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Report No. IITRI-C227-7 & 8
(Technical Summary Report)

RESEARCH ON CHEMISTRY OF O_3F_2 AND O_2F_2

Air Force Office of Scientific Research
Washington, D. C.

IIT RESEARCH INSTITUTE

Report No. IITRI-C227-7 & 8
(Technical Summary Report)

RESEARCH ON CHEMISTRY OF O_3F_2 AND O_2F_2

January 1 through June 30, 1964

Contract No. AF 49(638)-1175
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Prepared by

Irvine J. Solomon

of

IIT RESEARCH INSTITUTE
Technology Center
Chicago 16, Illinois

for

Air Force Office of Scientific Research
Washington 25, D. C.

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September 1, 1964

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FOREWORD

This is Report No. IITRI-C227-7 and C227-8, Technical Summary Report No. 7 and 8, which covers the period from January 1 through June 30, 1964, on IITRI Project C227, Contract No. AF 49(638)-1175, entitled, "Research on Chemistry of O_3F_2 and O_2F_2 ."

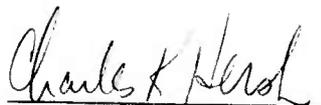
This research is being supported by the Advanced Research Projects Agency under ARPA Order No. 350-62, Project Code No. 9100. Technical Direction is being provided by the Director of Engineering Sciences, SREP, Air Force Office of Scientific Research.

In addition to the author, who is the principal investigator, personnel contributing to the program include: R. I. Brabets, Research Engineer; J. Keith, Research Chemist; R. Uenishi, Research Chemist; J. Finn, Associate Chemist; A. Kacmarek, Associate Chemist; J. Raney, Associate Physicist; R. Douthart, Assistant Chemist; G. Macur, Assistant Chemist; and W. Sumida, Assistant Chemist.

Respectfully submitted,

IIT RESEARCH INSTITUTE

Approved by:



Charles K. Hersh
Manager
Propellant Research

IJS:pfb



Irvine J. Solomon
Senior Chemist
Propellant Research

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RESEARCH ON CHEMISTRY OF O_3F_2 AND O_2F_2

I. INTRODUCTION

The following are the major objectives of this program:

- (1) the elucidation of the chemistry of O_3F_2 and O_2F_2 with inorganic compounds,
- (2) the study of the physical properties of O_4F_2 as a means of revealing the presence or absence of ionic species in O_4F_2 ,
- (3) the determination of the oxidizing species remaining in solution after fluorination of nitric acid,
- and (4) the determination of the feasibility of preparing new ions of the type NF_4^+ and $NH_2F_2^+$.

II. RESULTS AND DISCUSSION

A. NF_4^+ , $N_2F_5^+$, and $H_2NF_2^+$ Ions

The formation of ionic species such as NF_4^+ and $N_2F_5^+$ depends on several factors. For example, an important prerequisite for the formation of NF_4^+ is certainly the availability of unshared electrons in the parent compound, another is the nature of the attacking electrophile. Probably the solvation of these ions is also an important factor. An answer to the question of whether these ions can exist must be based on a detailed study of these factors. This study is in progress, and the significant results which have been obtained are summarized below.

1. Difluoramine Additives

The reactions of difluoramine and methyl difluoramine with various acids are being studied in order to estimate the base strength of these amines. Although difluoramine is a very weak base, it does form compounds with strong acids such as BF_3 and PF_5 . In each of these systems, however, no useful thermodynamic data can be obtained which would enable us to quantitatively determine the base strength of the amine. In the vapor phase $\text{HNF}_2\text{-BF}_3$ is too highly dissociated for the dissociation equilibrium to be examined, and irreversible decomposition occurs in the $\text{HNF}_2\text{-PF}_5$ system.¹ Methyl difluoramine also forms compounds with these acids, but irreversible decomposition to HCN , HF , etc. readily occurs.²

We have examined the behavior of difluoramine with several other acids, namely, hydrogen chloride, sulfur trioxide, trimethyl aluminum, and trimethyl gallium, and work on methyl difluoramine and these acids has been initiated.

a. Hydrogen Chloride

A pressure composition study of the $\text{HNF}_2\text{-HCl}$ system (from -138 to -112°C) showed only positive deviations from Raoult's Law, indicating no interaction (Figure 1). Strong negative deviations were observed

¹Hercules Powder Co., Contract No. DA-31-124-ARO(D)-62, Quarterly Report No. 1, June 15, 1963.

²Ibid., Quarterly Report No. 3, December 16, 1963.

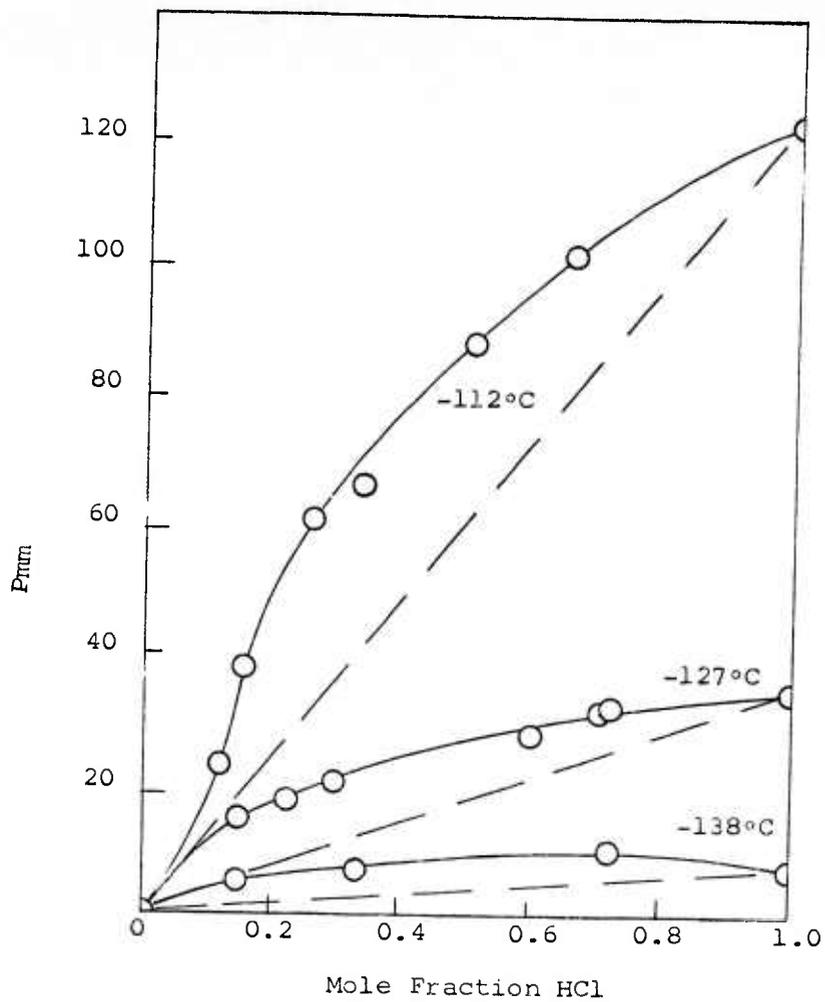
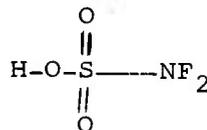


Figure 1
 THE HNF₂-HCl SYSTEM

with methyl difluoramine, and at -127°C , the formation of a weak 1:1 additive was indicated (Figure 2). During the study of the compatibility of methyl difluoramine with mercury a sealed Pyrex tube containing these two components exploded violently while it was being shaken.

b. Sulfur Trioxide

It has been reported that HNF_2 and SO_3 form a 1:1 compound and possibly a 1:2 compound.³ The pressure composition diagram shown in Figure 3 was obtained at 0°C . The proton and F^{19} NMR spectra show the structure to be

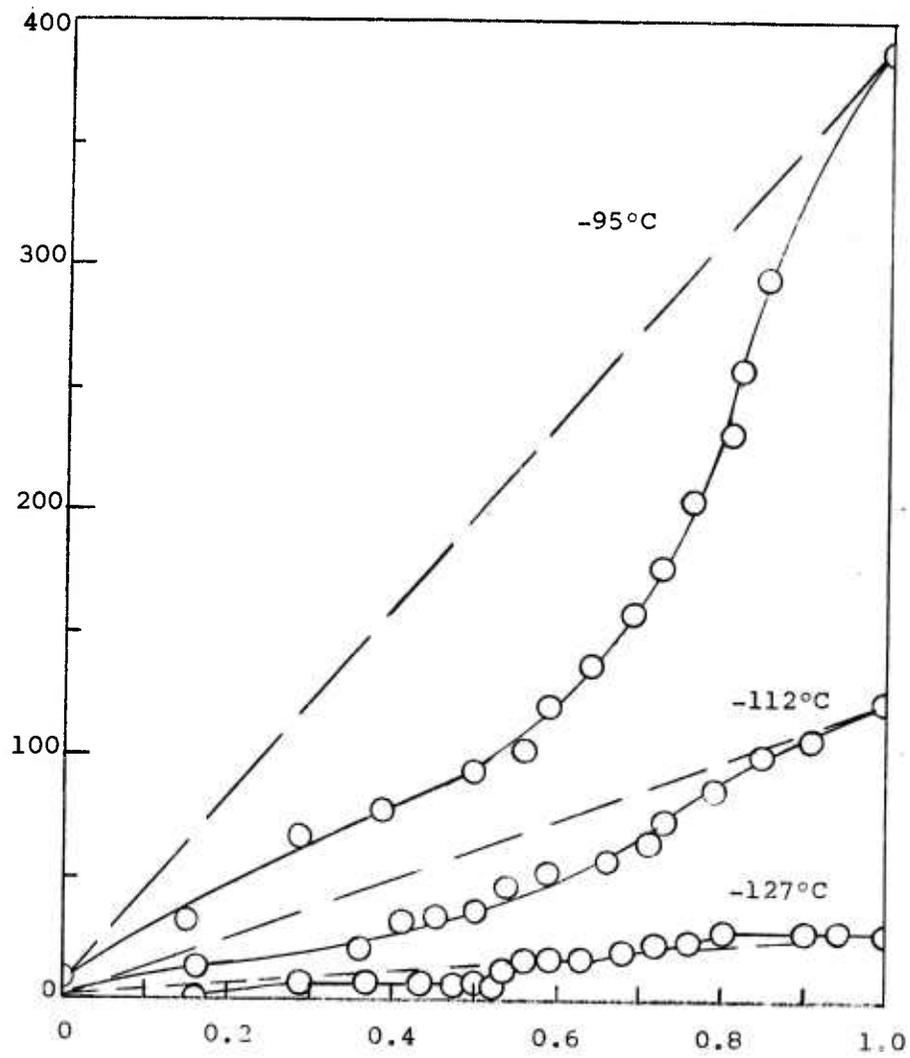


Slow decomposition occurs at room temperature, yielding SO_2 , N_2F_4 , and presumably H_2SO_4 .

c. Trimethyl Aluminum

Since a rather strong acid is required to form a stable complex with difluoramine, we investigated the reaction of difluoramine with trimethyl aluminum and trimethyl gallium. The reaction with trimethyl aluminum invariably resulted in explosion if the difluoramine

³Solomon, I.J., "(U) Research on Chemistry of O_3F_2 and O_2F_2 ," Yearly Summary Report No. IITRI-C227-6, IIT Research Institute Chicago, Ill., Feb. 1964.

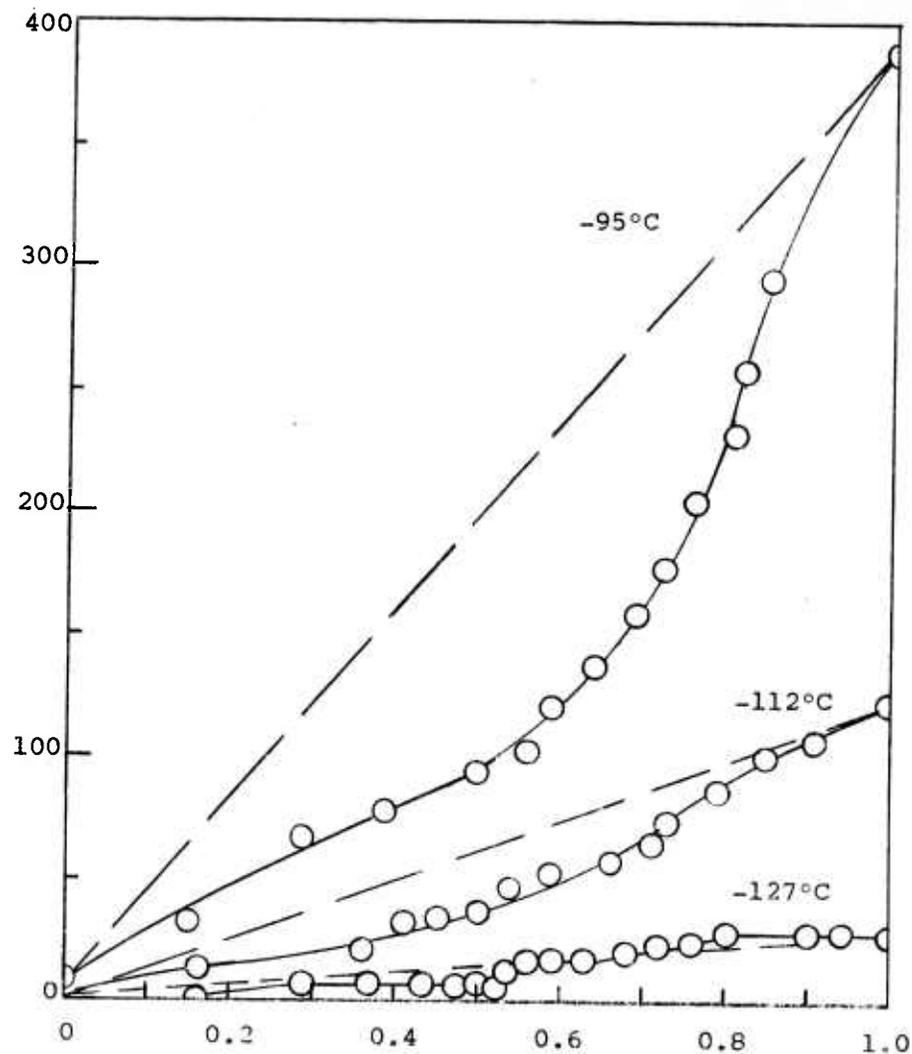


Mole Fraction HCl

Figure 2

THE MeNF_2 -HCl SYSTEM

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Mole Fraction HCl

Figure 2

THE MeNF_2 -HCl SYSTEM

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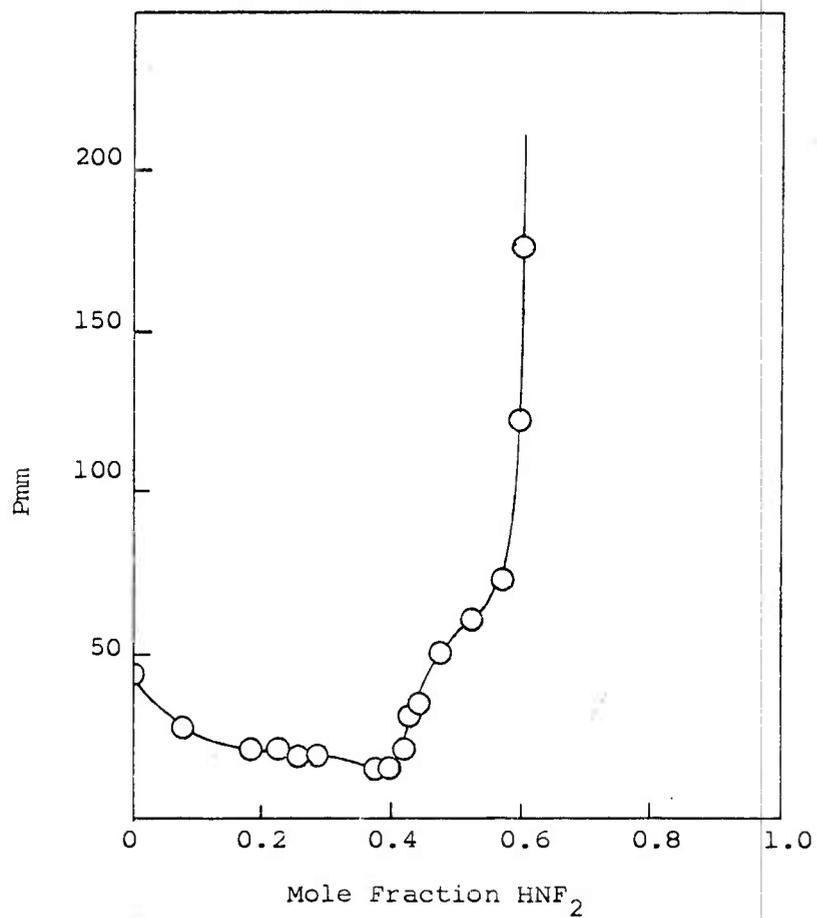
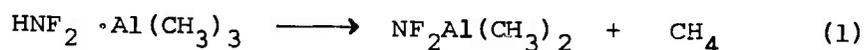


Figure 3
 THE HNF₂-SO₃ SYSTEM AT 0°C

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was added too rapidly or the mixture warmed too rapidly. The reaction occurred slowly when difluoramine was added in small quantities at -80°C , although slight decomposition occurred even under these conditions. Vapor pressure measurements could not be made because of irreversible decomposition, presumably according to Equation 1.



The decomposition product can react further with difluoramine. A sample of trimethyl aluminum was treated with an equivalent quantity of difluoramine and the adduct allowed to decompose according to Equation 1. A second equivalent of difluoramine was added, and the mixture slowly thawed. The mixture exploded with a bright green flash, although with less violence than a mixture of trimethyl aluminum and difluoramine. The mixture exploded with a bright green flash, although with less violence than a mixture of trimethyl aluminum and difluoramine. This system will be reexamined in an attempt to completely replace the methyl groups by NF_2 groups, forming $\text{Al}(\text{NF}_2)_3$. To our knowledge $\text{NF}_2\text{-Al}(\text{CH}_3)_2$ is the first example of an Al-NF_2 bond, and the method can certainly open a route to interesting compounds containing more than one Al-NF_2 bond.

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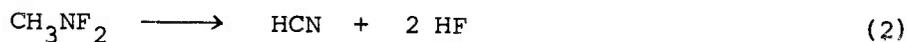
d. Trimethyl Gallium

Trimethyl gallium reacts slowly with difluoramine when the two are mixed and thawed. A viscous, colorless liquid is formed, and methane is slowly produced. The presence of excess difluoramine after two days, however, indicated that the reaction does not proceed beyond the formation of $F_2NGa(CH_3)_2$. This reaction is being studied further.

2. Methyl Difluoramine Additives

The additives of methyl difluoramine (CH_3NF_2) with various Lewis acids are also being studied.

Equimolar quantities of trimethyl aluminum and methyl difluoramine were condensed in a glass tube, and the tube was sealed and thawed. At a temperature below $0^\circ C$, vigorous frothing was noted in the portion of the tube where the trimethyl aluminum condensed. A viscous liquid was present when the tube was examined at room temperature. After 4 days, a clear glassy solid was observed in the bottom of the tube. Two moles of methane and about $1/3$ mole of HCN were the only volatile products. Heating of the residual solid produced a small amount of noncondensable material and a trace of sublimable solid, but all of the hydrogen cyanide could not be recovered. The reaction is presumably:



The missing hydrogen cyanide is probably complexed with CH_3AlF_2 . This irreversible decomposition is consistent with the behavior of methyl difluoramine toward other acids such as BF_3 and PF_5 .

3. Dimethyl Fluoramine Additives

In order to complete this phase, the additives of dimethyl fluoramine, $(\text{CH}_3)_2\text{NF}$, with various Lewis acids are also being studied.

Synthesis of dimethyl fluoramine was accomplished by the dry fluorination of $(\text{CH}_3)_2\text{NCOH}$. A positive pressure flow of 90% dilution of F_2 in He at 0°C resulted in a poor yield. By fluorinating the $(\text{CH}_3)_2\text{NCOH}$ under a vacuum of 100 to 250 mm Hg pressure, the yield was noticeably improved. Since the infrared spectrum of dimethyl fluoramine was not found in the literature, the compound will be tentatively identified from the vapor pressure data, and confirmed by its mass-cracking pattern and its NMR spectrum.

Presently the difficulty lies in the isolation of the compounds fractionated in the vapor pressure range of dimethyl fluoramine. A recourse to the synthesis of dimethyl fluoramine was attempted by using N,N-dimethyl acetamide $(\text{CH}_3)_2\text{NCOCH}_3$ instead of the formamide. A better yield is obtained by using the acetamide, but the problem of purifying the desired product is not easily accomplished by vacuum distillation. These products are currently being examined by gas chromatography.

B. Physical Properties of O_4F_2

The nature of O_4F_2 in both the vapor and the condensed phases is being studied in an attempt to answer the following questions: Does O_4F_2 vaporize into $(O_2F)_2$ and/or O_2F , or does it decompose completely to O_2 and F_2 ? Is O_4F_2 dimerized or ionized in the liquid or solution phase? That is, do ions such as OF^+ and O_3F^- exist?

A new Pyrex vessel for the synthesis and study of O_4F_2 has been fabricated. The vessel is equipped with three electrodes. The electrode used mainly for the synthesis of O_4F_2 extends into the center of the vessel. The other two electrodes, which are used for both synthesis and electrical measurements, are positioned on either side of the vessel. These two electrodes are shielded by small-diameter Pyrex tubing. Platinum wires lead from the shielded electrodes to the platinum rings of the capacitance cell, which is much smaller than the main vessel and consists of two small concentric platinum rings which were made from platinum sheets.

Future work will be devoted to the calibration of the capacitance cell and measurements of the capacitance of the cell containing pure liquid oxygen and later O_4F_2 .

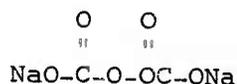
A measuring cell has a certain fixed capacitance, C_1 , through the insulation of the platinum rings or cylinders from one another and between the electrodes. Neglecting the small deviation of the dielectric constant of air from unity, the capacitance when measured with air in the cell is therefore

$C_0 + C_1$ and, when measured with a liquid of dielectric constant ϵ in it, is $\epsilon C_0 + C_1$. By using a pure liquid of known dielectric constant such as benzene, C_0 and C_1 can be determined and used for the measurement of the dielectric constant of an unknown material. Capacitance measurements of the cell containing liquid oxygen will also be made. Since O_4F_2 contains more than 61% oxygen, it will be of considerable interest to compare measurements of both liquid oxygen and O_4F_2 . Liquid oxygen is reported to have a dielectric constant of about 1.46 at $-182^\circ C$.

C. Reactions of O_2F_2

1. Disodiumperoxydicarbonate

A study leading to the possible synthesis of polyoxyfluoride compounds was continued on a limited basis. The fluorination of disodiumperoxydicarbonate



was investigated by using O_2F_2 as the fluorinating agent. As a comparison, static fluorination with pure F_2 gas and CsF catalyst was employed as a more drastic means of fluorinating at low temperatures. This study was continued from a previous experiment in which OF_2 was the principal product of a $-78^\circ C$ reaction in a 25% F_2 -He gas mixture by using a fluidizing bed technique of fluorination. At high temperatures (above $0^\circ C$), CO_2 , usually the principal product, resulted from the decomposition of the peroxydicarbonate. The purpose of the various means of fluorination

was to examine their fluorinating efficiency as well as the feasibility of low-temperature reactions in order to counter the instability problem of the peroxydicarbonate experienced at higher temperatures.

Two preliminary runs were conducted by reacting O_2F_2 with (70% pure) disodiumperoxydicarbonate. The first experiment was conducted in a manner similar to a previous experiment (Report No. IITRI-C227-6) in which an implosion (or explosion) had occurred. The liquid O_2F_2 was left in contact with the peroxydicarbonate, and the reaction system continuously pumped. During 1 hr at $-160^\circ C$, no perceptible products collected in the $-196^\circ C$ trap downstream from the reactor. At $-111^\circ C$, liquid O_2F_2 completely disappeared from the reactor after several minutes. An infrared analysis of the total condensed products indicated the presence of CO_2 , COF_2 , CF_4 , and other unidentified compounds.

For the second run, a Helicoid vacuum gage was attached to the reactor system to measure pressure changes during the reaction. At $-160^\circ C$, a small pressure change was observed when O_2F_2 was left in contact with excess $Na_2C_2O_6$ for a 3-hr period. Analyses of the noncondensable gases resulted in recovery of trivial amounts of O_2 and F_2 gases at this temperature. Further contact of liquid O_2F_2 with $Na_2C_2O_6$ was conducted at $-111^\circ C$ for 6 hr. The O_2F_2 completely decomposed or reacted in this experiment. The amount of O_2 recovered was about three times that of F_2 . CO_2 comprised a major portion of the total amount

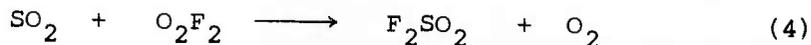
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of condensible products, and COF_2 , SiF_4 , and other unidentified constituents comprised the remaining portion. Warming to room temperature yielded only CO_2 and O_2 , the decomposition products of the peroxydicarbonates. From these experimental results O_2F_2 does not appear to be a suitable fluorinating agent for the peroxydicarbonate, and work on this approach was concluded.

In the static fluorination experiment, one atmosphere of pure F_2 gas at -183°C was kept in contact with a mixture of $\text{Na}_2\text{C}_2\text{O}_6$ and excess CsF for one week. The reactant-catalyst system was contained in a portable Pyrex storage bulb. The noncondensable gases pumped out of the bulb at -196°C appear to be entirely fluorine, and infrared spectral analysis of the small amount of condensible products indicated the presence of COF_2 , SiF_4 , CO_2 , and other unidentified compounds. No other product was recovered when the storage bulb was warmed to -78°C . Above this temperature, the decomposition products of the starting material, CO_2 and O_2 , are expected. Thus, only a slight reaction takes place at -183°C .

2. Sulfur Oxides and Oxyfluorides

Sulfur dioxide reacted vigorously with O_2F_2 , producing a variety of interesting products; however, the main reaction is:



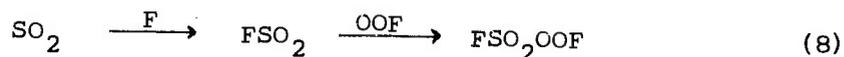
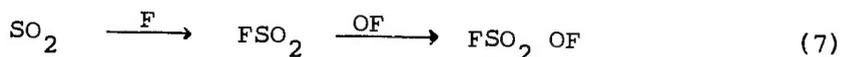
In a typical reaction 15.6 mmoles of sulfur dioxide was allowed to react with 15.5 mmoles of O_2F_2 at -160°C in the absence of a solvent. The reaction products were passed through liquid nitrogen traps and a sodium chloride tube, and the remaining noncondensable

gas (O_2) was transferred by means of a Toeppler pump and measured. The condensable gas was then further fractionated. The amounts of the various products are listed below:

F_2	1.9 mmoles
$F_2S_2O_5$	1.2 mmoles
$F_2S_2O_5, SO_2$	1.4 mmoles
$FSO_2 OF, FSO_2 OOF$	1.4 mmoles
F_2SO_2	10.3 mmoles
O_2	11.0 mmoles

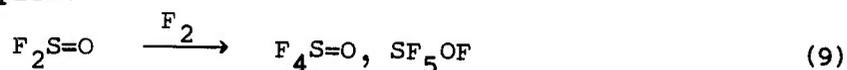
Thus, as noted previously, the main reaction is represented by Equation 4 in addition to other side reactions. The side reactions are the most interesting in that OF- and OOF-containing materials are formed. This is especially so since the products FSO_2OF and FSO_2OOF involve the addition of OF and OOF, respectively, to SO_2 .

The reaction may perhaps be represented as:

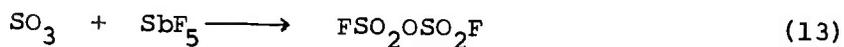
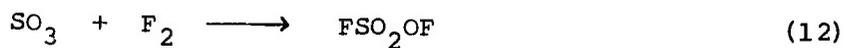


⁴F.B. Dudley, G.H. Cady and D.F. Eggers, Jr., J. Am. Chem. Soc., 78 29 (1956).

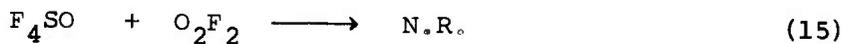
The product of Equation 7 was previously reported by Cady and co-workers, but only by the fluorination of SO_3 . In all previous work in which sulfur oxides or oxyfluorides were fluorinated it has not been possible to obtain products containing more S-O bonds than in the reactant. That is, S-O bonds are not formed by any dispersion reactions. The following reactions are given as examples:



Fluorine fluorosulfonate (FSO_2OF) and pyrosulfuryl fluoride ($\text{FSO}_2\text{OSO}_2\text{F}$) were previously prepared from SO_3 .



It is not surprising that F_2SO_2 is the main product in the reaction of SO_2 with O_2F_2 , since it results from a simple fluorination of SO_2 . Also, it was found in an independent experiment that F_2SO_2 does not react further with O_2F_2 . Also, F_4SO does not react with O_2F_2 .



Also, $\text{S}_2\text{O}_5\text{F}_2$ is formed from SO_2 and FSO_2OF , and therefore it may be formed in one of two ways.

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Another interesting fact was found in these experiments, that is, O_2F_2 is more soluble in F_2SO_2 and F_4SO than in Freon 13, the solvent currently thought of as the best for O_2F_2 . Some decomposition rates were determined in the solvents in order to ascertain the usefulness of these solvents for future studies. The results are given in Table 1. O_2F_2 decomposes at a slightly higher rate in F_2SO_2 and F_4SO than in Freon 13, but the decomposition rates are slow enough in any of these so that they can be used as solvents.

Table 1

DECOMPOSITION RATES OF O_2F_2 IN VARIOUS SOLVENTS

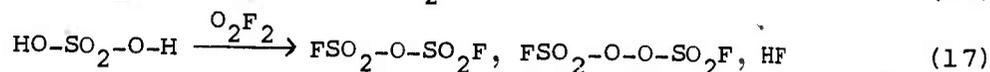
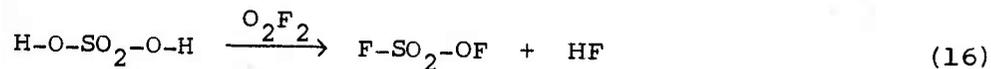
Temp, °C	Decomposition Rates, % per hr		
	F_2SO_2	F_4SO	Freon 13
-139	0.022	0.25	0.20
-112	0.22	1.02	0.20
-95	1.39	1.50	1.57

It was thought that F_2SO_2 and F_4SO might also be solvents for O_2BF_4 . However, two preliminary experiments showed no solution of O_2BF_4 in these solvents.

The reactions of H_2SO_4 and H_2SO_5 with O_2F_2 were also studied. Sulfuric acid reacts very slowly; the reaction of 3 mmoles of H_2SO_4 and 3 mmoles of O_2F_2 at $-130^\circ C$ yielded only 0.23 mmoles of product. This product was FSO_2OF , $F_2S_2O_5$, $F_2S_2O_6$,

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and SiF_4 . These are the expected products from the following reactions in which various bonds are fluorinated.



The rate of reaction of H_2SO_5 with O_2F_2 was faster than with H_2SO_4 ; that is, 13 mmoles of H_2SO_5 reacted with 21 mmoles of O_2F_2 at -130°C to produce about 5 mmoles of products. The main products were FSO_2OF and SiF_4 ; small amounts of F_2SO_5 and F_2SO_6 were detected. These are the expected products.

In a few preliminary experiments SO_3 was allowed to react with O_2F_2 . It should be remembered that previous to this work SOF compounds were prepared only from compounds containing three S-O bonds. The reaction of SO_3 with O_2F_2 is so vigorous that the first attempt at studying this reaction resulted in an explosion. Subsequent reactions were run in F_2SO_2 solvent. Some very interesting results were obtained. When 7.1 mmoles of SO_3 and 8.0 mmoles of O_2F_2 were allowed to react in F_2SO_2 , a large amount of product was obtained; however, when the product was warmed to room temperature, O_2 (6.3 mmoles) and F_2 (4.9 mmoles) were released. The only product that decomposed on warming will be further characterized.

D. Chemistry of O_3F_2

In this phase of the program O_3F_2 will be reacted with a number of inorganic compounds. In other words most of the work completed on the reactions of O_2F_2 will be repeated by using O_3F_2 . It must be remembered that the O_2F_2 used in these experiments will always contain at least small amounts of O_3F_2 . However, contrary to earlier work, it has been found that O_3F_2 can be distilled if done with care.

The liquid nitrogen bath surrounding the U-trap containing the O_3F_2 is dropped very slowly, preferably by evaporation of the liquid nitrogen. The O_3F_2 is distilled through as short distance as physically possible and caught in an adjacent trap. The system is pumped during the entire operation. Some decomposition does result, but if liquid oxygen is used as the refrigerant, an extra bonus is obtained. The O_3F_2 has a lower melting point than O_2F_2 and will drain to the bottom and contact the sample under investigation, while the O_2F_2 freezes out at the top of the tube.

The following materials have been investigated with O_3F_2 : calcium, magnesium, potassium, sodium, lithium, sodium fluoride, sodium bromide, sodium iodide, sodium nitrite, and sodium nitrate.

Calcium and magnesium do not react at all. The alkali metals react smoothly. The sodium halides react as expected: NaBr - some reaction to liberate bromine; NaI - appreciable reaction to liberate iodine. Sodium nitrite and nitrate do not

seem to give appreciable reactions. Now that the preliminary reactions have been carried out, some of the more interesting results will be studied during the next quarter.

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