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SYNTHESES OF HALOGEN COMPOUNDS IN HIGH VALENCE STATES

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13. ABSTRACT

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$$NF_4AsF_6 = NF_5 + AsF_5$$

followed by irreversible decomposition of NF_5: $NF_5 \xrightarrow{k_1} NF_3 + F_2$

This step is taken to be a 3/2 order reaction and the kinetic data are represented by the equation

$$P_a^{3/2} - (P_a^0)^{3/2} = 3k_1Keq\ t/2$$

where P_a=partial pressure of AsF_5.

Matrix isolation techniques did not disclose the presence of NF_5 in the decomposition products. Isotopic exchange studies, using N-15, As-76 and F-18 labelled materials disclosed rapid exchange with AsF_5 involving the AsF_6^- ion. Interpretation in terms of $As_2F_{11}^-$ was confirmed by demonstration of the existence of $NF_4As_2F_{11}$ in a pressure-composition study.

Analysis of the products of decomposition of $Cl_2F^+AsF_6^-$ by matrix isolation infrared spectroscopy disclosed only ClF and AsF_5.

Fluorination of BrO_2 and BrO_3/BrO_2 mixtures with O_2F_2 was found to yield BrF_5 with excess O_2F_2, and a mixture of BrO_2F, and BrO_3F under less extreme conditions.

The reaction of CF_3OOOCF_3 with N_2F_4 produces CF_3ONF_2, CF_3OOCF_3 and various decomposition products. With CF_3OOF, the first product to appear is NOF. No evidence of the appearance of CF_3OONF_2 was found.

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Bromine oxyfluorides						
Cl_2FAsF_6						
CF_3OOF						
CF_3OOOCF_3						
CF_3ONF_2						
$CF_3C(O)ONO_3$						

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ABSTRACT: (cont'd)

The reaction of trifluoroacetaldehyde with N_2O_5 produced a new compound which is believed to be trifluoroperoxyacetyl nitrate, $CF_3C(O)OONO_2$. It has been characterized by means of molecular weight, vapor pressure, nuclear magnetic resonance spectroscopy, and infrared spectroscopy.

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SYNTHESES OF HALOGEN COMPOUNDS IN HIGH VALENCE STATES

February 1, 1968 through December 31, 1973

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Prepared by
Irvine J. Solomon
and
James N. Keith
of
IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois 60616

for
Department of the Navy
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FOREWORD

This is the Final Technical Report on IITRI Project C6140, Contract No. N00014-68-C-0279, entitled "Syntheses of Halogen Compounds in High Valence States". This research was supported by the Office of Naval Research, Power Branch, with Mr. Richard L. Hanson as Scientific Officer until May 31, 1971, Mr. Roland Jackel until January 31, 1973, and Dr. Ralph Roberts until December 31, 1973. The Report covers the period from February 1, 1968 through December 31, 1973.

We wish to thank Drs. H. Hyman (now deceased), I. Sheft, and E. Appelman, all of Argonne National Laboratory, for valuable aid and advice during the course of this program. We also wish to thank Dr. John Huston, Loyolla University, for determination of the mass spectra of our NF_3 samples, and Dr. Alan Snelson of IITRI for the conduct of the matrix isolation work.

Respectfully submitted,

IJ Solomon

I. J. Solomon
Senior Scientific Advisor

JN Keith

J. N. Keith
Research Chemist

Approved by

Robert Remaly

Robert F. Remaly
Manager
Chemical Energetics

ABSTRACT

The kinetics of the thermal decomposition of NF_4AsF_6 have been studied and interpreted in terms of an equilibrium dissociation, such as:

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followed by irreversible decomposition of NF_5:

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The reaction of trifluoroacetaldehyde with N_2O_5 produced a new compound which is believed to be trifluoroperoxyacetyl nitrate, $CF_3C(O)OONO_2$. It has been characterized by means of molecular weight, vapor pressure, nuclear magnetic resonance spectroscopy, and infrared spectroscopy.

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1. INTRODUCTION

Several topics of interest have been investigated during the course of this program. The first of these was the mechanism of decomposition of NF_4^+ salts. This work was related to our earlier work on the chemistry of O_2BF_4, in which we demonstrated that the very unstable oxygen fluoride, O_2F, was the primary dissociation product. The mode of decomposition of NF_4AsF_6 seems also to imply the existence of NF_5. Attempts were made to obtain evidence to support this postulate.

Our interest in N-F cations led to the synthesis of fluoroammonium perchlorate to be used by Dr. John Fenn of Yale University in molecular beam experiments.

Another unusual ion which seems to be related to the above work is Cl_2F^+. If $Cl_2F^+AsF_6^-$ decomposes in a simple manner, one might postulate the appearance of Cl_2F_2 in its dissociation products. Attempts were therefore made to detect such a compound.

After perbromic acid had been reported by Appelman we obtained a small sample from him and prepared ammonium perbromate, NH_4BrO_4, for a study of its physical properties. This led to a study of the synthesis of bromine oxides and oxyfluorides.

During the last year of the program we turned our attention to the reactions of the perfluoroalkyl trioxides and peroxyhypofluorites; in particular, the attempted synthesis of R_fOONF_2.

2. RESULTS AND DISCUSSION

2.1 Study of NF_4^+ Compounds

Recent work has shown that surprisingly stable salts of the fluorinated cations N_2F^+, $N_2F_3^+$, and NF_4^+ can be prepared using strongly acidic metal fluorides.[1-4] The last named ion is particularly intriguing, since the parent "base", NF_5, is not known to exist. The salts of this ion must be prepared indirectly from mixtures of NF_3, F_2, and metal fluorides, using electric discharge or thermal activation.

$$NF_3 + \frac{1}{2} F_2 + AsF_5 \xrightarrow{\text{glow discharge}} NF_4^+ AsF_6^- \qquad (1)$$

$$NF_3 + \frac{1}{2} F_2 + SbF_5 \xrightarrow[\text{pressure}]{\Delta/\text{liq. HF}} NF_4^+ SbF_6^- \qquad (2)$$

The comparison with the dioxygenyl salts is obvious when it is noted that either of the above methods can be used, and in this case, even the very unstable oxygen fluoride, O_2F reacts smoothly according to the following equation:[5]

$$O_2F + BF_3 \xrightarrow{-138°C} O_2^+BF_4^- \qquad (3)$$

The decomposition of $O_2^+BF_4^-$ has been studied, and the overall decomposition is represented as:

$$O_2BF_4 \longrightarrow O_2 + \frac{1}{2} F_2 + BF_3 \qquad (4)$$

The data on both the conventional decomposition of O_2BF_4 and the F^{18} tracer studies are explained in terms of the equilibrium:

$$O_2BF_{4(s)} \rightleftharpoons O_2F_{(g)} + BF_{3(g)} \qquad (5)$$

and a bimolecular process for the decomposition of O_2F. As expected the presence of BF_3 retarded the decomposition of O_2BF_4.

It is tempting to postulate the existence of an analogous nitrogen fluoride, NF_5, as an intermediate in the above reactions or in the decomposition of the salts. Direct examination of such a compound is, of course, extremely remote, but the possibility exists of obtaining indirect evidence in the form of kinetic data. The high pressures involved in the synthesis preclude a kinetic study of this reaction at present. The thermal decomposition, however, should lend itself to a kinetic study. A study of the rate of decomposition of an NF_4^+ salt in the presence of excess NF_3, F_2, or metal fluoride should indicate whether the decomposition depends on a dissociative equilibrium of the sort:

$$NF_4BF_4(s) = NF_5(g) + BF_3(g) \qquad (6)$$

followed by rapid decomposition of NF_5. O_2BF_4 has been shown to decompose by such a mechanism,[5] and NF_5, if it exists at all, would decompose very rapidly, probably by a unimolecular path:

$$NF_5 \longrightarrow NF_3 + F_2 \qquad (7)$$

If evidence can be found for the equilibrium in equation 6, F^{18} exchange studies may shed some light on its nature. Thus, the existence of an equilibrium makes possible a reaction such as equation 8.

$$NF_4AsF_6 + AsF_5^* = NF_4AsF_6^* + AsF_5 \qquad (8)$$

Analysis of the decomposition products of the labeled salt might then indicate whether all of the fluorine atoms in NF_5 are bound to nitrogen:

$$NF_4AsF_6^* \xrightarrow{\Delta} NF_5^* + AsF_6^* \tag{9}$$

$$(NF_3)F_2^* \longrightarrow NF_3 + F_2^* \tag{10}$$

or

$$NF_5^* \longrightarrow NF_3^* + F_2^* \tag{11}$$

In equation 10, $(NF_3)F_2^*$ indicates a structure in which not all the fluorine atoms are bound to nitrogen, such as a loose molecular association NF_3-F-F, or an ionic structure $NF_4^+F^-$. In equation 11, a structure with a pentacoordinate nitrogen atom is indicated. It would be necessary to use a salt with relatively low thermal stability for this study, to avoid the problems of exchange due to dissociation of fluorine, and of exchange with the passivated metal reaction vessel.

We considered a number of points in choosing an NF_4^+ salt for both conventional and F^{18} tracer studies. An important consideration is that the use of F^{18} is limited to studies that can be carried out in the span of 1 day because of its short half-life, 110 min. Further, the use of F^{18} may not be useful if the experiment were carried out at high temperatures. Compounds such as nitrogen trifluoride (NF_3), boron trifluoride (BF_3), and AsF_5 do not exchange with F_2 at room temperature; however exchange occurs at temperatures at which F_2 is dissociated to F atoms. For example, we have found that the following exchange occurs above 200°C

$$BF_3 + F_2^* \longrightarrow BF_2F^* + FF^* \qquad (12)$$

Keeping all of these points in mind, we decided that the best candidate for preliminary study is NF_4AsF_6. Of the two methods, glow discharge or high temperature, available for the preparation of NF_4^+ compounds, the high-pressure techniques were eliminated for the time being because of the long times necessary for the preparations. As stated before the half-life of F^{18} prohibits experiments of more than 1-day duration.

Thus, the glow-discharge preparation of NF_4AsF_6 was studied, and the preparation was run under a variety of conditions in order to find the method best suited to the application.

Of the two methods available for the direct synthesis of NF_4^+ salts, Christe's glow-discharge process for $NF_4^+AsF_6^-$ looks very promising for small-scale work if, indeed, 95% pure product can be obtained as the authors state in their paper. Further, the glow-discharge process may also be a suitable method for tetrafluoroammonium fluoroborate ($NF_4^+BF_4^-$), since the volatility of BF_3 is sufficiently high to permit the use of very low temperatures. We therefore began with an examination of the glow-discharge synthesis of $NF_4^+AsF_6^-$ at -78°C.

Initial experiments using 100-cc discharge tubes demonstrated that considerable etching occurred unless the reactor was designed with a generous spacing between the electrodes and the glass. The final design that is being used is a reactor about 6-in. long with 60-mm o.d. with nickel electrodes sealed at opposite ends by means of tungsten leads. The electrode spacing is 1 in. The discharge is operated at about 5,000 v, a.c. and 10 ma using a total gas pressure of 100 mm or less. An all-glass circulating pump is used and is timed by a simple switch-and-cam device driven by a 60 rpm synchronous motor.

In these experiments the analytical procedure consisted of passing the hydrolysis products through -80°C and -183°C traps and collecting the -183°C distilate in a trap cooled with liquid nitrogen treated with helium (~ -205°C). The criterion of success, of course, was the appearance of NF_3 in this fraction. This was detected by means of its infrared spectrum. After several attempts a product was finally obtained in a 15-hr experiment with a total pressure change of 160 mm, which hydrolyzed yielded about 50% of the expected amount of NF_3. (A spectrum run at 400-mm pressure did not indicate a significant amount of NO.) Brown fumes in the hydrolysis vessel, however, indicated that nitrogen oxides were present.

After a number of partly successful attempts to prepare NF_4AsF_6 in a glass vacuum line (the best product gave a yield of about 40 percent of the expected NF_3 on hydrolysis), glass was abandoned except for the glow discharge vessel itself. A vacuum system was constructed of Monel, with a minimum of 316 stainless steel. It was evacuated by an oil diffusion pump, protected by a soda-lime trap. An auxiliary glass vacuum line was attached for analytical purposes. The metal vacuum line was thoroughly passivated with NF_3, F_2, and AsF_5. The work in the glass vacuum line had indicated that etching could be effectively avoided in a discharge tube 60 x 6 mm, with nickel electrodes 1 in. apart while maintaining the tube at dry ice temperature. At a pressure of 60-80 mm, a discharge was maintained at about 5000 volts a.c. with a current of 8-10 ma.

In the above apparatus a 20 hour reaction of a 1:1:2 NF_3: AsF_5:F_2 mixture yielded 1.2 grams of solid product, which evolved NF_3 and oxygen in a ratio of 2:1, on hydrolysis, according to the following equation:

$$NF_4^+AsF_6^- \xrightarrow{H_2O} NF_3 + \frac{1}{2} O_2 + \text{etc.} \qquad (13)$$

Small amounts of nitrogen oxides were seen unless the refrigerant level was carefully controlled. In most experiments no difficulty was experienced, and the product was a white powder, easily scraped from the glass wall of the reactor.

It thus appears that the glow discharge method is capable of yielding NF_4AsF_6 of good quality, and that hydrolysis can be used effectively to analyze the product.

Several attempts were made to prepare NF_4BF_4 from a mixture of NF_3, F_2 and BF_3 by glow discharge at -80°C and by ultraviolet irradiation. The glow discharge reactions yielded only O_2BF_4 and salts which gave nitrogen oxides on hydrolysis, but no NF_3. The oxygen comes from the glass reactor. The product of the ultraviolet-induced reactions was nearly pure O_2BF_4. (We had previously shown that O_2BF_4 could be conveniently prepared by irradiation of a F_2-O_2-BF_3 mixture). Experiments using larger reactors and lower discharge currents produced essentially the same results.

Since the synthesis of NF_4AsF_6, of good quality is no problem, this material was used for the kinetic and other experiments instead of NF_4BF_4. About 2 to 2.5 grams of material could be prepared in a week by the discharge method, and was quite adequate for a kinetic run. All transfers were made in a nitrogen-filled glove box.

The kinetic results have been published in the Journal of Fluorine Chemistry. A copy of the paper appears as Appendix I to this report. The matrix isolation experiments, conducted with Dr. Alan Snelson are also reported in this paper.

Tracer studies were performed using the radioactive isotope, ^{18}F, with Irving Sheft and Herbert Hyman at Argonne National Laboratory. These results have been summarized in a paper which has been submitted to the Journal of Inorganic and Nuclear Chemistry. This paper comprises Appendix II to this report.

2.2 Synthesis of Fluorammonium Perchlorate

During the course of this program the suggestion was made by Mr. Hanson that fluorammonium perchlorate, NH_3FClO_4 might be of particular interest to us since it contains a fluorinated cation of a base which has never been isolated. Using molecular beam experiments, Dr. John B. Fenn, Yale University, has identified ammonia and perchloric acid as the gaseous species in the vaporization of ammonium perchlorate. Thus, one might hope to identify fluoramine from the perchlorate in a similar manner. We therefore undertook the task of preparing a sample for these experiments, and planned to attempt a matrix isolation experiment as well.

Fluorammonium perchlorate has been prepared by the reaction[6] of anhydrous perchloric acid with N-fluoro isopropyl carbamate:

$$i\text{-}C_3H_7OC(O)NHF + HClO_4 \rightarrow NH_3FClO_4 + CO_2 + i\text{-}C_3H_7OClO_3 \quad (14)$$

The latter compound was obtained[7] by aqueous fluorination of i-propyl carbamate.

The N-fluorocarbamate was prepared using this method and isolated by vacuum distillation. The purity was monitored by proton nmr, and only material containing no detectable organic impurities was used in the next step. Perchloric acid was prepared according to the method of G. F. Smith[8], and used within 24 hrs. of distillation. It was usually very pale yellow.

Two preparations of fluorammonium perchlorate exploded violently during transfer and drying, however, one sample was obtained in a dry, powdered state. But, while waiting for the matrix isolation experiment for several days, hydrolysis occurred, and the product became visibly wet. In all three preparations care was taken to use the purest possible fluorocarbamate, and the perchloric acid was used as soon after preparation as possible. Although care was taken to wash the solid excess perchloric acid remained on the solid. More likely, even a very minute quantity of chlorine oxide in the perchloric acid may be sufficient to initiate decomposition. In any case, since this was not the main objective of our work, it was dropped by agreement with Mr. Jackel.

2.3 $Cl_2F^+AsF_6^-$

The ability of the strong fluorine-containing Lewis acids to form stable salts with remarkably unstable bases is strikingly demonstrated by such compounds[9] as O_2AsF_6 and NF_4AsF_6[3,4], both of which are stable to at least 100°C, although the corresponding "bases" are certainly stable only at very low temperatures. We have demonstrated[5,10] indirectly that these salts are related to the above bases by means of the following equilibria,

$$O_2BF_4 = O_2F + BF_3 \qquad (15)$$

$$NF_4AsF_6 = NF_5 + AsF_5 \qquad (16)$$

which can be demonstrated, even though the bases are very unstable under the conditions of the kinetic studies.

Recent work in the chemistry of chlorine fluorides has revealed several remarkable new ions. Of particular interest is the salt[11,12] $Cl_2F^+AsF_6^-$, formed from ClF and AsF_5. Inspection of probable mechanisms for the formation and decomposition of this compound lead one to expect an equilibrium of the sort

$$2ClF = Cl_2F_2 \qquad (17)$$

$$Cl_2F_2 + AsF_5 = Cl_2F^+AsF_6^- \qquad (18)$$

which is quite analogous to the situation with O_2^+ and NF_4^+; i.e., we have an ion, Cl_2F^+, derived from the unstable base, Cl_2F_2, stabilized by the presence of AsF_6^-.

The equipment used has been described in previous reports and in our paper[10] on NF_4AsF_6. The ClF (Apache Chemicals, Inc.) was highly colored when introduced into the vacuum line.

ClF_3 was removed by the following procedure. To a sample of ClF in a Kel-F trap, a small quantity (ca 10%) AsF_5 was added, and the mixture thawed and cooled several times to effect complete reaction of the ClF_3 and any other impurities more basic than ClF. The trap was cooled to -80°C for several hours, after which the ClF vapor was removed rapidly to avoid vaporization of a significant amount of Cl_2FAsF_6. Residual color was removed by pumping on the solid for short periods while thawing. The resulting material was white and melted to a pale yellow liquid. Reaction with AsF_5 was effected by mixing ClF and AsF_5 in approximately 2:1 ratio, then cooling the reactor to -78.5°C. Reaction was fairly rapid, although the last 20 mm pressure drop was rather slow. Excess reactant vapors were pumped off, and the reaction vessel was transferred to the matrix isolation apparatus. The sample (about 1 millimole) was sublimed to a stainless steel coldfinger held at -196°C, which was then rotated to position the sample facing the CsI window. The Cl_2FAsF_6 was sublimed from the coldfinger at -90 to -100°C in a stream of neon, condensing the mixture on the window using liquid helium. After about 1 hour of sublimation, the cell was transferred to the spectrophotometer and the infrared spectrum of the deposit recorded. Frequency assignments are listed in Table 1. The spectrum appears to be adequately represented by the summation of the spectra of ClF and AsF_5. Cl_2F_2, if present, does not appear to be sufficiently stable to detect by this means.

Table 1

MATRIX ISOLATION SPECTRUM OF SUBLIMATION PRODUCTS OF $Cl_2F^+AsF_6^-$

		ClF	AsF_5
816	vw		
808	s		ν_5
781.5	m		ν_3
774	w	ν_1	
768	vw		
395	m		
364	ms		ν_4
356	w		ν_6

Sample sublimed from coldfinger at -90 to -100°C in neon matrix.

2.4 Heptavalent Bromine

2.4.1 General

There has been a fair amount of interest during the past decade in the synthesis of heptavalent bromine compounds, especially since the discovery of the xenon fluorides and chlorine pentafluoride. Most of the effort has been concentrated on the fluorides, for obvious reasons, but to date no evidence has been found for the existence of BrF_7. The first synthesis of a heptavalent bromine compound was that of perbromic acid by

Appelman[13], by the action of fluorine on alkaline bromate solutions. Perbromyl fluoride was later obtained by fluorination of $KBrO_4$.

Because of certain disadvantage of ammonium perchlorate in explosive compositions, such as its bulk density and hygroscopicity, it was of some interest to determine the physical properties of ammonium perbromate for comparison. We therefore contacted Dr. Appelman, who generously furnished us with a sample of 3M perbromic acid, which we used to prepare ammonium perbromate. The isolation and characterization of this salt were reported in a paper published[14] in Inorganic Chemistry, which is reproduced as Appendix III to this report. Since the above paper appeared, the thermodynamic properties of the perbromate ion have been reported[15], making it possible now to estimate the heat of formation of ammonium perbromate as about -33 kcal per mole.

The stability of the perbromates was quite impressive, considering the failure of several synthetic methods[13] which had been tried for preparing them. It seemed likely that the oxygen-containing heptavalent bromine compounds might be more stable than BrF_7, which had never been made. Attempts to prepare new bromine oxyfluorides were therefore undertaken.

Bromyl fluoride, BrO_2F, is reported to result[16] from the reaction of BrF_5 on $NaBrO_3$. Attempts were therefore made to prepare bromine oxyfluorides from the bromate using oxygen fluorides. A much more likely method, however, was considered to be the fluorination of bromine oxides. These difficult, unstable materials, however have not been well characterized. Some effort, therefore, was expended in developing techniques for handling them and characterizing them by analysis.

2.4.2 Synthesis of Bromine Oxides

After several unsuccessful attempts to prepare BrO_2 by bubbling ozone through a Freon-11 solution of bromine, we decided to use the glow discharge method of Schwarz[17] and found that BrO_2 is very conveniently prepared in this way, with sufficient care in removal of the ozone by-product. A mixture of oxygen and bromine (usually about 3:1) was prepared in a 3-liter flask, and slowly passed through the discharge tube, whose lower part was refrigerated with liquid nitrogen. Usually about 4,000-6,000 volts was applied to the discharge. Upon completion of the run, the ozone was removed by slowly pumping on the tube while it was thawing in a cold Dewar flask. The gases were passed through dry-ice trap to catch the first traces of bromine. By the time bromine began to evaporate, the ozone had all been removed. A -45 or -30° bath was then placed around the sample while pumping off the bromine. The discharge tube was then closed, and the sample decomposed by thawing to room temperature. Occasionally rapid decomposition, once with a flash of light, occurred at about 0°C, but usually the decomposition was smooth. The bromine and oxygen were separated by passage through -196° traps and measured as gases.

Considerable difficulty was experienced in obtaining reproducible compositions, as can be seen in Table 2, despite various

Table 2

SYNTHESIS OF BROMINE OXIDES

Run	T, °C	Gas Used, O/Br	Br_2, cc	O_2, cc	O/Br
3	-196	3:1	63.8	110.0	1.72
4	-196	3:1	6.9	14.1	1.97
5	-196	3:1	44.9	86.6	1.93
6	-196	3:1	20.4	36.7	1.80
7	-196	3:1	18.0	31.0	1.72
8	-196	3:1	30.1	48.4	1.61
9	-196	3:1	14.9	28.7	1.93
10	-196	3:1	17.5	31.4	1.79
11	-196	3:1	21.2	36.9	1.74
12	-196	3:1	9.0	16.5	1.83
13	-196	3:1	27.6	48.9	1.77
14	-196	7:1	27.6	48.9	1.77
15	-78	7:1	10.2	23.5	2.30
16	-78	7:1	42.5	102.5	2.41
17	-183	10:1	38.0	67.8	1.78
18	-183	3:1	11.6	19.0	1.64
19	-183	3:1	32.5	56.8	1.75
20	-183	3:1	53.0	92.0	1.74
21	-183	3:1	13.7	25.6	1.87
22	-183	50:1	26.7	48.5	1.81
23	-183	10:1	19.4	38.8	2.00
24	-183	10:1	22.5	41.1	1.83
25	-183	10:1	9.0	17.5	1.95
26	-183	10:1	22.2	41.7	1.88
27	-183	10:1	18.9	35.3	1.87
28	-78	50:1	30.9	69.6	2.26
29	0	50:1	4.0	12.0	3.0
31	0	50:1	4.5	12.2	2.71

modifications of the trap geometry, etc. Raising the temperature to -78° increased the oxygen-bromine ratio, but obviously a higher oxide is formed at this temperature. At -183°C no ozone is formed, facilitating clean-up of the product, but the composition is not improved thereby. Finally, it was found that enlarging the upstream tubing connecting the trap to the electrode, and adding an extra fan at this spot produced consistently higher analyses. The average O/Br ratio in these runs (23-27) was 1.90.

The three experiments at -78°C are interesting, in that they indicate that a fairly large quantity of the higher bromine oxide, BrO_3, is present. Although bromine trioxide can be prepared above -40°C, it is obtainable only in small quantities, and it is necessary to use high oxygen: bromine ratios (50:1). We have prepared several samples at 0°C, using Pflugmacher's method,[18] with the following modification. At the end of the run, the bromine-oxygen mixture is replaced by pure oxygen, and the ozone thus produced prevents the decomposition of the product while changing the coolant to dry ice. After the sample has cooled to -78°C the oxygen flow and the discharge are shut off, and the residual gases are pumped out. The sample is then stored at -196°C until used. One sample, which was quite white was analyzed as $BrO_{3.0}$. Another, slightly colored, had a composition corresponding to $BrO_{2.71}$ (very close to Schumacher's[19] "Br_3O_8").

Further attempts were made to increase the yield in the synthesis of bromine trioxide. This compound, unfortunately can be prepared only at temperatures near 0°C, where it is very unstable unless ozone is present. When oxygen was added on completion of the synthesis to produce ozone while cooling the reactor to -80°C, little, if any product seemed to be lost. However, the amount of BrO_3 prepared in the discharge reaction is only about 30-40 mg, no matter how long the discharge is operated. Attempts have been made to use very thin-walled reactors without significant change in the yield.

Corona discharge was attempted using a long nickel wire as the inner electrode, and aluminum foil or a film of silver as the outer electrode. In both cases, when the discharge was operated at from 5000 to 12000 volts, no solid appeared in the corona discharge region, but very small amount appeared in the area of glow discharge near the tip of the nickel electrode. Several attempts were made to detect perbromate, BrO_4^-, in the hydrolysis products of BrO_3. Thus a sample of BrO_3(about 20 mg) was prepared, the tube opened at -196°C, and 10 ml of dilute NaOH were added. Several drops of methylene blue solution were added. Although no precipitate appeared immediately as it does with $NaBrO_4$, a dark blue precipitate settled overnight. Similar results were obtained with crystal violet. However, a dilute solution of bromine in water gave identical results on addition of dilute NaOH, followed by these dyes. Another sample of BrO_3 gave a pale yellow solution on hydrolysis with neutral water. In an attempt to detect BrO_4^- spectroscopically, the hydrolyzates were neutralized with NaOH and evaporated to dryness. The sodium salts were then ground and mulled with Nujol. Since very poor spectra were obtained with the mulls, the hydrolyzates were pelletized with KBr. All of the peaks seen in the infrared spectra were accounted for by the spectra of $NaBrO_3$ and NaOH, on comparison with pellets of these materials with KBr.

The tedious procedure involved in the synthesis of perbromates induced us to look more closely at the bromine oxides, which have been briefly characterized, but not studied in much detail.[16-19] It seems an obvious approach to prepare bromine oxyfluorides by direct fluorination of the oxides. Since their instability makes it necessary in any case to use low temperatures, the use of dioxygen difluoride seems especially suitable here. Bromine dioxide has been fluorinated by fluorine and by BrF_5 to bromyl fluoride,[16] BrO_2F. Dioxygen difluoride will surely effect the same reaction at a lower temperature, and also should produce perbromyl fluoride, BrO_3F, from BrO_3. It is also hoped that other heptavalent oxyfluorides will be produced, such as BrO_2F_3 or $BrOF_5$.

We therefore initiated a study of the reactions of the bromine oxides with the oxygen fluorides. For the reaction of O_2F_2 with BrO_2, frangible seals were added to the lower part of the discharge apparatus, so that, after removal of this part from the system, it could be reopened and O_2F_2 distilled in. In the first such experiment, BrO_2 was prepared, ozone and bromine evaporated away, and the bottom part of the reactor sealed off. O_2F_2 was then prepared in another reactor, and melted down into a small transfer tube, which was then sealed off. This tube was then connected to the BrO_2 tube, the connecting tubing evacuated, and the frangible seals broken. The O_2F_2 was thawed slowly and allowed to distill into the reactor above the BrO_2, after which the transfer tube was sealed off and removed. The reactor was placed in a cooling bath at -126°C. In an hour, nearly all of the color of O_2F_2 and of BrO_2 had disappeared, and only a white solid was visible in the reactor with a small yellow spot on the bottom. A small amount of non-condensible gas was present, but no fluorine. During removal of the condensible gases from the reactor, the solid evaporated smoothly, and appeared as a white condensate in the adjacent trap. Later some purple color appeared. Toward the end of the transfer, the solid melted to a clear colorless liquid, which bubbled slowly. The color of the condensate after this point was then reddish-brown of bromine. The infrared spectrum of the mixture indicated the presence of BrF_5, and the color of bromine was evident in the vapor. On attempting to transfer the product to an NMR tube extensive decomposition occurred, evidenced by an extreme darkening of the liquid, and the appearance of non-condensible gas.

In another similar experiment, an nmr tube was attached directly to the reactor, so that the product need not be distilled out, but merely melted down to the bottom of the tube. In this experiment, the product was less colored, and mostly liquid at -30°C. The nmr spectrum at this temperature, however, revealed only bromine pentafluoride. A less volatile material was also present which is believed to have been bromyl fluoride.

Experiments on BrO_2/BrO_3 mixtures with less O_2F_2 have indicated that bromyl and possibly some perbromyl fluoride were produced. Thus, BrO_2 was prepared at -183°C using a 6:1 O_2/Br_2 mixture. The product was mostly yellow, but white on the upper surfaces. After evaporation of the excess bromine at -30°C, it was determined that 15.3 cc of bromine had been consumed, corresponding to 30.6 cc BrO_2. A previously prepared sample of O_2F_2 was distilled in, and the reactor brought to -126°C for 90 min. Most of the color disappeared, and the reactor was coated with white solid with a small spot of pale yellow-orange color. At the end of this time the volatile product consisted of 34.1 cc O_2 and a trace of F_2.

On thawing to -78°C a further 17.6 cc O_2, 1.5 cc F_2 and 9.9 cc of condensible gas were obtained. The infrared spectrum of the condensible gas appeared to be mainly that of a mixture of fluorocarbons and SiF_4, with three smaller peaks (960, 875, and 590 cm^{-1}) which may be due to BrO_3F (976.5, 875.5 and 606 cm^{-1}, for the three strongest peaks[20]). Overnight these peaks disappeared, and the color of bromine appeared. Aside from the appearance of a small new peak at 1280 cm^{-1}, the spectrum was otherwise unchanged.

The -78°C residue did not appear to distill at room temperature, but melted to a clear colorless liquid which bubbled slowly producing (overnight): 36.4 cc O_2, 14.2 cc Br_2, and 10.0 cc SiF_4 (IR spectrum). Using the SiF_4 value to calculate the fluorine, and to correct the oxygen valve, this becomes: 26.4 cc O_2, 14.2 cc Br_2 and 20.0 cc F_2 corresponding to the composition BrO_2F.

The consumption of fluorine implied by the analytical data for the -126° reaction corresponds to much more than required for a reaction such as:

$$BrO_2 + \frac{1}{2} O_2F_2 \longrightarrow BrO_2F + \frac{1}{2} O_2 \qquad (20)$$

The oxygen obtained on thawing to -78°C further suggests an unstable oxyfluoride. Attempts to purify the products resulted in decomposition. It is probable that a mixture of an unstable oxyfluoride, BrO_2F and BrF_3 or BrF_5 was produced, along with a small amount of BrO_3F.

2.5 Attempted Synthesis of R_fOONF_2

2.5.1 General

A number of methods are now available for the synthesis of peroxyhypofluorites. For the higher homologues, addition of oxygen fluorides to higher olefins is convenient[21]:

$$C_3F_6 + O_2F_2 \longrightarrow C_3F_7OOF \qquad (21)$$

while CF_3OOF is now available from carbonyl fluoride:[22,23]

$$COF_2 + CsF \longrightarrow CsOCF_3 \qquad (22)$$

$$CsOCF_3 + OF_2 \longrightarrow CsF + CF_3OOF \qquad (23)$$

Although peroxyhypofluorites have been known for a number of years, very little is known of their chemistry. They presumably will behave much like the hypofluorites, although they are more reactive and less stable.

One of the very interesting new types of compounds related to the hypofluorites is R_fONF_2, for which several synthetic methods are available: (1) from $CF_3OF + N_2F_4$ under ultraviolet light[24,25]:

$$CF_3OF + N_2F_4 \xrightarrow{u.v.} CF_3ONF_2 \qquad (24)$$

(2) from peroxides[26]:

$$CF_3OOCF_3 \xrightarrow[u.v.]{N_2F_4} CF_3ONF_2 \qquad (25)$$

and (3) from hypofluorites and the potassium fluoride adduct of difluoramine[27]:

$$R_fOF \xrightarrow{HNF_2 \cdot KF} R_fONF_2 \qquad (26)$$

It would be of considerable interest to study the synthesis of similar compounds containing a peroxy group, e.g.:

$$CF_3OOF + N_2F_4 \longrightarrow CF_3OONF_2 \qquad (27)$$

Such a functional group should be very energetic and would represent an interesting new class of compounds.

2.5.2 Experiments with C_3F_7OOF

Attempts were made to prepare such compounds by all of the above methods. C_3F_7OOF, prepared from perfluoropropene, was reacted with $KF \cdot HNF_2$ as follows:

$KF \cdot HNF_2$ was prepared[27] and the excess HNF_2 distilled off. C_3F_7OOF was condensed onto the solid and thawed to -78°C for two days. On attempting to transfer the products to an infrared cell, an explosion occurred, destroying the apparatus.

In another experiment, after five days it was possible to distill the products from the reactor and identify most of them by fractional condensation in the vacuum line and infrared and nmr spectroscopy. The bulk of the volatile product consisted of unreacted C_3F_7OOF, COF_2, CF_3COF, C_2F_6 and N_2F_4, with some CF_4, NF_3 and NO_2. Although traces of unknown materials were present, no significant quantity of R_fONF_2 or R_fOONF_2 was formed. Repetition of this reaction using excess C_3F_7OOF or excess $KF \cdot HNF_2$ gave essentially the same results.

Reaction of C_3F_7OOF with approximately by equal amounts of N_2F_4 at 25, -30 and -78°C produced essentially the same results as with $KF \cdot HNF_2$; i.e., mainly cleavage products with small traces of unknown materials which could have contained ONF_2 groups, but which were too small to separate and identify. In order to avoid the complexities due to cleavage of C_3F_7OOF, we next turned our attention to the simpler CF_3OOF and CF_3OOOCF_3.

2.5.3 Synthesis of CF_3OOF and CF_3OOOCF_3

Perfluoromethyltrioxide, CF_3OOOCF_3, is conveniently prepared by the reaction of oxygen difluoride with $CsOCF_3$ (from COF_2 + CsF) at ambient temperature. By the use of excess OF_2, the intermediate, CF_3OOF, can also be obtained:

$$CsOCF_3 + OF_2 \longrightarrow CsF + CF_3OOF \qquad (28)$$

$$CsOCF_3 + CF_3OOF \longrightarrow CsF + CF_3OOOCF_3 \qquad (29)$$

The trioxide is a relatively stable compound at room temperatures, and decomposes readily at 65°C.

$$CF_3OOOCF_3 \xrightarrow{\Delta} CF_3OOCF_3 + \frac{1}{2} O_2 \qquad (30)$$

The reaction of OF_2 with $CsOCF_3$, results in a mixture of CF_3OOF and CF_3OOOCF_3 with the latter predominating. Since a number of reactions with CF_3OOF were planned, attempts were made to increase the yield by using a large excess of OF_2.

In a 7-day experiment using a 7:1 ratio of OF_2 to COF_2, at an OF_2 pressure of 100 psig, the condensible products, exclusive of OF_2, were CF_3OOF, 28%, CF_3OF, 28% and CF_3OOOCF_3, 44%. A large amount of non-condensible gas was also found. In another experiment under similar conditions, reaction overnight yielded a product which was 28.4% CF_3OOF, 71.6% CF_3OOOCF_3, and no more than a trace of CF_3OF. Little non-condensible gas was produced. In a third experiment, 28.4% CF_3OOF and 71.6% CF_3OOOCF_3 were produced. Since the peroxyfluoride, CF_3OOF is produced in significantly smaller amount than the trioxide, it was of considerable interest to determine if it could be obtained from the trioxide, either by reversal of reaction (29) or by fluorination of the trioxide. Attempts were made to achieve this fluorination with the extremely reactive oxygen fluoride, O_2F_2. Although unstable even at very low temperatures, O_2F_2 is capable of very vigorous reaction at temperatures as low as -183°C. For example, it adds readily to perfluoropropene at this temperature, forming fluoroperoxyperfluoropropane, C_3F_7OOF. Attempts were made therefore to use O_2F_2 to fluorinate or oxyfluorinate CF_3OOOCF_3.

$$CF_3OOOCF_3 \xrightarrow{O_2F_2} CF_3OOF + CF_3OF \qquad (31)$$

Thus, 2.12 mmoles of trioxide and 2.26 mmoles of O_2F_2 were combined in a Pyrex reactor and thawed to -138°C. After 2 hours, the color had lightened considerably. The non-condensible gases (O_2+F_2) were pumped out, and the condensate thawed and allowed to vaporize to decompose residual O_2F_2. The product was 2.51 mmoles of condensible gas. Infrared spectroscopy indicated that it consisted of trioxide contaminated with SiF_4, plus two new unidentified peaks at 5.85 and 9.25μ. When the recovered trioxide was treated with water, the 5.85μ peak and the SiF_4 peak (9.75μ) disappeared. The 9.25μ peak remained however. Whatever the source of this product, the compound is stable to hydrolysis. The 5.85μ peak was broad, suggesting that it is not due to a carbonyl group ($\rangle C=O$), which usually produces a rather sharp spike.

Another method, if reaction (29) is reversible, would be to drive the reaction to the left by addition of OF_2 to trioxide over CsF; thus:

$$CF_3OOOCF_3 + CsF \longrightarrow CF_3OOF + CsOCF_3 \qquad (32)$$

$$OF_2 + CsOCF_3 \longrightarrow CF_3OOF + CsF \qquad (33)$$

Trioxide, 4.65 mmoles, and 4.83 mmoles of OF_2 were condensed in a small stainless steel reactor over activated cesium fluoride and ball milled for 20 hours at room temperature. On opening the reactor a very small absorption was noted at 10.6 (CF_3OOF, presumably). The reactor was heated to 65°C for 2 hours without much change in the intensity of this peak. Distillation of the contents yielded 3.88 mmoles of CF_3OOOCF_3, 3.11 mmoles of OF_2

containing a trace of CF_3OF, and about 0.09 mmole of CF_3OOF containing some SiF_4 and a trace of OF_2. The amount of CF_3OOF produced is very small under these conditions. The reaction cannot be run at higher temperatures, because of the lower stability of CF_3OOF.

Finally, it was thought that, if O_2F_2 at low temperatures would not fluorinate the trioxide the reason may be the relative stability of the starting material at these temperatures. An interesting indirect source of unstable dioxygen fluoride is e dioxygenyl salt, O_2BF_4. This compound, which is much more stable than the oxygen fluorides from which it is made, decomposes slowly at 0°C via the very unstable O_2F:

$$O_2BF_4 \quad = \quad O_2F + BF_3 \tag{34}$$

$$O_2F \longrightarrow O_2 + \frac{1}{2} F_2 \tag{35}$$

Since O_2F exists in equilibrium with the salt the rate of decomposition is controlled by the pressure of BF_3. The O_2F decomposes very rapidly, but can be used for fluorination of organic compounds.

Dioxygenyl fluoroborate, O_2BF_4 (1.15 mmole), was prepared by the reaction of O_2F_2 with excess BF_3 at -138°C. CF_3OOOCF_3, 1.11 mmoles was condensed onto the solid, which was maintained at -78.5°C for 4 hours. No non-condensible gas was produced. (Oxygen and BF_3 would be by-products of the postulated reaction.) The mixture was then thawed to 0°C. In 2-1/2 hours, sampling of the vapor disclosed no CF_3OOF; nor in 1 hour at 25°C. The mixture was heated for 10 minutes at 65°C, whereupon all of the remaining O_2BF_4 decomposed. The gases were distilled in the vacuum line, yielding only a trace of CF_3OOF (which could have been an impurity in the trioxide). Some COF_2 was also found.

Considerable effort was expended to increase the yield of CF_3OOF by using higher OF_2 pressure and by fluorination of the trioxide, with little success. The fluorination of OF_2 may have produced a small amount of CF_3OOF, but the reaction is very slow at best. It is possible, of course, that the reverse reaction of trioxide with CsF does not occur at ordinary temperatures.

Thermal activation of the CF_3OOOCF_3 will probably not be effective because of decomposition of the product.

2.5.4 Reactions of CF_3OOF and CF_3OOOCF_3 with N_2F_4

2.5.4.1 Gas Chromatography

Both Pyrex and Monel/stainless steel vacuum lines were used, depending on the needs of the particular experiment. Certain problems with perfluoromethoxy compounds complicate their isolation and analysis. First, the volatilities are frequently similar, and, since they are usually mutually soluble, separations are sometimes rather tedious. Second, infrared spectroscopy tends to be a poor method for identifying mixtures, since many of the absorbances overlap seriously. Finally, the nmr lines of the CF_3-O groups are in the same region (around 60-70 ppm), and those for similar compounds can be rather close together. For these reasons an additional analytical and preparatory tool was desired. A simplified gas chromatograph was constructed and

and attached directly to a Pyrex vacuum line. The chromatograph, which is illustrated schematically in Figure 1, consists of a small Pyrex sampling valve, A, into which samples of condensible gases can be led directly from the vacuum line; a septum injection port B, which can be used for hypodermic injection of reference gases without the need of entering via the vacuum line; a chromatographic column, C, usually of 1/4 inch copper tubing, prepared at IITRI; a Gow-Mac No. 9677 T/C detector (thermistor type); and a series of Pyrex paper-clip style collection traps, E, (all with 4-way stopcocks), also connected to the vacuum line via a 2-way stopcock. Samples can thus be handled directly from the vacuum line, and returned to the vacuum line after separation, for transfer to the infrared cell or nmr tube, or measurement of physical properties.

To provide a simple method of comparison among compounds and identification of fractions, which is relatively independent of column conditions, reference materials can be added. For fluoroorganics it is convenient to use the Freons or fluorocarbons. We have usually used the simple Freons, such as Freon 11, 12, and 13, since these are conveniently handled materials, and are occasionally used as solvents as well. Although for more precise work it is useful to add the reference to the sample being analyzed, we prefer usually to avoid this when possible, especially for preparatory chromatography. The relative retention time, T_R, is calculated thus:

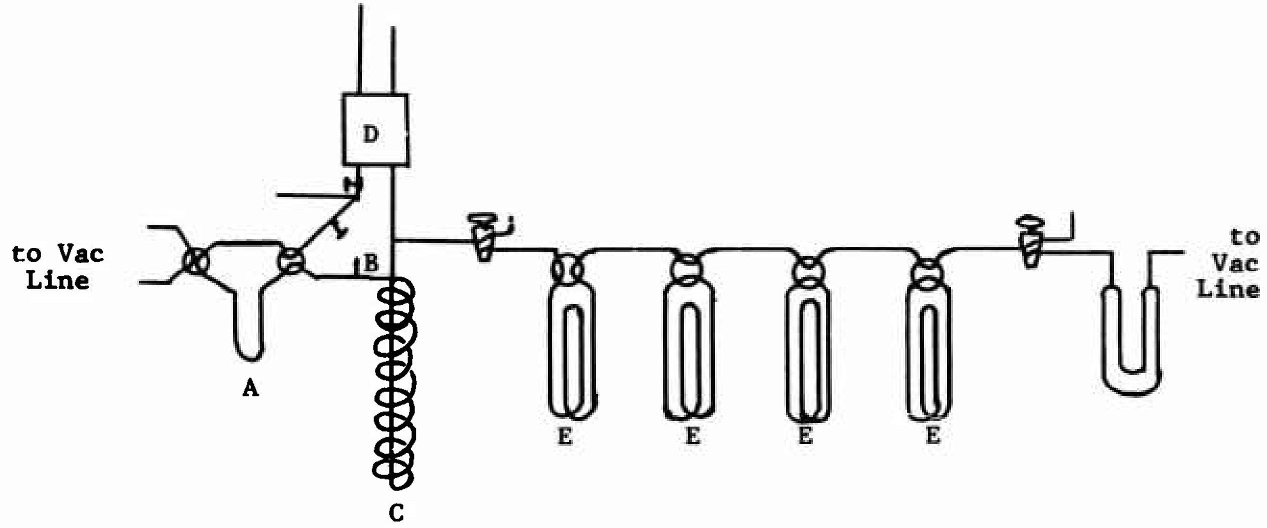


Figure 1 Gas Chromatograph and Collector System

$$T_R = \frac{T_s - T_a}{T_f - T_a} \qquad (36)$$

where T_s, T_a, and T_f refer to the times required for elution of the sample peak, the air peak, and the Freon peak, respectively.

Reactions of OOF or peroxy and trioxy compounds conducted at ambient temperature were usually done in metal of Kel-F reactors. For low temperature experiments (such as O_2F_2 + CF_3OOOCF_3) glass vessels were usually used.

2.5.4.2 Reactions with N_2F_4

Since CF_3OOF was in limited supply, reactions were begun with the trioxide. Attempts to react the trioxide with N_2F_4 at ambient temperature produced no result in several days except the appearance of a very weak nmr line at about -23 ppm. However, at 65°C for 24 hours complete reaction of the trioxide occurred, producing, among other products, predominantly CF_3ONF_2 and CF_3OOCF_3, indentified by infrared and nmr spectra. Smaller amounts of NF_3, SiF_4, COF_2, and NO_2 were identified. After removal of these by reaction with aqueous KOH, and distillation, fairly pure CF_3ONF_2 was obtained. Further purification by gas chromatography yielded a sample whose infrared spectrum was essentially identical with that reported by Shreeve, et. al.[24]. The relative retention volume (T_R) (rel. to $CFCl_3$) was 14 on FC43 (50%). The T_R of CF_3OOOCF_3 on this column was 57 (lit.[28] 60). Nitrogen oxides were evidently not produced directly by the reaction, since the brown color of NO_2 was not present until the gases had been exposed to glass for a few minutes. It is probable that the primary product is NOF and the NO_2 is formed by attack on the Pyrex:

$$4\ NOF + SiO_2 \longrightarrow SiF_4 + 2NO_2 + 2NO \qquad (37)$$

The CF_3OOF-N_2F_4 reaction was conducted at room temperature overnight. Analysis by gas chromatography indicated essentially the same products that were observed for the trioxide-N_2F_4 reaction. Under the conditions of the chromatography, CF_3ONF_2 and CF_3OOCF_3 (T_R=27) were least volatile components, and no heavier materials were seen. The infrared spectrum, of course, was complex, and the separation of products has not been completed. CF_3OOF is obviously much more reaction than CF_3OF, which requires ultraviolet activation, and the failure to isolate CF_3OONF_2 may be due to low stability.

During the course of this work we became aware of work done by Hohorst and Des Marteau[29] on reactions of CF_3OOOCF_3 and CF_3OOF with nitrogen oxides and N_2F_4. Although trifluoromethyl peroxynitrate (CF_3OONO_2) could be prepared in good yield from N_2O_4 or N_2O_5, the nitrate, CF_3ONO_2 could not be found among the products of any of these reactions. Reaction of CF_3OOF yielded CF_3ONF_2, but not CF_3OONF_2, which is surprising, in view of the ease of preparation of CF_3ONF_2 and CF_3OONO_2. We therefore repeated the CF_3OOF-N_2F_4 reaction, monitoring the infrared spectrum continously, since it is possible that CF_3OONF_2 may be formed initially, then decompose during attempted recovery yielding the fragmentation products observed.

At room temperature CF_3OOF reacted fairly rapidly with N_2F_4, yielding essentially the same products as the reaction with the trioxide: NF_3, COF_2, CF_3OOCF_3, CF_3ONF_2 and nitrogen oxides. Since the brown color of NO_2 did not appear until the gases were exposed to glass, it appeared that NO_2 is not a primary product. Experiments were therefore performed in a stainless steel infrared cell at ambient temperature, monitoring the spectrum of the gases periodically.

To a large stainless steel infrared cell, with silver chloride windows, CF_3OOF and N_2F_4 were admitted to a pressure of 25 mm each. Initial impurities were COF_2 and C_2F_6. The infrared spectrum was monitored periodically using a Perkin-Elmer Model 137 spectrophotometer. The following observations were made:

Carbonyl fluoride (principally 5.2μ and 12.8μ) was present as an impurity in the starting materials, and continued to increase slowly throughout the experiment.

Nitrosyl fluoride (NOF) appeared within 1 minute of mixing, and its absorbance gradually increased during the next 10 minutes, until its peaks at 5.4μ were nearly equal to that of COF_2 at 5.2μ. After 1 hour, all NOF absorbances were significantly smaller, and continued to decrease. At 3 hours all were very small, and overnight had disappeared completely.

CF_3ONF_2 appeared in the first minute as a broad low peak at 11.3-11.5μ which increased to a maximum in 10 minutes. The 10.55μ and 13.9μ peaks, which are also characteristic of this compound, were obscured by the presence of N_2F_4 in the early spectra. After 1 hour the disappearance of N_2F_4 revealed their presence.

Most of the CF_3OOF peaks coincide with those of other compounds such as COF_2, and N_2F_4, but the medium peak at 8.4 is characteristic only of this compound. It began to decrease in the first minute and had disappeared completely in 10 minutes.

The peroxide, CF_3OOCF_3 first became evident (at 8.6μ) at 10 minutes, although it may have been partly obscured by the CF_3OOF 8.4 peak before this. No further increase was observed. The broad band at 7.6-8.3μ became resolved, at 10 minutes into a strong peak at 7.7μ and a very strong broad peak at 7.9-8.3μ, due to CF_3ONF_2. CF_3OOCF_3 and COF_2. Before this time, the presence of CF_3OOF (7.8-7.9μ) prevented this resolution.

The very strong broad absorption of N_2F_4 from 9.7 to 11μ and 13.1-14.2 obscured much of the spectrum in the first 10 minutes. After 1 hour however, most of it had disappeared, and the CF_3ONF_2 peaks were now evident, as well as a sharp spike at 9.75μ (SiF_4+CF_3ONF_2) and a broad band peaking at 11μ (NF_3).

Unidentified peaks which appeared were small. One at 6.7μ was sharp, and remained throughout the experiment; a small spike at 12.15μ appeared at 3 minutes and was absent after 1 hour. This may have been due to NO_2F, but its disappearance should have been accompanied by the appearance of NO_2 peaks.

No NO_2 was evident during the first 3 hours, but overnight, a small peak appeared at 6.2μ. After addition of dry air, intense absorption was observed due to NO_2 at 3.4, 4.2, 5.7, 6.2 and 13.3μ.

In a similar experiment, CF_3OOF and N_2F_4 were used at pressures of 40 and 25 mm, respectively. All observations were similar to the above, except that the NOF peaks did not decrease, even on standing overnight. They did disappear, to be replaced by NO_2 peaks, on addition of dry air, however.

It is apparent that the reaction of CF_3OOF with N_2F_4 is fairly rapid, and one of the first products is CF_3ONF_2. NOF is also a very early product, suggesting the mechanism:

$$CF_3OOF + NF_2 \longrightarrow CF_3OO^\cdot + NF_3 \qquad (38)$$

$$CF_3OO^\cdot + NF_2 \longrightarrow CF_3O + ONF_2 \qquad (39)$$

$$CF_3O + NF_2 \longrightarrow CF_3ONF_2 \qquad (40)$$

$$ONF_2 + NF_2 \longrightarrow ONF + NF_3 \qquad (41)$$

The fact that ONF remains when N_2F_4 is not in excess makes it apparent that the following is the only mechanism for its removal:

$$ONF + NF_2 \longrightarrow NO + NF_3 \qquad (42)$$

The NO is obscured by the presence of COF_2 (from decomposition of CF_3O) and appears again as NO_2 on exposure to air. The fact that no NO_2 is seen until this point is strong evidence for the supposition that free oxygen is not present at any time during the reaction from, for example:

$$CF_3OO \longrightarrow CF_3O + O^\cdot \qquad (43)$$

Since it would rapidly produce NO_2 by reaction with NO.

CF_3OOF and N_2F_4 probably react accordingly to the following mechanism:

$$N_2F_4 = 2NF_2 \tag{44}$$

$$CF_3OOF + NF_2 \longrightarrow CF_3OO + NF_3 \tag{45}$$

$$CF_3OO + NF_2 \longrightarrow CF_3O + ONF_2 \tag{46}$$

$$CF_3O + NF_2 \longrightarrow CF_3ONF_2 \tag{47}$$

$$2CF_3O \longrightarrow CF_3OOCF_3 \tag{48}$$

$$CF_3O \longrightarrow CF_2O + F \tag{49}$$

$$NF_2 + F \longrightarrow NF_3 \tag{50}$$

$$ONF_2 + NF_2 \longrightarrow ONF + NF_3 \tag{51}$$

$$ONF + NF_2 \longrightarrow NO + NF_3 \tag{52}$$

The last reaction is presumably fairly slow. The reverse reaction, incidentally, has been used under more extreme conditions to produce N_2F_4 from NF_3.

Attempts were to study the reaction by F^{19} nmr methods in the liquid phase. When equal amounts of N_2F_4 and CF_3OOF were condensed in a KelF nmr tube and held at -78.5°C for several hours, no new lines were seen in addition to those of the reactants. Expansion of the mixture at room temperature produced additional weak resonance lines in the CF_3 region, and at -122.4 ppm (CF_3ONF_2) but nothing new in the latter region.

2.6 Preparation and Characterization of Trifluoro-PAN

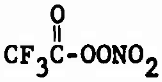
Peroxyacetyl nitrate (PAN) and its homologues are formed when sunlight acts on air which is polluted with trace concentrations of organic compounds and nitrogen oxides. These compounds are of extreme importance since PAN-type compounds are responsible for severe eye irritation and crop damage amounting to millions of dollars.

It was felt that these types of compounds would also be of interest due to the fact that they are potentially high energy materials, which supposedly contain the $-OONO_2$ group. Work on the preparation and characterization of $CF_3C(O)OONO_2$ was begun on this program and this work, as well as other work relating to air pollution problem is now being continued as an NSF program. The combined work will be published shortly.

At the present time, very little data exists on the structure of PAN and its homologues beyond some scattered and incomplete infrared data, proton magnetic resonance (which did not shed light on the structure of PAN) and some mass spectral data. There is difficulty obtaining information on PAN since the compound is difficult to prepare in significant concentrations, is explosive when concentrated, and conventional structural studies have not been conclusive.

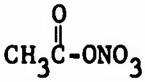
The purpose of this work is the structure determination of PAN and its homologues. The methods to be used are oxygen-17 NMR as well as infrared and other techniques when feasible. As a bonus, it should also be possible to use the oxygen-17 NMR data obtained and the oxygen-17 labeled compounds for gaining insight into the mechanism of PAN formation and decay. Eventually, the refinement of the oxygen-17 NMR method and oxygen-17 tagging should be invaluable in the study of reactions important in understanding air pollution and its control.

Since the structural features of interest all involve the configurations of the oxygen atoms surrounding the nitrogen, it appears that the most suitable approach to elucidation of the structure of this compound is that which will directly give information concerning oxygen atoms. Oxygen-17 nuclear magnetic resonances spectra of appropriately labeled samples should readily distinguish between the three structures which have, at various time, been proposed for this compound:



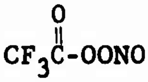
$\mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-OONO_2}$

I



$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-ONO_3}$

II



$\mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-OONO}$

III

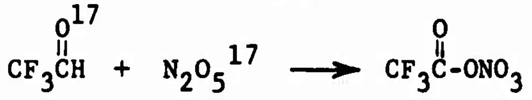
According to E. R. Stephens[30] PAN can be formed in the laboratory by at least four different methods.

1. Photolyses of mixtures of nitrogen dioxide or nitric oxide with organic compounds in air or in oxygen. These reactions apparently simulate the conditions in which PAN is formed in polluted air.
2. Photolysis of alkyl nitrite vapor in oxygen.
3. The dark reaction of aldehyde vapor with nitrogen pentoxide.
4. Peracetic acid can be nitrated in various ways to yield PAN.

Oxygen-17 labeled PAN, and perhaps homologues of PAN, will be prepared by as many reactions as possible. This will not only allow later mechanism studies to be carried out for the various reactions, but will also confirm that the compound formed in all the reactions is the same.

Oxygen-17 is quite expensive, but its cost is not prohibitive in carrying out research. However, it should be remembered that criteria other than those ordinarily used in selecting preparative schemes must sometimes be used. For example, it is necessary to use reactions that will allow recovery of oxygen-17 in by-products or eliminate by-products containing oxygen-17. A system for handling oxygen and products containing oxygen-17 is available at IITRI. After a considerable amount of work, it is now possible to completely recover and recycle oxygen-17 gas. Thus, if the correct preparation schemes are used and oxygen recycled it is possible to derive the most benefit from very small amounts of oxygen-17.

After considerable thought, it was decided that the best technique for the preparation of isotopically labeled PAN is the reaction of aldehyde with N_2O_5



$$CF_3\overset{O^{17}}{\overset{\|}{C}}H + N_2O_5^{17} \longrightarrow CF_3\overset{O}{\overset{\|}{C}}\text{-}ONO_3 \qquad (53)$$

This technique was chosen because the starting material $N_2O_5^{17}$ is readily available, and in reading the literature, it appears to be the best method for the preparation of relatively large amounts of PAN.

The labeled N_2O_5 was prepared as follows:

$$N_2 + O_2{}^{17} \xrightarrow[\text{discharge}]{\text{glow}} NO_2{}^{17} \quad (54)$$

$$O_2{}^{17} \xrightarrow[\text{discharge}]{\text{glow}} O_3{}^{17} \quad (55)$$

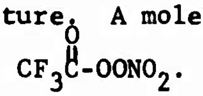
$$NO_2{}^{17} + O_3{}^{17} \longrightarrow N_2O_5{}^{17} \quad (56)$$

Since PAN is not only difficult to prepare but also explosive when in the pure state, it was decided to attempt the preparation of trifluoro PAN, which, it was thought, would be much more stable than the corresponding PAN. This will not only allow the preparative schemes to be developed, but, if trifluoro-PAN is as stable as expected, allow the characterization of this compound. This information will be very valuable in the later characterization of ordinary PAN.

It was predicted that CF_3-PAN would be stable for the following reasons. Whereas peroxides such as CF_3OOCH_3 are incapable of existence, the corresponding perfluoro compound, CF_3OOCF_3, is easily prepared and quite stable. As a matter of fact, even CF_3OOOCF_3 exists and is stable at room temperature.

The preparation of trifluoro-PAN was attempted by allowing CF_3CHO to react with N_2O_5 in the presences of uv light.

The CF_3CHO was prepared by addition of the hemiacetal of CF_3CHO to polyphosphoric acid at 180°C. The product was purified by fractional distillation. The N_2O_5 was prepared by allowing O_3 and NO_2 to react at -78°C. Approximately 1 mmole of N_2O_5 and CF_3CHO were then allowed to react in a Delmar uv apparatus. A reaction occurred almost immediately; brown NO_2 gas was visible, all of the solid N_2O_5 disappeared, and a colorless liquid resulted. The product was fractionated using U-traps maintained at -30, -63, -78, -95, -112 and -196°C. A trace of COF_2 was found in the -196°C trap and the -63 and -78°C traps contained mostly NO_2 along with a small amount of unknown. An unknown -30°C condensate was also found.

This unknown exerted a vapor pressure of 20 mm at room temperature. A molecular weight of 199 was found, compared to 175 for  $CF_3\overset{\overset{O}{\|}}{C}\text{-}OONO_2$. This number may not be accurate since a leak was suspected. The F^{19} NMR spectrum of the unknown exhibited one main line at 82.9 ppm and a small impurity line (CF_3CHO) at 86.1 ppm. The unknown when allowed to react with KI released I_2, indicating the presence of a strong oxidizing agent.

A repeat reaction of CF_3CHO and N_2O_5 was carried out in the absence of uv light, and it was found that the same results were obtained. The M.W. of this sample was found to be 183; this is close to the theoretical 175 for $C_2F_3O_5N$.

The infrared spectrum of this material has been obtained in the vapor state at 5 mm pressure in a 10 cm cell. It is reproduced in Figure 2.

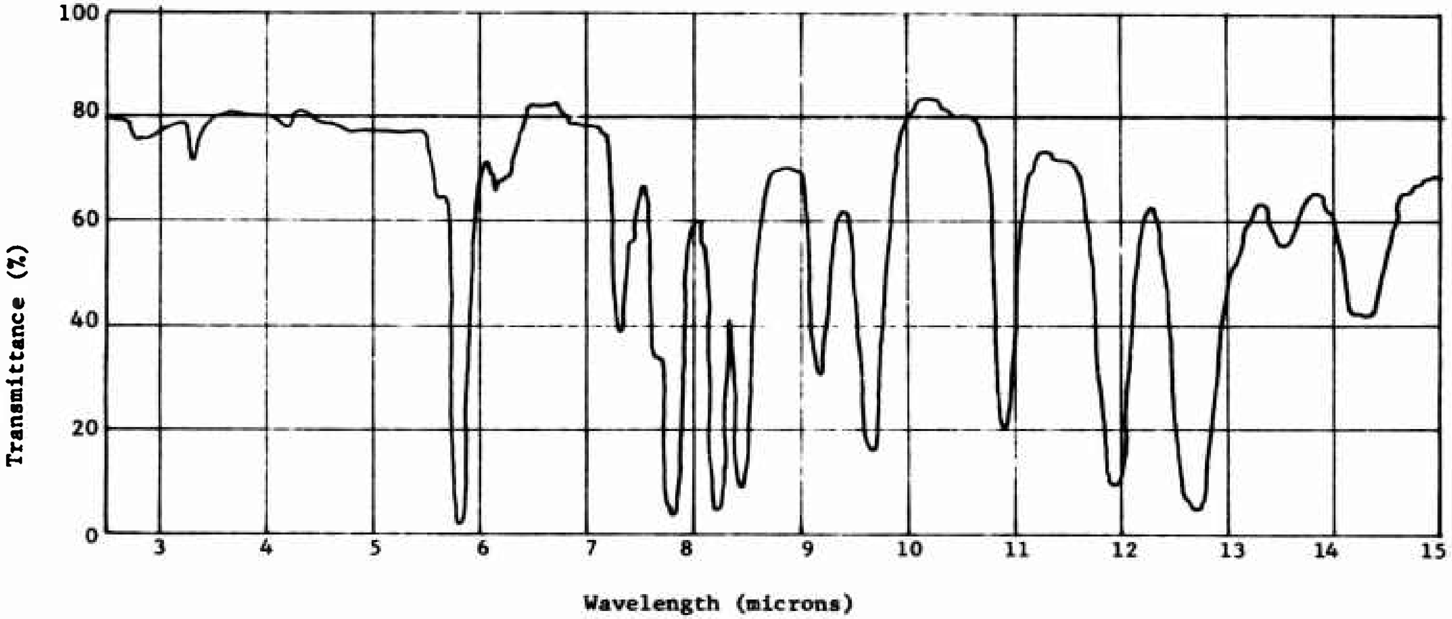


Figure 2

INFRARED SPECTRUM OF CF_3COH - N_2O_5 PRODUCT

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APPENDIX I

THE DECOMPOSITION OF NF_4AsF_6

Irvine J. Solomon, James N. Keith
and Alan Snelson

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THE DECOMPOSITION OF NF_4AsF_6

IRVINE J. SOLOMON, JAMES N. KEITH AND ALAN SNELSON
IIT Research Institute, Chicago, Ill. 60616 (U.S.A.)
(Received December 30, 1971)

SUMMARY

NF_4AsF_6 decomposes smoothly at 175° and above, to the starting materials NF_3, F_2 and AsF_5. The decomposition has been followed by total pressure measurements and found to obey the equation

$$P^{3/2} = At + B$$

This has been interpreted in terms of an equilibrium dissociation step

$$NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5$$

followed by irreversible decomposition of the unstable NF_5

$$NF_5 \rightarrow NF_3 + F_2$$

The latter step is taken to be a 3/2-order reaction:

$$\frac{dP}{dt} = k_1 P_n P_a^{1/2}$$

where P_n is the partial pressure of NF_5 and P_a that of AsF_5. Taking the equilibrium into account, the above equation is integrated to yield

$$P_a^{3/2} - (P_a^0)^{3/2} = 3k_1K_{eq}t/2$$

An attempt to identify NF_5 in the products by matrix isolation methods yielded, besides the expected NF_3 and AsF_5, an unknown minor product which appeared not to contain nitrogen.

INTRODUCTION

The stability of the recently reported tetrafluoroammonium salts[1,2] is quite remarkable in view of the low basicity of difluoramine[3,4] and the absence of detectable basic properties in nitrogen trifluoride[4]. The existence of such salts is particularly interesting since the conjugate base, nitrogen pentafluoride, is not known, and is expected to be extremely unstable. The case is analogous to that of the dioxygenyl salts, such as O_2BF_4, which have been shown[5] to be derived from the very unstable base O_2F:

$$O_2F + BF_3 \rightarrow O_2BF_4 \tag{1}$$

We thus have stable salts of very unstable bases, which can be prepared only by the use of forcing conditions, such as glow discharge or high-pressure methods.

As in the case of the dioxygenyl salts, neither synthetic route is conducive to kinetic studies, but it is possible to obtain some kinetic information on the thermal decomposition by pressure measurements. As with O_2BF_4, the kinetic data indicated the existence of an equilibrium dissociation which controls the rate of decomposition.

Attempts were made to obtain infrared spectra of primary dissociation products by matrix isolation techniques, but it was not possible to draw definite conclusions.

EXPERIMENTAL

Materials and equipment

All synthetic work and the kinetic and isotopic exchange studies were performed in metal vacuum lines of the type used for reactive fluorine compounds. Transfers of solid NF_4AsF_6 were made in a nitrogen-filled dry box.

Nitrogen trifluoride was purchased from Air Products and Chemicals, Inc. and arsenic pentafluoride from Ozark-Mahoning Co. Fluorine (Matheson Co.) was passed through sodium fluoride prior to use. Isotopically enriched nitrogen (95% ^{15}N, Merck Sharpe and Dhome) was fluorinated in a glow discharge reaction[6] at −196° to form $^{15}NF_3$.

Preparation of NF_4AsF_6

NF_4AsF_6 was prepared in a glow-discharge reaction at −80° using a reactant ratio of $F_2:NF_3:AsF_5 = 1.5:1:1$. The Pyrex glow-discharge tube was evacuated and removed from the vacuum line by sealing the connecting tubing, and opened in a dry box to transfer the contents. Analysis of the thermal decomposition products indicated the presence of NF_3, F_2 and AsF_5 in equal amounts. Hydrolysis produced a 2:1 mixture of NF_3 and O_2.

Kinetic measurements

The thermal decomposition of NF_4AsF_6 was followed by measurement of the total pressure in a passivated 100 cc Monel cylinder by means of a Wallace-Tiernan FA145-780 vacuum gauge. The cylinder was heated with a 1650 W, 10 × 30 cm Lindberg Hevi-Duty tube furnace, using a copper–constantan control thermocouple. A record of the temperature of the sample (by means of a thermocouple taped directly to the cylinder) was kept on a Varian millivolt recorder.

Infrared spectra

The infrared spectra of the starting materials and of the decomposition products were recorded using a Perkin–Elmer Model 621 Grating Spectrophotometer. Conventional matrix isolation equipment was used consisting of a cesium iodide window mounted in a copper block attached to a cold finger which can be rotated to position the window. The Dewar was of metal construction, the outer jacket being filled with liquid nitrogen surrounding the liquid helium-filled cold finger. The furnace consisted of a 3 mm × 2.5 cm platinum tube heated by induction. The temperature was measured by means of a thermocouple.

RESULTS AND DISCUSSION

As in the similar case of O_2BF_4, the rate of decomposition of NF_4AsF_6 in a sealed container decreases steadily during the reaction the initial rate being restored upon removal of the decomposition products by evacuation. The data are well represented by the equation

$$P^{3/2} = At + B \qquad (2)$$

and are presented in Tables 1–7.

TABLE 1

DECOMPOSITION OF NF_4AsF_6 AT 175°

T (min)	P (mmHg)
0.0	0.0
2.8	0.7
11.2	1.3
16.9	1.7
27.2	2.2
38.4	2.7
64.7	3.7
127.0	5.7

$A = 0.106$, $B = 0.290$, $r = 0.9995$*.

* A and B are the coefficients of equation (2), as determined by the treatment of the data by the method of least squares, using program number 09100-70803 for the Hewlett-Packard Model 9100B Electronic Calculator. The correlation coefficient, r, was determined using the same program.

TABLE 2

DECOMPOSITION OF NF_4AsF_6 AT 195°

T (min)	P (mmHg)
0.0	0.3
0.5	0.7
2.1	1.7
4.1	2.7
6.9	3.7
10.0	4.7
13.7	5.7
18.4	6.7
32.8	9.7
45.0	11.7
57.8	13.7
78.7	16.7
93.3	18.7
126.7	22.7

$A = 0.852$, $B = 1.18$, $r = 0.9999$.

TABLE 3

DECOMPOSITION OF NF_4AsF_6 AT 205°

T (min)	P (mmHg)
0.0	0.3
0.2	0.7
1.0	1.7
2.0	2.7
4.5	4.7
6.2	5.7
12.1	8.7
14.1	9.7
27.3	14.7
36.4	17.7
42.4	19.7
49.3	21.7
60.3	24.7
80.8	29.7
93.6	32.7
102.8	34.7
131.7	40.7

$A = 1.98$, $B = 1.57$, $r = 0.9999$.

TABLE 4

DECOMPOSITION OF NF_4AsF_6 AT 218.5°

T (min)	P (mmHg)
0.0	0.6
1.1	4.7
3.1	9.7
5.9	14.7
10.8	21.7
15.0	26.7
18.6	30.7
22.5	34.7
31.5	42.7
40.7	49.7
47.5	54.7
54.7	59.7
64.5	65.7
71.0	69.7
80.0	74.7
89.9	79.7
100.2	84.7

$A = 7.99$, $B = 10.55$, $r = 0.9988$.

TABLE 5

DECOMPOSITION OF NF_4AsF_6 AT 222°

T (min)	P (mmHg)
0.0	0.6
1.0	5.7
2.1	8.7
4.6	14.7
7.3	19.7
10.5	24.7
14.2	29.7
18.2	34.7
28.0	44.7
34.8	50.7
39.6	54.7
46.0	59.7
52.8	64.7
59.6	69.7
67.5	74.7
75.6	79.7

$A = 9.65$, $B = 11.96$, $r = 0.9987$.

TABLE 6

DECOMPOSITION OF NF_4AsF_6 AT 222°
IN THE PRESENCE OF AsF_5

T (min)	P (mmHg)
0.0	99.0
24.9	107.7
30.0	110.0
43.9	115.0
57.0	120.0
85.7	130.0
114.6	140.0
180.0	161.0
240.0	178.6

$A = 9.15$, $B = 5082$, $r = 0.9997$.

TABLE 7

DECOMPOSITION OF NF_4AsF_6 AT 222°
IN THE PRESENCE OF NF_3

T (min)	P (mmHg)
0.0	111.5
4.3	113.0
7.4	114.0
9.9	115.0
12.2	116.0
17.2	118.0
22.3	120.0
27.7	122.0
35.5	125.0
44.0	128.0
58.7	133.0
71.5	137.0
84.3	141.0
100.3	145.0
131.9	153.0

$A = 2.77$, $B = 43.7$, $r = 0.9997$.

It is evident that an equilibrium step is involved in the decomposition reaction, just as with the dioxygenyl salts *. It is extremely unlikely that the synthetic reaction

$$NF_3(g) + F_2(g) + AsF_5(g) = NF_4AsF_6(s) \qquad (3)$$

is involved here, considering the rather extreme conditions required for this reaction. It is more likely that an equilibrium dissociation step is involved.

$$NF_4AsF_6(s) \rightleftharpoons NF_5(g) + AsF_5(g) \qquad (4)$$

This is followed by decomposition of the unstable NF_5

$$NF_5 \xrightarrow{k_1} NF_3 + F_2 \qquad (5)$$

The form of equation (2) indicated that this step must be considerably more complex than indicated by equation (5). A 3/2-order reaction will produce the correct results **:

---

* In most of the experiments the first couple of points were lower than those calculated from the rate constants. This initial departure from linearity can probably be attributed to the fact that early in the experiment the deviation from equilibrium is greatest, and therefore the rate of the reaction is greater, since in this region it is less controlled by the dissociative equilibrium.

** The fractional order itself suggests the involvement of fluorine atoms in steps such as: $NF_5 + M \rightarrow NF_4 + F + M$, *etc.* Equations were derived from rate equations such as
$dP/dt = kP_{NF_5}P_{NF_3}{}^{1/4}$ and $dP/dt = k_{NF_5}P_{NF_2}{}^{1/2}$.

Neither of these equations gave straight lines with the data for the experiments with excess AsF_5 or NF_3. Equation (6), however, did produce a good fit with the data, indicating a half-order dependence on AsF_5. Heterogeneous reactions, however, also often follow fractional-order kinetics.

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_1 P_n P_a^{1/2} \tag{6}$$

where P_n = NF_5 pressure and P_a = AsF_5 pressure. Since P_n is controlled by the equilibrium, $P_n = K_{eq}/P_a$, and

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_1 K_{eq} P_a^{-1/2} \tag{7}$$

Taking $\mathrm{d}P = \mathrm{d}P_a$, and integrating

$$P_a^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \tag{8}$$

In terms of the experimental quantities

$$\frac{\sqrt{3}}{9} (P_T + 2P_a^0)^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \tag{9}$$

except for the experiment in which NF_3 was added:

$$\frac{\sqrt{3}}{9} (P_T - P_c)^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \tag{10}$$

where P_c is the calculated partial pressure due to the NF_3 added at the beginning of the experiment and P_T is the total pressure.

The rate constant cannot be determined separately from the equilibrium constant. The products of the constants $k_1 K_{eq}$ presented in Table 8 can be computed from the slopes of $(P_T + 2P_a^0)^{3/2}$ or $(P_T - P_c)^{3/2}$ versus t. An Arrhenius plot of these products was linear and yields, for the sum of the overall heat of sublimation and the activation energy for the decomposition of NF_5, a value of 41 kcal mole^{-1}.

In an attempt to obtain support for the postulate that NF_5 is present as an intermediate, matrix isolation studies were performed with NF_4AsF_6.

TABLE 8

KINETIC CONSTANTS

Temperature	$10^6 k_1 K_{eq}$ *
175	3.78
195	28.5
205	64.1
218.5	248
222	296
222 (AsF_5)	281
222 (NF_3)	85.1

* Mole$^{3/2}$liter$^{-3/2}$sec^{-1}.

Reference spectra of NF_3 and AsF_5 were obtained and compared with the literature[9,10]. The spectra were in satisfactory agreement and no evidence of significant impurities was seen. Several runs were made with NF_4AsF_6, decomposing at different temperatures. The results are shown in Table 9.

TABLE 9

INFRARED SPECTRA IN NEON MATRIX

Frequency (cm^{-1})				
$^{14}NF_4AsF_6$	$^{15}NF_4AsF_6$	$^{14}NF_3$	$^{15}NF_3$	AsF_5
1049	1043			
1027	1026	1027	1027	
	1003.5		1004	
899	898.5	899	899	
	878.5		878	
827	822.5			
809	808			809
782	782			782.5
		642	638	
489		490	489	
398	397.5			398
367	367			367
332	331			
309	307			

In the experiments which produced strong spectra, new peaks were observed at 1049, 827, 332 and 309 cm^{-1}, which did not appear to be due to overtones, matrix effects, *etc.* A search of the literature did not disclose a likely impurity to which these peaks could be attributed.

Examination of the spectra of the products from $^{15}NF_4AsF_6$, however, revealed the presence of the same new peaks with the same relative intensities. The fact that no isotopic shift is observed indicates that the source of these peaks is not a nitrogen compound derived from the NF_4AsF_6 but an impurity common to the two samples, or resulting from interaction of the decomposition products with the materials of the apparatus. We have not been able to identify this impurity nor has any evidence of NF_5 been found.

CONCLUSIONS

NF_4AsF_4 decomposes smoothly above 175° at a rate which decreases as the reaction proceeds, in a manner similar to that of O_2BF_4. The data can be correlated with a mechanism consisting of an equilibrium dissociation

$$NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5 \quad (4)$$

followed by decomposition of NF_5

$$NF_5 \rightarrow NF_3 + F_2 \quad (5)$$

This process must be somewhat more complex than indicated above since the data indicate that the overall order is 3/2. A process which is first order in NF_5 and 1/2 order in AsF_5 will fit the data.

$$\frac{dP}{dt} = k_1 P_n P_a^{1/2} \quad (6)$$

The implication of this mechanism (that NF_5 exists as an intermediate in this process) was not supported by matrix isolation studies. It would be expected, however, to be very unstable and to have only transitory existence.

ACKNOWLEDGEMENT

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APPENDIX II

EXCHANGE STUDIES WITH NF_4AsF_6

**J. N. Keith, I. J. Solomon, I. Sheft
and H. Hyman**

**Submitted to:
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EXCHANGE STUDIES WITH NF_4AsF_6

by

J. N. Keith, I. J. Solomon, I. Sheft, and H. Hyman
IIT Research Institute, Chicago, Illinois 60616 (USA)
Argonne National Laboratory, Argonne, Illinois 60440 (USA)

SUMMARY

Isotopic exchange experiments have been conducted with the salt NF_4AsF_6 and gaseous $^{76}AsF_5$, $As^{18}F_5$, $^{18}F_2$, $^{15}NF_3$ and $N^{18}F_3$. Exchange of the flourine atoms of AsF_5 is believed to occur via the less volatile complex salt $NF_4As_2F_{11}$. Evidence for the existence of this salt is presented in the form of pressure composition data.

EXCHANGE STUDIES WITH NF_4AsF_6

INTRODUCTION

Of the many novel highly fluorinated ions reported in recent years, one of the most interesting is the perfluorammonium ion,[1,2] NF_4^+, which is surprisingly stable in the presence of AsF_6^-, SbF_6^- and BF_4^-, although the corresponding "base" is expected to be extremely unstable.

In an earlier paper we have reported indirect evidence[3], from the kinetics of thermal decomposition of NF_4AsF_6, which implies the existence of NF_5 in a reversible dissociative equilibrium of the type:

$$NF_4AsF_6(s) = NF_5(g) + AsF_5(g) \qquad (1)$$

although matrix isolation techniques failed to disclose the presence of NF_5 in the pyrolysis products. In their recent paper[4] on NF_4BF_4, Wilson, et. al. present data suggesting the formation of NF_5 by irradiation of nitrogen trifluoride-fluorine mixtures at low temperatures. Unfortunately, only very small amounts were obtainable, and they were unable to obtain direct physical evidence due to the low stability of their product.

In an attempt to obtain further information on this interesting problem, we have conducted isotopic exchange studies with NF_4AsF_6.

If the equilibrium given above is important under the conditions of the exchange, fluorine from ^{18}F labelled AsF_5 will appear in the NF_5, via the following process:

$$NF_4AsF_6 + AsF_5^* = NF_4AsF_6^* + AsF_5 \qquad (2)$$

$$NF_4AsF_6^* = NF_4F^* + AsF_5^* \qquad (3)$$

If the five fluorine atoms of NF_5 are in any way interchangable the ^{18}F will appear eventually in the NF_4^+ ion, and this can be taken as evidence of the existence of NF_5 as an intermediate.

EXPERIMENTAL

Materials and Equipment

Experiments were performed in metal vacuum lines of the type used for reactive fluorine compounds. Transfer of solid NF_4AsF_6 were made in a nitrogen-filled dry box.

Synthesis of NF_4AsF_6 has been described previously. Experiments with radioactive arsenic and fluorine isotopes were performed at Argonne National Laboratory, using the same equipment and procedures as in our O_2BF_4 study[5]. Labelled AsF_5, F_2, or NF_3 were condensed onto samples of NF_4AsF_6 (2-3 mmoles) in sufficient quantity (about 3 mmoles) to produce a pressure of 3 atmospheres at room temperature. In the experiments with radioactive isotopes the volatile material was removed quantitatively from the reactor on termination of the experiment and its activity counted, as well as the activity of the solid NF_4AsF_6.

In the case of $^{15}NF_3$, the reaction vessel was periodically opened to remove a small amount of vapor for determination of the $^{14}N/^{15}N$ ratio.

DISCUSSION

The results of the isotopic exchange experiments are summarized in Table 1. Clearly, AsF_5 exchange occurs readily, and the fluorine atoms do not appear in the NF_4^+ ion. The lack of F_2 and $^{15}NF_3$ exchange definitely rule out any exchange via the synthetic process

$$NF_3 + F_2 + AsF_5 = NF_4AsF_6 \qquad (4)$$

the limited nature of this exchange could be taken to signify that the labelled fluorine, in the hypothetical NF_5 of the dissociation step is never actually never bound to nitrogen,

$$NF_4AsF_6^* = NF_4F^* + AsF_5^* \qquad (3)$$

or at least, is not equivalent with the other four fluorine atoms, and simply returns to arsenic on recombination. One of the striking features of this exchange, however is the rapid rate. Complete exchange in three hours at room temperature is considerably more than might be expected of a gas-solid reaction with such a mechanism as proposed in (2) and (3). Another very likely possibility is indicated by some spectroscopic data of Christe and Pavlath[6], who found, in a part of a sample of NF_4AsF_6 prepared by the high pressure method, additional infrared bands which they attribute to the presence of the AsF_{11}^- ion.

Table 1

ISOTOPIC EXCHANGE EXPERIMENTS WITH NF_4AsF_6

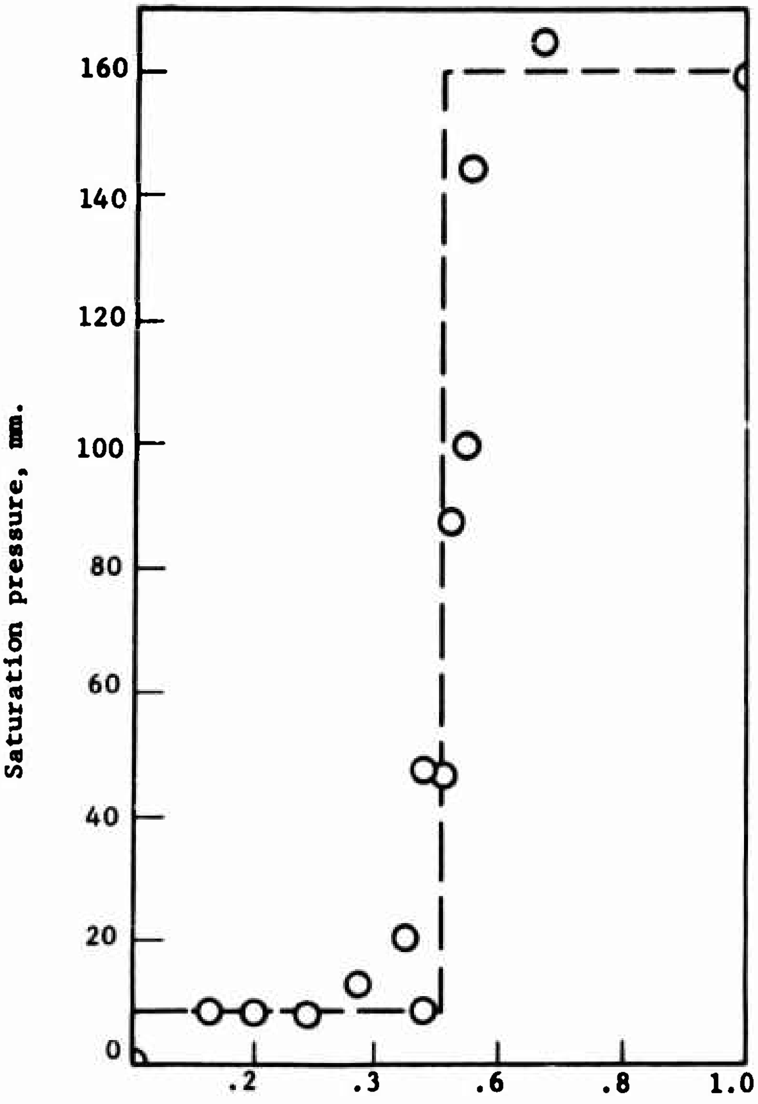
NF_4AsF_6, mmol	Vapor, mmol	Isotope	Time	Result
2.28	2.95 AsF_5	^{16}As	3 hr	100% exchange
2.20	3.01 AsF_5	^{18}F	3 hr	105% based on 6 atoms
2.20	3.00 F_2	^{18}F	3 hr	no exchange
2.20	3.03 NF_3	^{18}F	3 hr	100% based on 1 atom
2.20	3.02 NF_3	^{18}F	3 hr	100% based on 1 atom
2.47	2.45 NF_3	^{15}N	7 days	no exchange

Christe's data however, seem to indicate that $NF_4As_2F_{11}$ is quite stable, in contradiction to the fact that it has not been observed in other spectroscopic results, and the AsF_5 is usually quantitatively recovered rather easily in the exchange experiments. We therefore decided to examine the stability of this compound by means of a pressure-composition study. The results are shown in Figure 1. The saturation pressure of AsF_5 over the solid is dramatically reduced (8 mm at -78.5°C, compared with 160 mm for liquid AsF_5), indicating fair stability for the adduct. Equilibrium is reached fairly rapidly at -78.5°C at AsF_5 mole fractions less than 0.3, but approach to equilibrium is very slow near $x=0.5$ and at higher temperatures. The break at $x=0.5$ is reproduced on removal of AsF_5. For this reason complete curves were not obtained except at -78.5°C. Saturation pressure at mole fractions between 0.1 and 0.2 for other temperatures are 15.8 mm at -63.5°C and 27.0 at -45.2°C. From the slope of the Arrhenius plot:

$$\log_{10} P_{mm} = \frac{-703.3}{T} + 4.529 \qquad (5)$$

a heat of dissociation of 3.2 kcal/mole can be calculated for the process:

$$NF_4As_2F_{11} = NF_4AsF_6(s) + AsF_5(g) \qquad (6)$$



Mole Fraction AsF_5

Figure 1

NF_4AsF_6 - AsF_5 System

The saturation pressure at 25°C is estimated to be about 150 mm, so that under the conditions of the exchange experiments extensive formation of $NF_4As_2F_{11}$ is to be expected.

The partial exchange of $N^{18}F_3$ is somewhat difficult to rationalize in view of the lack of exchange with $^{15}NF_3$, but a fluorine bridged intermediate may be involved, analogous to $As_2F_{11}^-$.

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APPENDIX III

AMMONIUM PERBROMATE

J. N. Keith and I. J. Solomon

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Ammonium Perbromate

BY JAMES N. KEITH AND IRVINE J. SOLOMON

Contribution from IIT Research Institute,
Chicago, Illinois 60616

Ammonium Perbromate

By James N. Keith and Irvine J. Solomon

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Perbromic acid and alkali metal perbromates have recently been isolated and characterized.[1,2] The perbromates are chemically similar to the perchlorates, although somewhat less stable. An interesting difference is that the order of stability of the alkali metal salts is $MBrO_3 > MBrO_4$, while the reverse is true of the chlorine compounds, $MClO_3 < MClO_4$.

Ammonium chlorate (NH_4ClO_3) also is less stable than its perchlorate.[3] However, since the mechanism of decomposition is much more complex in this case, it is not possible to predict the stability of ammonium perbromate (NH_4BrO_4) from that of the bromate, which explodes on heating.[4] It was of considerable interest to us, therefore, to determine whether ammonium perbromate is sufficiently stable to isolate and to compare its physical and chemical properties with those of the perchlorate, especially its stability and mode of decomposition.

Experimental Section

Synthesis.—A sample of 3 *M* perbromic acid was generously supplied by E. Appelman, Argonne National Laboratory. Its synthesis and analysis have been described.[2] This solution was chilled and carefully neutralized with excess concentrated aqueous ammonia. The solution was evaporated at room temperature, and the solid was dried over P_2O_5 in a vacuum desiccator. Before use, the product was recrystallized from water. NH_4BrO_4 is neither shock nor friction sensitive.

Analysis.—The salt was analyzed for NH_4^+ by the hypobromite method[5] and for BrO_4^- by the method described by Appelman.[2] *Anal.* Calcd for NH_4BrO_4: NH_4^+, 11.5; BrO_4^-, 88.5. Found: NH_4^+, 11.1; BrO_4^-, 85.2.

Titration of a separate sample in 0.01 *M* acid and 0.1 *M* acid with molybdate gave values for the hypobromite and bromate contents of 1.0 and 0.6%, respectively. These are upper limits only, of course, because of the slow reduction of perbromate under these conditions. No precipitate was observed when 1 *M* $AgNO_3$ was added to a solution of NH_4BrO_4. The bromide content is believed to be less than 0.1%.

Infrared Spectrum.—The infrared spectrum of ammonium perbromate was examined by means of a Perkin-Elmer Model 621 grating infrared spectrophotometer. The sample was mulled with Nujol and supported between KBr disks. Strong bands were observed at 870 and 405 cm^{-1}, with a tiny, sharp peak at 795 cm^{-1} (on the edge of the former broad band). Appelman[2] reported ν_1, 798 cm^{-1}; ν_3, 883 cm^{-1}; ν_4, 410 cm^{-1}. No bands attributable to BrO_3^- were observed near 800 or 420 cm^{-1}.

Solubility.—The solubilities of NH_4BrO_4 in water and in several organic solvents were determined by weighing 1-ml aliquots of the saturated solutions.

Decomposition.—Preliminary decomposition experiments were performed with very small samples in melting point capillaries. Thermograms were obtained using a Fisher differential thermalyzer, Model 260, with a heating rate of 5°/min. Each 25-mg sample was diluted with 75 mg of Al_2O_3.

X-Ray Diffraction.—Powder patterns were obtained by the Geiger counter-goniometer method, using a Philips Norelco instrument. Copper Kα radiation (nickel filter) was employed. Samples were ground to <325 mesh and sifted into $^1/_{16}$ in. deep rectangular aluminum cells. The spectrum was scanned from $2\theta = 50$ to 5° at 1°/min.

Results

Ammonium perbromate is stable at room temperature and has solubilities similar to the perchlorate (Table I). Heats of solution in water calculated from the data in Table I are 4.4 kcal/mol for NH_4BrO_4 and 3.9 kcal/mol for NH_4ClO_4.

Table I

Solubility of NH_4BrO_4 and NH_4ClO_4

Solvent	Temp, °C	Solubility[a]	
		NH_4BrO_4	NH_4ClO_4[b]
Water	0.0	9.5	10.74
Water	15.0	13.9	...
Water	25.0	17.8	20.02
Water	45.0	26.3	28.02
Methanol	25.0	8.22	6.862
Ethanol	25.0	2.94	1.907
Acetone	25.0	3.22	2.26
Acetonitrile	25.0	1.36	...

[a] Solubility in H_2O in grams per 100 g of solution. Solubility in organic solvents in grams per 100 g of solvent. [b] Data for NH_4ClO_4 from J. C. Schumacher, "Perchlorates," Reinhold Publishing Corp., New York, N. Y., 1960.

NH_4BrO_4 is much less hygroscopic than NH_4ClO_4, although in humid atmospheres the perbromate does tend to "cake" slightly. Thus at 95% humidity, a 500-mg sample of NH_4BrO_4 gained 20 mg (4%) in the first 4 days, after which its weight remained approximately constant. A similar NH_4ClO_4 sample, however, gained a total of 115 mg (23%) in 4 weeks and was visibly wet.

NH_4BrO_4 begins to decompose around 170-180°, smoothly in most cases, although explosions sometimes occur. In one case, observed visually, dense brown fumes (Br_2) appeared at 176°, and the clear crystals became opaque. The decomposition seemed to subside until the sample gradually disappeared at 295° without melting or subliming.

NH_4BrO_4 exhibited two exotherms, a sharp one at 186° and a broad one beginning at 209°, with a small inflection at 228°. On one occasion, a 75-mg sample exploded upon reaching the 186° exotherm. For comparison, thermograms of NH_4ClO_4 were obtained under identical conditions. NH_4ClO_4 exhibited an endotherm at 239° (orthorhombic–cubic transition)

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(1) E. H. Appelman, *J. Am. Chem. Soc.*, 90, 1900 (1968).

(2) E. H. Appelman, *Inorg. Chem.*, 8, 223 (1969).

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(4) P. J. M. Radford in "Bromine and Its Compounds," Z. E. Jolles, Ed., Academic Press, New York, N. Y., 1966, p 165.

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, Chapter XL.

and two exotherms, a small one at 344° and a large one at 356°.

Although a substantial temperature difference exists between the two NH_4BrO_4 exotherms and no activity was observed in the sample after the first step in the decomposition, slow decomposition continues at the lower temperature when the sample is heated in a sealed tube, probably due to catalysis by the decomposition products. Thus a 70.4-mg sample, heated overnight at 170°, decomposed only partly but decomposed completely when heated at 260°. Another sample (1.80 mmol) decomposed completely in 3 days at 170°, leaving no solid residue. The major products were N_2 (0.58 mmol), O_2 (1.09 mmol), Br_2 (0.9 mmol), and H_2O (not measured), with small amounts of N_2O (0.1 mmol) and NO_2 (estimated 0.2 mmol). Thus the decomposition of NH_4BrO_4 more closely resembles that of NH_4BrO_3 (N_2, Br_2, O_2, H_2O) than that of NH_4ClO_4 (little N_2, nitrogen oxides major products).

TABLE II

X-RAY POWDER DATA FOR NH_4BrO_4

d, Å			
Obsd	Calcd	Intens	*hkl*
5.85	5.87	50	101
5.24	...	4	...[a]
4.77	4.74	100	011
4.60	4.60	41	200
4.21	4.21	8	111
3.94	3.92	72	201
3.810	3.815	55	002
3.660	3.659	90	210
3.517	3.524	25	102
3.302	3.298	70	211
3.038	3.044	82	112
2.938	2.936	32	202
2.685	2.686	32	121
2.642	2.641	43	212
2.450	2.451	9	103
2.398	2.397	6	221
2.295	2.300	24	400
	2.293		122
2.209	2.222	37	401
	2.202		312
2.159	...	7	...[a]
2.106	2.105	5	222
2.088	2.088	3	213
1.905	1.905	28	004
	1.903		123
1.877	1.873	15	412
1.865	1.862	12	313

[a] Denotes impurity.

However, firm conclusions about the stability or modes of decomposition of these salts must await the synthesis and purification of larger samples of both NH_4BrO_4 and NH_4BrO_3.

The powder diffraction spacings, presented in Table II, are correlated on the basis of an orthorhombic unit cell, with $a = 9.20$ Å, $b = 6.04$ Å, and $c = 7.63$ Å; the density, based on four molecules in the unit cell, is 2.54 g/cm^3 (by flotation, 2.5 g/cm^3). $KBrO_4$ is also orthorhombic,[6] as are NH_4ClO_4 and several metal perchlorates.

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