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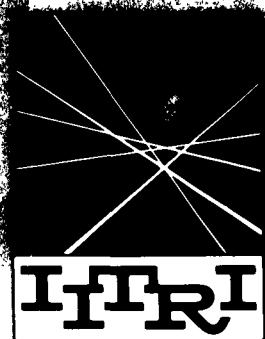# UNCLASSIFIED

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IITRI

Technology Center   Chicago, Illinois 60616

Report No. IITRI–C227-6
(Yearly Summary Report)

RESEARCH ON CHEMISTRY OF
O_3F_2 AND O_2F_2

Air Force Office of
Scientific Research

MAR 3 1964

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IIT RESEARCH INSTITUTE

Report No. IITRI-C227-6
(Yearly Summary Report)

RESEARCH ON CHEMISTRY OF O_3F_2 AND O_2F_2

October 1, 1962 through December 31, 1963

Contract No. AF 49(638)-1175
IITRI Project C227

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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FOREWARD

This is report No. IITRI C227-6, Yearly Summary Report, which covers the period from October 1, 1962 to December 31, 1963, on Contract No. AF 49(638)-1175, entitled "Research on Chemistry of O_3F_2 and O_2F_2."
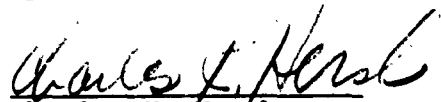
This research is being supported by the Advanced Research Projects Agency under ARPA Order No. 350-62, Project Code No. 9100. Technical direction is being provided by the Director of Engineering Sciences, SREP, Air Force Office of Scientific Research.
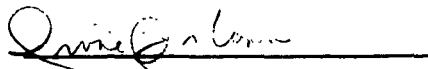
In addition to the author, who is principal investigator, personnel contributing to the program include: R. I. Brabets, Research Engineer; R. Healy, Research Chemist; J. Keith, Research Chemist; R. Uenishi, Research Chemist; J. Finn, Associate Chemist; A. Kacmarek, Associate Chemist; J. Raney, Associate Physicist; R. Douthart, Assistant Chemist; S. Macur, Assistant Chemist; and W. Sumida, Assistant Chemist.

<div align="right">

Respectfully submitted,

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</div>

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ABSTRACT

O_2F_2 appeared to be stable below $-160\,°C$, but decomposed above this temperature. Although OF_2 was sometimes found in the decomposition products, it apparently was formed in the discharge reaction and could be completely eliminated by pumping on the sample at $-196\,°C$. In glass, the only condensable decomposition product found was SiF_4. The possibility that the decomposition of O_2F_2 in Pyrex vessels is faster than in quartz or Vycor was indicated.

O_2F_2 was found to react with certain metal fluorides to form an interesting new class of compounds which are apparently oxygenyl (O_2^+) salts. The reactions are typified by the reaction with BF_3:

$$BF_3 + O_2F_2 \longrightarrow O_2BF_4 + 1/2\ F_2 \tag{16}$$
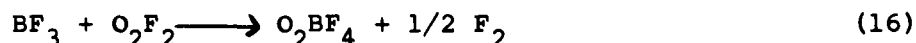
The stoichiometry of the above reaction has been established by mass balance and confirming evidence obtained by analysis of the decomposition products.

$$O_2BF_4 \longrightarrow BF_3 + O_2 + 1/2\ F_2 \tag{17}$$
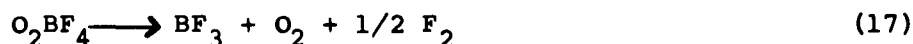
O_2BF_4 behaves as both an oxidizing and fluorinating agent.

$$O_2BF_4 + S \xrightarrow[\text{0 to 20°}]{\text{FC-75}} SO_2 + COF_2 + BF_3 + SiF_4 \tag{18}$$

$$O_2BF_4 + P \xrightarrow[\text{0 to 20°}]{\text{FC-75}} POF_3 + COF_2 + BF_3 + SiF_4 \tag{19}$$
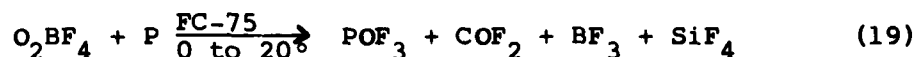
The reaction with chlorine produced an unstable purple product. Similar results were obtained with ClF_3, but no new compounds

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were isolated.

The hydrolysis of O_2BF_4 produces oxygen, ozone, fluorine, and HBF_4. Although the ozone-to-oxygen ratio is variable, the sum of the two is equivalent to twice the amount of oxygen present in the original compound. The amount of ozone obtained is smaller for samples kept at room temperature for a short time. Thus, a sample which had never been warmed above -126°C yielded 30% ozone and another sample which had been thawed for a short time produced only 10% ozone on hydrolysis.

The EPR studies showed a similar difference in the sample which had been warmed. The infrared spectrum of the solid was obtained and compared with that of O_2F_2. The analogous compound O_2PF_6 has been similarly prepared and characterized.

The reactions of O_2F_2 with metals at low temperatures is surprisingly mild. Thus, although lithium sparked with liquid O_2F_2, sodium and potassium did not, and calcium and magnesium were unreactive. O_2F_2 reacts vigorously with sulfur and with phosphorus to form known fluorides and oxyfluorides.

O_2F_2 liberates the halogens from NaI and NaBr and subsequently reacts explosively with the iodine formed in the first case. With $KClO_4$, only COF_2, $COCl_2$ and SiF_4 were identified as the products. Similar results were obtained with KNO_3. In all the reactions with the inorganic salts, the extent of reaction was slight.

Preliminary measurements of the vapor pressure of O_4F_2 with

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an Alphatron gauge indicated a vapor pressure of 20 to 25 microns at -196°C and 0.2 mm at -183°C. However, the vapor pressure is a function of time at -183°C. Thus, in another experiment, the pressure rose from 21 to 400 microns in 91 min. The resulting velocity constant, $1.3 \times 10^{-3} hr^{-1}$ is very close to that of O_3F_2.

Studies have been made of the reaction of HNF_2 with various Lewis acids. HNF_2-BF_3 has been isolated as a sublimable white solid whose vapor pressures (from -78.5 to 30.2°C) are represented by the equation

$$\log P \text{ mm} = \frac{-2,346}{T} + 12.2682 \tag{20}$$

The sublimation point is -23.3°C, and the heat of sublimation is 21.6 kcal/mole. The compound is completely dissociated in the vapor phase at 22°C.

No evidence of compound formation was obtained in the HNF_2-HCl system, although the components are miscible in all proportions at -112°, -127° and -138°C.

HNF_2 and SO_2 appear to form a 1:1 compound, HNF_2-SO_2. However, the vapor pressures were not reproduced in a second experiment.

Pressure composition studies on the HNF_2-SO_3 system indicated the formation of a 1:1 and, possibly, a 1:2 compound. Further work is in progress on this system.

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RESEARCH ON CHEMISTRY OF O_3F_2 AND O_2F_2

I.   INTRODUCTION

This program has the following major objectives:
(1) the elucidation of the inorganic chemistry of O_3F_2 and
O_2F_2, (2) the study of the physical properties of O_4F_2 to reveal
the presence or absence of ionic species, (3) the determination
of the oxidizing species remaining in solution after fluorina-
tion of HNO_3 and (4) determination of the feasibility of pre-
paring new ions of the type NF_4^+ and $NH_2F_2^+$.

II.   RESULTS AND DISCUSSION

A. Stability of O_2F_2 and O_3F_2

Two important considerations in the planned investigations
are the stability and mode of decomposition of O_2F_2 and O_3F_2
(Equations 1 and 2).

$$O_2F_2 \longrightarrow O_2 + F_2 \tag{1}$$
$$O_3F_2 \longrightarrow O_2F_2 + 1/2\ O_2 \tag{2}$$

To ensure that these decompositions would not be mistaken for
reactions of the compounds with various materials, studies on
stability as a function of temperature and container were
carried out. The following procedure was used. After the
O_2F_2 had been cooled to -196°C in a suitable reactor, the
apparatus was evacuated to approximately 10^{-5} mm Hg. The

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temperature was then raised in controlled increments, and decomposition was observed as a function of temperature.

The collection and measuring system for the decomposition products consisted of (1) a -196°C U-trap, (2) a 200°C sodium chloride tube, (3) another -196°C U-trap, and (4) a collection bulb, connected in series, respectively. The first U-trap removed condensable gases; the sodium chloride in the 200°C tube reacted with the fluorine to yield chlorine, which was trapped in the second U-trap; the oxygen passed through the 200°C tube and was collected and measured in the collection bulb. The volume of fluorine originally produced was calculated from the amount of chlorine trapped in the second U-trap.

Decomposition started at approximately -160°C. Below this temperature, O_2F_2 apparently is stable. However, if decomposition occurs as shown in Equation 1, equimolar quantities of oxygen and fluorine should have been formed. In some of the first experiments more fluorine than oxygen was obtained and oxides of nitrogen were also found. Consequently the validity of the oxygen and fluorine analyses (Report No. ARF 3227-1) was checked by determining the amounts of these gases in a one-to-one mixture which had been taken directly from the respective cylinders. The results were:

O_2 + F_2 charged	19.60 moles
Cl_2 recovered (F_2 originally present)	9.25 moles
O_2 remaining	10.16 moles

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$O_2 + F_2$ (experimentally determined) 19.41 moles

Error (0.19 x 100/19.4) 1%

A mass spectrum of the cylinder oxygen showed 99.6% oxygen, 0.2% nitrogen, and 0.2% argon. The general chemical specifications for the cylinder fluorine were 99.5% fluorine; 1.0% oxygen, nitrogen, and inert gases; and 0.5% carbon dioxide and hydrogen fluoride. These data indicate that the nitrogen can be attributed solely to impurities in the fluorine cylinder -- impurities which are well within specifications.

Some oxides of nitrogen found with the O_2F_2 in the early preparations were traced to a leak in the electrical discharge apparatus. Since then O_2F_2 free of these oxides has been synthesized in a leak-free system. The results of the stability tests on O_2F_2 are given in Table 1. Considering the small amounts of oxygen and fluorine determined, the results are satisfactory since the ratio of oxygen to fluorine is close to one in most cases. Also, from the data given in Table 1, it can be concluded that O_2F_2 is sufficiently stable at -160°C to permit studies of its reactions at this temperature. It was also found that the rate of decomposition of O_2F_2 might be faster in Pyrex than in quartz or Vycor.

However, a number of questions should be answered to more fully understand the decomposition of O_2F_2. Does O_2F_2 decompose to yield only oxygen and fluorine? Are reactive species formed during decomposition? Do these species attack glass more readily

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Table 1

DECOMPOSITION OF O_2F_2*

Container	Temperature, °C	Decomposition Products, mmole		Decomposition,%
		O_2	F_2	
Quartz	-160	0.04	0.02	0.3
Pyrex	-160	0.02	0.05	1.0
Vycor	-160	0.04	0.02	—
Quartz	-126	0.06	0.08	0.7
Pyrex	-126	0.06	0.10	2.6
Vycor	Tube Failure	—	—	—
Quartz	-112	0.35	0.58	4.5
Pyrex	-112	0.32	0.52	13.0

*Measured over a 6-hr period. Decomposition was calculated from average of O_2 and F_2 values. 10.3 mmoles O_2F_2 was used in the quartz tubes and 3.1 mmoles in the Pyrex tubes.

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than the fluorine and oxygen formed in the decomposition? Is the Kel-F stopcock grease being attached and giving volatile fluorocarbons or other products? Is OF_2 formed in the decomposition or in the synthesis of O_2F_2? The following work was carried out in an attempt to answer these questions.

A sample of O_2F_2 was decomposed and the products analyzed as follows. The gases were passed through a -196°C trap to remove any material that condensed at this temperature. The main products in the first trap were SiF_4 and OF_2. If the sample of O_2F_2 was pumped at -196°C before decomposition, only SiF_4 was present in the trap. Thus, some of the questions were definitely answered. That is, OF_2 is formed in the synthesis and not in the decomposition of O_2F_2. Also, the stopcock grease does not seem to react to give fluorocarbons or other products.

Another question was: Does O_2F_2 give reactive intermediates (which react with glass faster than fluorine) before it ultimately yields fluorine and oxygen? The answer is yes, but the nature of the intermediate is doubtful. The amount of silicon tetrafluoride in the first trap was proportional to the time that the decomposition products were exposed to the reactor. If the reactive intermediates were F, OF, or other free radicals, they would be expected to attack the glass and form SiF_4. But SiF_4 is formed for as long as 1 hr, which is much longer than the lifetime of any of the above-mentioned free radicals.
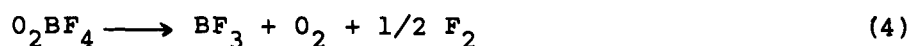
B. O_2^+ Compounds

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An interesting new group of compounds containing the O_2^+ cation were discovered. Most of the work was done on O_2BF_4, which is prepared as shown in Equation 3.

$$BF_3 + O_2F_2 \longrightarrow O_2BF_4 + 1/2 \ F_2 \tag{3}$$
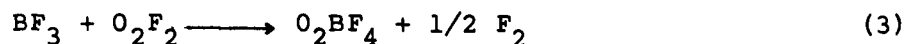
The stoichiometry of the reaction was validated, and the formula of the compound was calculated from the decomposition products.

$$O_2BF_4 \longrightarrow BF_3 + O_2 + 1/2 \ F_2 \tag{4}$$

Electron paramagnetic resonance (EPR) studies have shown that this compound contains a free electron. The EPR spectrum (Figure 1) consists of a single, asymmetric, broad line centered at $g = 1.97 \pm 0.10$. The width between inflection points, measured at 77°K, is 500 oersteds. A quantitative experiment in which the total number of spins was counted showed 5.96×10^{20} spins per gram; this indicates that approximately 12% of the molecules are paramagnetic. To weigh the amount of O_2BF_4 used in this experiment, the sample was maintained at room temperature for a short time. Another sample of O_2BF_4 which had not been exposed to temperatures above -126°C produced 30% free electrons.

The reaction of one sample of O_2BF_4 with water produced some interesting results. The products were oxygen, ozone, fluorine, HBF_4 and possibly HF. Hydrolysis of 29 mmoles of O_2BF_4 with excess water produced 64 mmoles of oxygen, 6.14 mmoles of fluorine, and 4 mmoles of ozone; these results indicate that 1 mole of O_2BF_4 reacts with 2 moles of water to release all the

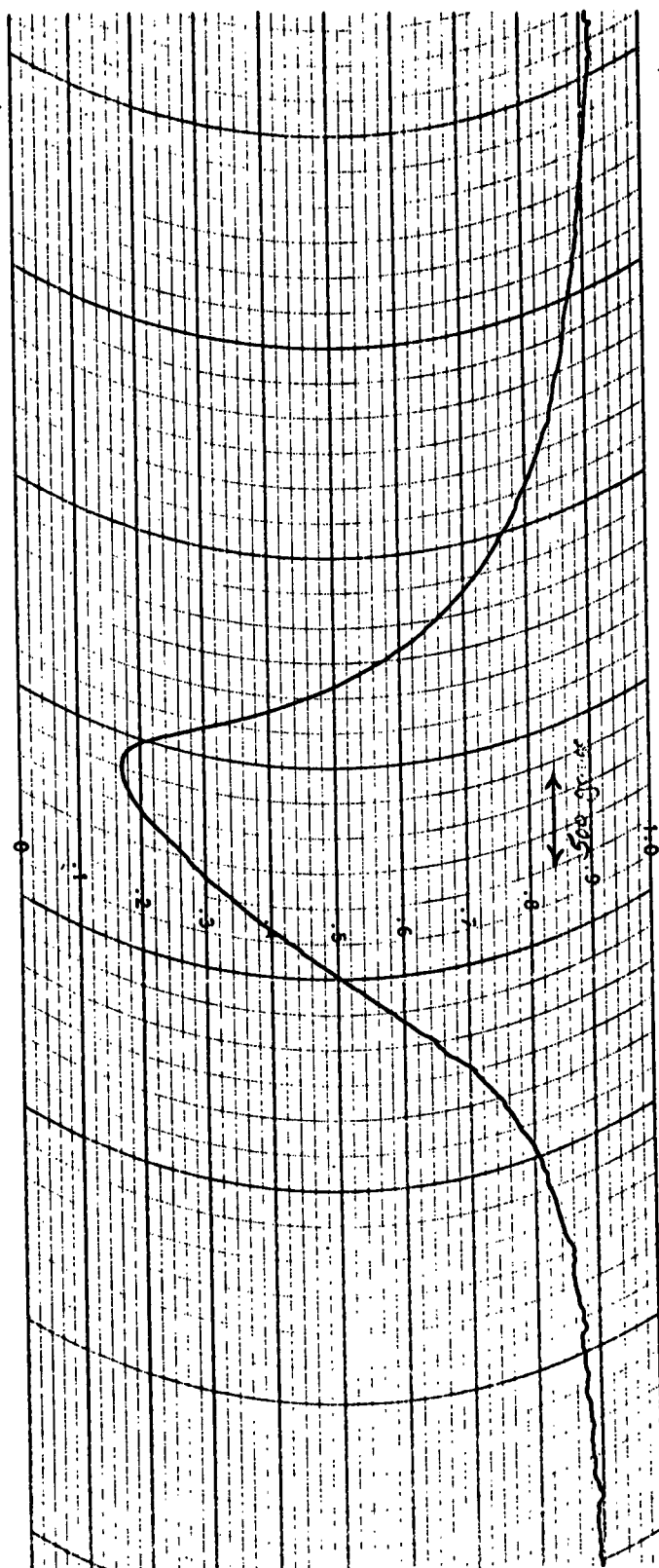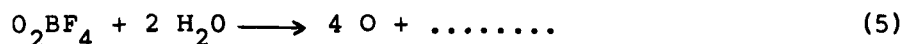**IIT RESEARCH INSTITUTE**

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Figure 1

ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF O_2BF_4

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oxygen in both the O_2BF_4 and the water.

$$O_2BF_4 + 2 H_2O \longrightarrow 4 O + \ldots\ldots \quad (5)$$
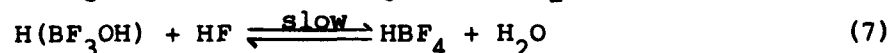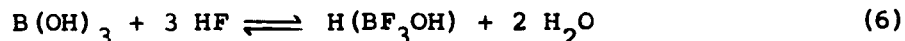
However, as in the case of the sample used for the EPR studies, this sample was exposed to room temperature for a short interval.

The hydrolysis was repeated with another sample which had not been warmed above -126°C. In this case, 10.7 mmoles of O_2BF_4 produced 0.2 mmoles of fluorine, 3.1 mmoles of ozone, and 13.1 mmoles of oxygen. Again the stoichiometry was approximately the same as that in Equation 5, but the ratio of ozone to oxygen was much higher than in the previous case.
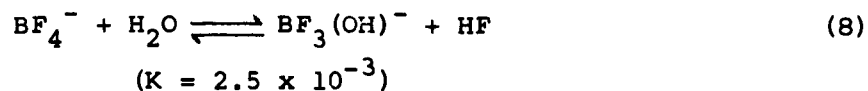
Thus, hydrolysis of the O_2BF_4 exposed to room temperature produced about 10% ozone (compared with the total oxygen) and contained approximately 12% free electrons. The sample that was kept below -126°C produced about 30% ozone on hydrolysis and contained approximately 30% free electrons per mole of O_2BF_4.

In two hydrolysis reactions, one at 25°C and the other at -80°C, the net ratio of total acidic hydrogen to total boron was found to be 1.55:1 and 1.24:1, respectively. No peroxide was found in the reaction at 25°C, and only 0.06 milliequivalent was detected in the reaction at -80°C.

The following equilibria tend to increase the ratio of acidic hydrogen to boron.

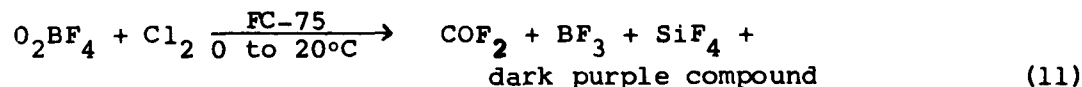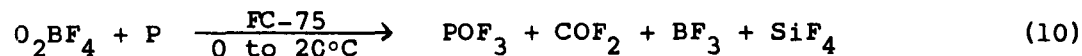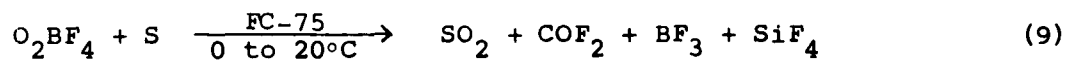$$B(OH)_3 + 3 HF \rightleftharpoons H(BF_3OH) + 2 H_2O \quad (6)$$

$$H(BF_3OH) + HF \underset{\text{}}{\overset{\text{slow}}{\rightleftharpoons}} HBF_4 + H_2O \quad (7)$$

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$$BF_4^- + H_2O \rightleftharpoons BF_3(OH)^- + HF \tag{8}$$
$$(K = 2.5 \times 10^{-3})$$

Since $H(BF_3OH)$ is the stronger acid, it depresses the dissociation of HF in reaction 7. Since it hydrolyzes, HBF_4 cannot be titrated alkalimetrically.[1] The peroxide was redetermined by a method[2] in which ozone does not interfere.

After a great deal of work, the infrared spectrum of O_2BF_4 (Figure 2) was obtained by using the cell shown in Figure 3. The spectrum seems to agree with the structure O_2BF_4. The infrared spectrum of O_2F_2 is also included for comparison. The O_2F_2 was frozen on the inside window of the cell. The O_2BF_4 was formed by allowing BF_3 to react with the frozen O_2F_2.

Reactions of O_2BF_4 with sulfur, phosphorous, and chlorine were carried out in slurries of FC-75 (a compound containing eight fully fluorinated carbon atoms and having a liquid range of -60 to 100°C.

$$O_2BF_4 + S \xrightarrow[\text{0 to 20°C}]{\text{FC-75}} SO_2 + COF_2 + BF_3 + SiF_4 \tag{9}$$

$$O_2BF_4 + P \xrightarrow[\text{0 to 20°C}]{\text{FC-75}} POF_3 + COF_2 + BF_3 + SiF_4 \tag{10}$$

$$O_2BF_4 + Cl_2 \xrightarrow[\text{0 to 20°C}]{\text{FC-75}} COF_2 + BF_3 + SiF_4 + \text{dark purple compound} \tag{11}$$

The volatiles were identified by infrared spectra.

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[1] Rys and Slutskaya, Dokl. Akad. Nauk. SSSR, Vol. 57, pp. 689-91, 1947.

[2] Schumb, Satterfield, and Wentworth, "Hydrogen Peroxide," Reinhold Publishing Company, New York, p. 551, 1955.
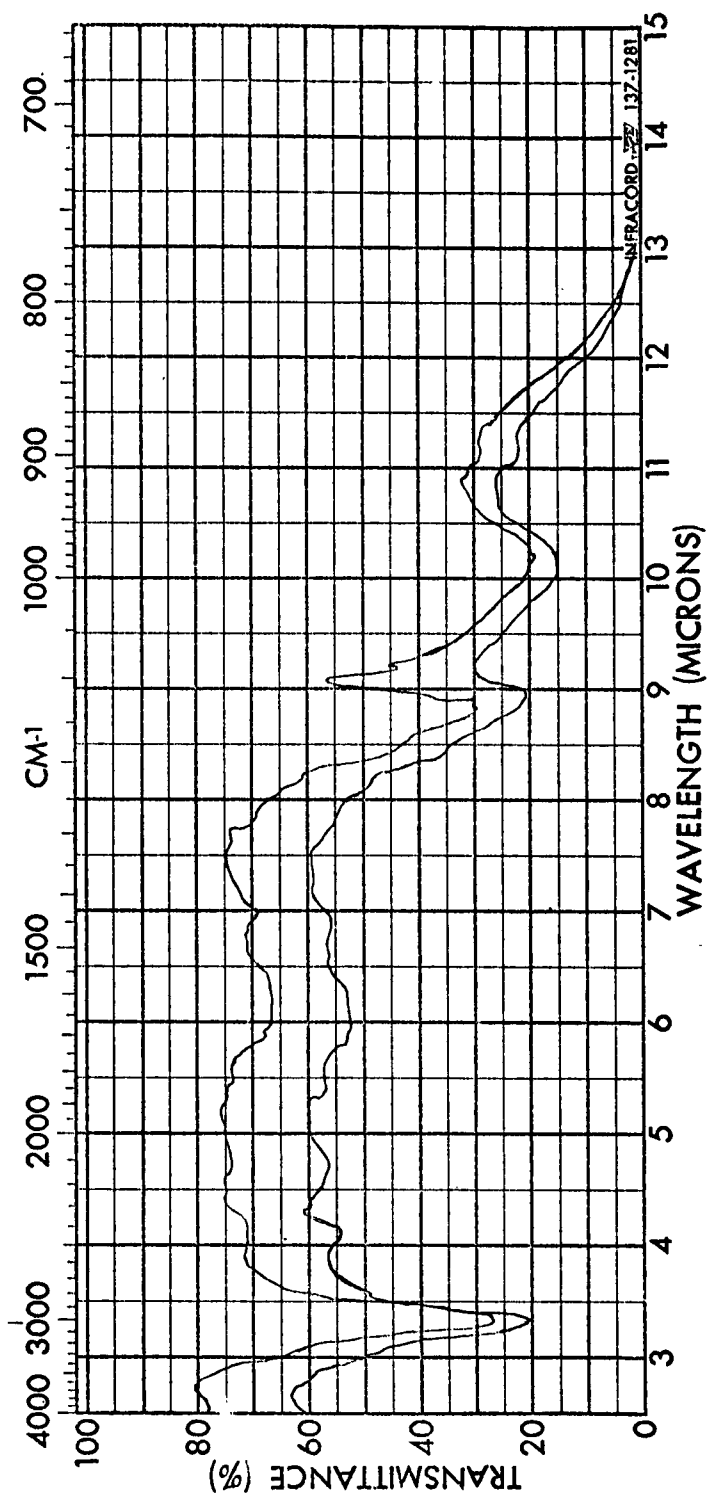
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Figure 2

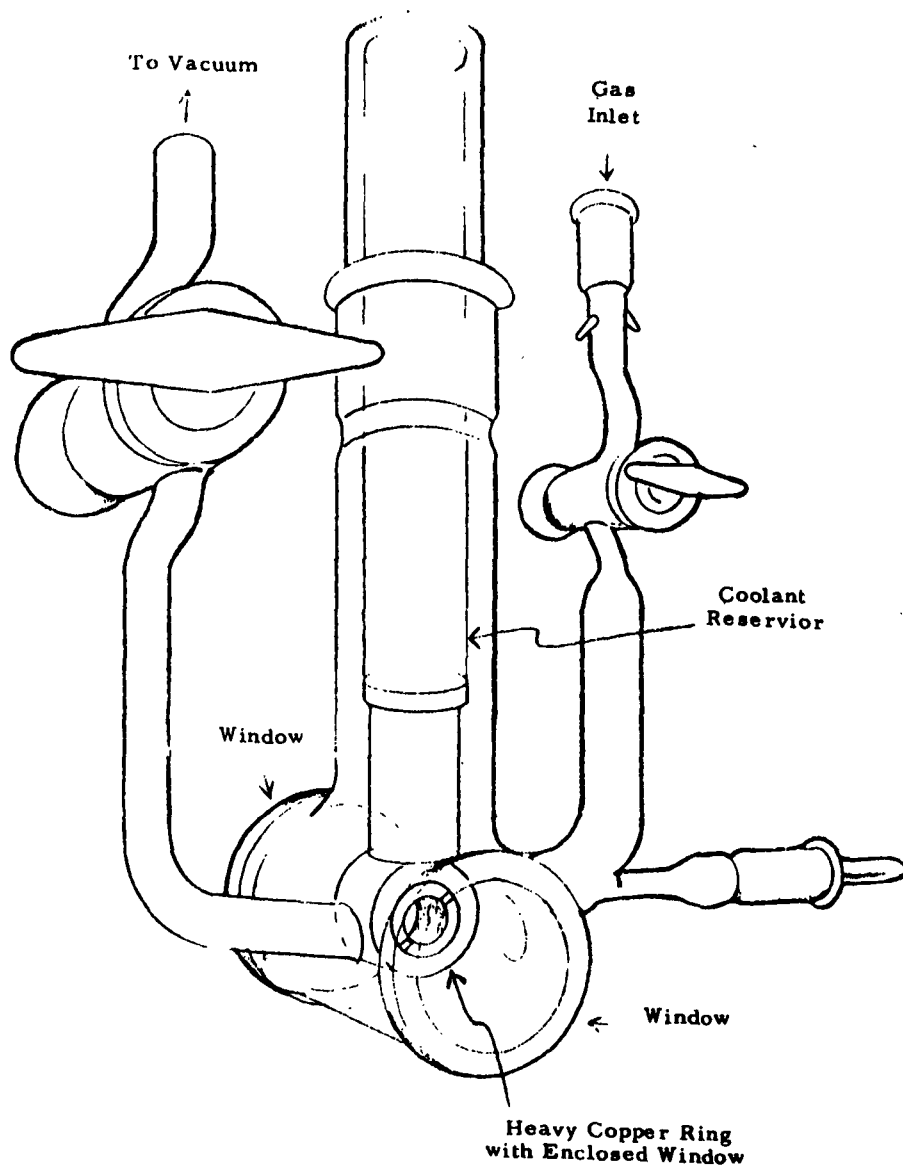INFRARED SPECTRUM OF O_2BF_4

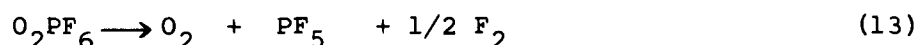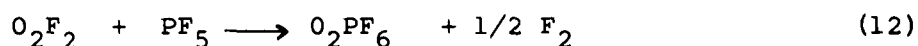IIT RESEARCH INSTITUTE

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Figure 3

LOW TEMPERATURE INFRARED ABSORPTION CELL

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The purple product appeared to persist longer without the use of FC-75. When ClF_3 was used instead of chlorine, apparently the same purple-colored product was formed, but it was much smaller in quantity and lower in thermal stability. At $-80\,^{\circ}C$ all the purple disappeared and a yellow solid remained.

Another O_2^+ compound, O_2PF_6, has now also been fully characterized. This compound is formed as shown in Equation 12 and decomposes as shown in Equation 13. The compound is not as stable as the BF_4^- compound.

$$O_2F_2 \; + \; PF_5 \longrightarrow O_2PF_6 \; + \; 1/2 \; F_2 \tag{12}$$

$$O_2PF_6 \longrightarrow O_2 \; + \; PF_5 \; + \; 1/2 \; F_2 \tag{13}$$

Hydrolysis of the new compound is similar to that of O_2BF_4:

$$O_2PF_6 \; + \; 2 \; H_2O \longrightarrow O_3 \; + \; O_2 \; \cdots \tag{14}$$
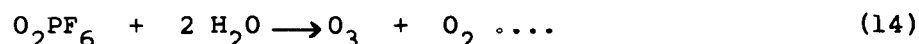
The infrared and EPR spectra of O_2PF_6 are given in Figures 4 and 5, respectively. The infrared spectrum shows a peak near $3 \; \mu$; O_2BF_4 and O_2F_2 absorb in the same region. The cell shown in Figure 3 was used to obtain the infrared spectrum. First, O_2F_2 was condensed on the inside window while the inside cold finger was maintained at $-196\,^{\circ}C$. Then PF_5 was introduced, and the temperature was raised to $-138\,^{\circ}C$. Any unreacted PF_5 and/or O_2F_2 was pumped from the cell before the spectrum was obtained.

The EPR results were also similar to those obtained for the BF_4^- analog. Although no spin concentration measurements were made, comparison with 0.05 ruby indicated that the sample

is not a pure paramagnetic substance. The line is very broad, asymmetric, and centered at about g = 2. Some unresolved structure, probably due to hyperfine interaction, is observed on the high field side of the absorption.

Figure 6 shows the decomposition of O_2PF_6. As in the case of O_2BF_4, the decomposition is very fast in the initial stages; then it levels off. Thus, all these results show that O_2PF_6 is similar to O_2BF_4 in every case.

C. Reactions of O_2F_2

1. Metals

The reactions of O_2F_2 with the alkali metals lithium, sodium, and potassium were conducted by condensing the O_2F_2 in a trap above a thin film of the metal. The trap was then thawed and the volatile gases were pumped through a -196 °C trap to prevent the accumulation of fluorine, which would react to form the metal fluoride. The lithium sparked during the reaction, but the sodium and potassium did not. The products were too small for analysis. However, it appears that the reactions with the alkali metals are not excessively violent. (O_2F_2 did not react with calcium at -160 °C or with magnesium at -126 °C.)

2. Sulfur

The reaction of O_2F_2 with sulfur under similar conditions was vigorous and produced a blue flame. Infrared spectroscopy

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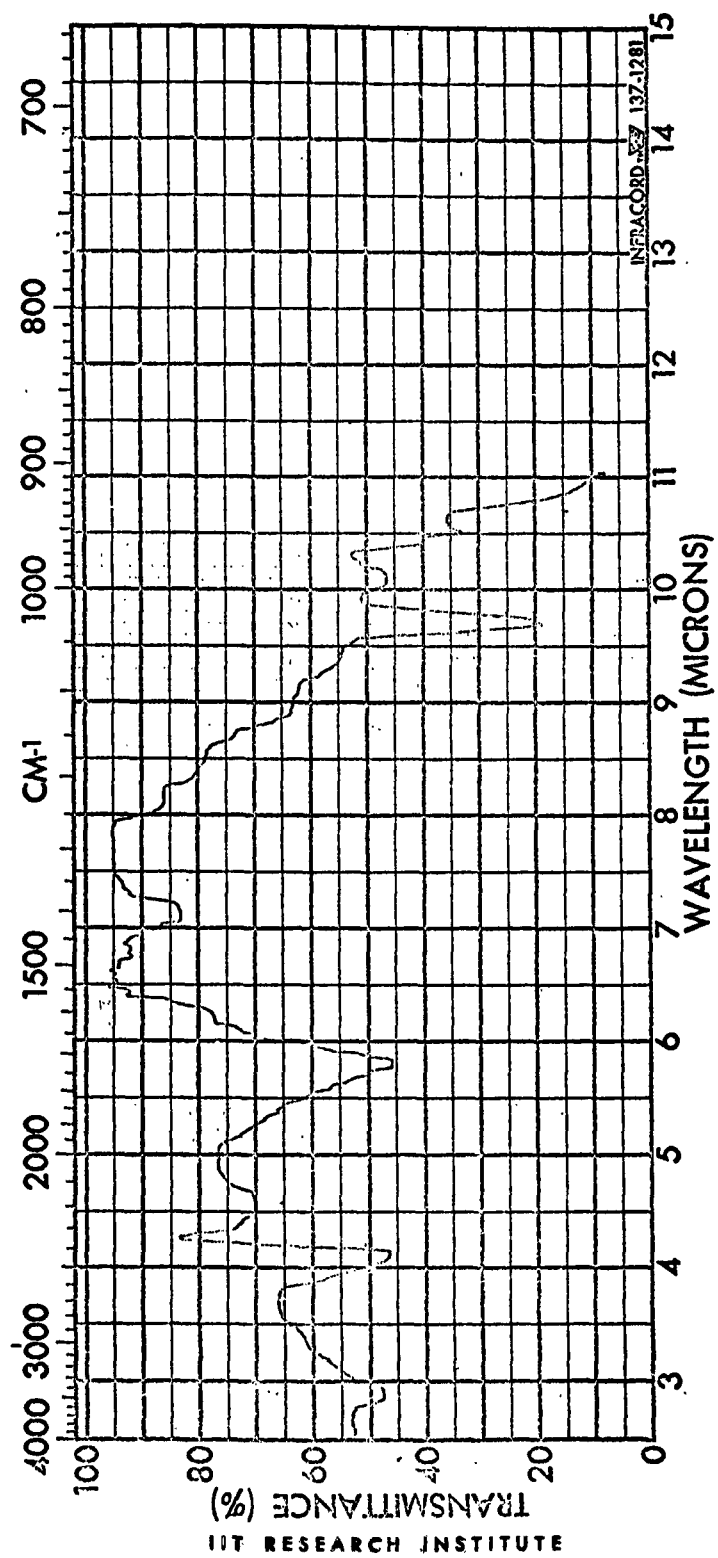
Figure 4

INFRARED SPECTRUM OF O_2PF_6

WAVELENGTH (MICRONS)

TRANSMITTANCE (%)

CM-1

INFRACORD 137-1281

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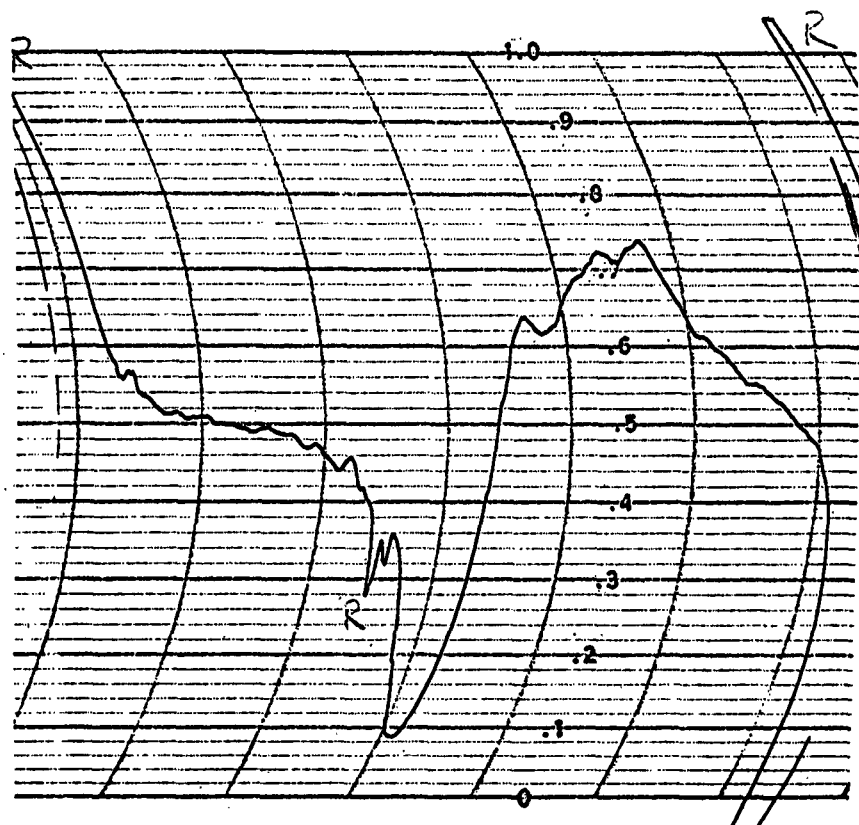
Figure 5

ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF O_2PF_6

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Pressure, mm Hg

200

150

100

50

0

10   20   30   40   50

Time, minutes
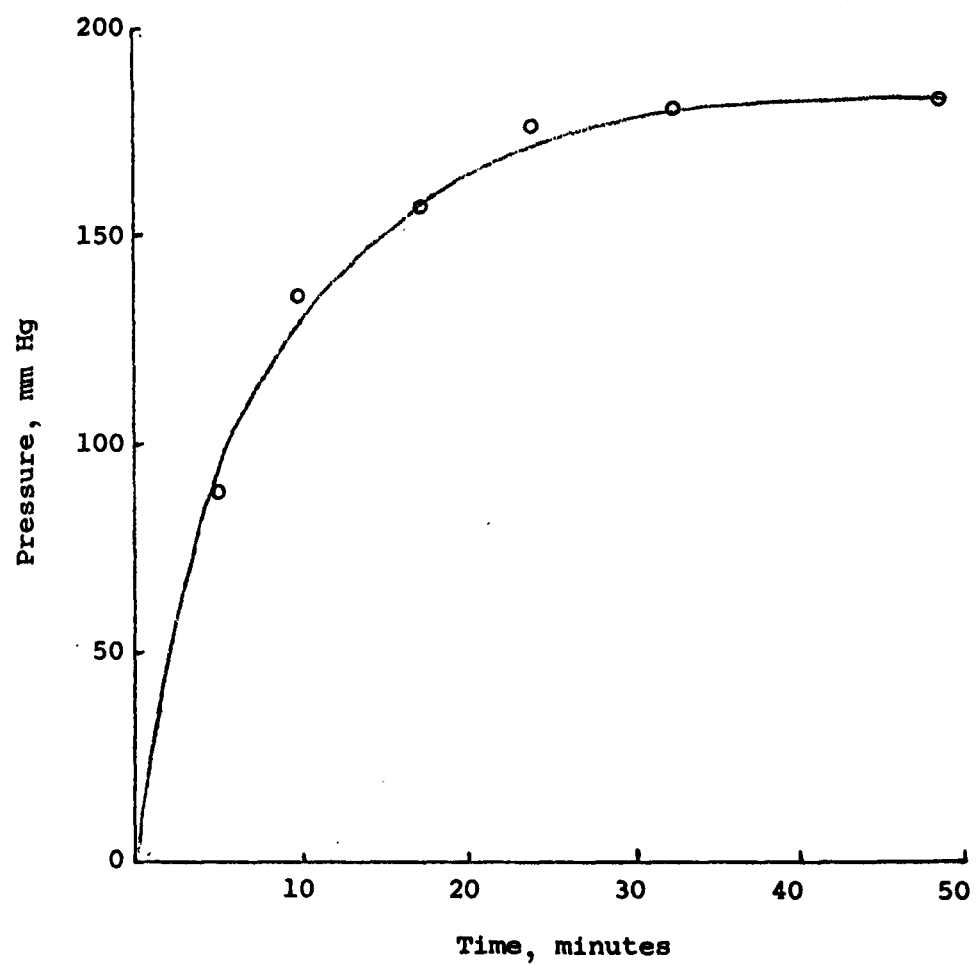
Figure 6

DECOMPOSITION OF O_2PF_6

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indicated the presence of SO_4, SO_2F_2, and $(SO_3)_n$ in the products.

To moderate the reaction, O_2F_2 was allowed to react with sulfur and $C\,ClF_3$ (Freon-13) was used as a solvent. The products were analyzed by passing the gases through (1) a -196 °C trap to remove the condensable products, (2) a heated sodium chloride tube to convert the fluorine to chlorine, (3) a -196 °C trap to condense the chlorine, and (4) a Toeppler pump to measure the oxygen. When excess sulfur was used, no chlorine appeared from the sodium chloride tube. Analysis of the condensable products (Table 2) indicated a rather complex mixture of sulfur oxides and fluorides contaminated with nitrogen oxides.

3. Phosphorous

O_2F_2 reacted very violently with red phosphorus, even at -196 °C, when Freon-13 was used to moderate the reaction, explosions also occurred. The reaction with a small amount of phosphorus yielded the simple fluorides of phosphorus, POF_3, and an unidentified compound which condensed as a yellow solid and turned a deep brown color on warming. It decomposed to yield fluorine and oxygen.

4. Inorganic Salts

The reaction of O_2F_2 with NaI liberated free iodine. A detonation then occurred, probably because of the interaction of iodine and O_2F_2. On the other hand, the reaction of O_2F_2 with NaBr produced only small amounts of bromine and no detonation. Hydrolysis of the resulting solid gave no noticeable

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Table 2

REACTION OF SULFUR WITH O_2F_2 IN $CClF_3$

Run No.	Initial Reactants, g		Sulfur Recovered, g	O_2 Produced, %	Mass Spectrometric Analysis of $CClF_3$ Gas Mixture, mole %					Mass Spectrometric Analysis of -138°C Fraction, mole %							
	Sulfur	O_2F_2			$CClF_3$	SOF_2	SF_6	SOF_4	Other[a]	$CClF_3$	SOF_2	SF_6	SOF_4	S_2F_2	SiF_4	O_2	Other[b]
1	11.9	1/3	0	99.7	98.3	0.1	0.0	0.1	1.0								
2	45.6	1/3	22.2	60.5	82.7	0.2	0.0	0.1	17.0								
3	112	1/3	56	94	97.9	0.2	0.0	0.1	1.18	0.3	1.5	0.0	3.0	0.0	0.3	3.5	97.4[c]
4	69.6	1/3	60.6	81.1						1.0	4.7	9.5	17.0	4.2	13.8	26.1[d]	33.7
5	42.3	1/3	14.0	95.9						1.9	10.0	1.6	24.5	21.9	10.2	19.7	10.2
6	243	2/3	96.8	99.7													

[a] Includes NO_2, N_2, CO, O_2, and unidentified materials.

[b] N_2O, HF, NO_2, O_2, SO_2, and unidentified materials.

[c] Heavily contaminated with CO_2 (74.3 mole %).

[d] Large amount of O_2 is indicative of the decomposition of some O_2-containing species.

reaction and only trace quantities of F^-.

At a temperature of $-160\,°C$, 4.5 mmoles O_2F_2 was allowed to react with 3.3 mmoles $KClO_4$ overnight. The cooling bath had thawed, but not enough to cause complete decomposition, and some noncondensable products were found. An unstable purple condensate was obtained in the $-196\,°C$ trap (probably O_2ClF_3). After the residual O_2F_2 had decomposed 5.2 cc of condensable gas was collected, and an infrared spectrum indicated the presence of SiF_4, COF_2, CO_2, $COCl_2$, possibly ClO_3F, and some unidentified bands.

In a second experiment, 11.8 mmoles O_2F_2 was allowed to react with 5 mmoles $KClO_4$ at $-160\,°C$ for 7 hr, while the non-condensable gas was continuously pumped off. No purple, $-196\,°C$ condensate was observed. After the O_2F_2 decomposed, 2.6 cc of condensable gas was obtained which contained COF_2, $COCl_2$, SiF_4, and unidentified products. No ClO_3F was indicated. Only 0.30 mg of fluoride was found in the solid residue.

At $-160\,°C$, 6 mmoles of O_2F_2 and 3.4 mmoles of KNO_3 were allowed to react overnight; pumping was continuous, and 3.1 cc of condensable gas was obtained, which contained COF_2, $COCl_2$, SiF_4, and unidentified products. Only 0.44 mg of fluoride was present in the solid residue.

Sodium sulfide detonated after standing in contact with O_2F_2 for about 1 hr, and $NaNO_3$ reacted with O_2F_2 to form small amounts of nitrate and fluoride.

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D. Physical Properties of O_4F_2

The nature of O_4F_2 in both the vapor and 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 oxygen and fluorine? Is O_4F_2 dimerized or ionized in the liquid or solution phase?

Preliminary attempts to prepare O_4F_2 were carried out in the apparatus shown in Figure 7. Although the apparatus was conditioned with fluorine before the first run, only 1/7 of the initial fluorine could be found in the product. It was apparent that the nickel electrodes had been badly attacked during the reaction. Consequently, the nickel wire electrodes were replaced by copper disks, which were silver-soldered to lead-ins of 1/4-in. copper rod. Two batches of O_4F_2 were made in the modified reactor, and the difficulty seemed to be corrected. However, after approximately 15 min. of operation, the discharge occurred near the top of the generator rather than at the disks.

Two preliminary vapor pressure measurements were made before delivery of the spiral gage. These measurements, made with an Alphatron gauge, will guide future experiments. This instrument indicated a pressure of 20 to 25 microns at -196 °C and 0.2 microns at -183 °C. These experiments indicated that it will be necessary to study the vapor density of O_4F_2 at temperatures around -183 °C.
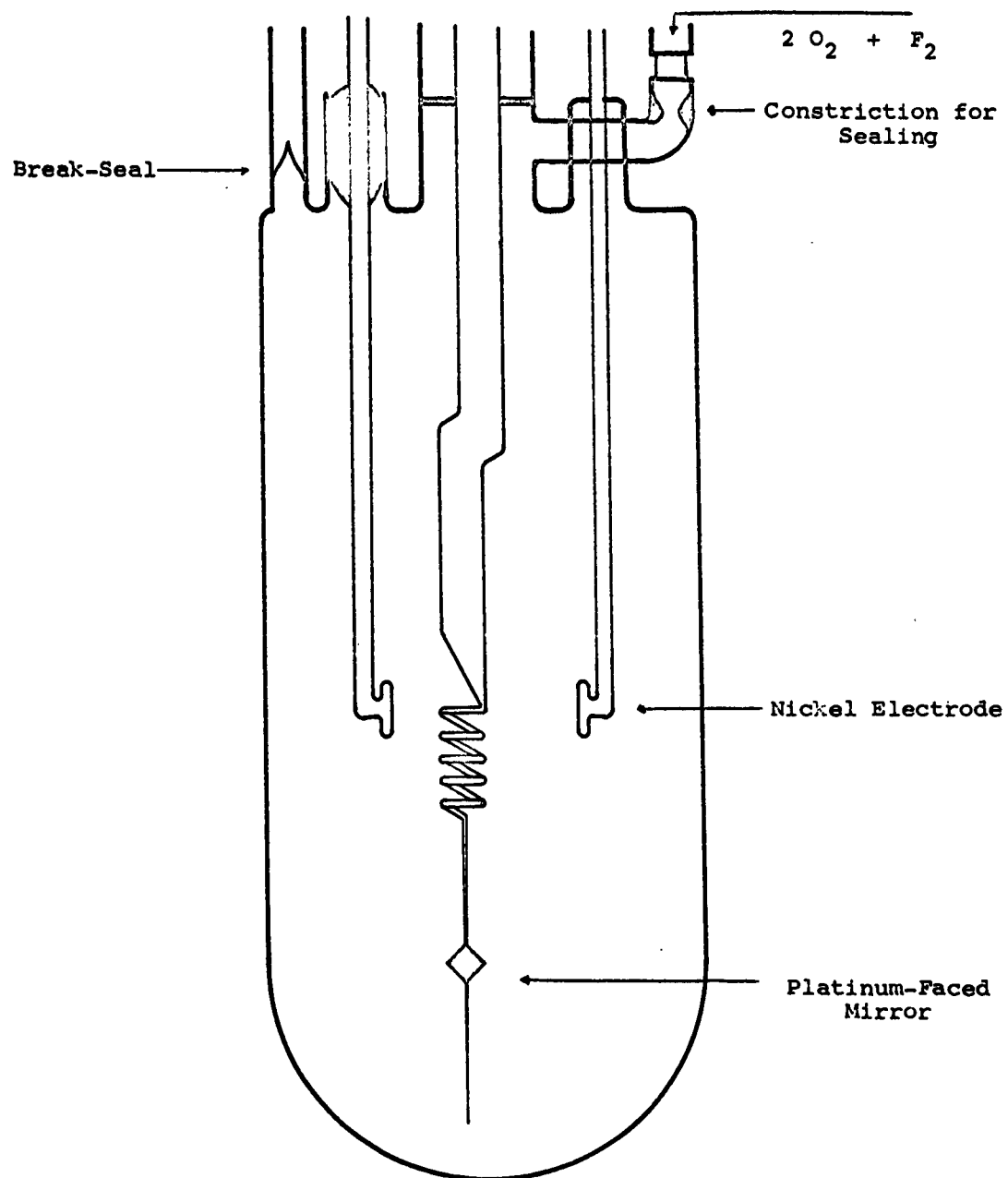
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Figure 7

O_4F_2 GENERATOR WITH INTEGRAL SPIRAL PRESSURE GAUGE

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E. 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 pre-requisite 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 which includes these factors. This study has been initiated, and some of the significant results obtained to date are summarized below.

1. BF_3-HNF_2 System

BF_3 and HNF_2 are known to form an addition compound, probably of the form:

$$\overset{\displaystyle H}{\underset{\displaystyle F_2N:BF_3}{|}}$$
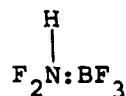
In our initial attempt to obtain this compound, we carried out the following reaction: HNF_2 was condensed in a trap at $-127\,°C$, and BF_3 was condensed in an adjacent trap at $-196\,°C$. The BF_3 was then warmed and allowed to bubble into the HNF_2. As the mixture was slowly warmed, a white solid formed. This solid decomposed on further warming to room temperature. The resultant mixture of gases was fractionated. The $-112\,°C$ condensate was a

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sublimable white solid which vaporized without melting; the vapor exerted a pressure of 227.9 mm at 22°C in the reaction system (calc., 233.6). The following vapor pressures were determined at different temperatures.

Pressure, mm	Temp, °C
1.7	-78.5
11.7	-63.5
98.7	-45.2
398.2	-30.7

These data, plotted as log P vs 1/T, gave a straight line, from which the following empirical equation was obtained.

$$\log P = \frac{-2,346}{T} + 12.2682 \tag{15}$$

The compound had a sublimation point of -23.3°C and a calculated heat of vaporization of 21.6 kcal/mole.

2. HNF_2-HCl System

No reaction was evident when HNF_2 and anhydrous HCl were condensed together at -112°C and the mixture allowed to warm slowly to room temperature.

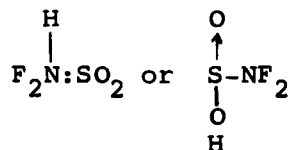A vapor pressure-composition diagram of the system was obtained at -112, -127, and -138°C. For these experiments, HNF_2 was condensed in one trap and HCl in an adjacent trap. The HCl was then added to the HNF_2 in small increments to keep the mixture at the desired temperature. In each case positive deviations from Raoult's law were obtained when the pressure was plotted

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against the mole fraction of HCl; this indicated that no compound had been formed.

3. HNF_2-SO_2 System

A vapor pressure-composition diagram for the HNF_2-SO_2 system was obtained by adding the SO_2 to the HNF_2 at -65 °C in a manner similar to that used for the HNF_2-HCl system. A negative deviation from Raoults's law was found up to 50 mole % SO_2, at which point the curve became parallel with the x axis. This indicated the formation of a 1:1 compound. An attempt was made to reproduce these results by an approach from the opposite direction; that is, by adding HNF_2 to SO_2. This curve had the same shape as the first, but the pressures in the region from 50 to 100 mole % SO_2 were considerably lower than those obtained during the first run. Obviously this experiment must be repeated until reproducable results are obtained.

Two types of 1:1 compounds could be formed from the reaction between HNF_2 and SO_2:

$$
\begin{array}{ccc}
\text{H} & & \text{O} \\
| & & \uparrow \\
\text{F}_2\text{N:SO}_2 & \text{or} & \text{S-NF}_2 \\
& & | \\
& & \text{O} \\
& & \text{H}
\end{array}
$$

To date we have not determined the nature of the compound formed in our experiments.

4. HNF_2-SO_3 System

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Considerable difficulty was encountered in studying the HNF_2-SO_3 system because of the tendency of the SO_3 to polymerize and react with stopcock grease. Even Kel-F90 grease became brownish-black after SO_3 had been handled in the vacuum line. To prevent polymerization of the SO_3, it was first depolymerized by heating, then measured as a gas, and finally condensed at 0 °C in the reaction vessel. When HNF_2 was added at -63.5 °C, equilibrium was not obtained. The pressure was much too high and dropped markedly when the reaction vessel was thawed at the end of the experiment. At -30.7 °C, the vapor pressure-composition diagram indicated the formation of a 1:1 and, possibly, a 1:2 compound. Equilibrium was attained very slowly in this system, and the curves are very difficult to reproduce. Further work is in progress on the system at -30.7 °C and higher temperatures to determine whether the 2:1 compound is actually formed.

F. Fluorination of Nitric Acid

Cady[3] has shown that NO_3F is the gaseous product of the fluorination of HNO_3. The information in the literature[3,4] indicates that the oxidizing species which remains in the acid is a peroxide, but it is not known whether the peroxide is H_2O_2 or a new, more interesting compound.

In our early fluorination experiments, concentrated HNO_3

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[3] Cady, G., J. Am. Chem. Soc., Vol. 56, p. 2635, 1934.

[4] Ibid., Vol. 57, p. 246, 1935.

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in a Pyrex NMR tube was treated with fluorine gas introduced through a long platinum tube. During the reaction NO_3F gas bubbles evolved and were later flushed away with nitrogen gas. As the reaction proceeded, a white material was detected in the tube. This material was isolated and shown to be Na_2SiF_6. Although several samples were prepared and submitted for NMR analysis, the results showed only a slight absorption in the SiF^{19} region.

For some of the fluorinations, we used NMR tubes of Teflon, but these proved unsatisfactory. The reactions carried out in Vycor tubes produced no detectable Na_2SiF_6. A test of the fluorinated solution with acidified $TiOSO_4$ reagent showed no color change; the fluoride ion, if present, interferes with this test.

Efforts are now being concentrated on fluorinating HNO_3 solutions in pure quartz NMR tubes. Previous experiments indicate that concentrated HNO_3 could be treated with fluorine gas if the acid was contained in Vycor so that no Na_2SiF_6 would be formed. Concentrated HNO_3 will again be treated with fluorine in pure quartz tubes, and the NMR spectra will be recorded immediately. If this procedure yields significant results, HNO_3 solutions of various concentrations will be fluorinated and their NMR spectra recorded.

At present we are studying the optical absorption of fluorinated 100% HNO_3 in the infrared region. We hope this

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technique will furnish a means of following the course of fluorination and provide other evidence about the identity of the dissolved oxidizing species referred to by Cady.[4] Pure HNO_3 was prepared and distilled into the cell (55 mm). After a short time in the cell, brown deposits formed on the BaF_2 windows. These deposits probably were due to the reaction of HNO_3 with the Viton "O" rings. Furthermore, the long cell allows the pure HNO_3 to absorb all the incident radiation. Further studies will require the use of a much shorter cell.

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