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ADVANCED OXIDIZER RESEARCH

COMBINED REPORT
Projects 076, 5007, 5017 and 5009

30 April 1963

DOD DIRECTIVE 5200.10

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Thiokol®
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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(U) ADVANCED OXIDIZER RESEARCH

30 April 1963

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Supervisor, Synthetic Chemical Research Section

Approved by: MURRAY S. COHEN
Manager, Chemistry Department

DAVID J. MANN
Director of Research

April 30, 1963 shall be used for purposes of downgrading and/or declassification of this document.
This report has been distributed in accordance with a combined LPIA-SPIA Distribution List in effect as of the publication date of this report.
GENERAL FOREWORD

This quarterly report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry being conducted at this Division under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, and was conducted under the following contracts:

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Reports on these programs were previously issued separately. Since the reporting dates did not coincide in all cases, the time periods covered for the separate programs are not exactly the same. The actual time period covered on each task is indicated in the Foreword to the appropriate section of the report. Future reports will also be issued on a calendar quarter basis on all these programs.
GENERAL INTRODUCTION

This report describes research conducted at Thiokol Chemical Corporation, Reaction Motors Division directed toward the development of advanced solid oxidizers. The four major tasks on which work has been performed are listed below, together with the objective of each task, and are included as four separate sections of this report.

SECTION I. RMD PROJECT 076 - DIFLUORAMINE CHEMISTRY

Investigation of the chemical reactions of the organic difluoramines.

SECTION II. RMD PROJECT 5007 - STRUCTURE-SENSITIVITY STUDY

Preparation of a series of organic difluoramines for evaluation of the relationship between structure and sensitivity.

SECTION III. RMD PROJECT 5017 - STABILIZATION OF HIGH ENERGY SOLID OXIDIZER

Investigation of the reactions of $\text{NO}_2\text{ClO}_4$ with various ligand molecules in an effort to increase the size of the $\text{NO}_2^+$ cation and thereby improve the stability of $\text{NO}_2\text{ClO}_4$.

SECTION IV. RMD PROJECT 5009 - INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

Investigation of the chemical reactions of $\text{O}_2\text{F}_2$ and other oxygen subfluorides in an effort to discover new reactions leading to solid oxidizers containing oxygen and fluorine.
Section I

RMD Project 076

(D) DIFLUORAMINE CHEMISTRY
Section I

(U)
DIFLUORAMINE CHEMISTRY

H. F. Smith

Report RMD-AOR-Q1-63

RMD Project 076
Report Period: 1 January 1963 to 31 March 1963

Contract No. NOnr 1878(00)
ARPA Order No. 186-61
Project Code No. 3910
This report has been distributed in accordance with a combined LPIA-SPIA Distribution List in effect as of the publication date of this report.
FOREWORD

This section of the quarterly report covers research conducted during the period from 1 January 1963 to 31 March 1963 on the chemical reactivity of alkyldifluoramines (RMD Project 076).

Technical personnel contributing to this work included: H. F. Smith (Project Scientist), and J. Castellano (Synthesis), and R. Storey, D. Yee, J. Creatura, and A. Fremmer (Instrumental and Wet Chemical Analysis).
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ABSTRACT

An improved synthesis of tert-butyldifluoramime, based upon the thermally initiated reaction between tert-butyl iodide and tetrafluoro hydrazine, has been developed. The method consistently gave 40% yields in one step, from a readily available starting material. At higher temperatures, some 1,2-bis(difluoramino)-2-methylpropane was formed, at the expense of the primary product.

Additional evidence has been accumulated supporting the interpretation of the reaction between tert-butyldifluoramime and phenyllithium as a one-electron reduction process involving free radical intermediates. The alkyldifluoramime reacted with n-butyllithium in a similar fashion, to produce n-octane.

Concentrated nitric acid was reduced by tert-butyldifluoramime to nitrogen tetroxide. Carbon dioxide and mixed alkyl nitrates were also formed.
I. INTRODUCTION

The objective of this research program is to investigate the chemical properties of alkyldifluoramines and to elucidate the mechanisms of those reactions which are found to occur. Such information can be applied in the development of useful new synthetic reactions in difluoramine chemistry, as well as in the effective utilization of related nitrogen-fluorine compounds in high energy propellants. In addition, some of the knowledge gained might contribute to the solution of fundamental chemical problems of much broader scope.

A system for the classification of chemical reactivity studies was presented in the Annual Technical Summary Report for 1962 (Ref 1). This system is based upon the nature of the reagents being studied, i.e., atoms or free radicals, electrophilic and nucleophilic reagents, and oxidizing and reducing agents. Our research efforts during the present report period have been directed toward two of these general areas.

The one-electron reduction of tertiary alkyldifluoramines by organometallic compounds (Ref 2) has been explored in greater detail, and additional evidence supporting the proposed mechanism has been accumulated. Reactions of tert-butyldifluoramine with both phenyllithium and n-butyllithium have been studied.

An investigation of the reaction of tert-butyldifluoramine with concentrated nitric acid was initiated during the present quarter. Although the identification of products and the delineation of the stoichiometry and mechanism of the reaction have not yet been completed, a discussion of the significance of preliminary observations is included in this report.

A new, convenient, and more efficient synthesis of the model compound, tert-butyldifluoramine, has been developed, and details of the procedure are described.
II. DISCUSSION

A. PREPARATION OF TERT-BUTYLDIFLUORAMINE

When tert-butyldifluoramine (II) was first adopted as a model compound for these studies (Ref 3), the only known method of synthesis involved the photolysis of a mixture of tetrafluorohydrazine and azoisobutane (Ref 4) (equation 1). The yield of purified product was only 20% of theory (Ref 2).

\[
N_2F_4 + (CH_3)_3CN\equiv NC(CH_3)_3 \rightarrow 2(CH_3)_3CNF_2
\]  

(1)

I

II

In addition, the synthesis of I (Ref 5, 6) proceeded with a yield of only 30%, giving a 6% overall yield for the two-step process.

Since the use of substantial quantities of II was anticipated, a more efficient method of synthesis was sought. The direct fluorination of the isomeric n-butylamine in aqueous medium (equation 2) had been reported (Ref 7).

\[
C_4H_9NH_2 + 2F_2 + 2NaHCO_3 \xrightarrow{H_2O} C_4H_9NF_2 + 2NaF + 2H_2O + 2CO_2
\]  

(2)

Attempts to apply this method to the preparation of the tert-butyl analog, however, were unsuccessful (Ref 1).

Other simple alkyldifluoramines have been produced by the photolysis of the corresponding alkyl iodides in the presence of tetrafluorohydrazine (Ref 8). This method has now been applied to the synthesis of tert-butyldifluoramine (equations 3, 4, 5 and 6).

\[
(CH_3)_3CI \rightarrow (CH_3)_3C^- + I^-\]  

(3)

\[
N_2F_4 \rightarrow 2 \cdot NF_2\]  

(4)

\[
(CH_3)_3C^- + \cdot NF_2 \rightarrow (CH_3)_3CNF_2\]  

II

(5)
Furthermore, experiment has shown that the same results obtained by photolysis can be achieved by thermal activation, with a consequent decrease in reaction time from 20 hours to 3-4 hours. Yields of 40% of the desired model compound have been obtained routinely using this technique. No increase in yield was observed when the reaction time was increased to six hours. The distilled product was identified by comparison of its boiling point and infrared and mass spectra with those of a sample prepared by the azoisobutane method.

The identification of the by-products of the reaction is of interest as a possible means of effecting still further improvement in the yield. A mixture of the gaseous products was examined by infrared and mass spectrometry, and found to contain N₂, NO, N₂O₄, N₂F₄, CF₄, C₂F₆, and SiF₄. The fluorocarbons are known contaminants in the tetrafluorohydrazine used. The nonvolatile tarry residue consisted principally of iodine and polymeric material. No evidence for the formation of 2, 2, 3, 3-tetramethylbutane, from the coupling of two tert-butyl radicals, was found (equation 7).

\[2(CH₃)₃C· \rightarrow (CH₃)₃C-C(CH₃)₃\]  \hspace{1cm} (7)

In one instance, in which the reaction temperature was 110°C instead of the usual 80-100°C, the yield of tert-butyl difluoramine decreased to 25%. In addition, there was obtained in 24% yield a liquid (bp 115°C) which was identified by its infrared spectrum as 1, 2-bis(difluoramino)-2-methylpropane (III). The infrared spectrum of this compound is reproduced in Figure 1. This observation may be explained by the mechanism outlined in equations 8 and 9.

\[2(CH₃)₃C· \rightarrow (CH₃)₂CH + CH₂=C(CH₃)₂\] \hspace{1cm} (8)

\[CH₂=C(CH₃)₂ + N₂F₄ \rightarrow CH₂C(CH₃)₂ \hspace{1cm} (9)

Either thermodynamic or kinetic considerations, or a combination of both, may be involved in this side reaction. It may be that an increase in temperature accelerates the reaction shown in equation 8 to a greater extent than that in equation 5. Alternatively, the increase in concentration of tert-butyl free radicals produced by increasing the temperature would be expected to increase the probability of the disproportionation reaction (equation 8). This explanation assumes that the increase in concentration of NF₂ radicals with increasing...
Figure 1. Infrared Spectrum of 1,2-bis(Difluoromino)-2-methylpropane
temperature is not proportionately great. In either case, the addition step (equation 9) must be reasonably rapid.

B. REACTIONS OF TERT-BUTYLDIFLUORAMINE WITH ORGANOMETALLIC COMPOUNDS

A preliminary investigation of the reaction of tert-butyldifluoramine with phenyllithium has been described in previous reports (Ref 1, 2). This reaction has now been repeated essentially as before, but on a larger scale (23 mmoles) to permit more complete recovery of products. In this instance, the organic portion of the reaction mixture was fractionated by distillation through a Vigreaux column. The first six fractions, collected at atmospheric pressure, consisted of mixtures of ether and benzene containing traces of starting material and biphenyl. The seventh fraction, weighing 0.25 g, boiled at 95-110°C at 0.1 mm. This fraction was found to be a complex mixture, showing infrared absorptions indicative of O-H, C=O, N-F, C-O-C, and substituted aromatic groupings. Attempts to separate this mixture into its constituents by gas chromatography are in progress.

The eighth distillation fraction, weighing 0.85 g, was mainly biphenyl. This is more than twice the amount of biphenyl contained in a corresponding sample of the phenyllithium reagent. It is clear then that a significant amount of biphenyl was formed in the reaction, and this fact lends further weight to the one-electron reduction mechanism proposed earlier.

The distillation residue, 0.70 g, consisted of mixed aliphatic compounds along with some biphenyl. Gas chromatographic methods will be utilized in an effort to isolate additional products from this fraction.

Analyses of the aqueous extract of the reaction mixture have not been entirely satisfactory. A blank (equal aliquot of the phenyllithium reagent, hydrolyzed with water) was found to contain 19.81 meq of Li⁺ and 20.45 meq of OH⁻. Comparison of these figures with the theoretical 23.00 mmoles indicates that the reagent is 12.5% lower in concentration than the nominal value. The aqueous solution from the reaction contained 17.67 meq of Li⁺, indicating a recovery of 89%. The sum of F⁻ (5.10 meq) and OH⁻ (8.60) did not agree with the amount of Li⁺ found. The reason for this discrepancy has not yet been determined.

In the same fashion, tert-butyldifluoramine was treated with n-butyllithium in hexane solution. The reaction observed was qualitatively similar to that which occurred when phenyllithium was used. Dark brown products formed.
with the evolution of heat. After the reaction was quenched with water, the hexane layer was found to contain some unreacted tert-butyldifluoramine and some n-octane. No products derived from the difluoramine could be detected in the organic portion. The aqueous fraction will be examined for possible water-soluble products and analyzed for the usual lithium, fluoride, and hydroxide.

The production of n-octane suggests that the same reaction path is followed as in the case of phenyllithium. The absence of high-boiling hydrocarbon-soluble products, however, remains to be explained.

C. REACTION OF TERT-BUTYLDIFLUORAMINE WITH NITRIC ACID

Past experience has shown that alkyldifluoramines are oxidized by permangamate, but not by mercuric oxide or neutral hydrogen peroxide (Ref 1, 9). Electrophilic attack by strong acid led to the elimination of hydrogen fluoride from a secondary alkyldifluoramine and difluoramine from a tertiary compound (Ref 1, 10). It is of interest then to determine what type of reaction, if any, occurs between a tertiary alkyldifluoramine and nitric acid.

An investigation into this area has been started. When tert-butyldifluoramine was mixed with concentrated nitric acid, there were no visible indications that reaction had occurred after a few hours at 28 or at 50°C. After standing at room temperature for 16-20 hours, however, the mixture rather abruptly became colored and evolved nitrogen tetroxide. Other products included N₂O₅, NO₂F, CO₂, SiF₄, and unidentified alkyl nitrites and nitrates. Some unreacted tert-butyldifluoramine was also detected, but no other material containing a nitrogen-fluorine bond was present. Molecular oxygen was not found among the products.

In the preliminary experiments which have been performed so far, it has not been possible to quantitatively determine the amounts of various products formed. Provision for this refinement will be made in future experiments. It will be instructive, for example, to determine whether the amount of dinitrogen tetroxide generated can be correlated with the amount of alkyldifluoramine consumed. It is known (Ref 11) that the thermal decomposition of nitric acid produces nitrogen tetroxide (equation 10), and it is obviously

\[
2\text{HNO}_3 \rightarrow \text{N}_2\text{O}_5 + \text{H}_2\text{O} + \text{O}_2
\]

(10)
possible that catalytic effects might lower the activation energy so that the reaction might become significant at room temperature. The absence of oxygen in the reaction products tends to argue against this process, but it is also possible that the atomic oxygen formed would react preferentially with the alkyl-difluoramine. Quantitative determination of the nitrogen tetroxide formed should help answer these questions.

The appearance of carbon dioxide among the products indicates extensive oxidative degradation of the tert-butyl moiety. The fact that a mixture of alkyl nitrites is produced, in place of solely tert-butyl nitrite, gives further support to this conclusion.
III. EXPERIMENTAL

A. PREPARATION OF TERT-BUTYLDIFLUORAMINE

A 2000 ml pyrex bulb was charged with 6.0 g (4.0 ml, 0.033 mole) of tert-butyl iodide under a stream of dry nitrogen. The bulb was degassed three times by a freeze-thaw technique (-78 to 25°C), and 4.16 g (0.040 mole) of N₂F₄ was condensed in at liquid nitrogen temperature. The bulb was then heated for four hours at 80-100°C. The gases were passed through traps at -78 and -196°C. The -78°C trap contained the crude tert-butylidifluoramine. This process was repeated four times, and the products of all four runs were combined and distilled to yield 5.8 g (0.053 mole, 40.7%) of tert-butylidifluoramine, (bp 54-56°C) (vapor pressure 227 mm at 25°C).

B. PREPARATION OF 1,2-BIS(DIFLUORAMINO)-2-METHYLPROPANE

The procedure described for the preparation of tert-butylidifluoramine was duplicated, except that two of the four runs were heated to 110°C. The products of all four runs were combined and distilled to yield 3.5 g (25%) tert-butylidifluoramine, bp 55-56°C, and 2.5 g (24%) 1,2-bis(difluoramino)-2-methylpropane, bp 110-115°C. The infrared spectrum of the latter showed absorptions which confirmed the assigned structure.

The residue from two runs was taken up in CH₂Cl₂ and washed with water, Na₂S₂O₃ solution, and again with water. The CH₂Cl₂ solution was dried over Na₂SO₄ and filtered. Removal of the solvent left a brown residue which appeared to be degraded polymeric material, as indicated by infrared analysis.

C. REACTION OF TERT-BUTYLDIFLUORAMINE WITH PHENYLLITHIUM

tert-Butylidifluoramine (2.50 g, 0.023 mole) was dissolved in 20 ml of sodium-dried ether, and the solution was cooled to 0°C. Under a stream of nitrogen, 11.5 ml (0.023 mole) of phenyllithium solution in benzene-ether (Lithium Corp. of America), diluted with an additional 10 ml of sodium-dried ether, was added dropwise to the stirred solution at such a rate as to maintain the temperature at 0-5°C. This required about 30 minutes. The dark brown mixture was stirred for one hour at 0°C and then quenched with 20 ml of cold H₂O. The aqueous and organic phases were separated. The aqueous phase
was washed with two 20 ml portions of ether, and the organic phase was washed with two 20 ml portions of water. The combined aqueous solution was submitted for analysis for Li+, F-, and OH-. The combined organic extracts were dried over Na₂SO₄ and distilled through a Vigreux column. The ether and benzene collected were found to contain traces of biphenyl. A liquid, bp 95-110°C/0.1 mm and weighing 0.25 g, was found to be a mixture of materials showing infrared absorption due to C=O, OH (alcohol), N-F, substituted aromatics and C-O-C. This material is being subjected to gas chromatographic separation and mass spectral analysis. In addition, 0.85 g of biphenyl was obtained and a residue weighing 0.70 g remained. This residue appeared to contain biphenyl and other substituted aromatics.

D. REACTION OF TERT-BUTYLDIFLUORAMINE WITH N-BUTYLLITHIUM

Tert-butylidifluoramine (2.20 g, 0.020 mole) was dissolved in 10 ml of hexane and the solution cooled to 0°C. Under a stream of nitrogen, 12.9 ml (0.020 mole) of n-butyllithium in hexane (Foote Mineral Corp.), diluted with 10 ml of hexane, was added dropwise to the stirred solution over a period of one hour. The color of the mixture darkened as stirring was continued for 1-1/2 hours at 20°C. The mixture was then treated with 20 ml of H₂O; no temperature rise was noted. The aqueous and organic phases were separated and treated as above (Section III C), using hexane as the solvent for extraction. The hexane solution was dried over Na₂SO₄ and distilled. The initial distillate, bp 33-68°C, was a mixture of hexane and tert-butylidifluoramine. After removal of the low-boiling fraction, a 1.0 g residue remained which appeared to be principally n-octane, as determined by infrared and mass spectral analysis. The aqueous solution was submitted for analysis as described above.

E. REACTION OF TERT-BUTYLDIFLUORAMINE WITH NITRIC ACID

Concentrated nitric acid (10 ml, 0.15 mole) was added dropwise to 0.55 g (5.0 mmoles) of tert-butylidifluoramine under nitrogen at one atmosphere pressure. A very slight temperature rise was indicated by the passage of a few bubbles through a bubbler tube attached in series with a U-trap kept in a bath at -78°C. The mixture was stirred for two hours at room temperature and for 1-1/2 hours at 48-50°C. There was no indication that reaction occurred. After standing at room temperature for an additional 20 hours, the solution had become yellow and the gas phase had become brown. The material collected in the trap was expanded at 0°C into an infrared cell. Only a small amount of tert-butylidifluoramine was detected. The aqueous solution was then diluted with water and extracted twice with CCl₄. The infrared spectrum of
CCl₄ extract was compared with that of a sample of CCl₄ which had been treated with N₂O₄ in HNO₃. Extra absorptions in the extract of the reaction mixture were attributed to C-H (3.40/7.69 μ) and alkyl nitrite (6.11/7.79 μ). Evaporation of the aqueous HNO₃ solution left a very small residue of unidentified salt.

In a second experiment, 1.02 g (9.3 mmols) of tert-butyl difluoramine was condensed under vacuum into a flask containing 10 ml (0.15 mole) of concentrated HNO₃. The mixture was warmed to room temperature and stirred. The pressure rose to 210-220 mm and remained constant for 16 hours. After this period, the pressure rose within 1-1/2 hours to 730 mm, with the evolution of brown gas. On cooling the reaction flask to -70°C, the pressure dropped to 340 mm. A sample of this gas was subjected to infrared analysis and found to contain C-H (3.33/6.75 μ), C-CH₃ (7.27 μ), N₂O (4.5 μ), N₂O₄ (5.72/6.15 μ), N-F (attributed to starting material, 10.30/11.35 μ), NO₃F (10.85/12.65/13.90 μ), CO₂ (4.35/15.96 μ), SiF₄ (9.75 μ), and NOCl (presumably from attack on NaCl window, 5.53/5.58 μ). Mass spectrometric analysis confirmed the presence of starting difluoramine, CO₂ and/or N₂O, SiF₄, and NO₃F, and established the absence of H₂ and O₂. A second gas sample taken at 0°C was found to contain some of these components, but no additional products. The acid solution was extracted with pentane to remove organic products. Infrared analysis of this extract revealed the presence of alkyl nitrite and nitrate (C-H at 3.51/6.90 μ, possible C-CH₃ at 7.28 μ, C-ONO at 6.41 μ, and C-ONO₂ at 6.10 μ). Analysis of the remaining aqueous phase is in progress.
IV. FUTURE PLANS

During the next quarter, the following activities are planned:

- Studies on the reaction of tert-butylidifluoramine with organo- metallic compounds and other one-electron reducing agents will be extended to include:
  - The effect of variations in mole ratio of reactants.
  - The effect of reversing the order of addition.

- The reaction of tert-butylidifluoramine with nitric acid will be explored in greater detail, with particular emphasis on the stoichiometry and possible mechanisms for the reaction.
V. REFERENCES


Section II

RMD Project 5007

(U)

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY
Section II

(U)
SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby

Report RMD-AOR-Q1-63

RMD Project 5007
Report Period: 15 December 1962
31 March 1963

Contract No. NOnr 3664(00)
ARPA Order No. 23-62
Project Code 3910
FOREWORD

This section of the quarterly report describes work conducted during the period from 15 December 1962 to 31 March 1963, on the synthesis of organic difluoramines for use in the study of structure-sensitivity relationships (RMD Project 5007).

The following technical personnel participated in this research: D. D. Perry (Project Scientist), A. P. Kotloby (Principal Investigator), J. A. Castellano (Synthesis), R. N. Storey, D. Y. Yee, and J. A. Creatura (Instrumental and Wet Chemical Analysis).
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CONFIDENTIAL

Project 5007
Report RMD-AOR-Q1-63
ABSTRACT

Work is reported on the preparation of aliphatic vicinal and geminal difluoramines for use in evaluating relationships between structure and sensitivity in the organic difluoramines. Compounds having carbon to NF$_2$ ratios of 3:1 or less, and which are solids or liquids boiling above 56°C, are desired for this study.

During the current report period, the following compounds were prepared, purified and submitted to the Naval Ordnance Laboratory for sensitivity evaluation: 2,2-bis(difluoramino)pentane, 1,1-bis(difluoramino)cyclopentane, 1,2-bis(difluoramino)cyclohexane, and 1,1-bis(difluoramino)cyclohexane. These compounds are stable, distillable liquids and are shock sensitive in qualitative tests.
I. INTRODUCTION

Investigations of organic difluoramines as ingredients of rocket propellants have produced a large variety of poly(difluaramino) compounds. A common feature of these compounds is their sensitivity to impact. Since propellants are normally subjected to many kinds of stresses during handling, storage and use, the study of the impact and thermal sensitivity of difluoramino compounds is important in assessing their practical value as propellants.

In order to determine whether systematic relationships between the structure and sensitivity of this class of compounds can be established, the Reaction Motors Division of Thiokol Chemical Corporation has undertaken a program sponsored by the Advanced Research Projects Agency and the Office of Naval Research for the preparation of a series of organic difluoramines for sensitivity evaluation. The preparation and purification of the compounds are the responsibility of Reaction Motors Division, while sensitivity tests are conducted at the Naval Ordnance Laboratory, White Oak, Maryland.
II. DISCUSSION

Previous efforts on this program were centered on the preparation of poly(difluoramo) carbamates (Ref 1), since these materials were expected to be low-melting solids and could, therefore, be evaluated in both the Bureau of Mines dropweight test (Ref 2) and the thermal explosion delay test (Ref 3).

As expected, the sensitivity of the carbamates as measured by the explosion delay test was found to increase with a decrease in the C:NF₂ ratio. It appeared that when the C:NF₂ ratio was greater than three, results in this test were not significant because of the long delay to the explosion causing erratic results. It was also found that the low energy carbamate group further reduced the impact sensitivity of these compounds. Furthermore, improvements in the accuracy of the explosion delay test, which employs liquids, made this test of greater interest in the study. Therefore, it was decided that further synthetic work would be limited to compounds with C:NF₂ ratio of three or less and that no special effort would be made to prepare solids. Organic difluoramines having functional groups likely to be employed in propellant compounds have been selected, and structural variations are being sought which will permit correlation of the sensitivity with the following factors:

- Oxidative balance of the molecule
- Normal versus branched chain and cyclic structures at a given C:NF₂ ratio, and with both geminal and vicinal NF₂-groups
- Other functional group(s) in the organic difluoramidine molecule

Below are listed in the order of decreasing emphasis the types of compounds (containing both vicinal or geminal NF₂-groups) that are to be synthesized on this program:

1) Alkanes, cyclic and acyclic
2) Alkenes, cyclic and acyclic
3) Esters
4) Acetals
5) Ethers
6) Nitriles
7) Alcohols
8) Ketones
9) Halides
10) Nitro compounds
11) Perfluoro and partially fluorinated hydrocarbons

A. PREPARATION OF VICINAL DIFLUORAMINES

The addition of tetrafluorohydrazine to olefins is a general route for the synthesis of vicinal bis(difluoramines). In the case of unhindered olefins containing isolated double bonds, the reaction can usually be carried out at approximately atmospheric pressure in a glass bulb. For volatile or somewhat less reactive olefins, the reaction is conveniently carried out in an all-glass pressure reactor of the Fischer-Porter type (Ref 4), or in steel Hoke bomb, at 70-100°C under a pressure of 150-250 psig. In order to form tetrakis-NF₂ adducts from conjugated dienes, higher temperatures and pressures and longer reaction time are generally required (Ref 5). In a typical reaction, a solution of the olefin in a solvent (e.g., Freon-113) is charged into the pressure reactor and degassed at -80°C. The solvent moderates the reaction and also desensitizes the reaction products. Tetrafluorohydrazine is then condensed into the reactor at -196°C, and the contents are heated for a period of 3-24 hours. The yield of crude product is usually in the range of 60-80% of the theoretical yield.

During the current report period, work on the preparation of vicinal bis(difluoramines) was limited to the preparation of 1,2-bis(difluoramino)-cyclohexane, prepared previously on another program (Ref 6). The procedure described in this reference was used, and a 45% yield was obtained.

B. PREPARATION OF GEMINAL DIFLUORAMINES

The reaction of carbonyl compounds with HNF₂ in ~100%-H₂SO₄ to yield geminal bis(difluoramines) has been investigated in many laboratories (e.g., Ref 7). At present, the best source of HNF₂ required for this reaction is N,N-difluorourrea, from which difluoramine is readily generated by acid hydrolysis (Ref 8, 9). Both reactions, the fluorination of urea and the generation of HNF₂, proceed smoothly and in high yields. After being scrupulously dried, the difluoramine is refluxed in ~100%-H₂SO₄ (or SO₃), and a methylene chloride solution of the ketone or aldehyde is added. Experimental conditions are critical. Failure to use acid of sufficient strength or use of too
small a quantity of acid results in failure of the reaction. Too much acid and/or too long a reaction time drastically reduce the yield. In general, the specific reaction conditions must be worked out for each new compound. Once prepared, geminal organodifluoramines are readily purified by distillation. Work with compounds having a high $\text{NF}_2/\text{C}$ ratio must be carried out in a shielded hood and on small scale, owing to their high-impact sensitivity.

During this period, 1,1-bis(difluoramino)cyclopentane, 1,1-bis(difluoramino)cyclohexane and 2,2-bis(difluoramino)pentane were prepared. Details of these preparations will be found in the Experimental Section.
III. EXPERIMENTAL

A. PREPARATION OF DIFLUOROUREA BY AQUEOUS FLUORINATION

A 1000-ml three-neck flask was filled with a solution of 50 g (0.83 mole) of urea in 600 ml of water. The solution was cooled to 0°C by means of an external ice-water bath. A 20% (by volume) mixture of fluorine in nitrogen was bubbled through the vigorously stirred solution, the temperature of which was kept at 0-5°C. Over a period of six hours, 2.0 moles of fluorine were bubbled through the solution. The solution was then stirred for an additional hour under a stream of nitrogen. The total volume of solution at the end of the reaction was 670 ml, indicating an increase in volume of 70 ml. The titration of the solution (iodometric method) showed the presence of 4.032 meq/ml of difluoramine. The yield of N,N-difluorourea was 64.8 g (0.675 mole, 70%). In order to avoid the detrimental effect of glass on aqueous difluorourea (Ref 5), the solution was stored in polyethylene containers.

B. SYNTHESIS OF 2, 2-BIS(DIFLUORAMINO)PENTANE

2-Pentanone (1.00 g, 0.012 mole), bp 102.4°C, was dissolved in 3 ml of dichloromethane and gradually added to a stirred mixture of 101.4% H₂SO₄ (20 ml) and difluoramine (1.06 g, 0.02 mole) kept under reflux at -80°C. The HNF₂ was generated by hydrolysis of 73.5% aqueous solution of N,N-difluorourea in the presence of 40 ml of conc H₂SO₄. A general view of the HNF₂ generator and reactor is shown in Figure 1.

After the addition of HNF₂ was completed, the reactants were stirred for four more hours. At the end of this period, the -80°C condenser had come to room temperature due to evaporation of the Dry Ice. The reaction mixture was extracted with dichloromethane. The organic layer was washed with aqueous NaHCO₃, then with distilled water until it was neutral, and dried over anhydrous MgSO₄. The filtered solution was freed off the solvent by evaporation, and the residue was distilled from Aroclor 1242* (bp 325-366°C) solution under reduced pressure. The use of high-boiling solvent permitted the complete distillation of the product without much loss on the walls of the flask and without decomposition of the residue. The 2,2-bis(difluoramino)-pentane obtained is a pungent, moderately impact-sensitive, colorless liquid (1.32 g, 63.4% yield), bp 44.0-45.0°C/19.0 mm Hg, nD²⁵ 1.3701. Its infrared

*Monsanto Chemical Co., Organic Chemicals Division, St. Louis, Missouri
spectrum contained characteristic absorptions of the \( \text{NF}_2 \)-group (10.1, 10.2, 11.1, 11.2, 11.6\( \mu \)) and C-H absorptions.

**Anal. Calcd.** for \( \text{C}_6\text{F}_4\text{H}_{10}\text{N}_2 \): C, 34.49; H, 5.79 N, 16.09. *Found:* C, 35.13; H, 6.22; N, 15.93.

**C. PREPARATION OF 1,1-BIS(DIFLUORAMINO)CYCLOHEXANE**

Into a 500-ml three-neck flask fitted with a water condenser and a dropping funnel was placed 100 ml of 4N N,N-difluorourrea solution. Into the stirred solution, 25 ml of conc \( \text{H}_2\text{SO}_4 \) was added dropwise under a stream of nitrogen. After the addition, the solution was heated to 90°C for one hour. The gases generated (\( \text{CO}_2 \) and \( \text{HNF}_2 \)) were passed through a water-cooled condenser, a 0°C trap, and a tube filled with anhydrous \( \text{CaSO}_4 \). The dry gas mixture was then passed into a 100-ml three-neck flask containing 30 ml of 100.6%-\( \text{H}_2\text{SO}_4 \) and fitted with a -80°C condenser and an addition funnel. When refluxing of \( \text{HNF}_2 \) became apparent, a solution of 0.010 mole of cyclohexanone in 1 ml of \( \text{CH}_2\text{Cl}_2 \) was added dropwise to the stirred \( \text{H}_2\text{SO}_4 \)-\( \text{HNF}_2 \). The rate of reflux in the reaction flask decreased as the reaction proceeded. After about three hours, 20 ml of \( \text{CH}_2\text{Cl}_2 \) was added to the reaction flask, and the product was separated, followed by \( \text{NaHCO}_3 \) and water washings. After purification by distillation, 1.87 g (50% yield), of 1,1-bis(difluoramino)cyclohexane, bp 50.0-50.5°C/10.0 mm, \( n_D^{25} \) 1.4080, was obtained.

**Anal. Calcd.** for \( \text{C}_6\text{F}_4\text{H}_{10}\text{N}_2 \): C, 38.71; H, 5.41; N, 15.05. *Found:* C, 39.02; H, 4.48; N, 15.18.

**D. SYNTHESIS OF 1,1-BIS(DIFLUORAMINO)CYCLOPENTANE**

Difluoramine was generated in the same way as in the reaction described above and passed into 5 ml of 101.6%-\( \text{H}_2\text{SO}_4 \), to which was gradually added 1.2 g (0.014 mole) of cyclopentanone in 3 ml of \( \text{CH}_2\text{Cl}_2 \). Work-up of the mixture gave 2.0 g (0.012 mole, 81% yield) of 1,1-bis(difluoramino)cyclopentane, bp 60.0-60.5°C/60.0 mm.

**Anal. Calcd.** for \( \text{C}_5\text{F}_4\text{H}_{9}\text{N}_2 \): C, 34.89; H, 4.68; N, 16.17. *Found:* C, 34.66; H, 4.47; N, 15.82.
E. SYNTHESIS OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

\[ \text{Cyclohexane} + N_2F_4 \rightarrow \text{cis-trans mixture} \]

This reaction was run according to the previously described procedure (Ref 6). The purified 1,2-bis(difluoramino)cyclohexane (cis-trans mixture), bp 40.0-41.0°C/5.0 mm, nD^25 1.4123, was obtained in 45% yield.

Anal. Calcd. for C_{6}F_{4}H_{10}N_{2}: C, 38.71; F, 40.82; H, 5.41; N, 15.05. Found: C, 38.00; F, 39.40; H, 4.48; N, 14.60.
V. FUTURE WORK

During the next period we plan to continue work on the synthesis of difluoramino hydrocarbons, and extend the work to NF₂ derivatives containing ester, ether, keto, and nitrile groups.
V. REFERENCES


Section III

RMD Project 5017

(U)

STABILIZATION OF HIGH ENERGY SOLID OXIDIZER
Section III

(U)
STABILIZATION OF HIGH ENERGY SOLID OXIDIZER

A. R. Young
J. Dvorak

Report RMD-AOR-Q1-63

RMD Project 5017
Report Period: 1 November 1962 to 31 March 1963

Contract No. NOnr 3913(00)
ARPA Order No. 354-62
Project Code 2910
FOREWORD

This section of the report summarizes the work carried out during the period from 1 November 1962 to 31 March 1963, on the chemical stabilization of nitronium perchlorate (RMD Project 5017).

Contributors to the research described during the report period are as follows: A. R. Young (Project Supervisor), J. Dvorak (Principal Investigator), D. Yee (Mass Spectroscopy), E. Egbert (X-ray Analysis), J. Creatura (Wet Chemical Analysis).
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ABSTRACT

The following compounds have been examined as potential nitronium ion ligands: NOCl, NO, NOF, (CH₃)₃N, and N₂F₂. None of these reagents form stable coordination complexes with nitronium perchlorate. However, as a result of studies of the reactions of NOCl, NO, and NOF with NO₂ClO₄ and with NO₂BF₄, strong evidence has been obtained for the existence of a new "nitroxy" cation, N₂O₃⁺⁺. The compound N₂O₃(BF₄)₂ has been characterized by chemical, x-ray, and thermal analysis. It is believed that the corresponding perchlorate, N₂O₃(ClO₄)₂ has been synthesized as well, but characterization is not as yet complete.
I. INTRODUCTION

The objective of this program is to improve the physical and chemical properties of nitronium perchlorate by coordinating ligand molecules to the nitronium ion. During this report period, the following compounds have been examined as potential nitronium ion ligands: NOCl, NO, NOF, (CH₃)₃N, and N₂F₂. No evidence for formation of a stable nitronium ion complex has been obtained in these experiments. However, considerable evidence has been found for the existence of stable fluoroborate and perchlorate salts of a new "nitroxy" cation, N₂O₃⁺. The thermal stability of N₂O₃(BF₄)₂ is markedly greater than that of NO₂BF₄. Sufficiently pure N₂O₃(ClO₄)₂ has not as yet been obtained to permit studies of its physical properties in comparison to NO₂ClO₄, but N₂O₃(ClO₄)₂ behavior is expected to parallel that of N₂O₃(BF₄)₂.
II. DISCUSSION

Two approaches have been pursued in an attempt to synthesize a stable complex of nitronium perchlorate.

The first approach involves the formation of a complex nitronium cation associated with an anion other than perchlorate and subsequent conversion to a complex nitronium perchlorate by metathesis. Studies made with nitronium fluoroborate are illustrative of this method.

The second approach involves investigation of direct reactions of nitronium perchlorate with potential ligands such as NO, NOF, N₂F₂, NH₃, and N₂H₄. The principal effort during this report period was devoted to the latter approach.

A. PREPARATION OF THE COMPLEX SALTS, N₂O₃(BF₄)₂

Solutions of nitrosyl salts have been reported to yield the complex cation, N₂O₃⁺², when treated with NO₂ (Ref 1). Preliminary attempts to demonstrate the existence of this cation in the solid state involved the reaction of NOBF₄ with NO₂ (Ref 2). Subsequent attempts to prepare the N₂O₃⁺² cation by the reaction of NO₂BF₄ with NO resulted in the isolation of a new complex salt, N₂O₃(BF₄)₂ via the reaction shown in equation 1.

\[ 2\text{NO}_2\text{BF}_4 + \text{NO} \rightarrow \text{N}_2\text{O}_3(\text{BF}_4)_2 + \text{NO}_2 \]  

(1)

Thermal decomposition of N₂O₃(BF₄)₂ gives rise to equimolar amounts of NO and NO₂ as determined by mass spectroscopic analysis. Boron trifluoride is also present in the decomposition gases. Determination of boron by standard wet chemical analysis on samples of N₂O₃(BF₄)₂ from two separate preparations gave values of 8.36 and 8.61%, respectively. These compare favorably with the calculated value of 8.64%. The 2:1 stoichiometry suggested in equation 1 is established by the fact that one mole of NO is completely consumed by two moles of NO₂BF₄. This process can be followed visually by noting the gradual disappearance (at low temperatures) of a blue color due to N₂O₃. If at this point additional NO is added to the system, the blue color of N₂O₃ becomes permanent, showing that no more NO is being consumed.
The reaction product, \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \), is distinguished from an equimolar mixture of \( \text{NOBF}_4 \) and \( \text{NO}_2\text{BF}_4 \) by its insolubility in acetonitrile. Addition of \( \text{NO} \) to a solution of \( \text{NO}_2\text{BF}_4 \) in acetonitrile results in the precipitation of \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \). Differences in the thermal decomposition temperatures which have been observed for \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) and an equimolar mixture of \( \text{NOBF}_4 \) and \( \text{NO}_2\text{BF}_4 \) when measured in standard melting point capillaries serve as additional evidence the \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) is not a mixture (Table I). A comparison of the x-ray powder patterns of \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) and an equimolar mixture of \( \text{NOBF}_4 \) and \( \text{NO}_2\text{BF}_4 \) also substantiates the claim that \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) is a true compound (Figure 1).

**TABLE I**

<table>
<thead>
<tr>
<th>( \text{NO}_2\text{BF}_4 )</th>
<th>( \text{NOBF}_4 )</th>
<th>Equimolar Mixture of ( \text{NOBF}_4 ) and ( \text{NO}_2\text{BF}_4 )</th>
<th>( \text{N}_2\text{O}_3(\text{BF}_4)_2 )</th>
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</thead>
<tbody>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>135°C</td>
<td>130°C</td>
<td>125°C</td>
<td>295°C</td>
</tr>
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</table>

It is interesting to note that a reaction of \( \text{N}_2\text{O}_4 \cdot 2\text{BF}_3 \) with \( \text{H}_2\text{SO}_4 \) (equation 2) has been reported to yield an equimolar mixture of nitrosyl and nitryl tetrafluoroborates (Ref 3).

\[
\text{N}_2\text{O}_4 \cdot 2\text{BF}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NOBF}_4 + \text{NO}_2\text{BF}_4 + \cdots
\]  

However, it is pointed out by the author that the x-ray pattern of the material does not show the major lines of \( \text{NO}_2\text{BF}_4 \). A comparison of the diffraction patterns of the \( \text{N}_2\text{O}_4 \cdot 2\text{BF}_3 - \text{H}_2\text{SO}_4 \) product with that of \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) shows that they are nearly identical (Figure 2). It is possible, therefore, that \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) may be prepared by the reaction of \( \text{N}_2\text{O}_4 \) with \( \text{BF}_3 \) in \( \text{H}_2\text{SO}_4 \).

**B. REACTION OF \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) WITH \( \text{NH}_4\text{ClO}_4 \)**

An attempt was made to prepare a new complex perchlorate by utilizing \( \text{N}_2\text{O}_3(\text{BF}_4)_2 \) (equation 3).

\[
\text{N}_2\text{O}_3(\text{BF}_4)_2 + 2\text{NH}_4\text{ClO}_4 \rightarrow \text{N}_2\text{O}_3(\text{ClO}_4)_2 + 2\text{NH}_4\text{BF}_4
\]  

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Figure 1. Diffraction Patterns of Fluoroborates

Figure 2. Diffraction Pattern of $\text{N}_2\text{O}_3(\text{BF}_4)_2$
A single experiment was conducted in which $N_2O_3(BF_4)_2$ and $NH_4ClO_4$ were allowed to react in liquid HF. A small amount of NO and $NO_2$ was liberated, but there was no indication that the desired reaction occurred.

C. REACTION OF TRIMETHYLAMINE WITH $NO_2^+$

An attempt was made to prepare a complex nitronium cation by the reaction of $NO_2BF_4$ with $N(CH_3)_3$ (equation 4).

$$NO_2BF_4 + N(CH_3)_3 \rightarrow NO_2[N(CH_3)_3]BF_4$$  

(4)

When $N(CH_3)_3$ was added to a solution of $NO_2BF_4$ in acetonitrile, a vigorous reaction ensued, and $N_2$, $N_2O$, NO and $NO_2$ were evolved. The solid product obtained after removal of the acetonitrile gave a negative test for nitrite and nitrate ions. Trimethylamine is evolved upon basic hydrolysis. The product is believed to be $(CH_5)_3N:BF_3$. Analysis of the solid is given in Table II.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Calcd. for $(CH_3)_3N:BF_3$ (%)</th>
<th>Found (%)</th>
</tr>
</thead>
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<tr>
<td>C</td>
<td>28.39</td>
<td>23.97</td>
</tr>
<tr>
<td>H</td>
<td>7.09</td>
<td>7.07</td>
</tr>
<tr>
<td>N</td>
<td>11.04</td>
<td>9.05</td>
</tr>
<tr>
<td>B</td>
<td>8.51</td>
<td>8.42</td>
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</table>

D. REACTION OF $NO_2ClO_4$ WITH $NOCl$

The reaction of $NO_2ClO_4$ with excess $NOCl$ has been reported (Ref 2). Analysis of the product, including the x-ray diffraction pattern, suggested that the $N_2O_3^+$ cation was present (equation 5).

$$2NO_2ClO_4 + NOCl \rightarrow N_2O_3(ClO_4)_2 + NO_2Cl$$  

(5)

Peculiar color changes were previously observed when nitromethane was added to the solid reaction product. It has since been determined that some NO and
NO₂ are evolved upon treatment with nitromethane. However, the solid recovered from the nitromethane solution has an x-ray powder pattern consistent with that of the solid before addition of nitromethane (Figure 3), indicating that only partial decomposition occurs. The gas evolution in nitromethane has subsequently been avoided by scrupulously drying the solvent.

In an attempt to define the stoichiometry of the reaction of NO₂ClO₄ with NOCl, several experiments were conducted in which the mole ratio of NO₂ClO₄ to NOCl was 2:1. In each reaction NO₂Cl was evolved. However, on the basis of x-ray patterns, the solid products obtained varied in composition from run to run. In one of these experiments, NOCl was added to a solution of NO₂ClO₄ in nitromethane in order to obtain more efficient mixing, and the product was isolated by distillation of the solvent in vacuo. The x-ray powder pattern of the product was different than those previously obtained for NO₂ClO₄-NOCl reaction products when excess NOCl was used (Figure 4). It is presently believed that the discrepancies noted in the various x-ray diffraction patterns are either the result of inefficient mixing of the NOCl with NO₂ClO₄ or the failure to allow sufficient time for complete reaction.

It is interesting to note that chemical analysis of a representative sample gives a mole ratio of NO/NO₂ which is approximately unity (Table III).

TABLE III
ANALYSIS OF NO₂ClO₄-1/2 NOCl REACTION PRODUCT

<table>
<thead>
<tr>
<th>Group</th>
<th>Calcd. for N₂O₃(ClO₄)₂ (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>10.9</td>
<td>7.7</td>
</tr>
<tr>
<td>NO₂</td>
<td>16.7</td>
<td>11.8</td>
</tr>
<tr>
<td>ClO₄</td>
<td>72.6</td>
<td>66.1</td>
</tr>
</tbody>
</table>

E. REACTION OF NO₂ClO₄ WITH NO

It has been determined that excess NO reacts with NO₂ClO₄ to yield a white solid (equation 6), identical to that obtained when NO₂ClO₄ is allowed to react with excess NOCl.

\[ 2\text{NO}_2\text{ClO}_4 + \text{NO} \rightarrow \text{N}_2\text{O}_3(\text{ClO}_4)_2 + \text{NO}_2 \] (6)
Figure 3. Diffraction Patterns of $\text{NO}_2\text{ClO}_4$-NOC1 Reaction Products (Part I)

Figure 4. Diffraction Patterns of $\text{NO}_2\text{ClO}_4$-NOC1 Reaction Products (Part II)
Analysis of the product resulted in an NO/NO₂ ratio of approximately unity (Table IV).

**TABLE IV**

**ANALYSIS OF NO₂ClO₄-NO REACTION PRODUCT**

<table>
<thead>
<tr>
<th>Group</th>
<th>Calcd. for N₂O₃(ClO₄)₂ (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>10.9</td>
<td>7.8</td>
</tr>
<tr>
<td>NO₂</td>
<td>16.7</td>
<td>13.0</td>
</tr>
<tr>
<td>ClO₄</td>
<td>72.6</td>
<td>75.7</td>
</tr>
</tbody>
</table>

Similar results are obtained when NO is allowed to react with a suspension of NO₂ClO₄ in liquid NO₂. A comparison of the x-ray powder patterns of those products is given in Figure 5.

When NO was condensed on NO₂ClO₄ in the mole ratio of 1:2, the white solid obtained gave an x-ray powder pattern inconsistent with prior results. However, when the reaction was conducted in nitromethane or liquid SO₂, using the same NO₂ClO₄ to NO molar ratio, the products obtained had x-ray powder patterns similar to those of products obtained when excess NO or excess NOCl were used (Figure 6).

**F. REACTION OF NO₂ClO₄ WITH NOF**

The reaction of NOF with NO₂ClO₄ was examined to determine if NOF might react differently than NOCl and produce a complex having NOF as a ligand group. In a preliminary experiment, commercially available NOF was employed. Subsequent experiments were conducted with freshly prepared NOF to preclude any possibility of reaction with an NO impurity. The NOF was generated *in situ* by the reaction of NOCl with HF (equations 7, 8):

\[
\text{NOCl} + \text{HF} \longrightarrow \text{NOF} + \text{HCl} \uparrow \quad (7)
\]

\[
2\text{NO}_2\text{ClO}_4 + \text{NOF} \longrightarrow \text{N}_2\text{O}_3(\text{ClO}_4)_2 + \text{NO}_2\text{F} \quad (8)
\]
Figure 5. Diffraction Patterns of $\text{NO}_2\text{ClO}_4$-NO Reaction Products (Part I)

Figure 6. Diffraction Patterns of $\text{NO}_2\text{ClO}_4$-NO Reaction Products (Part II)
In the initial run carried out in HF, the solid gave a different x-ray pattern (Figure 7) than the NO$_2$ClO$_4$-NOCl product, and it was thought that it might be NO$_2$ClO$_4$-NOF. However, the product gave a negative test for fluoride. The solid obtained in the second run gave an x-ray pattern identical to that of the NO$_2$ClO$_4$-NOCl product. It was concluded that NOF reacts with NO$_2$ClO$_4$ in the same manner as NOCl.

G. REACTION OF NO$_2$ClO$_4$ WITH CIS-N$_2$F$_2$

An attempt was made to prepare a complex perchlorate by the reaction of cis-N$_2$F$_2$ with NO$_2$ClO$_4$ (equation 9). However, no reaction occurred between NO$_2$ClO$_4$ and gaseous or liquid cis-N$_2$F$_2$. Both reagents were recovered.

\[
\text{NO}_2\text{ClO}_4 + \text{N}_2\text{F}_2 \rightarrow \text{NO}_2/\text{N}_2\text{F}_2/\text{ClO}_4
\]  

(9)

H. REACTION OF N$_2$O$_3$(ClO$_4$)$_2$ WITH NO$_2$BF$_4$

The reactions of NO, NOCl and NOF with NO$_2$ClO$_4$ in most instances yielded the same product as shown by x-ray analysis. The mole ratio of NO/NO$_2$ in these products is approximately unity. Therefore, the formation of a salt, N$_2$O$_3$(ClO$_4$)$_2$, analogous to the complex fluoroborate, N$_2$O$_3$(BF$_4$)$_2$, is strongly indicated. A definitive proof that we are dealing with a compound, and not an equimolar mixture of NOClO$_4$ and NO$_2$ClO$_4$, remains to be given.

A very convenient proof would be to prepare N$_2$O$_3$(BF$_4$)$_2$ from the NO$_2$ClO$_4$-NO product. Fortunately NO$_2$ClO$_4$, NO$_2$BF$_4$ and the NO$_2$ClO$_4$-NO product are all soluble in acetonitrile, so that the reaction shown in equation 10 appears to be a reasonable method of preparation for N$_2$O$_3$(BF$_4$)$_2$.

\[
\text{N}_2\text{O}_3(\text{ClO}_4)_2 + 2\text{NO}_2\text{BF}_4 \xrightarrow{\text{CH}_3\text{CN}} \text{N}_2\text{O}_3(\text{BF}_4)_2 \downarrow + 2\text{NO}_2\text{ClO}_4}
\]  

(10)

A preliminary attempt was, therefore, made to carry out this reaction. The addition of an acetonitrile solution of N$_2$O$_3$(ClO$_4$)$_2$ resulted in evolution of NO and NO$_2$ accompanied by what appeared to be extensive decomposition. No precipitation occurred.

It is believed that the NO$_2$BF$_4$ contained moisture and the gassing was due to a reaction with this impurity. An attempt will be made to carry out this reaction under scrupulously dry conditions.
Figure 7. Diffraction Patterns of NO$_2$ClO$_4$-NOF Reaction Products
I. REACTION OF NO₂ClO₄ WITH SULFOLANE

Nitronium perchlorate was found to dissolve readily in Sulfolane (tetramethylene sulfone). Addition of chloroform, essentially a nonsolvent, did not result in precipitation of NO₂ClO₄. The solution after hydrolysis gave a positive test for ClO₄⁻ with AsCl₃ but a negative brown ring test for NO₃⁻. Consequently, the reaction was repeated by adding an equimolar amount of Sulfolane to a suspension of NO₂ClO₄ in CHCl₃. Only a trace of solid remained. It was separated by filtration, and x-ray analysis is pending. The filtrate was hydrolyzed and gave a positive test for ClO₄⁻ but a negative test for NO₃⁻. The nature of this reaction is not presently understood.
III. EXPERIMENTAL

Most of the reactions described were conducted in Pyrex Fischer and Porter Aerosol Compatibility Tubes fitted with a pressure gauge, a metal valve, and a ball joint for connection to the vacuum line. Those reactions in which a solvent was present were carried out in round bottom flasks fitted with a sintered glass disk, stop-cock and ball joint. This assembly could be attached to the vacuum system and subsequently removed and inverted to filter the reaction mixture.

All sampling of solid reagents and preparation of solid products for x-ray analysis were carried out in a dry box.

A. PREPARATION OF THE COMPLEX SALT, $\text{N}_2\text{O}_3(\text{BF}_4)_2$

To a solution of 2.47 g (18.7 mmole) of $\text{NO}_2\text{BF}_4$ in approximately 30 ml of acetonitrile was added, at $-196^\circ$C, 9.3 mmole of NO. The reaction mixture was allowed to warm to room temperature and was stirred for several hours. The precipitated product was separated by filtration. Characterization of the product was presented earlier in the Discussion Section.

The reaction was also conducted by condensing the NO on $\text{NO}_2\text{BF}_4$ at $-196^\circ$C and allowing the reaction mixture to warm slowly to room temperature. The NO was kept in contact with the $\text{NO}_2\text{BF}_4$ by repetitive condensation. The reaction could be followed by determination of the composition of the gaseous fraction. The solid was washed with acetonitrile and dried in vacuo.

B. REACTION OF $\text{N}_2\text{O}_3(\text{BF}_4)_2$ WITH $\text{NH}_4\text{ClO}_4$

To a mixture of 0.768 g (3 mmole) of $\text{N}_2\text{O}_3(\text{BF}_4)_2$ and 1.416 g (12 mmole) of $\text{NH}_4\text{ClO}_4$ in a Kel-F reactor was added 25 ml of liquid HF. The reaction mixture was allowed to stir several hours during which time some NO and NO$_2$ were evolved. The solid isolated after removal of the HF was insoluble in both nitromethane and acetonitrile. The desired product, $\text{N}_2\text{O}_3(\text{ClO}_4)_2$, is known to be soluble in these solvents.
C. REACTION OF NO₂BF₄ WITH N(CH₃)₃

To 0.936 g (7.0 mmoles) of NO₂BF₄ in 30 ml of acetonitrile was added, at -196°C, 7.0 mmoles of N(CH₃)₃. The reaction mixture was allowed to warm slowly to room temperature, and considerable gassing occurred. Mass spectroscopic analysis of the evolved gas showed the presence of N₂, N₂O, NO and NO₂. A wax-like solid, melting with decomposition in the range 180-185°C, was obtained after removal of the solvent. Analysis of the solid was as follows:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Calcd. for (CH₃)₃N·BF₃ (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>28.39</td>
<td>23.97</td>
</tr>
<tr>
<td>H</td>
<td>7.09</td>
<td>7.07</td>
</tr>
<tr>
<td>N</td>
<td>11.04</td>
<td>9.05</td>
</tr>
<tr>
<td>B</td>
<td>8.51</td>
<td>8.42</td>
</tr>
</tbody>
</table>

D. REACTION OF EXCESS NO₂ClO₄ WITH NOCl

The reaction of NO₂ClO₄ with excess NOCl has been described previously (Ref 2). The reaction was conducted similarly with NO₂ClO₄ in excess. To 0.660 g (4.55 mmoles) of NO₂ClO₄ at -196°C was added 2.27 mmoles of NOCl. The reaction mixture was allowed to warm slowly and was stirred for several hours at 0°C. The volatile fraction was removed by pumping on the solid. The solid was analyzed for NO⁺ and NO₂⁺ content after hydrolytic conversion of these cations to nitrite (NO₂⁻) and nitrate (NO₃⁻), respectively. The nitrite ion was titrated with standard ceric sulfate solution, and the nitrate was determined by treating an aliquot of the hydrolysate with excess standard ferrous sulfate followed by titration with standard ceric sulfate. The perchlorate anion was determined colorimetrically. The analysis gave the following results:

<table>
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</tr>
<tr>
<td>ClO₄</td>
<td>72.6</td>
<td>66.1</td>
</tr>
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</table>

This reaction has also been conducted by the addition of NOCl to a solution of NO₂ClO₄ in nitromethane. The reaction mixture was allowed to warm to room temperature and stirred for several hours. The solvent was removed by distillation in vacuo.
E. REACTION OF NO₂ClO₄ WITH NO

1. Excess NO

To 0.520 g (3.57 mmoles) of NO₂ClO₄ at -196°C was added 4.42 mmoles of NO. The reaction mixture was allowed to warm slowly to room temperature with stirring. The gas was recondensed on the solid several times. The system was then evacuated, and a white solid was obtained. The solid product was analyzed according to the method described in subsection D above. The results were as follows:

<table>
<thead>
<tr>
<th>Group</th>
<th>Calcd. for N₂O₅(ClO₄)₂ (%)</th>
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</tr>
<tr>
<td>ClOF</td>
<td>72.6</td>
<td>75.7</td>
</tr>
</tbody>
</table>

2. Excess NO in Liquid NO₂

This reaction was conducted by the procedure described above. Approximately 25 ml of liquid NO₂ was employed per 0.30 g of NO₂ClO₄.

3. Excess NO₂ClO₄ in Liquid SO₂

To a suspension of 0.340 g (2.32 mmoles) of NO₂ClO₄ in 25 ml of SO₂ was added 1.16 mmoles of NO. The temperature of the reaction mixture was maintained at -10°C for several hours. The volatile materials were removed by vacuum distillation.

4. Excess NO₂ClO₄ in CH₃NO₂

A solution of 0.490 g (3.38 mmoles) of NO₂ClO₄ in 20 ml of nitromethane was cooled to -196°C, and 1.69 mmoles of NO were added. After warming to room temperature, the solution was stirred for several hours. The product was isolated by distillation of the solvent in vacuo.
F. REACTION OF NO$_2$ClO$_4$ WITH NOF

A Kel-F reactor charged with 0.226 g (1.56 mmoles) of NO$_2$ClO$_4$ was attached to a metal vacuum line, and 2.0 mmoles of commercial NOF were condensed on the solid at -196°C. The reaction mixture was allowed to warm slowly to room temperature with stirring. The condensation process was repeated several times. The solid was isolated by removal of the volatile material in vacuo. A similar procedure was followed when NOF was generated in situ. The Kel-F reactor was charged with 0.876 g (6.04 mmoles) of NO$_2$ClO$_4$ and approximately 20 ml of liquid HF. Then 6.04 mmoles of NOCl was introduced at -196°C. The reaction mixture was kept at approximately -50°C for one hour and then allowed to warm slowly to room temperature. The white solid product was obtained by removal of the volatile materials in vacuo.

G. REACTION OF NO$_2$ClO$_4$ WITH CIS-N$_2$F$_2$

To 0.283 g (1.95 mmoles) of NO$_2$ClO$_4$ at -196°C was added 2.5 mmoles of cis-N$_2$F$_2$. The reaction mixture was allowed to warm to room temperature with stirring. The gas was recondensed on the NO$_2$ClO$_4$ several times. The N$_2$F$_2$ was recovered and identified by its infrared spectrum. The solid had an x-ray powder pattern consistent with that for NO$_2$ClO$_4$.

H. REACTION OF N$_2$O$_3$(ClO$_4$)$_2$ WITH NO$_2$BF$_4$

An acetonitrile solution of 0.425 g (3.2 mmoles) of NO$_2$BF$_4$ was added to a solution of 0.417 g (1.6 mmoles) N$_2$O$_3$(ClO$_4$)$_2$ in acetonitrile. Considerable gassing occurred, but no precipitation was observed. While the solvent was being distilled in vacuo, a leak developed in the system and the pasty mass obtained was discarded.

I. REACTION OF NO$_2$ClO$_4$ WITH SULFOLANE

When 7 ml of Sulfolane was added to 0.330 g of NO$_2$ClO$_4$, a red solution resulted. After stirring for 1/2 hour, 10 ml of CHCl$_3$ was added to this solution but no precipitation occurred. The solution was hydrolyzed, and the hydrolysate gave a positive test for ClO$_4^-$ with $\phi_4$AsCl reagent and a negative brown ring test for NO$_3^-$. In a second experiment, 2.93 mmoles of Sulfolane were added to a suspension of 0.426 g (2.93 mmoles) of NO$_2$ClO$_4$ in 7 ml of CHCl$_3$. The undissolved solid was isolated by filtration. Analysis is pending. The filtrate was hydrolyzed, and the hydrolysate gave a positive test for ClO$_4^-$ and a negative brown ring test for NO$_3^-$. 

CONFIDENTIAL

Project 5017
Report RMD-AOR-Q1-63
IV. FUTURE WORK

- The products from the reactions of NO$_2$ClO$_4$ with NO, NOCl and NOF will be fully characterized.

- The reaction of NO$_2$ClO$_4$ with Sulfolane will be investigated.

- Systems for the reaction of NO$_2$ClO$_4$ with fuel ligands such as NH$_3$ and N$_2$H$_4$ will be investigated.
V. REFERENCES


2. Report RMD 5017-Q1, Stabilization of High Energy Solid Oxidizer, Thiokol Chemical Corporation, Reaction Motors Division, 30 November 1962. (Contract NOnr 3913(00))

Section IV

RMD Project 5009

INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES
Section IV

INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

A. R. Young
S. I. Morrow
T. Hirata

Report RMD-AOR-Q1-63

RMD Project 5009
Report Period: 16 January 1963 to 1 April 1963

Contract No. NOnr 3824(00)
ARPA Order No. 314-62
Project Code 9100
FOREWORD

This report summarizes the results of studies of the reactions of dioxygen difluoride conducted during the period 16 January 1963 to 1 April 1963 under Navy Contract NOnr 3824(00), ARPA Order No. 314-62. The report has been published as Section IV of Report RMD-AOR-Q1-63. In addition, it has been published separately as an unclassified document.

Personnel contributing to the work discussed in this section are as follows: A. R. Young, II (Project Supervisor), T. Hirata, S. I. Morrow, R. Storey, D. Y. Yee, and E. Egbert.
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<td>Infrared Spectrum of $O_2SbF_6$</td>
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<tr>
<td>2</td>
<td>Infrared Spectrum of the $NO_2-O_2PF_6$ Product</td>
<td>8</td>
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<td>Hydrolytic Analysis of $O_2F_2$-AsF$_5$ Product</td>
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<td>Analysis of $O_2F_2$-SbF$_6$ Product</td>
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ABSTRACT

Further characterization studies of the $\text{O}_2\text{F}_2$-Group V pentafluoride products were carried out during this quarter. Although the qualitative evidence that these products are dioxygenyl compounds of the form, $\text{O}_2\text{MF}_6$, remains convincing, quantitative analytical results presently available are still not completely satisfactory. Samples of the $\text{O}_2\text{F}_2$-$\text{AsF}_5$ product give consistently low arsenic analysis which is believed to be due to HF contamination. The best results have been obtained on the $\text{O}_2\text{F}_2$-$\text{SbF}_5$ product for which values of 46.07% and 46.05% have been obtained for Sb content, and 39.22% for fluorine content (theory for $\text{O}_2\text{SbF}_6$: Sb, 45.47; F, 42.59%).
I. INTRODUCTION

The overall objective of this research program is to generate basic information about the inorganic chemistry of the oxygen subfluorides ($O_2F_2$, $O_3F_2$, $O_4F_2$). It is hoped that this information may suggest routes to new inorganic solid oxidizers. Two general reactions of dioxygen difluoride which yield solid products are of current interest, namely, (a) the reaction of dioxygen difluoride with elemental chlorine or compounds containing monovalent chlorine, and (b) the reaction of dioxygen difluoride with pentafluorides of Group V elements. The former reaction yields violet-colored solids which are unstable above -80°C and must be characterized by examination of their decomposition products. The reaction of $O_2F_2$ with Group V pentafluorides produces solids which may be studied at room temperature. The work performed during this report period was primarily directed toward the characterization of the solid products obtained from $O_2F_2$-Group V pentafluoride reactions.
II. DISCUSSION

The reactions of \( \text{O}_2\text{F}_2 \) with the pentafluorides of phosphorous, arsenic, and antimony have been previously reported (Ref 1 and 2). These reactions yield solid products having an order of stability which increases as the atomic weight of the Group V element increases. The least stable product, that obtained with phosphorous pentafluoride, decomposes rapidly in vacuo at ambient temperatures. The \( \text{AsF}_5 \) and \( \text{SbF}_5 \) products, on the other hand, require elevated temperatures (>100°C) for rapid decomposition. It is currently believed that these solid products are derivatives of the dioxygenyl cation, \( \text{O}_2^+ \) (Ref 3), which arise by the general reaction shown in equation 1.

\[
\text{O}_2\text{F}_2 + \text{MF}_5 \xrightarrow{-160^\circ\text{C}} \text{O}_2\text{MF}_6 + 1/2 \text{F}_2
\]

The evidence supporting this characterization may be summarized as follows:

- The noncondensable gases collected after completion of the reaction contain an excess of \( \text{F}_2 \) over \( \text{O}_2 \). (The presence of \( \text{O}_2 \) and \( \text{F}_2 \) in equimolar amounts is expected due to the decomposition of excess \( \text{O}_2\text{F}_2 \).)

- Oxygen can be detected by mass spectroscopy in the vapor phase above the solids at room temperature. At elevated temperatures, peaks are observed for the corresponding Group V pentafluoride.

- The infrared spectra of the \( \text{O}_2\text{F}_2\text{-AsF}_5 \) and \( \text{O}_2\text{F}_2\text{-SbF}_5 \) products show absorptions at 705 cm\(^{-1}\) for \( \text{AsF}_6^- \) and 669 cm\(^{-1}\) for \( \text{SbF}_6^- \), respectively.

- The unstable \( \text{O}_2\text{F}_2\text{-PF}_5 \) product is converted to \( \text{NO}_2\text{PF}_6 \) by treatment with \( \text{NO}_2 \), and oxygen is liberated during the process.

- The x-ray diffraction pattern of the \( \text{O}_2\text{F}_2\text{-AsF}_5 \) product is almost identical to that of \( \text{NOAsF}_6 \).

- The \( \text{O}_2\text{F}_2\text{-AsF}_5 \) and \( \text{O}_2\text{F}_2\text{-SbF}_5 \) products liberate a mixture of \( \text{O}_2 \) and \( \text{O}_3 \) when treated with water.
In spite of these encouraging qualitative observations, attempts to obtain satisfactory analytical data in support of the characterization of these compounds as dioxygenyl derivatives have not been completely successful to date. Three methods of analysis have been used, namely, reaction with water (equation 2), reaction with NO$_2$ (equation 3) and thermal decomposition (equation 4).

\[ 2\text{O}_2\text{MF}_6 + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{O}_3 + 2\text{HMF}_6 \] (2)

\[ \text{NO}_2 + \text{O}_2\text{MF}_6 \rightarrow \text{O}_2 + \text{NO}_2\text{MF}_6 \] (3)

\[ \text{O}_2\text{MF}_6 \rightarrow \text{O}_2 + 1/2\text{F}_2 + \text{MF}_5 \] (4)

The results obtained in attempts to use hydrolysis and the reaction with nitrogen dioxide as analytical methods indicate that equation 2 and equation 3 are at least qualitatively correct, that is, oxygen and ozone are liberated when the O$_2$F$_2$-MF$_5$ products are treated with water and oxygen is liberated when the O$_2$F$_2$-MF$_5$ products are treated with NO$_2$. However, the quantities of gas liberated have been significantly lower than required by equations 2 and 3. Attempts to use thermal decomposition as an analytical method have been frustrated by the occurrence of side reactions between the initial decomposition products and the glass apparatus.

A. HYDROLYSIS OF DIOXYGENYL COMPOUNDS

Hydrolytic analysis was carried out on samples of the O$_2$F$_2$-AsF$_5$ products from two distinct preparative runs. If the O$_2$AsF$_6$ contents of the samples are calculated on the basis of the total oxygen and ozone found as compared to the amount predicted by equation 2 (Table I), one obtains values of 61.6% and 47.9%, respectively. On the other hand, the purities of the samples on the basis of their AsF$_6^-$ contents shown in Table II (obtained by precipitating \( \Phi_4\text{As(AsF}_6^\text{)} \) from the hydrolysate with \( \Phi_4\text{AsCl} \) are 90.5% and 86.7%, respectively. A possible reason for this discrepancy is that equation 2 does not accurately describe the reaction of O$_2$AsF$_6$ with water. An alternate equation which requires the liberation of less than a mole of gas per mole of O$_2$AsF$_6$ is shown in equation 5. Tests will be made for the presence of H$_2$O$_2$ in the hydrolysate.

\[ \text{O}_2\text{AsF}_6 + 3/2 \text{H}_2\text{O} \rightarrow \text{HAsF}_6 + \text{H}_2\text{O}_2 + 1/2 \text{O}_3 \] (5)
TABLE I

HYDROLYTIC ANALYSIS OF $O_2F_2$-AsF$_5$ PRODUCT

<table>
<thead>
<tr>
<th>Sample Weight (gm)</th>
<th>$O_2 + O_3$ Found (Total mmoles)</th>
<th>$O_2 + O_3$ (calcd. by eq. 2) (Total mmoles)</th>
<th>AsF$_6^-$ Found (%)</th>
<th>AsF$_6^-$ (calcd. for $O_2$AsF$_6$) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1728</td>
<td>0.48</td>
<td>0.78</td>
<td>77.41</td>
<td>85.51</td>
</tr>
<tr>
<td>0.1608</td>
<td>0.35</td>
<td>0.73</td>
<td>74.32</td>
<td>85.51</td>
</tr>
</tbody>
</table>

The low values obtained for the AsF$_6^-$ content of the $O_2F_2$-AsF$_5$ product cannot be satisfactorily accounted for at this point. Emission spectra obtained on the samples show no lines other than those due to arsenic. The most reasonable explanation at present is that the samples contain HF. This will have to be confirmed by thermal decomposition studies in a Teflon or metal apparatus.

The analytical results obtained on the hydrolysates of the $O_2F_2$-SbF$_5$ product have been in much better agreement with theory than those obtained for the $O_2F_2$-AsF$_5$ product (Table II). However, as in the case of the arsenic product, the total gas ($O_2 + O_3$) measured after hydrolysis of a sample of $O_2$SbF$_6$ is much lower than predicted by equation 2.

TABLE II

ANALYSIS OF $O_2F_2$-SbF$_5$ PRODUCT

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\text{Calcd. for } O_2\text{SbF}_6$ (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>45.47</td>
<td>46.07, 46.05</td>
</tr>
<tr>
<td>F</td>
<td>42.59</td>
<td>39.22</td>
</tr>
</tbody>
</table>

B. REACTION OF DIOXYGENYL COMPOUNDS WITH NO$_2$

The reaction of NO$_2$ with $O_2$MF$_6$ compounds (equation 3) has been carried out by introducing NO$_2$ into the reactor immediately after separation of all
volatile by-products from the dioxygenyl compounds by pumping at -80°C. The reaction has also been carried out on samples of the dioxygenyl compounds which have been removed from the reactor in a dry atmosphere and weighed. By both techniques, the oxygen found has been lower than predicted by equation 3, although in the former case this can be partially attributed to incomplete conversion of the MF₅ compound to O₂MF₆.

The solid product obtained by the reaction of 1.14 mmoles AsF₅ with excess O₂F₂, after pumping to remove all volatile by-products (O₂, F₂, SiF₄, unreacted AsF₅), yielded 0.781 mmole oxygen upon reaction with excess NO₂ at room temperature. Assuming complete conversion of the initial AsF₅ to O₂AsF₆, the observed oxygen is only 70% of that required by equation 3. In a separate experiment, a 0.140 g sample of the solid O₂F₂-AsF₅ product was allowed to react with excess NO₂. The reaction evolved 0.0174 g O₂ giving an oxygen content of 12.4% (required for O₂AsF₆, 14.5%).

Similar results were obtained with a freshly prepared sample of the O₂F₂-PF₅ product. In another experiment, 1.31 mmoles of PF₅ were allowed to react with excess O₂F₂, and materials volatile at -80°C (O₂, F₂, SiF₄, POF₃, PF₅) were removed from the reactor. Treatment of the remaining solid with excess NO₂ at 0°C produced 1.05 mmoles O₂. The residual solid was identified as NO₂PF₆ by infrared spectroscopy.

C. THERMAL DECOMPOSITION OF DIOXYGENYL COMPOUNDS

The thermal decomposition of dioxygenyl compounds, O₂MF₆, should proceed as shown in equation 4. The only test of this reaction as an analytical method was carried out in a glass system with the O₂F₂-PF₅ product. A sample of freshly prepared solid, which had been pumped at -80°C until it exhibited no vapor pressure, was allowed to decompose at room temperature for two hours. It formed 1.77 mmoles of gas of which 0.845 mmole was condensable at -196°C. The fraction noncondensable at -196°C (0.925 mmole) did not decrease when it was put in contact with mercury. It was identified as pure oxygen by mass spectroscopy. The condensable fraction, which according to equation 4 should have been PF₅, contained POF₃ and SiF₄, as well as PF₅. It is evident that reactions with glass (equations 6 and 7) obscured the results obtained in this analysis; therefore, they cannot be used to establish the composition of the O₂F₂-PF₅ product.

\[
2F₂ + SiO₂ \rightarrow SiF₄ + O₂ \quad (6)
\]

\[
2PF₅ + SiO₂ \rightarrow SiF₄ + 2POF₃ \quad (7)
\]
Future attempts to establish the composition of \( \text{O}_2\text{F}_2-\text{MF}_3 \) products by thermal decomposition will be carried out in Teflon or in metal systems.

D. INFRARED SPECTRA OF DIOXYGENYL COMPOUNDS

The infrared spectrum of the \( \text{O}_2\text{F}_2-\text{AsF}_5 \) product as a sodium fluoride pellet has been reported previously (Ref 2). An infrared spectrum of the \( \text{O}_2\text{F}_2-\text{SbF}_5 \) product appears in Figure 1. It shows a strong absorption at 669 cm\(^{-1}\) which has been reported for the \( \text{SbF}_6^- \) anion (Ref 4).

Because of the instability of the \( \text{O}_2\text{F}_2-\text{PF}_5 \) product, no attempt was made to obtain its infrared spectrum. When the unstable \( \text{O}_2\text{F}_2-\text{PF}_5 \) product is allowed to react with \( \text{NO}_2 \), it is converted to a thermally stable solid, the spectrum of which (Figure 2) shows absorptions for the \( \text{NO}_2^+ \) ion at 2350 cm\(^{-1}\) and for the \( \text{PF}_6^- \) anion at 837 cm\(^{-1}\) (Ref 4).

E. X-RAY DIFFRACTION PATTERNS OF DIOXYGENYL COMPOUNDS

The x-ray diffraction pattern of a new sample of the \( \text{O}_2\text{F}_2-\text{AsF}_5 \) product was obtained during this report period, and it is substantially identical to that previously reported (Ref 2). A powder sample of NOAsF\(_5\) purchased from the Ozark-Mahoning Company was photographed for comparison with the arsenic compound. Its diffraction pattern (Table III) is almost identical to that of the \( \text{O}_2\text{F}_2-\text{AsF}_5 \) product.

Effort to confirm the powder diffraction pattern reported for the \( \text{O}_2\text{F}_2-\text{SbF}_5 \) product was unsuccessful (Ref 2). No diffraction pattern was obtained on the sample which gave the infrared spectrum shown in Figure 1. The reason for the failure to obtain a diffraction pattern for the \( \text{O}_2\text{F}_2-\text{SbF}_5 \) product has not as yet been determined.

F. REACTION OF \( \text{O}_2\text{SbF}_6 \) WITH HF

It is believed that \( \text{NO}_2\text{SbF}_6 \) is a minor impurity in the \( \text{O}_2\text{F}_2-\text{SbF}_5 \) product, since traces of brown vapors are evolved when it is hydrolyzed. The nitrogen evidently arises from air leaks in the system during the discharge preparation of \( \text{O}_2\text{F}_2 \) or is an impurity in the oxygen used in this preparation.

One approach to the purification of \( \text{O}_2\text{SbF}_6 \) is by recrystallization from a solvent. Hydrogen fluoride was, therefore, tested as a possible recrystallization medium. The condensation of HF onto a sample of the \( \text{O}_2\text{F}_2-\text{SbF}_5 \) product...
Figure 1. Infrared Spectrum of $\text{O}_2\text{SbF}_6$

Figure 2. Infrared Spectrum of the $\text{NO}_2\cdot\text{O}_2\text{PF}_6$ Product
### TABLE III

**POWDER DIFFRACTION PATTERNS OF O$_2$F$_2$-AsF$_5$ PRODUCT AND NOAsF$_6$**

<table>
<thead>
<tr>
<th>Face Centered Cubic</th>
<th>O$_2$F$_2$-AsF$_5$ Product</th>
<th>NOAsF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0 = 8.00 \text{Å}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h,k,l$</td>
<td>$d$, Å (calcd)</td>
<td>$d$, Å</td>
</tr>
<tr>
<td>111</td>
<td>4.60</td>
<td>4.59</td>
</tr>
<tr>
<td>200</td>
<td>4.00</td>
<td>3.99</td>
</tr>
<tr>
<td>220</td>
<td>2.83</td>
<td>2.83</td>
</tr>
<tr>
<td>311</td>
<td>2.40</td>
<td>2.42</td>
</tr>
<tr>
<td>222</td>
<td>2.30</td>
<td>2.32</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>2.19</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>2.10</td>
</tr>
<tr>
<td>400</td>
<td>1.99</td>
<td>2.01</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>1.95</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>1.89</td>
</tr>
<tr>
<td>331</td>
<td>1.83</td>
<td>1.85</td>
</tr>
<tr>
<td>420</td>
<td>1.78</td>
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<tr>
<td>422</td>
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<tr>
<td>333,511</td>
<td>1.54</td>
<td>1.55</td>
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<tr>
<td>---</td>
<td>---</td>
<td>1.49</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>1.44</td>
</tr>
<tr>
<td>440</td>
<td>1.41</td>
<td>1.42</td>
</tr>
<tr>
<td>531</td>
<td>1.36</td>
<td>1.36</td>
</tr>
<tr>
<td>442,600</td>
<td>1.33</td>
<td>1.34</td>
</tr>
<tr>
<td>620</td>
<td>1.26</td>
<td>1.27</td>
</tr>
<tr>
<td>533</td>
<td>1.22</td>
<td>1.23</td>
</tr>
<tr>
<td>622</td>
<td>1.20</td>
<td>1.20</td>
</tr>
</tbody>
</table>

--- 9 ---
Project 5009
Report RMD-AOR-Q1-63
in a Kel-F tube gave rise to some interesting phenomena. A portion of the solid seemed to go into solution, and the surface of the undissolved solid appeared pink in the presence of HF. However, the color did not diffuse throughout the solution. The solvent and volatile reaction products were then condensed into a second Kel-F trap. It was evident that a highly corrosive, volatile material had been formed during treatment of the solid with HF, because the walls of the second trap became discolored when it warmed to room temperature. In spite of this evidence of reaction with HF, the solid remaining in the initial trap gave an infrared spectrum identical to the original $O_2F_2$-$SbF_5$ product (Figure 1). The study of the behavior of dioxygenyl compounds in HF will be pursued further in order to determine the extent of solubility and the nature of the observed interaction of the $SbF_5$ product with HF.

G. PREPARATION OF NEW DIOXYGENYL DERIVATIVES

1. Reaction of $O_2$ with $ClO_3F$

An attempt to prepare a dioxygenyl derivative having the $ClO_3F^-$ anion by activating a mixture of oxygen and perchloryl fluoride in an electric discharge at $-80^\circ C$ was unsuccessful; both reagents were recovered.

2. Reaction of $O_2F_2$ with $SnCl_4$

Since most of the reactions of $O_2F_2$ studied on this program are carried out in glass apparatus, $SiF_4$ is an ever-present contaminant. It is surprising, therefore, that silicon does not appear as an impurity in the dioxygenyl compounds (as indicated by emission spectroscopy) in the form of $(O_2)_2SiF_6$. One possible explanation is that dioxygenyl compounds of bivalent complex fluoride anions are inherently unstable. This possibility was tested by attempting the preparation of $(O_2)_2SnF_6$ via the reaction shown in equation 8.

$$O_2F_2 \ (excess) + SnCl_4 \rightarrow (O_2)_2SnF_6 + 2Cl_2 \quad (8)$$

A reaction took place at the melting point of $O_2F_2$ giving rise to a violet-colored intermediate product, a behavior which is characteristic of $O_2F_2$ reactions with chlorine-containing reagents. The violet product decomposed on warming to room temperature, and chlorine was found to be the major component of the volatile decomposition products. A white solid remained at room temperature. Attempts to identify the solid by infrared, mass spectroscopy (elevated temperatures), and x-ray were unsuccessful, because the solid became contaminated.
with water during handling. This reaction will be studied further in order to determine whether the solid is related to the products obtained by the reactions of Group V pentafluorides with \( \text{O}_2\text{F}_2 \).

3. Reaction of \( \text{O}_2\text{F}_2 \) with Xenon

Because of the current interest in compounds of the rare gasses, it was decided to attempt the preparation of dioxygenyl derivates of \( \text{XeF}_4 \) or \( \text{XeF}_6 \), as shown in equation 9,

\[
\text{O}_2\text{F}_2 \text{ (excess)} + \text{Xe} \rightarrow (\text{O}_2)_m\text{XeF}_n
\]  

The reaction was initially carried out in a glass system by condensing \( \text{Xe} \) in the bottom of a glass U-shaped discharge tube, generating \( \text{O}_2\text{F}_2 \) in the apparatus at \(-196^\circ\text{C}\), and allowing the \( \text{O}_2\text{F}_2 \) to melt and flow on the solid \( \text{Xe} \). The system was pumped at \(-80^\circ\text{C}\) until no vapor pressure remained at that temperature. Upon removal of the \(-80^\circ\text{C}\) bath, a solid was observed which built up a decomposition pressure as it warmed to room temperature. The solid appeared to decompose rapidly at room temperature. The resultant gases contained \( \text{O}_2 \), \( \text{Xe} \), and \( \text{SiF}_4 \). Since it was suspected that the compound was reacting with the glass rather than decomposing thermally, the reaction was repeated in a Kel-F system. The solid appeared to disappear as rapidly at room temperature in Kel-F as it did in glass. During an attempt to remove a sample of the solid for mass spectral analysis, it was inadvertently exposed to air whereupon it fumed copiously. The mass spectrum of the vapors from this exposed sample showed \( \text{Xe} \), \( \text{H}_2\text{O} \), and HF.

Further studies of this reaction are in progress and it is hoped that additional evidence of the composition of this solid will be forthcoming.

H. \( \text{Cl}_2\text{-O}_2\text{F}_2 \) REACTION

No progress was made during this quarter in our continuing effort to characterize the unstable violet \( \text{Cl}_2\text{-O}_2\text{F}_2 \) addition product. Some studies were made of the "cold mercury absorption method" vs the "hot sodium chloride method" for analyzing oxygen-fluorine mixtures. On the basis of the results obtained, future analysis of the \( \text{Cl}_2\text{-O}_2\text{F}_2 \) decomposition products will be carried out by the cold mercury absorption method. The hot sodium chloride method invariably gave low results for fluorine due to a reaction with the glass apparatus producing \( \text{SiF}_4 \) and \( \text{O}_2 \).
III. EXPERIMENTAL

A. $O_2F_2$-$AsF_5$ PRODUCT

The $O_2F_2$-$AsF_5$ reactions were carried out by condensing $AsF_5$ on the bottom of a U-shaped glass trap having copper electrodes sealed into each leg. A 1:1 mixture of $O_2$ and $F_2$ of sufficient quantity to produce a two-fold excess of $O_2F_2$ was leaked into the discharge tube (at $-196^\circ C$) at a pressure of 10-15 mm, and discharge was maintained until the pressure decreased to zero. The Dewar was then lowered until the liquid nitrogen made contact only with the bottom of the U-trap. The $O_2F_2$ melted and flowed to the bottom where it reacted with the solid $AsF_5$. After the orange color of the $O_2F_2$ had been completely discharged, the liquid nitrogen Dewar was raised in order to condense unreacted $AsF_5$ and $SiF_4$, and a measured aliquot of the gas which was not condensable at $-196^\circ C$ was taken in a mercury absorption tube of known volume. The liquid nitrogen bath was replaced by a Dry Ice-Trichlor bath ($-78^\circ C$), and the system was evacuated until it exhibited no vapor pressure at $-78^\circ C$.

1. Reaction of $NO_2$ with $O_2F_2$-$AsF_5$

A 1.14 mmole sample of $AsF_5$ was reacted with excess $O_2F_2$ as described above. The solid product (which exhibited no vapor pressure at $-78^\circ C$) was treated with excess $NO_2$ at room temperature for 12 hours. After this period, the system was cooled to $-196^\circ C$ and 0.781 mmole noncondensable gas was measured and identified as $O_2$ by mass spectrometry. Based on equation 3 (i.e., $NO_2 + O_2AsF_6 \rightarrow O_2 + NO_2AsF_6$) the yield of $O_2AsF_6$ in the experiment was 68%.

In a similar experiment, the trap containing a freshly prepared sample of the $O_2F_2$-$AsF_5$ product was removed to a dry box, and a 0.140 g sample was placed in a glass bulb and allowed to react with excess $NO_2$. The sample liberated 0.0174 g $O_2$, which gives an $O_2$ content of 12.4% in the original sample (calculated for $O_2AsF_6$, 14.5%).
2. Reaction of \( \text{O}_2\text{F}_2-\text{AsF}_5 \) Product with Water

Two hydrolysis experiments were carried out with weighed samples of the \( \text{O}_2\text{F}_2-\text{AsF}_5 \) product from different preparative runs. In the first, a 0.1728 g sample liberated 0.48 mmole of gas identified as a mixture of oxygen and ozone. The aqueous solution gave 0.4052 g of \( \text{\Phi}_4\text{As} (\text{AsF}_6) \) when treated with \( \text{\Phi}_4\text{AsCl} \). The \( \text{AsF}_6^- \) content was, therefore, 77.41% (calculated for \( \text{O}_2\text{AsF}_6 \), 85.51%). The sample from the second preparative run weighing 0.1608 g, liberated 0.35 mmole \( \text{O}_2 \) and \( \text{O}_3 \) (total) and yielded 0.3620 g \( \text{\Phi}_4\text{AsAsF}_6 \). Its \( \text{AsF}_6^- \) content was, therefore, 74.32%.

B. \( \text{O}_2\text{F}_2-\text{PF}_5 \) PRODUCT

The \( \text{O}_2\text{F}_2-\text{PF}_5 \) reactions were carried out in a glass system using a procedure identical to that used for the \( \text{O}_2\text{F}_2-\text{AsF}_5 \) reaction.

1. Reaction of \( \text{O}_2\text{F}_2-\text{PF}_5 \) Product with \( \text{NO}_2 \)

A 1.31 mmole sample of \( \text{PF}_5 \) was allowed to react with excess \( \text{O}_2\text{F}_2 \) at \(-160^\circ\text{C}\). After completion of the reaction, 0.71 mmole of condensable gas was removed from the reactor at \(-78^\circ\text{C}\) and condensed at \(-196^\circ\text{C}\) in a downstream trap. It contained \( \text{SiF}_4 \), \( \text{POF}_3 \), and a minor amount of \( \text{PF}_5 \). \( \text{NO}_2 \) was introduced into the reactor and allowed to remain in contact with the solid product at \( 0^\circ\text{C} \) for two hours. At the end of this period, 1.05 mmoles of oxygen were measured in the system and identified by mass spectroscopy. Based on equation 3 (i.e., \( \text{NO}_2 + \text{O}_2\text{PF}_6 \rightarrow \text{O}_2 + \text{NO}_2\text{PF}_6 \)) the yield of \( \text{O}_2\text{PF}_6 \) in the reaction was 80%. The solid remaining after reaction with \( \text{NO}_2 \) showed an absorption at 2350 cm\(^{-1}\) for the \( \text{NO}_2^- \) ion and at 837 cm\(^{-1}\) for the \( \text{PF}_6^- \) ion.

2. Thermal Decomposition of \( \text{O}_2\text{F}_2-\text{PF}_5 \) Product in Glass

The solid product obtained by the reaction of \( \text{O}_2\text{F}_2 \) with 1.31 mmoles \( \text{PF}_5 \) was allowed to decompose for 48 hours in a glass system of known volume. It liberated 1.77 mmoles of gas (calculated for 1.31 mmoles \( \text{O}_2\text{PF}_6 \rightarrow \text{O}_2 + 1/2 \text{F}_2 + \text{PF}_5 \), 1.96 mmoles). The gas contained a 0.845 mmole fraction condensable at \(-196^\circ\text{C} \) (\( \text{POF}_3 \), \( \text{SiF}_4 \), and \( \text{PF}_5 \)) the balance (0.925 mmole) was virtually pure \( \text{O}_2 \).
C. $O_2F_2$-$SbF_5$ PRODUCT

1. Preparation of $O_2F_2$-$SbF_5$ Product in Kel-F Apparatus

Liquid $SbF_5$ was charged into a weighed Kel-F tube in a dry box. The tube was stoppered and reweighed (3.394 g $SbF_5$). The Kel-F tube was attached to the $O_2F_2$ generation system, while a positive pressure of dry $N_2$ was kept on the system to avoid diffusion of moist air into the $SbF_5$. $O_2F_2$ was prepared in a Kel-F discharge tube and distilled in vacuo onto the $SbF_5$ at -196°C. When the -196°C bath was replaced with one at -78°C, the contents of the reactor appeared as an orange colored liquid. When this system was allowed to stand at -78°C overnight, a light colored solid slowly formed. The product was pumped for several hours at room temperature to remove all volatile materials, including any $SbF_5$ which might not have reacted. The resulting gray-white solid weighed 3.569 g. This corresponds to an 85.3% yield of $O_2SbF_6$. Two attempts were made to obtain x-ray diffraction patterns of this material, but neither was successful. Hydrolysis of the product and chemical analysis of the resultant solution showed 46.05% Sb (45.47% theoretical). The infrared spectrum of the product showed an absorption at 669 cm$^{-1}$ which is typical of $SbF_6^-$. When the product was allowed to react with $NO_2$ in a vacuum apparatus, a yellow solid was formed that released $NO_2$ on hydrolysis.

2. Reaction of $O_2SbF_6$ with HF

Anhydrous HF was condensed in a Kel-F tube containing a 1.04 g sample of $O_2SbF_6$. The solid had a faint pinkish-lavender color in the liquid HF at -78°C. It was difficult to determine whether the solution itself had a similar faint color or not. The solution was held overnight at -78°C. Although results of instrumental analysis of the gases from the reaction showed only air and oxides of nitrogen, there was some evidence (blackening of a Kel-F trap) that there may have been a reactive gas present. As the system was allowed to warm to room temperature, there appeared to be gassing at the surface of the solid, and the quantity of solid decreased appreciably. In order to determine whether a chemical reaction had taken place, the HF was pumped off and the solid residue analyzed. When the trap containing the solid product was removed from the system, the color changed from white to purple. This material proved to be more reactive on handling in the dry box under nitrogen than freshly prepared $O_2SbF_6$. However, its infrared spectrum was identical to those of samples of $O_2SbF_6$. The solid weighed 0.90 g after treatment with HF, a loss in weight of 0.14 g.
D. PREPARATION OF NEW DIOXYGENYL COMPOUNDS

1. Reaction of $O_2$ with $ClO_2F$

Equimolar quantities (approximately 1 mmole) of oxygen and perchloryl fluoride were charged into a 500 ml glass bulb. The mixture was allowed to leak into an evacuated quartz U-tube having sealed copper electrodes until the pressure in the discharge tube was 15 mm. The tube was cooled to $-80^\circ C$, and a discharge was initiated by means of a 12,000 volt luminous tube transformer. No decrease in pressure was observed over a two-hour period and after the discharge was terminated, and no solid product was in the discharge tube.

2. Reaction of $SnCl_4$ with $O_2F_2$

After thorough degassing, approximately 5 ml (0.27 mmole) of $SnCl_4$ was condensed in an $O_2F_2$ generator. $O_2F_2$ was prepared in the arc and slowly brought into contact with the solid $SnCl_4$. An intense purple color appeared upon contact. On rapid warming of the mixture, there was a pressure surge resulting in information of noncondensable gases. The purple material rapidly decomposed at $-78^\circ C$. A dark ring remained on the wall which turned purple upon recondensation of the gases present. On long standing, the dark material bleached white. Solid material was recovered at room temperature. Although mass spectral and infrared analyses were made, the presence of $H_2O$ in the sample renders interpretation of the data impossible. X-ray analysis is being carried out on a sample of the solid. The condensable gas was primarily $Cl_2$. No $Cl-O$ bonded materials were found.

3. Reaction of Xenon and $O_2F_2$

Gaseous xenon was condensed at $-196^\circ C$ in the bottom of a Kel-F electrical discharge tube, and $O_2F_2$ was then generated in the same trap. When the cold bath was lowered, there was no evidence of the orange-colored liquid, $O_2F_2$. Instead only a light yellow solid was seen. This solid was frozen at $-196^\circ C$ and outgassed to remove any free $O_2$ or $F_2$ present. Mass spectrometric analysis of the gases given off by the solid at room temperature indicated the presence of xenon. The sample was stored overnight at $-78^\circ C$. The U-trap was inadvertently broken during an attempt to remove it from the vacuum system to a dry box. The grayish-white solid in the trap began to fume as it came in contact with moist air. Although it was placed in a dry box immediately, it appeared to be decomposing rapidly, giving off noxious fumes. In spite of
these difficulties, a small sample of the solid was loaded into a metal tube for pyrolysis in a mass spectrometer. When the sample was heated, small amounts of xenon along with water and HF were evolved.

E. ANALYSIS OF OXYGEN-FLUORINE MIXTURES

1. Analysis of a Sample of O₂ and F₂ by Sodium Chloride Method

Approximately 0.5 mmole of a 1:1 mixture of O₂ and F₂ was slowly passed through NaCl previously heated to 120°C. The Cl₂ resulting from the reaction of F₂ with NaCl was trapped at -196°C. The O₂ was transferred to a calibrated volume by means of a Toepler pump. The noncondensables amounted to 0.297 mmole, of which about 5% was a CF₄ impurity and the remainder was O₂. This was determined by mass spectroscopy. The condensable fraction was 0.161 mmole of Cl₂ with a trace of SiF₄. These data give an O₂/F₂ ratio of 1.8.

2. Analysis of O₂ and F₂ by Mercury Absorption

A 1:1 mixture of O₂ and F₂ was expanded into a glass cylinder having stopcocks at each end. One end was attached to the vacuum manifold by means of a ball joint and the other end to a mercury reservoir. The aliquot was 0.336 mmole. A small amount of mercury was admitted and the container was shaken for several hours. The surface of the mercury became tarnished by reaction with fluorine. The unreacted O₂ was transferred to a calibrated volume and measured. Mass spectral analysis indicated traces of SiF₄ and CF material. The O₂ amounted to 0.159 mmole. This gives an F₂/O₂ ratio of 1.17, or approximately 1:1.
IV. FUTURE WORK

- The analysis of the $\text{O}_2\text{F}_2$-Group V pentafluoride reaction product will be continued.

- The physical and chemical properties of the $\text{O}_2\text{F}_2$-Group V pentafluoride products will be investigated.

- The reactions of $\text{O}_2\text{F}_2$ with $\text{SnCl}_4$ and with xenon will be studied further.
V. REFERENCES


