show that protonation of NHF_2 in HF-MF_5 (M = As or Sb) solutions proceeds according to:

$$NHF_2 + HF + MF_5 \rightarrow NH_2F_2^+MF_6^-$$

The resulting difluoroammonium salts are white crystalline solids. They are stable at -50°, but at room temperature tend to undergo spontaneous exothermic decomposition with melting and gas evolution. In our study, the longest time period during which a solid $NH_2F_2^+$ salt could be kept at room temperature without decomposition was about half an hour. The HF solutions of these salts appear to be reasonably stable at room temperature; however, their stability varied strongly from sample to sample indicating some catalytic effect of by-products or impurities. Precautionary measures for handling these compounds are given in the first paragraph of the experimental section.

The main products in the decomposition of these $NH_2F_2^+MF_6^-$ salts are N_2, NF_3, and some trans-N_2F_2, in addition to the expected HF and MF_5. The fact that trans-N_2F_2 shows little tendency to complex with MF_5 under the given reaction conditions, agrees with previous[25] studies. The observation of only small amounts of trans-N_2F_2, but approximately equimolar amounts of N_2 and NF_3 as main products, indicates the following principal decomposition mode:

$$3NH_2F_2^+MF_6^- \rightarrow 3MF_5 + 6HF + N_2 + NF_3$$

The formation of small amounts of trans-N_2F_2 might indicate that N_2F_2 is an intermediate in the above decomposition mode; however, previous decomposition studies[21] on N_2F_2 gave no evidence for a disproportionation according to:

$$3N_2F_2 \rightarrow 2N_2 + 2NF_3$$

This difference in the decomposition products might be due to the exothermicity of the $\overset{\frown}{\underset{\smile}{NH_2F_2^+ MF_6^-}}$ decomposition causing the formation of excited intermediates. The observed instability of $NH_2F_2^+$ salts towards HF elimination is not surprising. Thus, NHF_2 and its CsF adduct are known[21] to decompose explosively.

The stability of the mixed $NH_nF_{4-n}^+$ fluoroammonium cations decreases with decreasing n. Thus, NH_3F^+ is relatively stable[19,20], $NH_2F_2^+$ is of very marginal stability, and no evidence was found in this study for the existence of a $NHF_3^+SbF_6^-$ salt at temperatures as low as -78°. Since the NH_3F^+ and $NH_2F_2^+$ cations are reasonably stable, particularly in HF solution at low temperatures, the direct fluorination of $NH_4^+AsF_6^-$ by F_2 in HF solution was studied over the temperature range -78 to 25°. However, no fluorination of $NH_4^+AsF_6^-$ was observed under these conditions indicating a significant activation energy for this reaction.

Nuclear Magnetic Resonance Spectra. The ^{19}F and ^{1}H nmr spectra of $NH_2F_2^+AsF_6^-$ were recorded for HF solutions acidified by AsF_5 to suppress exchange between the cation and the HF solvent. The results are summarized in Table 1 and compared to the data previously reported for the related species NH_4^+[1,26], NH_3F^+[19] NF_4^+[10,12] and NHF_2.[27] As can be seen, the observed chemical shifts and the hydrogen-fluorine spin-spin coupling constant of $NH_2F_2^+$ are in excellent agreement with those known for the closely related species. Furthermore, the observed multiplicities (1:2:1 triplets) in both the ^{1}H and the ^{19}F spectrum confirm that the species contains two hydrogen and two fluorine atoms. The components of the triplets were relatively broad and their line width did not significantly decrease with decreasing temperature in the range -30 to -60°. This indicates that the line broadening is due to ^{14}N quadrupole relaxation and not to an exchange process. In addition to the $NH_2F_2^+$ signal, the proton spectrum showed a singlet at $\delta=-8.6$ due to HF and the fluorine spectrum exhibited a singlet at $\phi = 173$ for rapidly exchanging HF, AsF_6^-, and AsF_5. For a sample of $NH_2F2^+SbF_6^-$ in unacidified HF, separate signals were observed for the SbF_6^- anion[1,28] and HF at $\phi = 126$ and 194.5, respectively.

Vibrational Spectra. The low-temperature infrared and Raman spectra of the solids and the Raman spectra of HF solutions have been recorded for both $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$. The observed spectra are shown in Figures 1 and 2, and the observed frequencies and their assignment are listed in Table II. The assignments were made by comparison with those[29] of isoelectronic CH_2F_2. As can be seen from the Raman spectra of the HF solutions, the $NHF_2 \cdot MF_5$ adducts are ionic and exhibit the bands characteristic for octahedral AsF_6^-[30-32] and SbF_6^-[31-33]. In the solid state, site symmetry and crystal field effects, in addition to distortion due to anion-cation interactions[1], cause a splitting of many bands[1,31,33-35]. In the absence of crystal structural data, no attempt will be made in the following discussion to thoroughly analyze these solid state effects. An $NH_2F_2^+$ cation of symmetry C_{2v}(see below) already possesses 9 fundamentals, the maximum number expected for a five atomic species. Consequently, the cation bands should be affected only by crystal field effects, but not by symmetry lowering. Since the assignment of the anion bands (see Table II) is straightforward, we will discuss only that of the cation bands.

An XH_2F_2 species of symmetry C_{2v} possesses 9 fundamentals classified as $4A_1 + A_2 + 2B_1 + 2B_2$. All of these should be active in both the infrared and Raman spectra, except for the A_2 mode which should only be Raman active. The Raman spectrum of $NH_2F_2^+AsF_6^-$ in HF solution (Figure 1, traces C,D,E) readily permits the assignment of the three fundamentals involving mainly motions of the NF_2 group, since the relative Raman intensities of the NH_2 modes are very low. After subtraction of the three anion bands, we are left with three reasonably intense bands at 1064, 1039, and 534 cm^{-1}. Of these. the ones at 1064 and 534 cm^{-1} are polarized and, therefore, represent the symmetric NF_2 stretch and the NF_2 scissoring mode of species A_1 respectively. The remaining depolarized Raman band at 1039 cm^{-1} must then be due to the antisymmetric NF_2 stretch, ν_9 (B_2).

Identification of the NH_2 modes is possible from the infrared spectra where these modes are expected to be appreciably intense. In the frequency region of the NH_2 stretching modes (2500-3500 cm^{-1}), $NH_2F_2^+SbF_6^-$ exhibits two medium strong bands at 2790 and 2637 cm^{-1} which are assigned, by analogy with CH_2F_2[29], to the antisymmetric and the symmetric NH_2 stretch, respectively. In addition to these bands, several weaker bands were observed, some of which can be attributed to combination bands (see Table II), probably in Fermi resonance with ν_1 and ν_5. In the infrared spectrum of $NH_2F_2^+AsF_6^-$, the splitting of these bands is even more pronounced. Similar splittings have previously been observed[29] for the CH_2 stretching modes of isoelectronic CH_2F_2. The assignment of these infrared bands to the NH_2 stretching modes is confirmed by the observation of a broad Raman band of very low intensity at about 2800 cm^{-1} for the HF solution of $NH_2F_2^+AsF_6^-$.

In the region of the NH_2 deformation modes (1700-1100 cm^{-1}) two intense sharp infrared bands were observed at about 1550 and 1480 cm^{-1}, respectively. Based on a comparison of their absolute and relative frequencies with those of CH_2F_2[29], SiH_2Hal_2[36], and GeH_2Hal_2[37], they should represent the scissoring and the wagging deformation, respectively, of the NH_2 group. Comparison of their relative intensities with those of the above dihalohydrides is ambiguous. Whereas in the infrared spectrum of CH_2F_2 the CH_2 scissoring mode is of very low intensity, in the remaining molecules its intensity is similar to that of the wagging mode and very high. Assignment of the 1550 and 1480 cm^{-1} bands of $NH_2F_2^+$ to the NH_2 wagging and the rocking mode, respectively, and of a weak infrared feature at 1655 cm^{-1} to the NH_2 scissoring mode, would result in an unreasonably high frequency for the rocking mode and in a too small frequency difference between the wagging and the rocking mode, provided that the NH_2 modes in $NH_2F_2^+$ are not strongly affected by NH...FM bridging between the cations and the anions. Adopting the above assignment of 1550 and 1480 cm^{-1} to the scissoring and wagging mode, respectively, we still have to locate the NH_2 rocking mode. By comparison with the other XH_2F_2 molecules[29,36,37], we would expect this mode to have a frequency of about 1200 cm^{-1}. The infrared spectra of the $NH_2F_2^+$ salts show indeed a weak band at about 1180 cm^{-1} which is tentatively assigned to the NH_2 rocking mode. However, its relative infrared intensity is unexpectedly low. An alternate assignment for this mode exists by attributing one of the more intense components of the 1050 cm^{-1} band system to it. However, this alternative seems to us less satisfactory for the following reasons. The Raman spectra of the solids show the same splittings. Since the NH_2 modes are of very low intensity in the Raman spectrum (see above), these bands should belong to an NF_2 mode. Furthermore, by comparison with the frequencies of the scissoring and the wagging mode, a frequency of 1070 to 1020 cm^{-1} for the NH_2 rocking mode appears unreasonably low.

The torsion mode, ν_5 (A_2), should only be Raman active and be of low intensity. This explains our failure to detect this mode for $NH_2F_2^+$.

The spectra of the solid salts show, in addition to the splittings frequently observed[1,31,33-35] for MF_6^- salts, bands in the region 100-300 cm^{-1}. These bands were not observed for the Raman spectrum of $NH_2F_2^+AsF_6^-$ in HF solution, and are rather broad. Therefore, they are attributed to lattice modes or cation-anion interaction through XH...FM bridges. Since the spectra of these solids were recorded at temperatures where the lattice is likely to become rigid, the observed phenomena are not surprising. A more detailed discussion of these effects has previously been given for OH_3^+ salts[1].

The unknown frequency of ν_5 (A_2), the tentative assignment for the NH_2 deformation modes, the uncertainty in the frequencies of ν_6 (B_1) and ν_1 (A_1), and the importance of the off-diagonal terms in the F matrix of the CH_2F_2 general valence force field[29], do not justify a normal coordinate analysis for $NH_2F_2^+$ at the present time.

Summary. The existence of 1:1:1 adducts between NHF_2, HF, and SbF_5 or AsF_5 was established by the observed material balances. The ionic structures, $NH_2F_2^+MF_6^-$, were established for these adducts by ^1H and ^{19}F nmr and vibrational spectroscopy. Seven or eight of the nine fundamentals, expected for a $NH_2F_2^+$ cation of symmetry C_{2v}, were observed. The nature of the products, resulting from the decomposition of these adducts, was briefly studied. With the exception of NHF_3^+, all of the fluoroammonium ions are now known.

Acknowledgement. The help of Drs. L. Grant, C. Schack and R. Wilson, and the financial support of the Office of Naval Research, Power Branch, is gratefully acknowledged.

REFERENCES

(1) K. O. Christe, C. J. Schack, and R. D. Wilson, Inorg. Chem., in press.

(2) K. O. Christe, Inorg. Chem., in press.

(3) W. C. Holmes in Kirk-Othmer's Encyclopedia of Chemical Technology, second edit., Vol. 2, p. 314, John Wiley, New York, 1967.

(4) W. C. Price, T. R. Passmore, and D. M. Roessler, Discussions Faraday Soc., 35, 201 (1963).

(5) J. N. Wilson, Advan. Chem. Ser., No. 54, 30 (1966).

(6) K. O. Christe, J. P. Guertin, and A. E. Pavlath, Inorg. Nucl. Chem. Lett., 2, 83 (1966).

(7) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Nucl. Chem. Lett., 2, 79 (1966).

(8) K. O. Christe, J. P. Guertin, and A. E. Pavlath, U. S. Patent 3,503,719 (1970).

(9) J. P. Guertin, K. O. Christe, and A. E. Pavlath, Inorg. Chem., 5, 1921 (1966).

(10) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, Inorg. Chem., 6, 533 (1967).

(11) K. O. Christe and D. Pilipovich, Inorg. Chem., 10, 2803 (1971).

(12) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Chem., 6, 1156 (1967).

(13) C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner, and J. N. Wilson, Inorg. Chem., 11, 1696 (1972).

(14) K. O. Christe, R. D. Wilson, and A. E. Axworthy, Inorg. Chem., 12, 2478 (1973).

(15) S. M. Sinel'nikov and V. Ya. Rosolovskii, Dokl. Akad. Nauk SSSR, 194, 1341 (1970).

(16) V. Ya. Rosolovskii, V. I. Nefedov, and S. M. Sinel'nikov, Izvest. Akad. Nauk SSSR, Ser. Khim., 7, 1445 (1973).

(17) S. P. Mishra, M. C. R. Symons, K. O. Christe, R. D. Wilson and R. I. Wagner, Inorg. Chem., in press.

(18) I. J. Solomon, J. N. Keith, and A. Snelson, J. Fluorine Chem., 2, 129 (1972).

(19) V. Grakauskas, A. H. Remanick, and K. Baum, J. Amer. Chem. Soc., 90, 3839 (1968).

(20) V. Grakauskas, J. Inorg. Nucl. Chem., 35, 3035 (1973).

(21) E. W. Lawless and I. C. Smith, "Inorganic High-Energy Oxidizers," Marcel Dekker, New York, N.Y., 1968, p. 69.

(22) A. D. Craig, Inorg. Chem., 3, 1628 (1964).

(23) E. A. Lawton and J. Q. Weber, J. Amer. Chem. Soc., 85, 3595 (1963).

(24) E. A. Lawton, E.F.C. Cain, D. F. Sheehan and M. Warner, J. Inorg. Nucl. Chem., 17, 188 (1961).

(25) For a discussion of the complex formation of cis- and trans-N_2F_2 with Lewis acids see K. O. Christe, R. D. Wilson, and W. Sawodny, J. Mol. Structure, 8, 245 (1971).

(26) M. T. Emerson, E. Grunwald, and R. A. Kromhout, J. Chem. Phys., 33, 547 (1960).

(27) A. Kennedy and C. B. Colburn, J. Amer. Chem. Soc., 81, 2906 (1959).

(28) R. G. Kidd and R. W. Matthews, Inorg. Chem., 11, 1156 (1972).

(29) I. Suzuki and T. Shimanouchi, J. Mol. Spectrosc., 46, 130 (1973); H. B. Stewart and H. H. Nielsen, Phys. Rev., 75, 640 (1949); J. Morcillo, L. J. Zamorano, and J. M. V. Heredia, Spectrochim. Acta, 22, 1969 (1966); D. H. Rank, E. R. Shull, and E. L. Pace, J. Chem. Phys., 18, 885 (1950); W. Holzer, J. Mol. Spectrosc., 25, 123 (1968).

(30) K. O. Christe and W. Sawodny, Inorg. Chem., 6, 1783 (1967); K. O. Christe, Inorg. Chem., 9, 2801 (1970).

(31) A. M. Qureshi and F. Aubke, Canad. J. Chem., 48, 3117 (1970).

(32) G. M. Begun and A. C. Rutenberg, Inorg. Chem., 6, 2212 (1967).

(33) K. O. Christe and C. J. Schack, Inorg. Chem., 9, 2296 (1970).

(34) K. O. Christe, E. C. Curtis, and R. D. Wilson, J. Inorg. Nucl. Chem., in press.

(35) R. J. Gillespie and B. Landa, Inorg. Chem., 12, 1383 (1973); R. J. Gillespie and M. J. Morton, Inorg. Chem., 9, 811 (1970).

(36) J. A. Hawkins and M. K. Wilson, J. Chem. Phys., 21, 360 (1953); J. A. Hawkins, S. R. Polo, and M. K. Wilson, J. Chem. Phys., 21, 1122 (1953); D. W. Mayo, H. E. Opitz, and J. S. Peake, J. Chem. Phys., 23, 1344 (1955); S. Cradock, E.A.V. Ebsworth, and A. G. Robiette, Trans. Faraday Soc., 60, 1502 (1964).

(37) E.A.V. Ebsworth and A. G. Robiette, Spectrochim. Acta, 20, 1639 (1964).

Table I. $^{1}H(\delta)$ and ^{19}F (ϕ) nmr Shifts[a] (ppm) and HF Spin-Spin Coupling Constant (J, Hz) of $NH_2F_2^+$ Compared to Those of Closely Related Species

Compound	NH_4^+ [b]	NH_3F^+ [c]	$NH_2F_2^+$	NF_4^+ [d]	NHF_2 [e]
δ	-6.3	-10.3(d)[f]	-14.2(tr)	-	-7.2(tr)
ϕ	-	110.8(q)	-11.6(tr)	-213.5	6 (d)
J_{HF}	-	44	34	-	24

(a) Measured for $NH_2F_2^+AsF_6^-$ in HF solution at -40° relative to external TMS and $CFCl_3$ respectively

(b) Ref 1 and 26

(c) Ref 19

(d) Ref 10 and 12

(e) Ref 27

(f) d=doublet, tr=triplet, q=quartet

TABLE II. VIBRATIONAL SPECTRA OF $NH_2F_2^+AsF_6^-$ AND $NH_2F_2^+SbF_6^-$ COMPARED TO THAT OF CH_2F_2

Obsd freq (cm^{-1}) and rel intens[b]							Assignment (point group)[c]		Approximate descriptio of mode
CH_2F_2	$NH_2F_2^+AsF_6^-$			$NH_2F_2^+SbF_6^-$			XH_2F_2	MF_6^-	
	solid		HF solution	solid		HF solution			
	Ir	Ra	Ra	Ir	Ra	Ra	(C_{2v})	(O_h)	
	2963 mw			2980 vw			$2\nu_7$ and		
	2941 mw			2935 w			ν_1 or ν_5 +		
	2913 m			2890 mw			lattice modes		
	2885 m								
3014	2836 m			2790 vs			ν_6 (B_1)		νas XH_2
	2784 m			2696 w					
2548	2657 s			2637 ms			ν_1 (A_1)		νsym XH_2
1508	1557 s			1543 ms			ν_2 (A_1)		δsciss XH_2
1435	1474 s			1487 ms			ν_8 (B_2)		δwag XH_2
1178	1185 vw			1176 vw			ν_7 (B_1)		δrock XH_2
1113	1073 m	1073 sh	1064 (2.7)p	1066 m	1062 (2.3)	1062 m	ν_3 (A_1)		νsym XF_2
	1065 m	1062 (4.5)		1055 sh	1052 (1)				
	1038 s	1041 (3.2)	1039 (0.6) dp	1036 s	1037 (1.9)	1039 w			
1090	1020 w						ν_9 (B_2)		νas XF_2
	720 vs			705 vs					
	682 ms			680 s				ν_3(F_{1u})	νas MF_6
		714 (9.6)	683 (10)p	652 m	671 (10)	650 vs		ν_1(A_{1g})	νsym in phase MF_6
		674 (10)		626 ms	639 (8.4)				
				610 mw					
	597 m	569 (4.9)	570 (0.5) dp	602 mw	566 (1.9)			ν_2(E_g)	νsym out of phase MF_6
	547 s			550 m	539 (0.9)				
528	532 m	533 (3.1)	534 (0.8)p	528s	524(1.3)		ν_4 (A_1)		δsciss XF_2

TABLE II. VIBRATIONAL SPECTRA OF $NH_2F_2^-AsF_6^-$ AND $NH_2F_2^+SbF_6^-$ (Cont'd.)

COMPARED TO THAT OF CH_2F_2

Obsd freq (cm^{-1}) and rel intens[b]							Assignment (point group)[c]		Approximate description of mode
CH_2F_2	$NH_2F_2^+AsF_6^-$			$NH_2F_2^+SbF_6^-$			XH_2F_2	MF_6^-	
	solid		HF solution	solid		HF solution			
	Ir	Ra	Ra	Ir	Ra	Ra	(C_{2v})	(O_h)	
	414 m			360 m				$\nu_4(F_{1u})$	δas MF_6
	391 vs			280 vs					
	376 w								
	369 w	369 (7.0)	366 (1.4)dp		276 (4.9)			$\nu_5(F_{2g})$	δsym MF_6
	300 s	290 (1.1)br			238 (0.4)				lattice vibrations or XH...FM stretch
		216 (0+)			103 (2.3)				

(a) Ref. 29.

(b) Uncorrected Raman intensities.

(c) Assignments for the anions bands are made for octahedral symmetry, although in the solid state the actual symmetry is obviously lower.

DIAGRAM CAPTIONS

Figure 1. Vibrational spectrum of $NH_2F_2^+AsF_6^-$. Trace A: Infrared spectrum of the solid as a dry powder between CsI disks, recorded at -196°. Trace B: Raman spectrum of the solid suspended in HF at -70°. Traces C, D, and E: Raman spectrum of an HF solution, recorded at 25° at three different recorder voltages. Traces marked by an asterisk were recorded with the incident polarization perpendicular. P, dp, and S indicate polarized and depolarized bands, and spectral slit width, respectively. For the Raman spectra, the 4880 Å exciting line of an Ar ion laser was used, the sample containers being Teflon-FEP or Kel-F tubes.

Figure 2. Vibrational Spectrum of $NH_2F_2^+SbF_6^-$. Trace A: Infrared spectrum; bands due to impurities or decomposition products were deleted. Traces B and C: Raman spectra. Recording conditions were identical to those of Figure 1. Trace C is incomplete owing to sudden self-destruction of the sample during the recording of the spectrum.

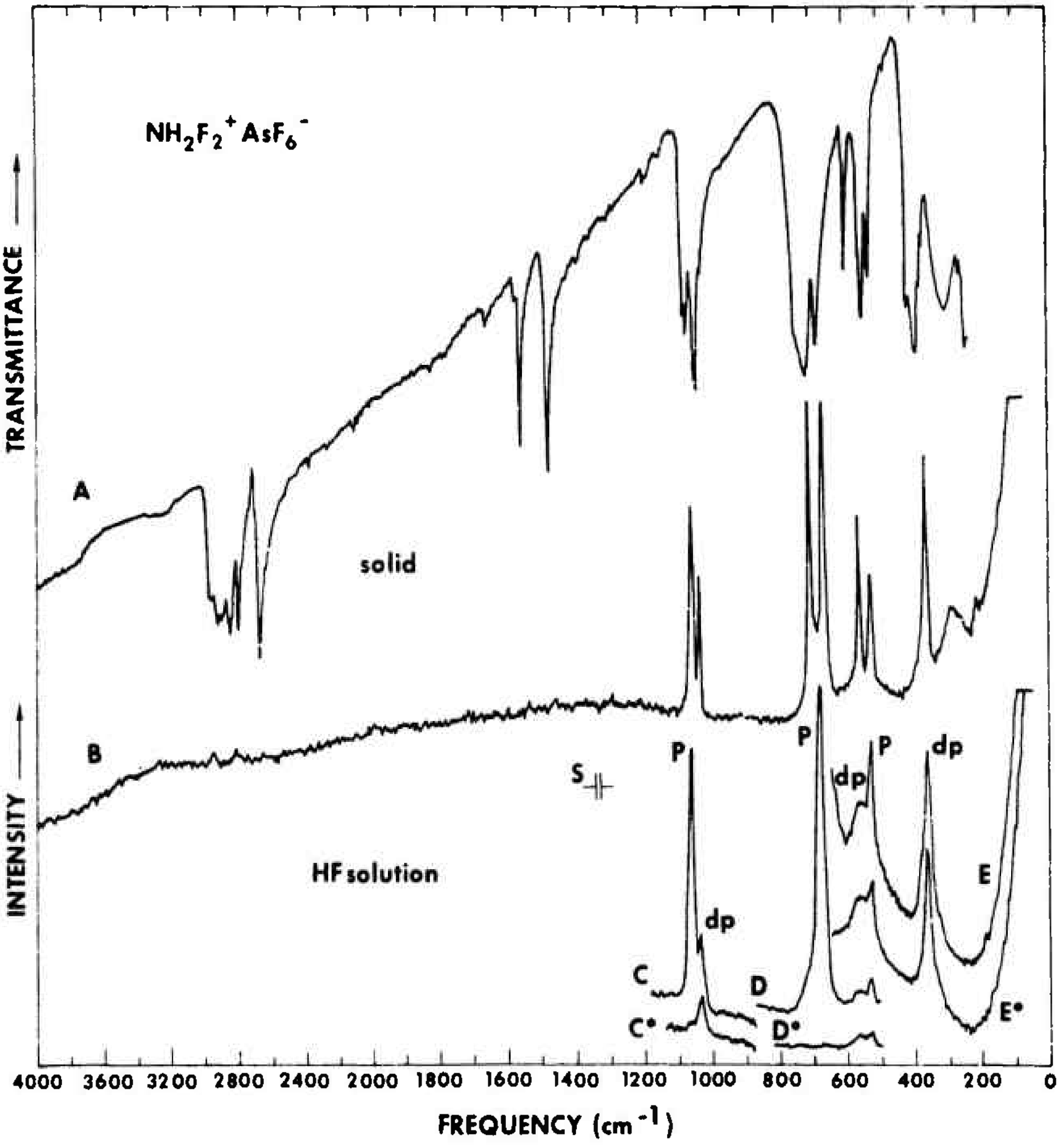

NH2F2+ AsF6-
TRANSMITTANCE
A
solid
B
INTENSITY
HF solution
S
P
dp
P
dp
P
dp
C
C*
D
D*
E
E*
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400 200 0
FREQUENCY (cm-1)

Figure 1

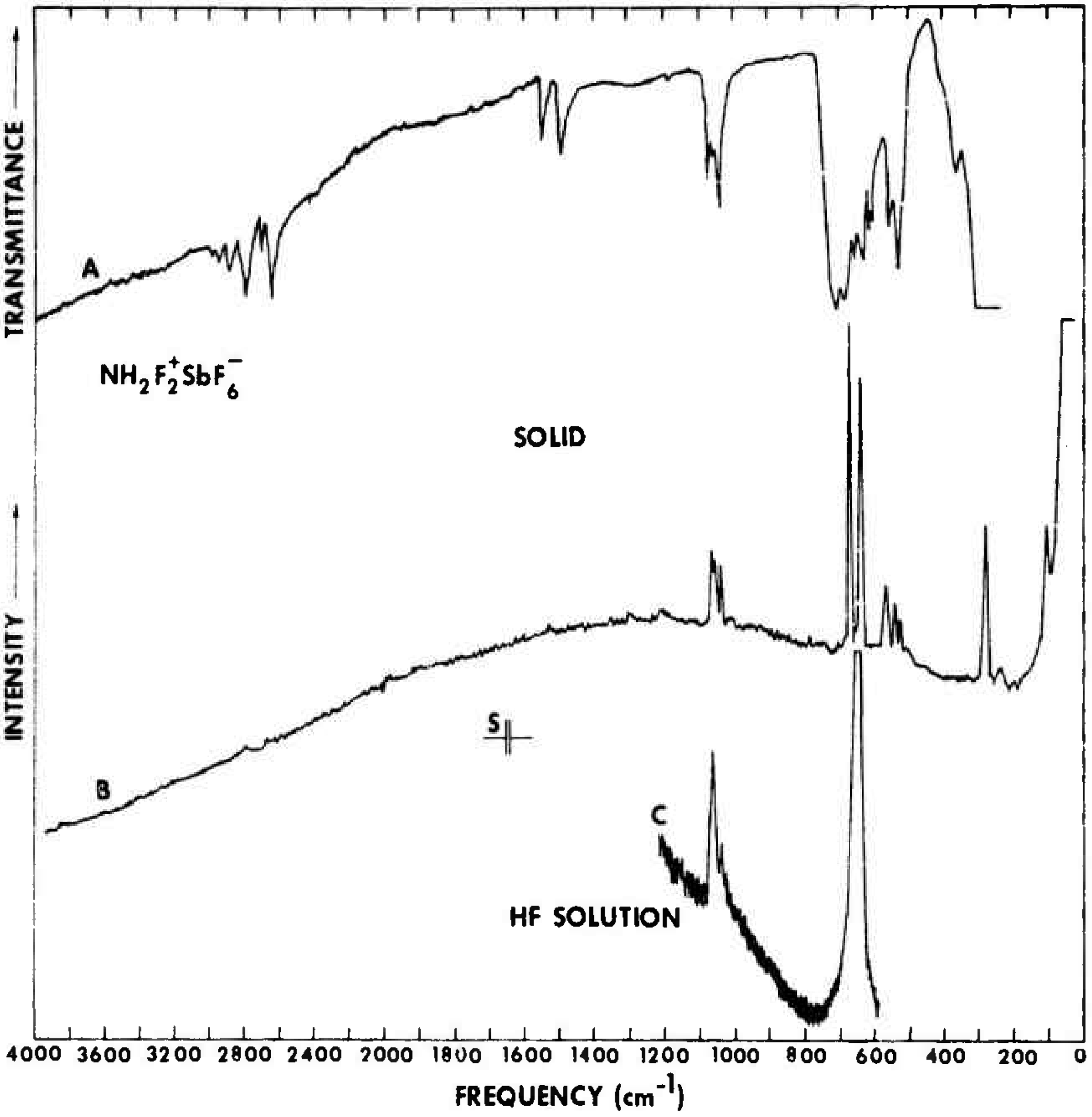

TRANSMITTANCE
INTENSITY
A
$NH_2F_2^+SbF_6^-$
SOLID
B
S
C
HF SOLUTION
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400 200 0
FREQUENCY (cm^{-1})

Figure 2