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Report RMD 5043-Q1-64

Contract No. NONr 4364(00)

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ADVANCED OXIDIZER RESEARCH

Report Period: 1 January 1964 to 31 March 1964

Research reported in this publication was supported
by the Advanced Research Projects Agency.

DOWNGRADED AT 3 YEAR INTERVALS:
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Thiokol

CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVER, NEW JERSEY

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ADVANCED OXIDIZER RESEARCH

Report Period: 1 January 1964 to 31 March 1964

Contract No. NONr 4364(00), ARPA Order No. 417

Submitted by:

Donald D. Perry

DONALD D. PERRY
Supervisor,
Synthetic Chemical
Research Section

Approved by:

Murray S. Cohen

MURRAY S. COHEN
Manager,
Chemistry Department

31 March 1964 shall be used for
purposes of downgrading and/or
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David J. Mann
DAVID J. MANN
Director of Research

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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 includes the following tasks:

Task No.	Title
51	Difluoramine Chemistry
52	Synthesis of Compounds for Structure-Sensitivity Study
53	Chemistry of the Oxygen Fluorides
54	Stabilization of Nitronium Perchlorate by Complexation
55	Thermal Stability of Advanced Solid Oxidizers

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ABSTRACT

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

SECTION I - DIFLUORAMINE CHEMISTRY

A mixture of 1,2- and 1,4-bis(difluoramino)cyclohexenes has been prepared. The mixture decolorized bromine solution and reacted with permanganate to give carboxyl derivatives. Dehydrofluorination with an anionic exchange resin produced a conjugated bis(fluorimine) with interesting photochemical properties.

1,2-Bis(fluorimino)cyclohexane was synthesized by the addition of tetrafluorohydrazine to cyclohexene and subsequent dehydrofluorination. It was decomposed by sodium hydroxide solution but remained unreactive toward concentrated sulfuric acid, tetrafluorohydrazine, or aqueous nickel fluoride.

SECTION II - SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

Work is reported on the synthesis and gas chromatographic purification of aliphatic difluoramines for evaluation of the relationship between structure and sensitivity. The following crude tris-difluoramines were synthesized by the reaction of perfluoroguanidine with the corresponding primary and secondary alcohols during the current period followed by the fluorination of intermediate bis(difluoramino)fluoramino adducts:

Tris(difluoramino)methoxybutane
Tris(difluoramino)methoxypentane
Tris(difluoramino)methoxyhexane
Tris(difluoramino)methoxyheptane
Tris(difluoramino)methoxyoctane
Tris(difluoramino)methoxynonane
2-Tris(difluoramino)methoxyhexane
3-Tris(difluoramino)methoxyhexane

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Work is in progress on purification of these compounds to >99% purity by a combination of distillation and gas chromatography. Other compounds prepared were 1,1-bis(difluoramino)hexane, 1,1-bis(difluoramino)propane, and ethyl 2,3-bis(difluoramino)butyrate. These compounds are being carefully purified for comparison of sensitivity data with that obtained on less pure samples. Some problems associated with the gas chromatographic purification of organo-difluoramines are described.

SECTION III - CHEMISTRY OF THE OXYGEN FLUORIDES

The reaction of O_2F_2 with xenon in a metal Kel-F system at $-115^\circ C$ has produced high yields of an unidentified liquid, containing xenon, oxygen, and probably fluorine.

Attempts to utilize O_2AsF_6 in the synthesis of BrF_7 , $O_2^+C(NO_2)_3^-$, $O_2^+HSO_4^-$, $O_2^+NO_3^-$, and $O_2(C_6H_5N)^+AsF_6^-$ were unsuccessful. Solutions of O_2AsF_6 in HF were found to be stable up to approximately $-20^\circ C$.

Low temperature infrared spectra of O_2F_2 films on AgCl were obtained with much greater band resolution than previously reported.

SECTION IV - STABILIZATION OF NITRONIUM PERCHLORATE BY COMPLEXATION

The reaction of pyridine with nitronium perchlorate in Freon-113 at $-30^\circ C$ gave a solid which shows both NO_2^+ and pyridine ring absorptions in the infrared and is believed to contain a pyridinium complex, $NO_2(py)_xClO_4$. The purification and characterization of this complex is in progress.

The reaction of NO_2ClO_4 with N_2H_5Cl produced a complex mixture of gaseous decomposition products rather than the desired $NO_2N_2H_5(ClO_4)_2$.

SECTION V - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

The literature on the thermal decomposition of high energy solid perchlorate oxidizers has been carefully reviewed. The information available indicates that stability of the oxidizer is related to the strength of the acid-base complex. These data suggest that perchloric acid is the effective decomposing agent in all cases.

Anhydrous perchloric acid was prepared and its vapor pressure was determined because of a lack of definitive data in the literature.

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DIFLUORAMINE CHEMISTRY

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Section I

DIFLUORAMINE CHEMISTRY

Harry F. Smith

Report RMD 5043-Q1-64

RMD Project 5043, Task 51
Report Period: 1 January 1964
to 31 March 1964

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 4910

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FOREWORD

This section of the quarterly report describes research conducted from 1 January to 31 March 1964 on the synthesis and chemical reactions of organic difluoramines (RMD Project 5043, Task 51).

Technical personnel contributing to this effort were: H. F. Smith (Project Scientist) and J. A. Castellano (Synthesis), J. Creatura and A. Fremmer (Elemental Analysis), and R. Storey and D. Kates (Instrumental Analysis). The results of some company-sponsored investigations on the photochemistry of fluorimines by H. Burwasser are included.

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I. INTRODUCTION

The objective of this research program is the investigation of the chemical reactions of alkyldifluoramines and related compounds, with emphasis on the identification of products formed and, wherever possible, elucidation of the reaction mechanisms involved. Such information should prove useful in guiding the search for new nitrogen-fluorine compounds as well as in the utilization of known materials in high-energy propellant applications.

Attention is currently focused on determining the scope and generality of the addition reactions in which the C=NF group of perfluoroguanidine participates. Studies concerned with the synthesis and reactions of 1,4-bis(fluorimino)cyclohexene-2 and 1,2-bis(fluorimino)cyclohexane are described in this report.

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II. DISCUSSION

The importance which perfluoroguanidine has achieved as an intermediate in the synthesis of prospective high-energy propellant oxidizers can be attributed directly to the reactivity of the fluorimino group in the molecule. Such active-hydrogen compounds as alcohols (Ref 1), isocyanic acid (Ref 2) and hydrogen chloride (Ref 3) have been found to add readily to the double bond in perfluoroguanidine.

It will be of great practical and theoretical significance to determine to what extent this reactivity is shared by other compounds which contain the C=NF grouping. The compounds most closely analogous to perfluoroguanidine, and ultimately the subject of the greater part of our experimentation, are the tri-

fluoroamidines, $RC \begin{smallmatrix} \text{NF} \\ \text{NF} \end{smallmatrix} = NF_2$. The more readily available alkylfluorimines, $R-C \begin{smallmatrix} \text{NF} \\ \text{NF} \end{smallmatrix} - R^1$, are serving as suitable model compounds for preliminary studies. The preparation and properties of compounds derived from the addition of tetrafluorohydrazine to 1,3-cyclohexadiene and to cyclohexene are described.

A. BIS(DIFLUORAMINO)CYCLOHEXENES

1. Synthesis

The addition of tetrafluorohydrazine to 1,3-cyclohexadiene, as described in the previous report (Ref 4), has been repeated and the formation of four isomeric bis(difluoramino)cyclohexenes has been confirmed. It has been found that simple distillation will suffice to separate the mixture into two pairs of compounds, but the identity of the individual components has not yet been established. If it happens that one distillation fraction consists of the cis and trans modifications of the 1,2-addition product and the other fraction consists of the geometric isomers of the 1,4-bis(difluoramino) the need for further separations will be eliminated. In the ensuing dehydrofluorination step, either a cis or a trans isomer will give the same product, so the use of a cis-trans mixture will impose no hardship.

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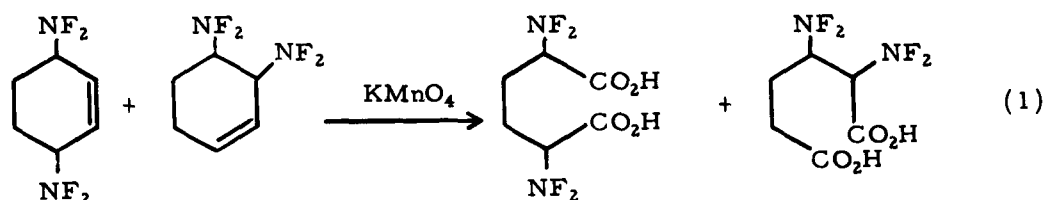
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2. Reactions

a. Oxidation

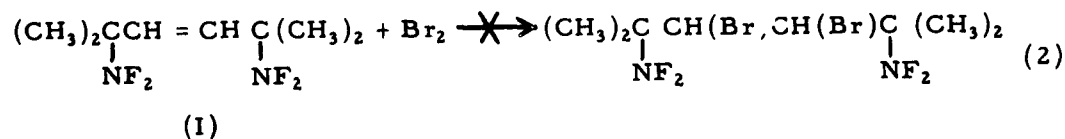
The useful information and products which might be derived from studies of the oxidation of unsaturated alkyldifluoramines and some screening experiments in this area have been discussed in previous reports (Ref 4 and 5). This investigation has been extended to include a larger scale reaction of bis-(difluoramino)cyclohexene (mixed 1,2- and 1,4-isomers) with aqueous permanganate. The liquid product was shown by infrared analysis to contain carboxyl groups in addition to the NF₂.



Further characterization was not possible because of the complexity of the product mixture. The experiment will be repeated when sufficient quantities of the individual isomers become available.

b. Reaction with Bromine

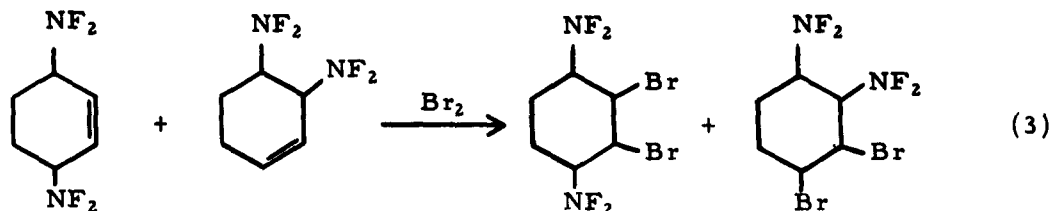
Previous investigations on this program have given indications that the proximity of difluoramino groups may have a pronounced effect upon the reactivity of an olefinic bond (Ref 4 and 6). Early attempts to effect the addition of bromine to trans-2,5-bis(difluoramino)-2,5-dimethylhexene-3 (I) were unsuccessful (Ref 6). It has now been discovered that a carbon tetrachloride solution of bromine is decolorized by the bis(difluoramino)cyclohexene isomer mixture.



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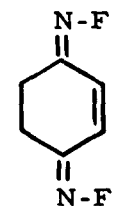
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Here again isolation and detailed characterization of products must await the availability of isomerically pure model compound.

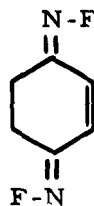
c. Dehydrofluorination

The use of a basic ion exchange resin to effect the removal of hydrogen fluoride from secondary alkyl difluoramines (Ref 4) has been found to give the best results of any reagent tried. Reaction was clean and free from the decomposition which accompanied the use of potassium hydroxide or an amine. The product obtained from the mixture of isomers of 1,2- and 1,4-bis(difluoramino)-cyclohexene was a distillable liquid, from which a crystalline solid was obtained by trituration with pentane. The solid, to which the structure 1,4-bis(fluorimino)-cyclohexene-2 (II) has been assigned, has been subjected to repeated recrystallizations and to zone refining without change in its melting point (52-53°C).



syn-syn

(IIa)



syn-anti

(IIb)



anti-anti

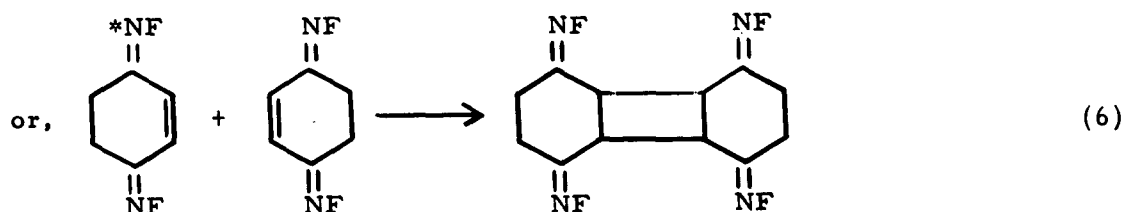
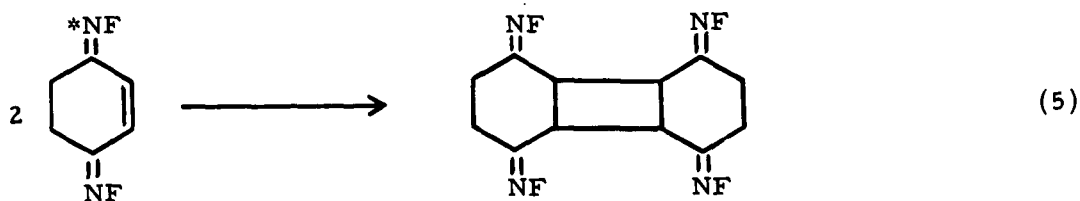
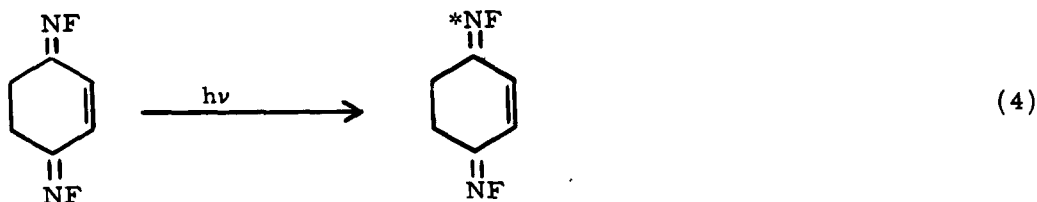
(IIc)

F¹⁹ n.m.r. measurements (Ref 4) reveal the presence of fluorine atoms in three different environments, indicating that all three of the possible geometric isomers are present. Interconversions among the three must, then, be extremely facile and they must form a set of ideal solutions to give the sharp melting point which has been observed. An indication from vapor phase chromatography that two or more separable components were present may have been an artifact arising from decomposition on the column. This point is being rechecked.

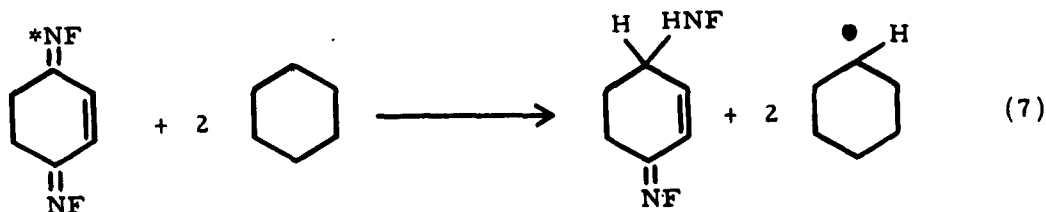
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3. Photochemical Properties of 1,4-Bis(fluorimino)cyclohexene-2

The title compound exhibits a single broad absorption centering at 238-240 mμ ($\epsilon = 2 \times 10^4$ mole-cm/liter) in the visible-ultraviolet spectrum. Photolysis of dilute (ca. 10^{-4} M) solutions in cyclohexane at 254 mμ resulted in a decrease of the original absorption but did not produce any new absorption in the visible or ultraviolet regions. The average quantum yield for 50% conversion was approximately 10^{-2} . One possible mechanism which would account for the observed results is the cyclodimerization which is known to occur in other olefinic systems (Ref 7):



Solvent participation is also possible:



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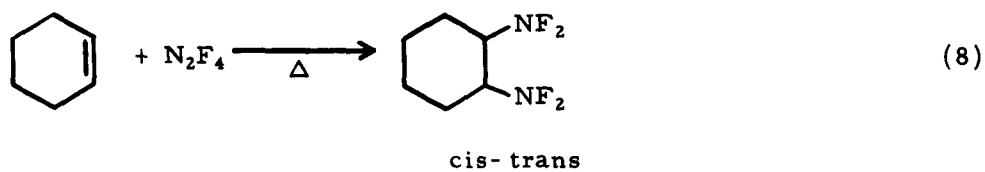
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Photolysis of the unsaturated bis(fluorimine) in acetonitrile solution also led to a decrease in the 238 mμ absorption, but in this case a product absorbing at 272 mμ was formed. The minute quantities of material involved in the photolytic reactions have precluded isolation of products or characterization by infrared spectrometry or chromatography. Preparative scale experiments are planned when required equipment becomes available.

B. 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

1. Synthesis

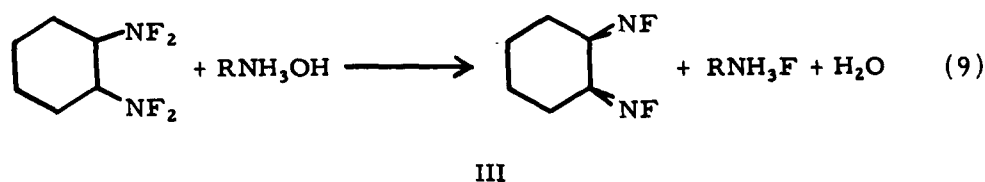
Fresh supplies of this compound were prepared using established synthetic procedures (Ref 8).



The combined product from six experiments totalled 16.2 grams (55% of theory).

2. Dehydrofluorination

The dehydrofluorination procedure, using an anionic exchange resin, was applied with equal success to the synthesis of 1,2-bis(fluorimino)cyclohexane (III).



A yield of 51.5% of purified material, having the correct analysis for $\text{C}_6\text{H}_8\text{N}_2\text{F}_2$ and an infrared absorption spectrum identical with that reported earlier (Ref 6), was obtained.

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3. Reactions of 1,2-Bis(fluorimino)cyclohexane

a. With Sulfuric Acid

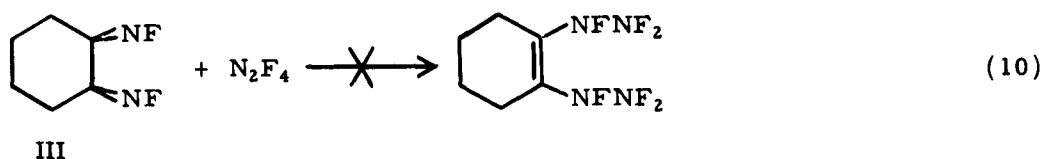
A small amount of the bis(fluorimine) (III) was treated with concentrated sulfuric acid. After 20 hours the organic starting material was recovered unchanged. The fluorimino group is therefore inert to attack by a strong electrophile. This is in contrast to the behavior of difluoramino compounds, which eliminate either hydrogen fluoride or difluoramine under similar conditions.

b. With Sodium Hydroxide

A measured quantity of III (11.37 mmoles) was stirred for 20 hours with 6.00 meq of sodium hydroxide solution. The orange reaction mixture was then titrated with standard acid and found to contain a residual 3.00 meq of free base. Extraction with ether gave a viscous oil contaminated with Kel-F grease. The amount of fluoride ion liberated has not yet been determined.

c. With Tetrafluorohydrazine

An attempt was made to determine whether the fluorimino grouping would undergo a free-radical addition reaction in the same manner as an olefinic bond. The bis(fluorimine) (III) was heated to 80-100° for five hours in the presence of a slight excess of tetrafluorohydrazine. No reaction occurred, and most of the starting material was recovered.



d. With Maleic Anhydride

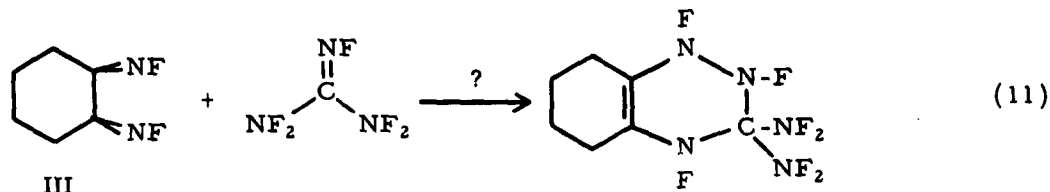
The possibility that a 1,2-bis(fluorimine) might function as a Diels-Alder diene offers attractive prospects. Since perfluoroguanidine has been found to

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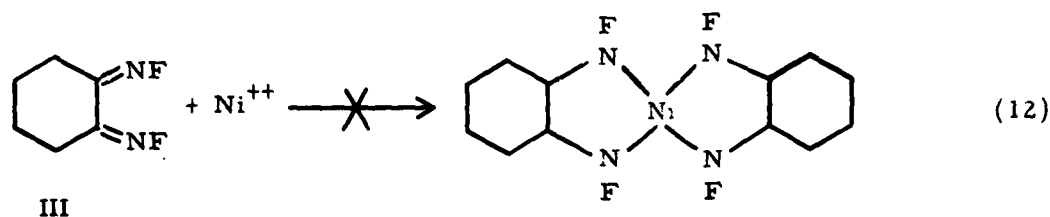
have substantial dienophilic character (Ref 9), interesting new organic NF compounds would be available through reactions of this type:



To test this hypothesis the Diels-Alder reaction was attempted with III and a reactive dienophile, maleic anhydride. A liquid product (bp 58-60°/0.15 mm), which showed absorptions in the infrared for both NF and anhydride groups, was obtained. Elemental analysis gave results (C, 48.43; H, 4.46; N, 14.44; F, 19.25) which correspond to a 2:1 mixture of bis(fluorimine) and anhydride. The product was shown, however, to be an azeotropic mixture of the starting materials, and the two components were separated by gas-liquid chromatography and identified by their retention times. A second product, a black solid with a softening point at 280°, was found to contain no NF groups.

d. With Nickel Fluoride

The geometrical arrangement of structures like III suggests the possibility that bidentate coordination compounds might easily be formed. Accordingly, an aqueous solution of nickel fluoride was treated with a drop of 1,2-bis(fluorimino)cyclohexane. No colored complex was obtained.



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III. EXPERIMENTAL

A. REACTION OF BIS(DIFLUORAMINO)CYCLOHEXENE WITH PERMANGANATE

Addition of 40 ml 0.1N KMnO_4 solution to three drops of bis(difluoramino)-cyclohexene (mixture of 1,2- and 1,4- isomers) gave an immediate brown precipitate of MnO_2 . The mixture was extracted with CH_2Cl_2 , the extract dried, and the solvent evaporated to yield a liquid product. The infrared spectrum indicated the presence of COOH .

B. REACTION OF BIS(DIFLUORAMINO)CYCLOHEXENE WITH BROMINE

Two drops of a solution of bromine in carbon tetrachloride were added to two drops of bis(fluorimino)cyclohexene (isomer mixture). The bromine color disappeared on standing for 4 hours at room temperature. Trityldifluoramine had not decolorized bromine after 48 hours at room temperature.

C. SYNTHESIS OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

Tetrafluorohydrazine (3.12 g., 30 mmoles, measured by volume assuming ideality) was condensed into an evacuated 2-liter bulb containing 2.18 g. (27 mmoles) of cyclohexene (Eastman, "White Label"), and the bulb was then heated in an enclosing mantle at $100 \pm 5^\circ$ for 5 hours. After vacuum distillation to remove unreacted N_2F_4 , collecting product at -78° , the material from six similar runs was combined and distilled, bp $69-82^\circ/27.5$ mm. A yield of 16.2 g. (55%) was obtained.

D. SYNTHESIS OF 1,2-BIS(FLUORIMINO)CYCLOHEXANE

1,2-Bis(difluoramino)cyclohexane (16 g., 86 mmoles) was dissolved in 100 ml ethyl ether. To this solution was added 64 g. (240 meq) Amberlite IR 45 and the mixture was stirred at 30° under a nitrogen atmosphere for 24 hours. The spent resin was then removed by filtration and washed with

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ether. The filtrate and washings were combined, dried and evaporated to dryness. The residue, a yellow liquid (9.3 g.), was distilled (bp 68-70°/0.2 mm; 64-66°/0.1 mm) to yield 6.3 g. (50%) of pure product ($n_D^{20} = 1.4661$), mp 5-6°.

Anal. Calcd for $C_6H_8N_2F_2$: C, 49.31; H, 5.52; N, 19.17; F, 26.00

Found: C, 49.53; H, 5.51; N, 18.97; F, 25.99 (by diff)

M.W. Calcd: 146.14

Found: 146/152

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IV. FUTURE WORK

During the next quarter the research effort will be devoted to the following areas:

- Addition of isocyanic acid to fluorimines
- Addition of difluoramine to fluorimines
- Further study of 1,2-bis(fluorimines) as possible Diels-Alder dienes
- Synthesis of a suitable N,N,N'-trifluoroalkylamidine
- Exploration of reactions of the double bond in trifluoroamidines.

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Section II

Task 52

**SYNTHESIS OF COMPOUNDS FOR
STRUCTURE-SENSITIVITY STUDY**

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Section II

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby
D. D. Perry

Report RMD 5043-Q1-64

RMD Project 5043, Task 52
Report Period: 1 January 1964
to 31 March 1964

Contract No. NOmr 4364(00)
ARPA Order No. 417
Project Code 4910

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REACTION MOTORS DIVISION

FOREWORD

This report describes the work carried out during the period from 1 January to 31 March 1964 on the synthesis of organodifluoramines for use in the study of structure-sensitivity relationships (RMD Project 5043, Task 52).

The following personnel contributed to this effort: A. P. Kotloby (Project Scientist), W. H. Wieting (Synthesis), R. N. Storey, D. Z. Chowanec, and D. N. Pregler (Instrumental and Wet Chemical Analysis).

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I. INTRODUCTION

This portion of the advanced oxidizer research program deals with the synthesis phase of a study aimed at an understanding of the structural and chemical factors affecting the sensitivity of organic difluoramines. One of the principal problems involved in the use of these compounds in propellant formulations is their sensitivity to stresses such as heat and mechanical shock. The evaluation of the sensitivity data gathered from a sufficiently large number of organofluoramines representing a variety of structural types and functional groups could be useful in guiding research toward the synthesis of compounds having a minimum degree of sensitivity in relation to their energy.

In accordance with this goal, Thiokol Chemical Corporation, Reaction Motors Division, has undertaken the task of preparing a variety of organic difluoramines for sensitivity evaluation by the Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland. These compounds have been selected on a systematic basis to provide information concerning the effect on sensitivity of such factors as the NF_2 -to-carbon ratio, the type of NF_2 -substitution, and the presence of various organofunctional groups. The principal sensitivity test being employed with these materials is the Wenograd thermal explosion delay test (Ref 3). Some of the data obtained on these and other N-F materials have been summarized elsewhere (Ref 2). These results show some interesting and potentially valuable correlations between vicinally and geminally-substituted bis(difluoramines). It is now of interest to extend these studies to the highly energetic tris(difluoramino)methyl compounds which are available via addition reactions of perfluoroguanidine.

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II. DISCUSSION

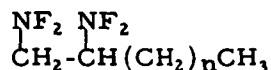
A. BASIC CONSIDERATIONS

The synthesis phase of this research program is concerned with the selection, preparation, and characterization of a series of organodifluoramines. The selection of compounds or classes of compounds for synthesis is based primarily on the following considerations.

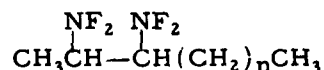
- The usefulness of the proposed compounds in providing information relating structure to sensitivity
- Synthetic feasibility
- Requirements of the test
- Availability of compounds from other sources.

1. Relationship of Structure to Sensitivity

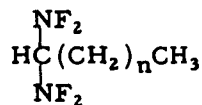
In order to fulfill the first requirement, we have synthesized (Ref 1) a variety of vic and gem-NF₂ compounds in several different homologous series:



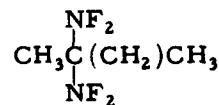
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n = 0 to 2



n = 0 to 4



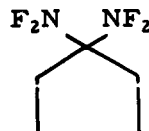
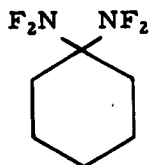
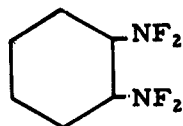
n = 0 to 3

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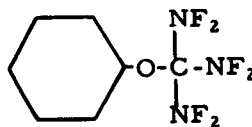
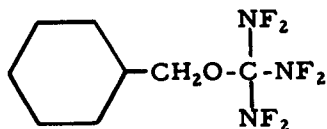
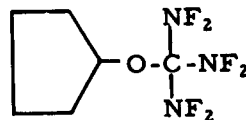
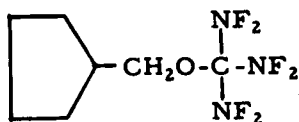
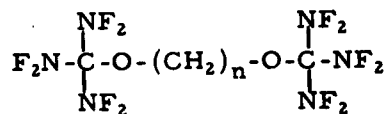
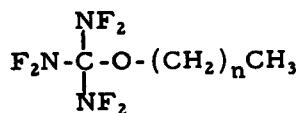
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Data on these compounds will be supplemented by the preparation of tris(difluoramino)methoxyalkanes of the types shown below during the current year's program:



In addition, we plan to prepare urethanes from $(\text{NF}_2)_3\text{NCO}$ and compare their sensitivities with those of vic-urethanes prepared previously on the program.

A comparison of the sensitivity of compounds within each homologous series provides information on the effect of oxidative balance, while a comparison between the corresponding members of different series shows how sensitivity is affected by vicinal and geminal substitution and other structural or substituent effects (Ref 2).

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2. Synthetic Feasibility

The syntheses of N-F compounds employed in this work are based on the known reactions of difluoramine, tetrafluorohydrazine, perfluoroguanidine, and tris(difluoramino)methyl isocyanate. While the applicability of all these reagents has certain limitations, it is possible by these methods to prepare a sufficiently wide variety of organodifluoramine structures to elucidate almost all of the structural factors which can affect the sensitivity of this class of materials.

3. Requirements of the Sensitivity Test

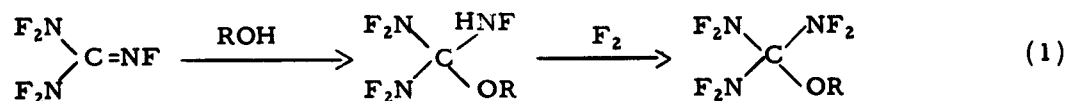
The test requirements are quite important in the selection of compounds for evaluation. Currently, strong emphasis is being placed on the use of a high temperature explosion delay test (Ref 3). This test requires a liquid compound, or a solid that melts without decomposition. Another requirement is that the compound should be sufficiently sensitive to yield meaningful results. Regarding this, it has been found that an NF_2/C ratio $< 1:3$ is generally undesirable.

4. Availability of Compounds from Other Sources

The Naval Ordnance Laboratory maintains contact with other research groups in the propellant industry and receives from them certain compounds for sensitivity determinations. Close liaison is maintained between Thiokol and NOL to avoid any duplication on our synthetic program of materials they have received from other organizations.

B. PREPARATION AND PURIFICATION OF TRIS(DIFLUORAMINO)-METHOXYALKANES

During the current quarter work was initiated on the synthesis of tris(difluoramino)methoxyalkanes by the reaction of alcohols with perfluoroguanidine, followed by fluorination of the intermediate fluoramino adduct (equation 1):



Nucleophilic addition of hydroxyl compounds to perfluoroguanidine has been the subject of intense investigations in several laboratories (e.g., Ref 4 and 5).

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Primary and secondary alcohols have been found to add readily to the electron-deficient double bond in perfluoroguanidine. Urea is usually used as a catalyst in the addition reaction, with Freon-11 or acetonitrile as the solvent. The saturated fluoramino adducts, most of which are not very stable at room temperature, are fluorinated with dilute fluorine gas at about 0°C.

Initial work on the synthesis of tris(difluoramino)methyl ethers was carried out with a very impure batch of PFG. Although this batch was reported to be approximately 65% PFG, we found that it contained large quantities of non-condensables and that purification yielded only about 30% of usable material. An addition reaction with n-pentanol apparently proceeded smoothly, but the product obtained by fluorination of the initial adduct consisted principally of fluorinated alcohols, with possibly a small amount of the desired tris(difluoramino)-pentyl ether. It therefore appeared that little addition had occurred. During purification of this crude PFG prior to attempting another addition reaction under modified conditions, an explosion occurred in the vacuum line.

Subsequently, we have been working with PFG of >90% purity, obtained from American Cyanamid Co. and the Minnesota Mining and Manufacturing Co. This material contained no non-condensables and was colorless in contrast to the greenish color of the previous batch, due probably to the presence of oxides of nitrogen. Using the purer PFG, we have carried out the synthesis of a number of tris-compounds. These compounds are listed in Table I.

TABLE I

TRIS(DIFLUORAMINO)METHOXYALKANES

<u>Compound</u>	<u>BP (Crude Product (°C/mm Hg))</u>
Tris(difluoramino)methoxybutane	51.0/10.3
Tris(difluoramino)methoxypentane	32.0/0.8
Tris(difluoramino)methoxyhexane	41.0/0.3
Tris(difluoramino)methoxyheptane	57.0/0.3
Tris(difluoramino)methoxyoctane	66.0/0.55
Tris(difluoramino)methoxynonane	68.0/0.25
2-Tris(difluoramino)methoxyhexane	45.0/4.4
3-Tris(difluoramino)methoxyhexane	42.0/6.7

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The crude products obtained in these reactions were given a simple vacuum distillation and submitted for infrared and gas chromatographic analysis. It is our objective in this work to obtain samples of >99% purity for the sensitivity evaluation studies, so that there will be no question that small amounts of impurities are either stabilizing or sensitizing the compounds.

It soon became apparent that v.p.c. purification of the tris-compounds would not be routine. For one thing, initial chromatographic analyses showed the presence of a number of impurities. The infrared spectra of the crude products confirmed this. Virtually all of the products exhibited residual N-H absorptions, as well as bands attributable to C-F bonds. Several types of chromatographic columns have been investigated under various temperature conditions. These are listed in Table II. To date, good separations have not been achieved.

TABLE II

V.P.C. CONDITIONS INVESTIGATED FOR PURIFICATION
OF TRIS-COMPOUNDS

<u>Liquid Phase</u> (%)	<u>Solid Phase</u>	<u>Column</u> <u>Material</u>	<u>Temp</u> (°C)
SE-30 (Silicone) (30%)	Chromosorb P	Al	110
FC-43 (15%)	Chromosorb P	Cu	145
QF-1 (Fluorosilicone, 15%)	Chromosorb P	Cu	140
Di-n-decylphthalate (25%)	Firebrick	Cu	140
Kel-F-10 (10%)	Teflon	Cu	145
FC-43 (15%)	Silica Gel	Cu	160

Work is continuing to determine the optimum conditions for purification of the tris-compounds. The approaches under study include the following areas:

- Modification of the synthesis conditions in an effort to achieve a purer product initially.

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- Use of a more efficient distillation column to further purify the crude product prior to v.p.c. purification.
- Study of other columns and conditions for v.p.c. purification.

Once the optimum conditions for purifying the tris-compounds have been determined on an analytical instrument, preparative gas chromatography will be employed to purify samples for submission to the Naval Ordnance Laboratory. The main product peak will be "sliced off" in order to afford a sample of maximum purity.

C. SYNTHESIS OF BIS(DIFLUORAMINO) COMPOUNDS

Although the synthesis effort is currently concerned principally with the preparation of tris-compounds, some work is also proceeding on vic- and gem-bis(difluoramines). This is being done to complete syntheses initiated during the previous year of the program and to obtain purer samples of some adducts which were slightly below the minimum purity requirements established for the test compounds. These compounds are listed in Table III. The experimental procedures used in their preparation are the same as described in a previous report on this program (Ref 6). Chemical analysis of two of these compounds, 1,1-bis(difluoramino)hexane and ethyl 2,3-bis(difluoramino)butyrate, indicated purity of >90% after distillation.

TABLE III

BIS(DIFLUORAMINO)ALKANES

<u>Compound</u>	<u>BP</u> <u>(°C/mm Hg)</u>
1,1-Bis(difluoramino)propane	31.0/160
1,1-Bis(difluoramino)hexane	53.0/25
1,1-Bis(difluoramino)-2-methylpropane	35.0/72
Ethyl 2,3-bis(difluoramino)butyrate	50.0/6
4,5-Bis(difluoramino)pentanol	60.0/0.22
1,2-Bis(difluoramino)-4-pentanol	38.0/0.3

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After a preliminary purification by vacuum distillation through a short glass column, all the compounds were subjected to vapor phase chromatographic purification. So far we have evaluated three polar and four nonpolar columns. The results of the work on gas chromatographic separation are summarized in Tables IV and V.

These results again serve to indicate that the purification of organodifluoramines by the gas chromatographic method is not a simple procedure and requires further work. Those compounds for which the conditions have been determined (e.g., ethyl 2,3-bis(difluoramino)butyrate) will be purified on a preparative column and submitted for sensitivity evaluation.

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TABLE IV
EVALUATION OF NONPOLAR GAS CHROMATOGRAPHIC COLUMNS
FOR SEPARATION OF ORGANODIFLUORAMINES

Compound	Column and Conditions			
	SE-30 (Silicone), on Chromosorb P (45-60 mesh)	Di-n-decylphthalate 25%, on Firebrick (30-60 mesh)	Kel-F-10, 10% on Teflon (low density)	SF-96 Methylsilicone (Wilkins)
1, 1-Bis (difluoramino) - 2-methylpropane	Al Column, 20 ft x 3/8 in. T = 110°C He Carrier, max, f.r. In hexane No separation	Cu Column, 6 ft x 1/4 in. T = 140°C He Carrier, max, f.r. In benzene No separation	Cu Column, 6 ft x 1/4 in. T = 145°C He Carrier, max, f.r. In benzene No separation	Al Column, 15 ft x 3/8 in. T = 140°C He Carrier, max, f.r. Excellent resolution; 1 peak
1, 1-Bis (difluoramino) hexane	-----	-----	No separation	Good resolution; 1 major, 1 minor peak
Ethyl 2, 3-bis (difluoramino) butyrate	No separation	3 resolved peaks, 1 major Good separation	-----	Good resolution; 1 major and few small peaks
4, 5-Bis (difluoramino) pentanol	No separation	No separation	-----	No separation

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TABLE V
EVALUATION OF POLAR GAS CHROMATOGRAPHIC COLUMNS
FOR SEPARATION OF ORGANODIFLUORAMINES

Compound	Column and Conditions	
	FC-43 (Polyfluorobutylamine) 15%, on Chromosorb P (30-60 mesh)	QF-1 (Fluorosilicone) 15%, on Chromosorb P (30-60 mesh)
1,1-Bis(difluoramino)-2-methylpropane	Cu Column, 15 ft x 1/4 in. T = 145°C He Carrier, max, f.r. In hexane No separation	Cu Column, 15 ft x 1/4 in. T = 140°C He Carrier, max, f.r. In hexane No separation
1,1-Bis(difluoramino)hexane	-----	FC-43 (Polyfluorobutylamine) 15%, on Silica Gel (30-60 mesh) Cu Column, 7.5 ft x 1/4 in. T = 160°C He Carrier, max, f.r. In benzene 3 unresolved peaks and 1 small peak 2 peak areas; 1 unresolved, another low
Ethyl 2,3-bis(difluoramino)butyrate	Good separation; 1 peak, shoulder, tail	Good separation; 1 peak, shoulder, small peak
4,5-Bis(difluoramino)pentanol	Poor separation; 1 peak, shoulder, tail	Flat peak, tail

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III. EXPERIMENTAL

Synthesis of Tris(difluoramino)methoxyalkanes

Onto a twice-degassed solution of an alcohol (0.04 mole) in 10 ml Freon-113 containing 1 g. urea and cooled to -120° (Freon-11/liquid N_2 slush bath) was condensed 0.05 mole of perfluoroguanidine ($>92\%$ pure). The reactor was cooled and allowed to come gradually to 0° while being stirred with a Teflon-coated magnetic stirring bar. The mixture was kept overnight at this temperature. The uptake of perfluoroguanidine, as observed for C_4 through C_9 normal primary alcohols, was nearly quantitative. The small excess of perfluoroguanidine was then removed, the solution was flushed with dry nitrogen, and the pressure in the reactor was brought to atmospheric. To the filtered solution was added 1 g. of NaF and the 1,1-bis(difluoramino)-1-fluoroaminomethoxyalkane was fluorinated by slowly bubbling dilute fluorine (2% by vol in N_2 , total 0.04 mole) into the solution while the temperature was kept at 0° with an ice bath. The fluorination required 16 to 19 hours and was usually carried out overnight. The solution of the crude tris(difluoramino)methoxyalkane was flushed with nitrogen, diluted with 50 ml of Freon-113, washed several times with water, dried over $MgSO_4$, stripped of solvent under 10-20 mm pressure, and distilled under vacuum. Compounds made from C_7 (or lower) alcohols were very sensitive to shock.

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IV. FUTURE WORK

During the next quarter, work will be conducted in the following areas:

1. Determination of the optimum conditions for purification of tris-compounds to >99% purity.
2. Preparation of tris(difluoramino)methoxy derivatives from secondary and cyclic alcohols and from glycols.
3. Synthesis of alkyl N-tris(difluoramino)methylcarbamates from tris(difluoramino)methyl isocyanate and alcohols.
4. Synthesis of difluoramino-N-fluoroazoxyalkanes by the reaction of N_2F_4 -NO mixtures with olefins.

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V. REFERENCES

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4. Minnesota Mining and Manufacturing Company, Report No. 14, Chemical Research as Related to Advanced Solid Propellants, 30 September 1962.
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Section III

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CHEMISTRY OF THE OXYGEN FLUORIDES

Section III

CHEMISTRY OF THE OXYGEN FLUORIDES

S. I. Morrow
A. R. Young

Report RMD 5043-Q1-64

RMD Project 5043, Task 53
Report Period: 1 January 1964
to 31 March 1964

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 4910

FOREWORD

This section of the report summarizes the results of studies of the chemistry of dioxygen difluoride and of dioxygenyl salts during the period from 1 January 1964 to 31 March 1964. This program was monitored by Mr. R. Hanson of the Office of Naval Research.

Personnel contributing to these studies were: A. R. Young (Project Supervisor), S. I. Morrow (Principal Investigator), K. Tiger, J. Crothamel, R. Storey and R. Crooker.

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I. INTRODUCTION

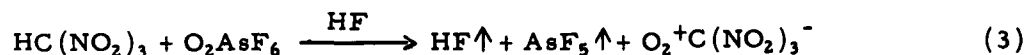
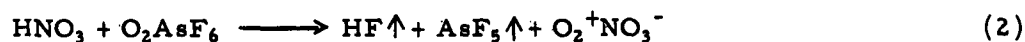
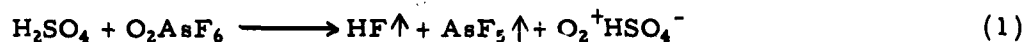
Our investigation of the inorganic chemistry of the oxygen subfluorides has as its goal the utilization of these unstable O-F compounds as precursors of new solid oxidizers. For this reason much of the past quarter was devoted to studies of the chemical properties of the stable dioxygenyl salt, $O_2^+AsF_6^-$, that is derived from the reaction of O_2F_2 with AsF_5 . In these investigations O_2AsF_6 has been considered both as a source of the dioxygenyl cation ($\cdot O_2^+$) and as a powerful fluorinating agent ($O_2AsF_6 \rightarrow \cdot F + O_2 + AsF_5$). Accordingly, we attempted metathetical conversions of O_2AsF_6 to dioxygenyl salts of highly oxidizing anions and also attempted the fluorination of BrF_3 with O_2AsF_6 .

Reactions of O_2F_2 with xenon and with potassium nitroform were also investigated during this report period and further studies were made of the infrared spectra of O_2F_2 films.

II. DISCUSSION

A. PREPARATION OF DIOXYGENYL DERIVATIVES FROM DIOXYGENYL HEXAFLUOROARSENATE

Because of the excellent oxidizing potential of the paramagnetic dioxygenyl ion ($\cdot\text{O}_2^+$) we are seeking methods of preparing dioxygenyl salts of energetic oxidizing anions. Thus, it is possible that conditions can be found which will favor the conversion of O_2AsF_6 to more energetic dioxygenyl salts, as shown in equations 1 - 3:



1. Reaction of O_2AsF_6 with H_2SO_4

When O_2AsF_6 was added to excess 98% H_2SO_4 , gas evolution occurred instantaneously. The gas liberated was 92% oxygen and 8% fluorine. However, the quantity of oxygen evolved was only 64.9% of the calculated dioxygenyl ion content of the O_2AsF_6 sample. This was not a freshly prepared sample of O_2AsF_6 and it is possible that it underwent some decomposition during storage. Nevertheless, the possibility that the balance of the oxygen was retained in the H_2SO_4 solution as O_2^+ will be examined in subsequent experiments.

2. Reaction of O_2AsF_6 with HNO_3

Anhydrous nitric acid was swept with dry nitrogen gas and pumped on at reduced temperature in an attempt to remove dissolved NO_2 . The latter is objectionable because it reacts with O_2AsF_6 to form NO_2AsF_6 .

These attempts to remove NO_2 were not successful; therefore, the reaction of O_2AsF_6 with HNO_3 was not evaluated. Other methods reported for preparing pure 100% HNO_3 will be tried in order that the desired reaction can be investigated.

3. Reaction of Nitroform with O_2AsF_6

When solutions of nitroform and O_2AsF_6 in HF were mixed at $-78^\circ C$, vigorous gas evolution occurred. This gas was identified as oxygen. In a separate experiment it was found that O_2AsF_6 does not evolve oxygen at a rapid rate in HF until the temperature is as high as $-20^\circ C$. A white precipitate remained when the solvent was removed by vacuum distillation. Nitrogen oxides were found in the gases from the reaction. The solid residue became liquid during storage prior to analysis. Its infrared spectrum showed a weak -OH stretching frequency and broad bands throughout the observed range, as well as the AsF_6^- ion absorption. The rapid evolution of oxygen at $-78^\circ C$ in this experiment indicates that $O_2C(NO_2)_3$ cannot be prepared in an HF medium.

B. STABILITY OF O_2AsF_6 IN SOLUTION

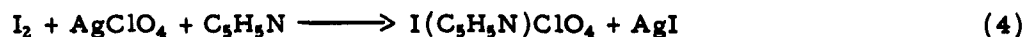
Hydrogen fluoride is the only satisfactory solvent that has been found for O_2AsF_6 . However, solutions of the dioxygenyl compound in HF decompose rapidly above $-20^\circ C$. Consequently, attempts were made to increase the stability of O_2AsF_6 solutions in HF. In addition, other solvents suitable at room temperature were sought for dioxygenyl compounds. In the search for such solvents the behavior of O_2AsF_6 with AsF_3 was investigated.

1. Hydrogen Fluoride as a Solvent for O_2AsF_6

Previous work with O_2AsF_6 and HF resulted in the formation of a purple solution, which began to give off O_2 at about $-50^\circ C$ (Ref 2). Reinvestigation of this reaction in a system free from brass or copper showed that O_2AsF_6 solutions in HF are actually colorless. Evidently the distillation of HF through copper introduces an impurity that imparts a purple color to the solution. It was found that the colorless HF solution was considerably more stable than violet solutions observed previously. However, vigorous gas evolution took place above $-20^\circ C$. Anhydrous reagent HF contains traces of moisture, according to Jarry (Ref 3). If the solvent were rigorously purified as he describes, it is possible that the stability of this system would be further improved. This is a matter of practical consequence since it might be possible to evaluate reactions of O_2AsF_6 in HF at normal temperatures.

2. Attempt to Form a Pyridine - O_2^+ Complex

Pyridine is known to form complexes with nonmetallic cations as shown in equation 4:



If a pyridinium complex could be formed from O_2AsF_6 (equation 5):



it might be stable and soluble in anhydrous HF at room temperature. Such a complex might open up a possible synthetic route to dioxygenyl perchlorate or nitrate by metathesis.

The reaction of O_2AsF_6 and pyridine was studied without a diluent, as well as in the presence of perfluoropropane. In each case, when the O_2AsF_6 -pyridine mixture was warmed from $-196^\circ C$, a brown solution was formed and oxygen was evolved. In the reaction without solvent 75% of the oxygen present as O_2^+ was given off as O_2 . The brown solid recovered from the reaction in C_3F_8 solvent gassed only slightly when put in water. ($O_2(C_6H_5N)AsF_6$ was therefore probably not present, since it would have given off oxygen upon hydrolysis.) Infrared analysis showed that the solid contained alkyl nitrite and nitrate components as well as AsF_6^- (possibly as the pyridinium salt). The product from the reaction in which C_3F_8 was used as a diluent had a similar composition. Evidently O_2AsF_6 decomposed in the presence of pyridine to give off oxygen which oxidized the nitrogen in pyridine with accompanying ring cleavage.

3. Arsenic Trifluoride as a Solvent for O_2AsF_6

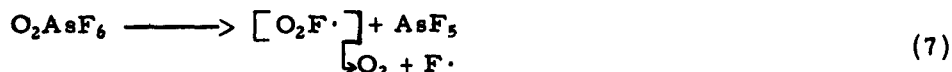
The O_2AsF_6 - AsF_3 system was evaluated at $-10^\circ C$. O_2AsF_6 dissolved completely in the liquid AsF_3 , but as the mixture was allowed to stand for two hours, oxygen was evolved. The amount given off was approximately equal to the dioxygenyl content of the O_2AsF_6 used. When the AsF_3 was distilled off at $25^\circ C$ in a vacuum, only a trace of white solid was left behind. The AsF_3 was evidently oxidized to AsF_5 by O_2AsF_6 .

C. INVESTIGATION OF O_2AsF_6 AS A FLUORINATING AGENT

Studies of the reaction of O_2AsF_6 with SO_2Cl_2 , as well as with unsaturated carbon compounds, showed the power of this material as a fluorinating agent (Ref 2). Although SO_2Cl_2 is rather difficult to fluorinate, the following reaction has been observed:

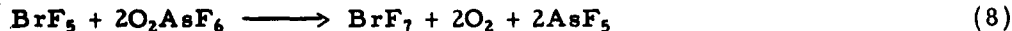


It is believed that O_2AsF_6 acts as follows, releasing fluorine atoms which are very active fluorinating species:



1. Reaction of O_2AsF_6 and BrF_5

It was hoped that the fluorinating power of O_2AsF_6 might be sufficient to convert the known interhalogen BrF_5 to the as-yet-unreported heptafluoride, BrF_7 (equation 8):



When BrF_5 was condensed onto O_2AsF_6 at $-196^\circ C$ and allowed to warm to $25^\circ C$, a purple color was observed. At the same time, fluorine and a non-condensable gas containing a significant amount of fluorine were evolved. Analysis of the condensable product gases showed that the other product was either AsF_3 or AsF_5 , contaminated with BF_3 , SiF_4 , CF_4 and C_2F_6 . Analysis of the original BrF_5 reagent showed that it contained BF_3 , SiF_4 , and HF . It is concluded that under these conditions BrF_5 cannot be fluorinated further with O_2AsF_6 .

D. REACTIONS OF DIOXYGEN DIFLUORIDE

Efforts were continued to find potentially useful reactions of O_2F_2 . The $Xe-O_2F_2$ system previously led to the formation in low yield of a solid xenon-containing product which was never characterized (Ref 2). Considerable progress in the study of this reaction was made during this quarter. A mixing technique was developed that results in the complete conversion of xenon by O_2F_2 to products non-volatile at $-78^\circ C$.

Considerable qualitative evidence has been obtained that we are possibly dealing with hitherto unreported Xe-O-F compounds. The exact composition of these products remains to be determined at this point, however. An unsuccessful attempt was also made to prepare a new oxidizer by the reaction of O_2F_2 with $KC(NO_2)_3$.

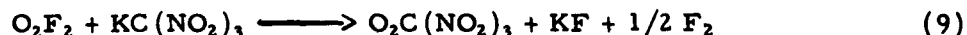
1. Reaction of Xenon with O_2F_2

The complete conversion of Xe to Xe-F or Xe-O bonded products by reaction with O_2F_2 at low temperatures was the result of careful selection of reaction conditions so that adequate mixing of Xe with O_2F_2 over a period of several hours could be achieved. When the two reagents were held at $-116^\circ C$ for two hours, xenon was completely converted to a white solid, non-volatile at $-78^\circ C$ (melting point of xenon is $-112^\circ C$).

Impurities removed from the solid by pumping at $-78^\circ C$ were SF_6 , SiF_4 , CO_2 , COF_2 , CF_4 and C_2F_6 . When the solid was sublimed at room temperature in vacuo, the condensate (at $-196^\circ C$) melted on warming to room temperature, indicating that some change in constitution occurred during the sublimation. The liquid obtained gave off oxygen and xenon at room temperature. (A test for fluorine was inconclusive.) The fact that this liquid decomposed under these conditions indicates it is not $XeOF_4$, which is reported to be a stable liquid. We are apparently dealing with a new xenon species, the characterization of which is of great interest.

2. Reaction of O_2F_2 with $KC(NO_2)_3$

The reaction of O_2F_2 with potassium nitroform (equation 9) was investigated as another possible route to dioxygenyl salts containing energetic oxidizing anions.



There was no evidence of a violent reaction when a mixture of O_2F_2 and $KC(NO_2)_3$ was warmed to room temperature. Gaseous impurities removed from the yellow solid residue from the reaction were: COF_2 , SiF_4 , N_2O , NO , NO_2 , and various fluorocarbon compounds. Infrared analysis of the solid indicated it was a mixture of unreacted $KC(NO_2)_3$ and a fluosilicate. The fact that the product did not evolve oxygen under ambient conditions indicates that $O_2C(NO_2)_3$ was probably absent.

E. INFRARED SPECTRA OF DIOXYGENYL COMPOUNDS

The low temperature infrared spectra of O_2F_2 films and films of the ultra-violet $O_2F_2-Cl_2$ and O_2F_2-HCl adducts were presented in a previous report (Ref 2). These spectra were chiefly characterized by rather broad, undefined absorptions in the 8-10 μ and 12-15 μ regions. This probably was due to excessive film thickness, because recently we have obtained quite well defined spectra of O_2F_2 films on AgCl (Figures 1 and 1a). It was noticed during this work that sometimes the O_2F_2 at -196°C, which is normally orange, contains a white solid, Figure 2. The latter seems to be less volatile than the O_2F_2 . It was speculated that this might be another form of O_2F_2 , since there are similarities in the spectra of the two. No conclusions can be drawn as yet from this work. However, it is hoped that we may shortly be able to determine which bands are due to O_2F_2 and which may be due to impurities.

An unsuccessful attempt was made to obtain the spectra of materials formed from Xe and O_2F_2 . Also, work was done on the synthesis of ClF so that the infrared spectrum of the ClF- O_2F_2 adduct could be obtained at -196°C. (Problems in the synthesis arose, however, and no pure ClF was obtained.) These low temperature studies will be continued, since they may afford a means of identification and analysis of unstable species that do not exist at normal temperatures.

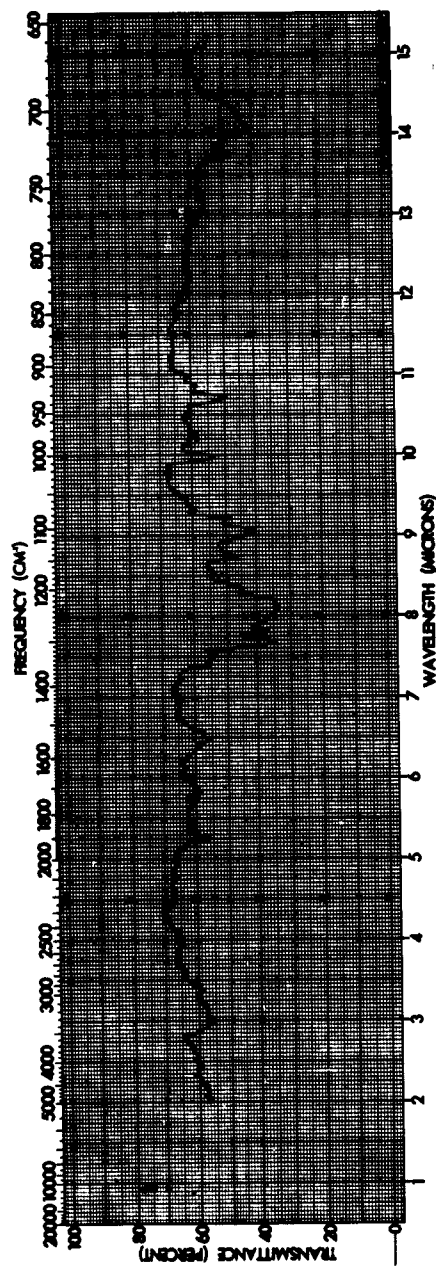


Figure 1. Infrared Spectrum of O_2F_2 Films

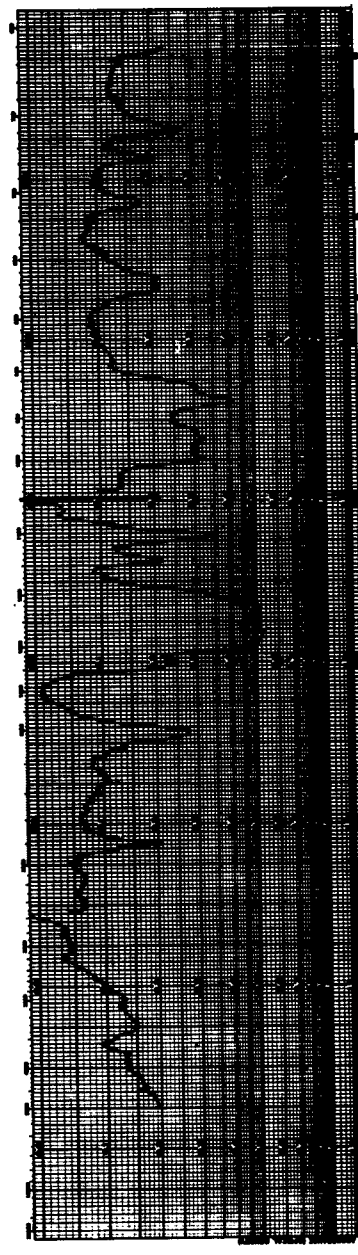


Figure 1a. Infrared Spectrum of O_2F_2 Films

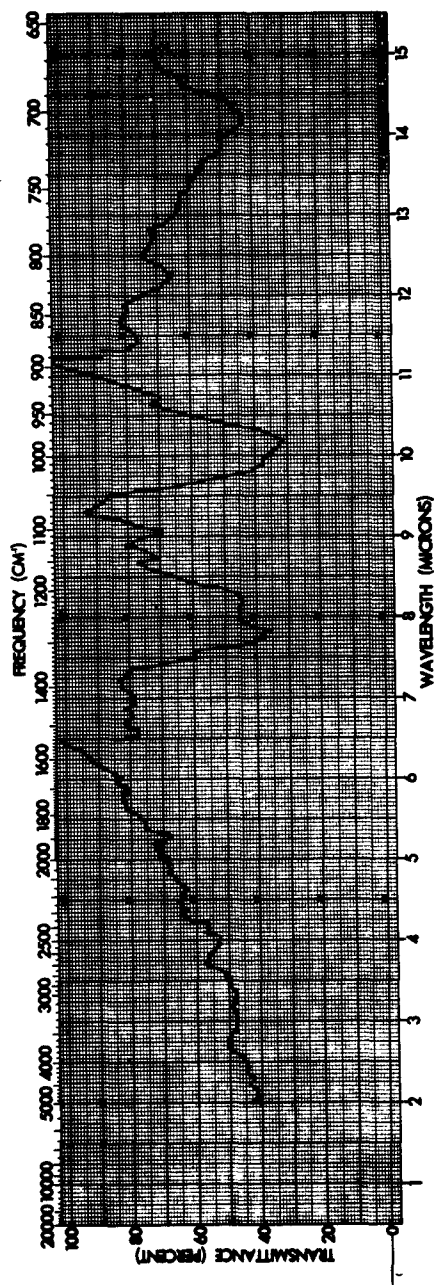


Figure 2. White Film on the AgCl Window after Pumping Out the O_2F_2

III. EXPERIMENTAL

A. PREPARATION OF NEW DIOXYGENYL DERIVATIVES FROM DIOXYGENYL HEXAFLUOROARSENATE

1. Sulfuric Acid

A 0.1124 g. sample of O_2AsF_6 was added slowly in a vacuum to 4.0 cc of 95 to 98% H_2SO_4 reagent. Reaction took place instantaneously. The only gaseous product obtained was 0.33 millimole of oxygen; 64.9% of the theoretical amount of oxygen was obtained. There was no evidence of any accompanying ozone, although absorption of the gas over mercury showed a 0.5 mm decrease in pressure, which was assumed to have been due to the presence of 8% fluorine. Since the dioxygenyl salt was not a freshly prepared sample, it is possible that the low oxygen recovery may have been due to low O_2^+ content of the reagent. Chemical test of the sulfuric acid solution afterward with tetraphenyl arsonium solution gave a precipitate, which indicates AsF_6^- ion was present.

2. Nitric Acid

Ordinarily NO_2 can be removed from 100% nitric acid by sweeping it with nitrogen. This did not prove to be effective with the sample available; nor were efforts to distill off NO_2 selectively at a reduced temperature in a vacuum successful.

3. Nitroform

This reaction was tried in anhydrous hydrogen fluoride solvent. First it was necessary to prepare potassium nitroform by the procedure of Marans and Zelinski (Ref 4). Then this was used to synthesize nitroform by the method of Shechter and Cates (Ref 1). Potassium nitroform proved to be difficult to store. In fact, one batch exploded when kept in a desiccator overnight. It is interesting to note that a negative shock sensitivity test was obtained with freshly prepared nitroform. It was found, too, that it could be stored better in a Dewar filled with Dry Ice than in a refrigerator. The latter method was

recommended by the above authors. Infrared analysis of nitroform prepared by this method indicated that it was pure.

A 0.2577 g. sample of nitroform was loaded into a Kel-F reactor, which was evacuated to remove any volatile impurities. After this treatment, the sample appeared as white crystals at room temperature. Then a small Kel-F capsule containing 0.343 g. of O_2AsF_6 was added to the reactor. These quantities of reactants represented approximately equimolar portions. The reactor was evacuated again, pressurized with nitrogen, and then the contents were held at $-78^\circ C$ prior to carrying out the experiment. The reactants were not in physical contact with each other until HF was added. The HF used in this reaction was pumped on at $-196^\circ C$ to remove any noncondensable ($-196^\circ C$) gases. The solvent was introduced as a gas into the reactor held at $-196^\circ C$. The system was warmed to $-78^\circ C$ and shaken gently to mix the contents. Strong evolution of bubbles and boiling of solvent occurred at $-78^\circ C$ as the solution was mixed. It was found that oxygen was evolved at this point. The reagents seemed to dissolve completely at $-78^\circ C$ and at the same time a white precipitate formed.

After all activity had ceased at $-78^\circ C$, the solution was warmed to $-68^\circ C$ to facilitate removal of HF by distillation. A solid was left behind after all the HF had been removed. When stored in a Kel-F container prior to analysis, this solid became a liquid. Infrared analysis of it showed -OH stretch, broad bands throughout the spectrum, as well as AsF_6^- ion absorptions.

The most volatile portion of gases from the reaction was collected and analyzed. It is believed that this sample may have become contaminated with impurities in the wall of the Kel-F storage trap prior to analysis. Also, since this fraction contained HF, it is quite likely that further analytical difficulties were introduced when the sample was run in the mass spectrometer. As described in another section, it has been found that HF cannot be analyzed in this way.

This reagent tends to degas the mass spectrometer system, so that many extraneous ion peaks are observed. Analysis of the above fraction in the mass spectrometer showed the presence of N_2 , N_2O , NO_2 , H_2 and HF. A control analysis of the HF from the lecture bottle showed the presence of AsF_3 , H_2O , N_2O , NO_2 , AsF_3 , and HF. Analysis of another batch of HF from a different lecture bottle gave the same results. As the mass spectrometer system became passivated, the arsenic peaks began to disappear. Infrared analysis showed only the presence of HF and SiF_4 . It is quite likely that traces of

moisture were present in the HF; however, Jarry and Davis (Ref 3) found that special treatment is required to remove this impurity. They obtained a 99.9% pure sample by a relatively simple procedure, utilizing NaF and then CoF₃ treatment. The presence of moisture is serious in working with dioxygenyl compounds because of their extreme sensitivity to hydrolysis.

4. Potassium Nitroform

Approximately equimolar portions of 45.6 milligrams of KC(NO₂)₃ and 44.9 milligrams of O₂AsF₆ were loaded into a Kel-F reactor. The arrangement was such that mixing of the reagents did not occur until solvent was added to the reactor. A -196°C bath was placed around the reactor. Hydrogen fluoride from a lecture bottle was introduced in the vapor state. As it condensed to a liquid in the Kel-F reactor, flashes of light were seen. Thus it appeared that the reactants had acted upon each other even at this low temperature as liquid HF ran down onto them. Gases from the reaction at -196°C were analyzed in a mass spectrometer. Oxygen, C₂F₄, SiF₄, and NO₂ were found to be present. Hydrogen was also detected by the mass spectrometer. Later work with the mass spectrometer with reagent HF showed that it reacts with materials already in the system, which results in evolution of H₂ as well as other materials within the instrument itself. It was found that extensive passivation with HF is required before it itself can be analyzed in the mass spectrometer. The appearance of hydrogen, therefore, in the sample analyzed from this reaction appears to be misleading.

The reactants in the HF were allowed to warm from -196°C to 25°C. The solids dissolved as the HF melted, forming a yellow solution. Potassium nitroform itself is yellow. When the HF was distilled out of the reactor, a small amount of solid residue was left. This seemed to vaporize upon standing at 25°C, however, giving off N₂O, NO, NO₂, and SiF₄. No oxygen was detected. Infrared analysis of this solid showed traces of H₂O, NO₃⁻ and bands at 11.75 microns, as well as the AsF₆⁻ ion at 13.5 to 15 microns. As mentioned earlier, analysis of HF by the mass spectrometer is unreliable, so no data can be presented on anything that was entrained in the solvent.

B. STABILITY OF O₂AsF₆ IN SOLUTION

1. Hydrogen Fluoride

After O₂AsF₆ was mixed with liquid HF at -78°C, the temperature of the reactor was brought up slowly to -20°C. At this temperature a small amount

of gas (O_2) began to come off. While the temperature was being raised to $-10^\circ C$, the pressure in the reactor rose (evolved O_2) and caused rupture of the reactor.

2. Arsenic Trifluoride

A 0.5 millimole sample of O_2AsF_6 was mixed with liquid AsF_3 in a Kel-F reactor. The mixture was kept at $-10^\circ C$ for two hours. The amount of oxygen evolved was approximately equal to the O_2^+ content of the O_2AsF_6 used. There was a small amount of SiF_4 in this gas too.

An attempt was made to identify the solid residue after the AsF_3 solvent had been removed; however, it decomposed before it could be analyzed.

3. Pyridine

A 0.5 millimole sample of O_2AsF_6 was immersed in perfluoropropane solvent in a Kel-F reactor. When 0.5 millimole of pyridine was added, the mixture turned brown. After all of the solvent was removed, the brown solid residue was analyzed. It gave off only a trace of gas when hydrolyzed, whereas the O_2^+ in the expected complex should have been quantitatively converted to O_2 . This indicated the expected solid complex had not formed. Infrared analysis of the solid product showed the presence of alkyl nitrite and nitrate components, unidentified absorptions at 6.70 and 6.81 microns, and the AsF_6^- ion at 14.25 microns.

In another experiment, similar but without solvent, 1.25 ml of pyridine and 0.28 millimole of O_2AsF_6 were mixed. As the solution became brown, O_2 was given off. The amount evolved was 75% of the O_2^+ content of the O_2AsF_6 used. The solid residue isolated from the pyridine contained AsF_3 . Also, infrared analysis showed the presence of $-NH$ at 3.03 microns, as well as alkyl nitrite and nitrate components, and the AsF_6^- ion. There were unidentified bands at 6.70 and 6.81 microns too. Although traces of the desired compound may have been present in the solid product, this method of preparation is considered to be unpromising.

C. O_2AsF_6 AS A FLUORINATING AGENT

1. Bromine Pentafluoride

A 0.99 millimole sample of O_2AsF_6 was treated with excess BrF_5 in a Kel-F reactor. The reactants were repeatedly chilled to $-196^\circ C$ so as to

liquefy the BrF_5 and promote mixing. The O_2AsF_6 became purple, giving off a mixture of O_2 and F_2 . In addition BF_3 , CF_4 , SiF_4 , C_2F_6 , possibly AsF_3 , as well as unreacted BrF_5 were present. The O_2AsF_6 disappeared when the system was allowed to stand overnight at room temperature.

In another similar experiment except without solvent 0.51 millimole of O_2AsF_6 and 0.45 millimole of BrF_5 were mixed. After the reactants stood overnight at room temperature, the composition of the gases was qualitatively similar to that in the preceding reaction. No unidentified species that could have been BrF_7 were detected in either experiment.

D. REACTIONS OF DIOXYGEN DIFLUORIDE

1. Xenon

Prior to carrying out the two xenon experiments, we checked out the apparatus very carefully. The electrodes and Kel-F U-trap for generation of O_2F_2 were thoroughly cleaned, as was the Kel-F reactor. The system was leak-checked and found to have good vacuum-tight integrity. Also, two blank runs were made in which O_2F_2 was generated and transferred to the reactor in the absence of xenon. The O_2F_2 was of excellent quality and no solid residues were seen.

In the first experiment, 0.75 millimole of xenon was condensed in the Kel-F reactor at -196°C . Then an excess of O_2F_2 was made and transferred to the reactor. The -196°C bath on the reactor was replaced with a Freon-11 slush bath, which had a temperature of about -118°C . Xenon's melting point is -112°C and boiling point is -108.1°C . Dioxygen difluoride is a liquid and has a relatively low vapor pressure at -115°C .

The temperature of -115°C was chosen so that the reaction temperature would be as high as possible and so that at the same time solid or liquid xenon would be retained in contact with liquid O_2F_2 . There was a small rise in pressure as the xenon and O_2F_2 became mixed at -118°C . The system was allowed to stand for two hours at this temperature.

At the end of the reaction period the reactor was held at -116°C and evacuated through a -196°C trap. Some unreacted O_2F_2 seemed to have been carried over to the -196°C trap when this was done. Previously it was thought that O_2F_2 at room temperature would decompose before passing through such a

line several feet long. An attempt was made to hold the off-gases, suspected to contain O_2F_2 , overnight at $-196^\circ C$. Unfortunately the liquid nitrogen evaporated and also some air leaked into the trap. Analysis showed no xenon was present. The contents of the trap consisted of a 1.3 millimole mixture of COF_2 , CF_3Cl , SF_6 , CO_2 , and SiF_4 . All of these materials except CO_2 are impurities present either in the original reagents or are derived from Kel-F. Carbon dioxide has been found by other workers to appear from handling xenon oxide-type materials in metal apparatus (Ref 5).

The reactor was outgassed at $-78^\circ C$ through a $-196^\circ C$ trap. A 0.542 millimole sample of gas was collected, which was composed of CO_2 , COF_2 , CF_3Cl , and SiF_4 . The reactor was kept at $-78^\circ C$ after being pressurized with a mixture of O_2 and F_2 . Then the overlying gas was pumped off through a $-196^\circ C$ trap. When the remaining white solid was allowed to warm up to room temperature, it disappeared in about 15 minutes. A 1.38 millimole sample of gas was collected at $-196^\circ C$ from these operations. It was found to consist of COF_2 , CO_2 , CF_4 , C_2F_6 , SF_6 and SiF_4 . No xenon was recovered from the reaction. It is possible that the solid formed a relatively non-volatile liquid, which escaped detection in this experiment. (Information from a later similar experiment indicated that this was the case.)

Essentially the same procedure was used in the second experiment except that a much more detailed study of products was made. We enlarged the scale of the reaction twofold by using a 1.62 millimole quantity of xenon and excess dioxygen difluoride. The reaction was allowed to proceed as before for two hours at about $-117^\circ C$. There was a substantial buildup in pressure in the system when the reactants were mixed at $-117^\circ C$. When the reaction was terminated, the cold bath was lowered and about one cc of unreacted O_2F_2 was seen in the bottom of the trap. Yellow and white solids were present also in the upper part of the trap. The $-117^\circ C$ cold bath was replaced with one at $-78^\circ C$ to store the products overnight.

The next morning the yellow solid was gone, but the walls of the reactor were coated with a white solid. The O_2F_2 also was gone. After the reactor was evacuated at $-78^\circ C$, the off-gases from $-78^\circ C$ collected at $-196^\circ C$ were fractionated and analyzed. They were first passed through a $-106^\circ C$ bath (methyl formate-liquid nitrogen) so that xenon, if present, could be separated from the less volatile materials. The gas that passed through the $-106^\circ C$ trap was a 0.155 millimole mixture of SF_6 , SiF_4 , CO_2 , COF_2 , CF_4 , and C_2F_6 . No xenon was detected. The fraction retained at $-106^\circ C$ was 0.68 millimole in

quantity, which was found (by infrared analysis) to contain some SiF_4 . It is possible that there was another unidentified component. The product was stored overnight again at -78°C and evacuated through a -196°C trap the next morning. Only a trace of gas was condensed out at -196°C . This showed that the solid products were not losing significant quantities of xenon upon storage at -78°C .

A study was made of the gases evolved from the products at gradually increased temperatures. The first was -68°C (m-xylene slush bath). The only gas that came off was a 0.116 millimole fraction, which contained SiF_4 . The next temperature used was -55°C (acetonitrile slush bath), where nothing was evolved when the product stood in a vacuum. The product was then outgassed for several hours at -31°C (carbon tetrachloride slush bath). Negligible, if any, gas came off under these conditions. At this time the product had been stored at -78°C for a week, when it was not being tested at another temperature. There was no evidence of decomposition of the solids during this prolonged storage.

Since it was desired to confirm the hypothesis that the solid residues were xenon compounds, the products were allowed to stand at room temperature for a while. The solid on the walls appeared to vaporize by sublimation in a vacuum, while the white solid in the bottom of the trap remained seemingly unchanged. By rechilling the trap to -196°C some of the white material could be made to re-form on the walls. The fact that oxygen came from this material at room temperature was confirmed by mass spectrometric analysis. When the condensable materials from the reactor were collected at -196°C , there was a light orange band in the white material that froze out on the walls of the trap. This material melted and formed a clear, foaming liquid at room temperature in a closed system. It was shown that there was at least 0.678 millimole of gas in this fraction. Since only xenon was found in this fraction by the mass spectrometer, this sample was fractionated through a -78°C trap to remove the xenon from the liquid. When this was done, the portion that passed through the -78°C trap contained a 0.612 millimole quantity of xenon with a small amount of oxygen. It was not possible to tell whether all of the liquid retained at -78°C vaporized at room temperature or not, but it was shown that at least 0.0586 millimole of gas was formed from it at this temperature. Mass spectrometric analysis showed that this gas probably contained at least 50% xenon along with some oxygen, the exact proportion of which could not be determined. Unfortunately as far as being able to identify the liquid goes, mass spectrometer fragmentation peaks greater than xenon were not observed.

The only material left in the reactor after pumping on it at room temperature was the white solid in the bottom. In order to prevent decomposition before the solid could be analyzed, it was refrigerated at -78°C at atmospheric pressure under nitrogen gas. Study of this product is still in progress.

2. Potassium Nitroform

Yellow potassium nitroform powder (30 mg.) was loaded into a Kel-F reactor. Dioxygen difluoride was prepared in an adjacent reactor and transferred to the potassium nitroform. The former was allowed to melt and run down onto the latter, which was kept at -196°C . The O_2F_2 gradually disappeared as the system was allowed to warm up slowly. The reactor was later refrigerated at -196°C again and evacuated through a -196°C trap. Only a trace of gas was collected in this trap. Then the reactor which contained a yellow solid was warmed to -78°C . Again the system was evacuated through a -196°C trap. This gas coming off at -78°C was composed of COF_2 , SiF_4 , N_2O , and various fluorocarbon compounds. The latter no doubt were derived from interaction of the reactants with the Kel-F reactor. The solid left in the reactor was next allowed to warm to 25°C . No oxygen came from it, but a small amount of NO and NO_2 did. The color of the solid was now light gray. It gave a negative test for shock sensitivity. Infrared analysis showed that some unreacted $\text{KC}(\text{NO}_2)_3$ was still present. But another material was also present, whose spectrum resembled that of a fluosilicate. The reaction is considered unpromising.

E. INFRARED SPECTRA OF DIOXYGENYL COMPOUNDS

1. O_2F_2

Equimolar mixtures of O_2 and F_2 were passed through a high voltage arc in a glass U-tube at several millimeters gas pressure to prepare samples of O_2F_2 . Then the O_2F_2 was transferred to the low temperature infrared cell, where it was condensed onto the AgCl windows maintained at -196°C .

The spectra of different samples of O_2F_2 , Figure 1, were similar, but displayed small variations. In one case a white solid residue was left behind on the AgCl window after the O_2F_2 had evaporated. This residue, Figure 1a, displayed some of the peaks in the original O_2F_2 .

It is difficult to obtain uniform coatings of O_2F_2 on the cell window. Variations in thickness result in different intensities of absorptions observed in the

infrared region. However, we have been successful in obtaining thin uniform coatings, which have given spectra with better resolution.

2. Preparation of Chlorine Monofluoride

Chlorine monofluoride was made by passing an equimolar mixture of Cl_2 and ClF_3 from a glass bulb through a reactor at 400°C . Impurities found in the ClF were CO_2 , NO or NOF , CF_4 and SiF_4 . A pure sample of ClF could not be isolated from this mixture.

Another similar experiment was performed in which a Monel cylinder was substituted for the glass bulb. This was done to prevent the formation of the troublesome SiF_4 impurity. Unfortunately only CO_2 , COF_2 , ClO_2F , ClO_2 and possibly an NF material (11.0 microns in the infrared) were obtained. A second attempt was also unsuccessful.

Another procedure was tried in which an equimolar mixture of Cl_2 and F_2 was passed through a reactor at 270°C . The products were ClF , ClO_2F , and SiF_4 . Again a pure sample of ClF could not be isolated.

IV. FUTURE WORK

- The Xe-O₂F₂ reaction will be studied further in order to characterize the products.
- Other rare gas or rare gas compound-O₂F₂ reactions will be studied.
- Further attempts will be made to prepare O₂⁺ salts of oxidizing anions.
- A study of the chemistry of O₃F₂ will be initiated.
- Low temperature infrared studies on O₂F₂ and its complexes will be continued.

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Section IV

Task 54

**STABILIZATION OF NITRONIUM
PERCHLORATE BY COMPLEXATION**

Section IV

STABILIZATION OF NITRONIUM PERCHLORATE
BY COMPLEXATION

A. R. Young
J. J. Dvorak

Report RMD 5043-Q1-64

RMD Project 5043, Task 54
Report Period: 1 January 1964
to 31 March 1964

Contract No. NONr 4364(00)
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FOREWORD

This section of the advanced oxidizer report summarizes work carried out during the period from 1 January 1964 to 31 March 1964 on synthetic efforts directed toward the stabilization of nitronium perchlorate (RMD Project 5043, Task 54).

Contributors to the research were: A. R. Young (Project Supervisor), J. Dvorak (Principal Investigator), E. Egbert, J. Creatura, and R. Storey.

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I. INTRODUCTION

The objective of this program is the stabilization of nitronium perchlorate by chemical methods, as opposed to physical coating techniques. The principal approach being used is the synthesis of cationic nitronium perchlorate complexes.

It is believed that such complexes, by virtue of the increased size of the cation, would have greater ionic character and stability than nitronium perchlorate. Some evidence has now been obtained that pyridine forms a complex with nitronium perchlorate. If this can be definitely confirmed, then it may be possible to displace pyridine from the complex with more energetic ligands such as ammonia or hydrazine.

II. DISCUSSION

The major effort during this report period was directed toward the preparation of pyridine complexes of nitronium salts. The reaction of nitronium perchlorate with N_2H_5Cl was also explored as a possible route to $NO_2N_2H_5(ClO_4)_2$.

A. REACTION OF NO_2ClO_4 WITH PYRIDINE

Pyridine has the interesting property of forming complexes with nonmetallic cations as is evidenced by the existence of such species as $I(py)_2ClO_4$ and $Cl(py)NO_3$ (Ref 1). It was therefore decided to explore the possibility of preparing a pyridine complex of the nitronium ion, using nitronium perchlorate as a source of that ion. If the desired pyridine complex is obtained it could serve as a precursor for the preparation of more energetic complexes of nitronium perchlorate. Such an approach to nitronium perchlorate complexes is illustrated in equations 1 and 2.



In our initial attempt to prepare a complex, pyridine was added to an acetonitrile solution containing an equimolar amount of NO_2ClO_4 . The reaction mixture became slightly yellow-orange in color, and an orange solid was obtained when the acetonitrile was removed in vacuo. The infrared spectrum of the solid showed absorptions attributable to ClO_4^- and NO_3^- , as well as aromatic ring vibrations indicative of a pyridine salt. Results of an elemental analysis (Table I) were in poor agreement with calculated values for a pyridine-nitronium perchlorate complex. Although most of the analytical data indicate good agreement with theoretical values for pyridinium perchlorate, the presence of a large amount of nitrate, as indicated by the infrared data and the "hydrolyzable" nitrogen analysis, appears to rule out this being the product.

TABLE I
ANALYSIS OF NO_2ClO_4 -PYRIDINE PRODUCT

Atom or Group	Found (%)	Calcd. for $\text{NO}_2(\text{C}_5\text{H}_5\text{N})\text{ClO}_4$ (%)	Calcd. for $\text{C}_5\text{H}_5\text{NHClO}_4$ (%)	Calcd. for $\text{C}_5\text{H}_5\text{NHNO}_3$ (%)
C	34.70, 32.59	26.78	33.42	42.25
H	3.79, 3.72	2.73	3.34	4.22
ClO_4^-	54.3	44.32	55.43	---
N*	9.77	6.23	---	9.85

* Hydrolyzable

In a subsequent run, an equimolar amount of pyridine was added to a suspension of NO_2ClO_4 in Freon-113. The temperature of the reaction mixture was maintained at -30°C during the mixing period as well as during the removal of the solvent in vacuo. The solid residue was originally off-white, but during storage overnight in a dry box at ambient temperatures it turned dark brown. The infrared spectrum of the brown solid was obtained as a mull. It showed absorptions attributable to ClO_4^- and the pyridinium ion, as well as unassigned bands at 12.36μ , 12.75μ and 13.89μ . When anhydrous NH_3 was added to the solid at -196°C and the reaction mixture allowed to warm slowly to room temperature, the solid became black. The gas evolved in this reaction was found to contain N_2 , O_2 , nitrogen oxides, pyridine, trimethylamine and dimethylamine. The x-ray powder pattern of the black solid indicated the presence of NH_4ClO_4 and its infrared spectrum confirmed this observation.

The reaction of NO_2ClO_4 with pyridine in Freon-113 was then repeated. In this run, the solid residue obtained by removal of the Freon-113 in vacuo was stored at -78°C in order to inhibit decomposition. The infrared spectrum of this off-white solid (Figure 1) was similar to that found in the brown solid obtained in the previous experiment, with the exception that an additional absorption attributable to the NO_2^+ ion was present at 2340 cm^{-1} (Figure 1).

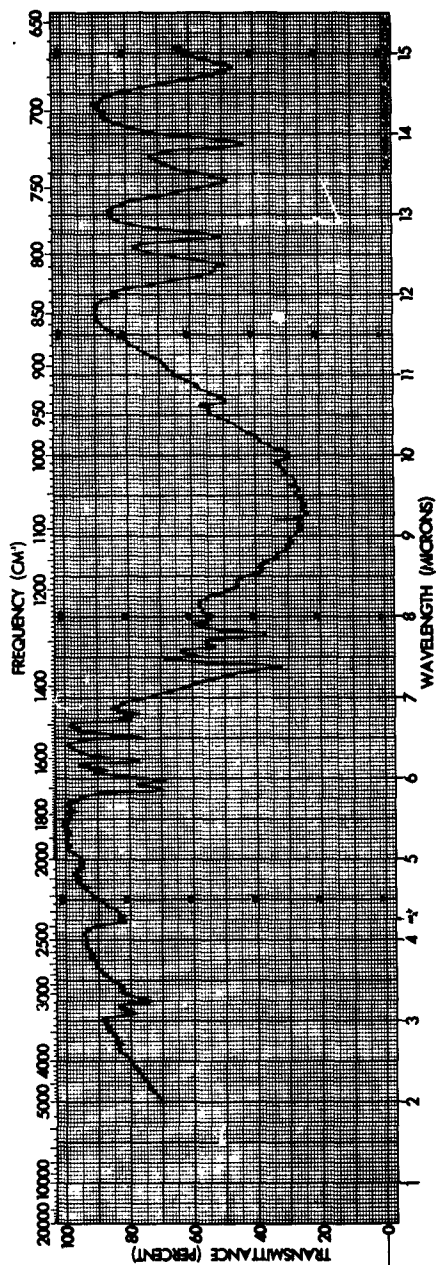


Figure 1. Infrared Spectrum of $\text{NO}_2\text{ClO}_4\text{-C}_5\text{H}_5\text{N}$ Reaction Product*

* Mixed Mull:

Kel-F 10 - $2\mu \rightarrow 7.5\mu$
Paraffin Oil - $7.5\mu \rightarrow 15\mu$

The x-ray powder pattern of this solid product appears to be little different from that of a reference pattern for NO_2ClO_4 (Figure 2). On standing at room temperature the solid darkens appreciably and brown fumes are evolved. Unfortunately, the only analytical data on this reaction product were obtained after the initiation of decomposition, as evidenced by the darkening of the solid and evolution of brown fumes. These results are presented in Table II.

TABLE II
ANALYSIS OF NO_2ClO_4 -PYRIDINE REACTION PRODUCT

Atom or Group	Found (%)	Calcd. for $\text{NO}_2(\text{C}_5\text{H}_5\text{N})\text{ClO}_4$ (%)
C	10.40, 11.88	26.78
H	1.07, 1.26	2.23
ClO_4^-	51.5	44.32
N*	14.19**	6.23

* Hydrolyzable

** Additional decomposition (fuming) was observed just prior to this analysis.

While it is apparent that the low temperature permitted by the use of Freon-113 as the solvent, reduced the amount of visible decomposition, it was not possible to eliminate decomposition of the product completely prior to analysis. Consequently, meaningful analytical data on the pyridine product are not yet available. It is hoped that by refinement of our experimental techniques (use of lower temperatures, careful exclusion of moisture, etc.) we can minimize or eliminate degradation of the product. In addition, we will further investigate the treatment of the pyridine-NP complex with ammonia in situ, in order to avoid the necessity of isolating the complex. It is quite probable that the well-known proclivity of NP to oxidize organic molecules is responsible for the decomposition of the product which occurs. Despite the

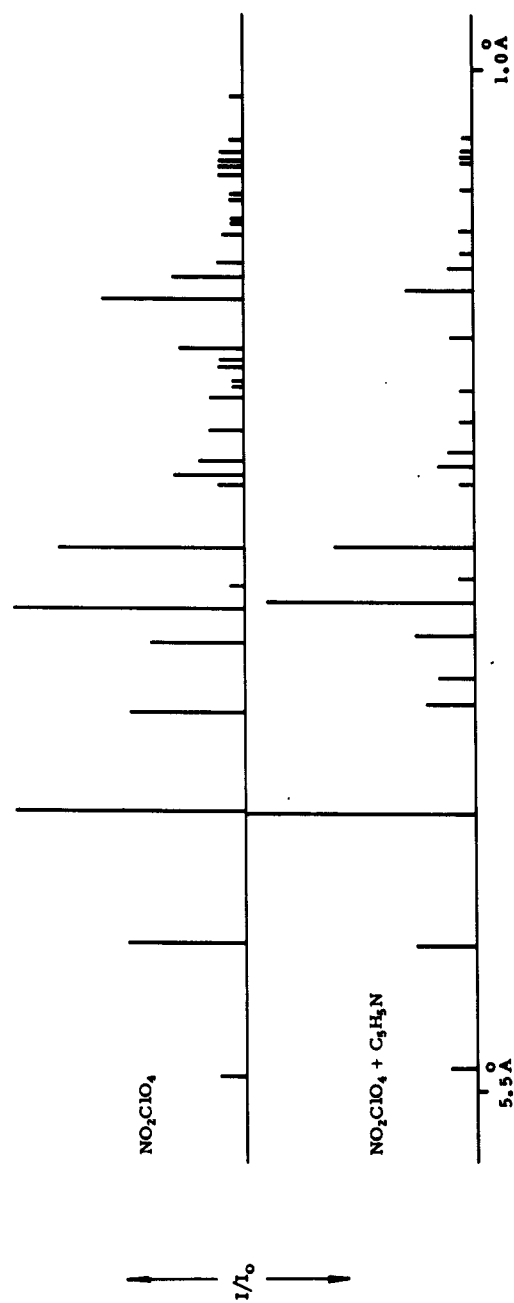
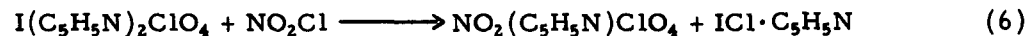
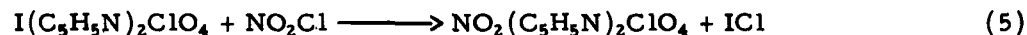
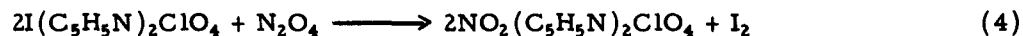


Figure 2. X-Ray Powder Pattern of NO₂ClO₄-C₅H₅N Reaction Product

occurrence of this decomposition, however, the spectral evidence indicates that NP forms a cationic pyridine complex.

B. PREPARATION OF $I(C_5H_5N)_2ClO_4$

An investigation of the preparation and chemical reactivity of dipyridine iodonium perchlorate, $I(C_5H_5N)_2ClO_4$, was undertaken as an alternate synthetic route to a pyridine complex of nitronium perchlorate. Examples of possible reactions leading to the desired complex nitronium perchlorate are given in equations 3, 4, 5, and 6.



When a slight excess of I_2 was added to a pyridine solution of $AgClO_4$, a light yellow, water insoluble solid, presumably AgI , precipitated. The mixture was filtered and the filtrate evaporated in vacuo. The residual solid was washed several times with chloroform and dried. The x-ray powder pattern of the solid product (Figure 3) was one not previously encountered. Infrared and chemical analyses of the solid product have not yet been completed. However, a preliminary investigation of its chemical reactivity was initiated on the assumption that it is, in fact, the previously reported (Ref 2) $I(py)_2ClO_4$. On the basis of x-ray patterns (Figure 3) obtained on the solid recovered after treatment of $I(py)_2ClO_4$ suspended in Freon-113 with N_2O_4 , it does not appear to react appreciably with N_2O_4 under the conditions used. Interestingly enough, the Freon-113 did become light purple in color which indicated the presence of some free iodine. It may be that the reaction will go completely under more forcing conditions and further efforts to carry out the desired displacement (equation 4) appear warranted.

X-ray analysis of the solid residue recovered from the reaction indicates that the $I(py)_2ClO_4$ does not react appreciably with $NOCl$ under ambient conditions (Figure 3).

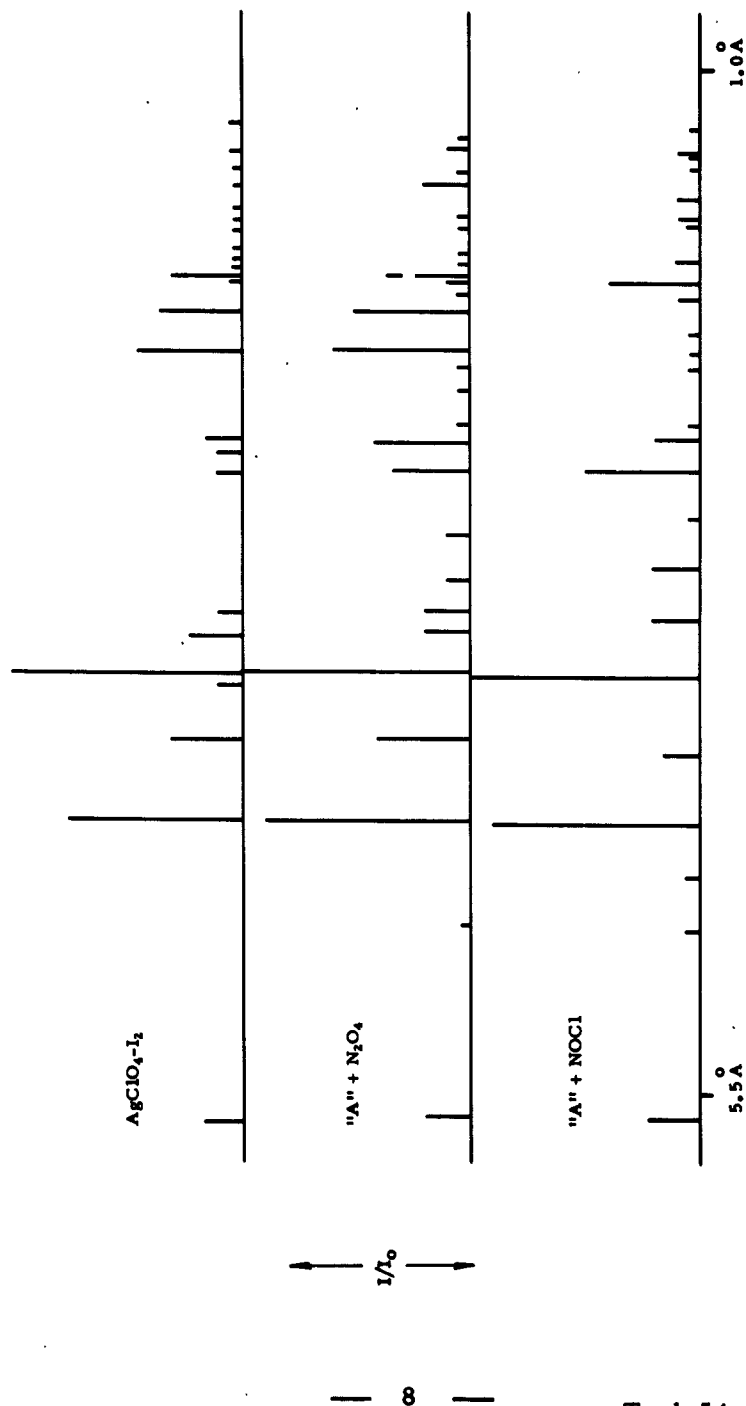


Figure 3. X-Ray Powder Patterns of AgClO₄-I₂ Reaction Products

C. REACTION OF NO_2BF_4 WITH PYRIDINE

The reaction of an acetonitrile solution of NO_2BF_4 with pyridine was also examined in order to compare the results obtained when NO_2ClO_4 was treated with pyridine in acetonitrile. A yellow solid residue was present after removing the acetonitrile in vacuo. On the basis of infrared analysis, the solid appeared to be a mixture of pyridinium salts of the BF_4^- and NO_3^- anions. Results of elemental analysis of the solid are presented in Table III.

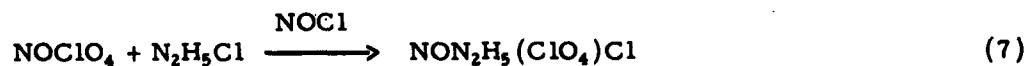
TABLE III
ANALYSIS OF NO_2BF_4 -PYRIDINE REACTION PRODUCT

Atom or Group	Found (%)	Calcd. for $\text{C}_5\text{H}_5\text{NHBF}_4$ (%)	Calcd. for $\text{C}_5\text{H}_5\text{NHNO}_3$ (%)
C	35.80, 37.79	35.61	42.25
H	3.46, 4.19	3.56	4.22
N*	10.18	---	9.85
B	5.55	6.51	---

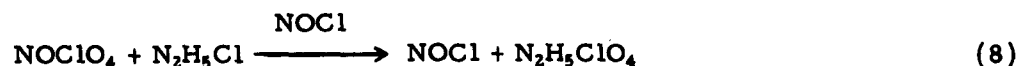
* Hydrolyzable

D. REACTION OF NO_2ClO_4 WITH $\text{N}_2\text{H}_5\text{Cl}$

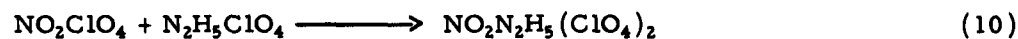
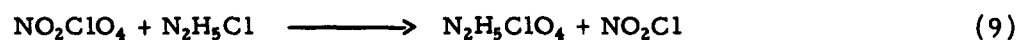
Interesting results were obtained when NOClO_4 was allowed to react with $\text{N}_2\text{H}_5\text{Cl}$ in liquid NOCl (Ref 3). This reaction was conducted as an attempt to prepare a nitrosylhydrazinium cation (NON_2H_5^+) as shown in equation 7.



Instead, an exchange reaction occurred as shown in equation 8.



In view of this result, an attempt was made to prepare nitrylhydrazinium perchlorate $[\text{NO}_2\text{N}_2\text{H}_5(\text{ClO}_4)_2]$ by reacting $\text{N}_2\text{H}_5\text{Cl}$ with excess NO_2ClO_4 (equations 9 and 10).



When NO_2ClO_4 was mixed with $\text{N}_2\text{H}_5\text{Cl}$ in the solid state, a violent reaction occurred. Noncondensable gases as well as Cl_2 , NO_2 and N_2O were generated. When a nitromethane solution of NO_2ClO_4 was added to a solution of $\text{N}_2\text{H}_5\text{Cl}$, decomposition again occurred although the reaction proceeded less vigorously. Nitrogen, nitrogen oxides, chlorine, chlorine oxides and HCl were identified as gaseous decomposition products. No solid residue was present upon removal of the solvent.

III. EXPERIMENTAL

All solid reagents and products were sampled in a dry box. The nitronium perchlorate was obtained from Callery Chemical Co.

A. REACTION OF NO_2ClO_4 WITH PYRIDINE

1. In Acetonitrile

To a cooled solution of 0.7387 g. (5.09 mmoles) of NO_2ClO_4 in 25 ml of acetonitrile was added 0.40 ml (5.09 mmoles) of pyridine. The reaction mixture was allowed to stir several hours at ambient temperature and the solvent was then removed in vacuo. The solid product was redissolved in acetonitrile and precipitated by addition of CCl_4 . The analysis is given in Table I.

2. In Freon-113

To 0.8160 g. (5.63 mmoles) of NO_2ClO_4 at -196°C was added 25 ml of Freon-113 and 0.48 ml (6 mmoles) of pyridine. The reaction mixture was allowed to warm to -30°C . After stirring for several hours the solvent was removed in vacuo. The solid product was then stored at -78°C prior to analysis (Table II). The infrared spectrum of this solid is given in Figure 1 and the x-ray powder pattern in Figure 2.

B. REACTION OF AgClO_4 WITH I_2 IN PYRIDINE

To 3.2284 g. (15 mmoles) of AgClO_4 in approximately 15 ml of pyridine was added a pyridine solution of 4.0608 g. (16 mmoles) of I_2 . After stirring several hours the reaction mixture was filtered and the filtrate was evaporated in vacuo. The residual solid was washed with chloroform and dried. The x-ray powder pattern of the solid is given in Figure 3. Infrared and chemical analysis are pending.

C. REACTION OF NO_2BF_4 WITH PYRIDINE

To an acetonitrile solution of 0.5312 g. (4.0 mmoles) of NO_2BF_4 was added 0.33 ml (4.0 mmoles) of pyridine. After stirring several hours the solvent was removed in vacuo and a yellow solid was obtained. The solid was recrystallized from ethanol and dried. Analysis is given in Table III.

D. REACTION OF NO_2ClO_4 WITH $\text{N}_2\text{H}_5\text{Cl}$

To 0.1644 g. (2.4 mmoles) of $\text{N}_2\text{H}_5\text{Cl}$ in approximately 15 ml of CH_3NO_2 at -30°C was added a solution of 0.6981 g. (4.8 mmoles) of NO_2ClO_4 . The reaction mixture was allowed to warm slowly to room temperature with stirring. As the pressure in the reaction vessel increased, the evolved gases were expanded into a storage bulb for subsequent analysis. Removal of the solvent in vacuo resulted in the isolation of only a trace amount of an oil.

IV. FUTURE WORK

1. The $\text{NO}_2\text{ClO}_4\text{-C}_5\text{H}_5\text{N}$ reaction product will be more completely characterized.
2. The reaction of $\text{NO}_2(\text{py})_x\text{ClO}_4$ with NH_3 will be investigated.
3. The $\text{AgClO}_4\text{-I}_2$ reaction production will be characterized.
4. The reaction of $\text{Ag}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4$ with NO_2Cl in pyridine will be attempted.
5. The preparation of $\text{NOF} \cdot 3\text{HClO}_4$ will be attempted.

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3. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD-AOR-ATS-63, Advanced Oxidizer Research, February 1964.

Section V

Task 55

**THERMAL STABILITY OF
ADVANCED SOLID OXIDIZERS**

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REACTION MOTORS DIVISION

Section V

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki
W. Cruice

Report RMD 5043-Q1-64

RMD Project 5043, Task 55
Report Period: 1 January 1964
to 31 March 1964

Contract No. NONr 4364(00)
ARPA Order No. 417
Project Code 4910

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FOREWORD

This section of the advanced oxidizer report summarizes work carried out during the period from 1 January 1964 to 31 March 1964 on the thermal stability of advanced solid oxidizers (RMD Project 5043, Task 55).

Contributors to the research were: C. Grelecki (Project Supervisor) and W. Cruice (Principal Investigator).

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I. INTRODUCTION

The objective of this program is to study the kinetics of the thermal reactions of high energy oxidizers in order to understand the mechanism by which they decompose. A thorough examination of available information, correlation of existing data, and supplementary laboratory work to render as complete an understanding as possible of the area are the three primary approaches to this program.

A literature search has been made and is continuing. Some attempt has been made to assemble information, delete what is not pertinent or has been disproved, and to form a cohesive body of information. Laboratory work has begun on several phases of the program.

This report includes a brief discussion of highlights of the literature survey and a summary of experimental work to date, as well as a brief summary of projected future work.

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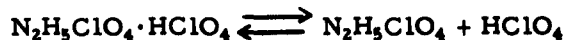
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II. LITERATURE SURVEY

The initial phase of this program is the correlation of existing data on thermal behavior, particularly thermal decomposition, of ammonium perchlorate, guanidinium perchlorate, hydrazinium dperchlorate, hydroxylammonium perchlorate, and nitronium perchlorate. Also included in the program are hydrazinium monoperchlorate, nitrosyl perchlorate and perchloric acid, inasmuch as these compounds appear to be reaction products of the thermal decomposition of the preceding ones.

It appears that all the above compounds with the exception of nitronium perchlorate and nitrosyl perchlorate are directly related to ammonium perchlorate in decomposition characteristics. Guanidinium perchlorate and hydroxylammonium perchlorate form ammonium perchlorate as an initial decomposition product (Ref 1, 2 and 3). Hydrazinium monoperchlorate and hydrazinium dperchlorate are structurally similar to ammonium perchlorate, whereas nitronium perchlorate and nitrosyl perchlorate are markedly different in structure. By the same token, ammonium perchlorate, guanidinium perchlorate, hydrazinium monoperchlorate, and hydrazinium dperchlorate decompositions are catalyzed by the presence of certain metals and metal oxides (Ref 4, 5, 6, 7 and 8) which have not been reported as catalysts for nitronium perchlorate and nitrosyl perchlorate.

In general the order of stability of the above oxidizers is as follows: ammonium perchlorate > guanidinium perchlorate > hydrazinium monoperchlorate > hydroxylammonium perchlorate > hydrazinium dperchlorate > nitronium perchlorate > perchloric acid. Exact comparisons are not possible in all cases because the reactions were not performed under the same conditions. Of these, the first five contain the perchloric acid "molecule," whereas nitronium perchlorate does not, and the thermal stability of these five seems to be related to the ease with which free perchloric acid can be produced from them. For example, the primary process during the decomposition of hydrazinium dperchlorate is the dissociation to hydrazinium monoperchlorate and perchloric acid according to the following equilibrium:



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Likewise, the initial step in the decomposition of ammonium perchlorate is the dissociation to ammonia and perchloric acid (Ref 9). Those standard heats of formation reported are in the order expected from relative thermal stability, as shown in Table I. A more convincing observation is that the heats of neutralization in aqueous solution are also in the order that would be expected from the thermal stabilities, assuming that the thermal stability is related to the production of perchloric acid. The assumed aqueous reaction is of the form:

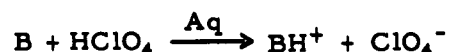


TABLE I

HEATS OF FORMATION AND NEUTRALIZATION
FOR SOME PERCHLORATE SALTS

<u>Salt</u>	<u>ΔH_{298}°</u>	<u>ΔH Neutralization</u>
NH_4ClO_4	-70.73	-25.5
$\text{HONH}_3\text{ClO}_4$	-66.5	---
$\text{H}_2\text{NNH}_2 \cdot \text{HClO}_4$	-42.9	-9.88
$\text{H}_2\text{NNH}_2 \cdot 2\text{HClO}_4$	-66.9	-5.36*

* Based on $\text{HP} + \text{HClO}_4 \xrightarrow{\text{Aq}} \text{HP-2}$

There is reason to believe that the thermal decompositions of nitronium perchlorate and nitrosyl perchlorate are interrelated; nitronium perchlorate is produced during the decomposition of nitrosyl perchlorate, and vice versa (Ref 10 and 11). Precisely how these two reactions are related is still not too clear, despite the somewhat extensive work done on nitronium perchlorate.

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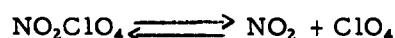
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Workers at Thiokol's Elkton Division managed to stabilize nitronium perchlorate by a "superdrying" process (Ref 12) and Dr. H. Cordes, U.S. Naval Ordnance Test Station, China Lake, California (Ref 13 and 14), has obtained a rate expression for nitronium perchlorate decomposition by freezing out certain products of the reaction. Unfortunately, information from these and other sources does not agree on all points.

Nitronium perchlorate does not contain the perchloric acid molecule. In this case, the initial dissociation reaction for the anhydrous salt is as follows:



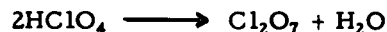
In the presence of water the salt hydrolyzes as follows:



Accordingly, wet samples decompose more rapidly than dry samples. The presence of as little as 10⁻²% H₂O increases the rate by a factor of 50 above that of the "superdry" samples at 70°C.

An evaluation of all available data leads to the supposition that perchloric acid is the effective decomposing agent in all cases. Unfortunately little is known of the properties of anhydrous perchloric acid. The bulk of work done on perchloric acid has been done on the aqueous solutions, principally 72% HClO₄. Anhydrous HClO₄ has been known since the early nineteenth century to be unstable, discoloring to a pale yellow, then a deep orange, and finally to a dark reddish-brown; in this latter condition, it is considered dangerously explosive. Only two vapor pressure points are known to have been reported. Van Wyk (Ref 16) reported a vapor pressure of 18 mm at 16°C in 1906, and Vorlander and vonSchilling (Ref 17) reported a vapor pressure of 56 mm at 39°C in 1900. Of these two, the second is considered moderately reliable, but the former was reported with other information which has since been cast in serious doubt (Ref 18). Applying the Clausius-Clapeyron equation to these two points yields a ΔH vaporization of 8.85 kcal/mole.

The stoichiometry of thermal decomposition is also subject to question. Zinov'ev and Tsentsiper (Ref 19) proposed a progressive decomposition, commencing with dissociation



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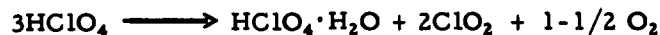
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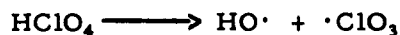
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and proceeding by decomposition of the chlorine heptoxide to chlorine dioxide and oxygen, and finally to chlorine and oxygen. The activation energy for the overall reaction, which was found to be autocatalytic, was 22.2 kcal/mole. A more recent study by Babaeva and Zinov'ev, (Ref 20 and 21) presents a very similar stoichiometry



in which decomposition of the heptoxide is said to be the rate-determining step. Variations of this stoichiometry and different reactions for the vapor phase (Ref 22) have been suggested. At high temperatures the reaction is mainly a homogeneous one with an activation energy of 43 kcal/mole. The rate-controlling step is presumably the dissociation of the acid according to the following:



This reaction is reported to be endothermic by 48 kcal/mole.

Because of the importance of the perchloric acid reaction in the decomposition of all of the perchlorate salts, the program was initiated by making a study of the perchloric acid reaction.

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III. EXPERIMENTAL

In as much as anhydrous perchloric acid is presumed to be the decomposing agent in the reactions under consideration, it was decided to perform vapor pressure and thermal decomposition studies on this compound before proceeding to the more complicated systems.

A. PRODUCTION OF ANHYDROUS PERCHLORIC ACID

The notorious instability of the anhydrous acid makes it necessary for it to be produced as required and reports in the literature concerning production methods generally emphasize the difficulty of obtaining pure material. However, the initial thermal reaction of hydrazinium dperchlorate in vacuum is the dissociation:



An attempt was made to make use of this reaction to produce high purity HClO_4 . The hydrazinium dperchlorate was placed in a test-tube shaped vessel, connected through an all-glass transmission tube to a cold trap at liquid N_2 temperature. The reaction vessel was placed in a Nujol bath at 140°C for a period of five hours; the cold trap was connected to a vacuum line of about 0.5 mm Hg at constant pressure.

The character of the salt is such that usually only about 15 to 25% conversion can be attained. Glasner and Makovsky (Ref 2) have reported that powdered Pyrex glass catalyzes the decomposition of guanidinium perchlorate, so Pyrex spheres about 30μ in diameter were added to the fourth and fifth runs. The results are reported in Table II. The conversions were unsatisfactory in all cases due to the decomposition of HClO_4 at the reaction temperature.

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TABLE II

SUMMARY OF ATTEMPTS TO PREPARE
ANHYDROUS PERCHLORIC ACID BY DISSOCIATION
OF HYDRAZINIUM DIPERCHLORATE

Run	Wt HP-2 (gm)	Wt Glass (gm)	Wt Residue (gm)	Wt HClO ₄ Recovered (gm)	% Recovery*
1	0.5170	---	0.3833	0.1242	55.7
2	0.6383	---	0.5775	0.0406	14.8
3	0.5825	---	0.4986	0.0655	26.1
4	0.6746	0.1103	0.7191	0.0551	18.9
5	0.6679	0.0313	0.6405	0.0463	16.1

* Computed by wt HClO₄ recovered/wt HP-2 x 100/232 x 100

Since this method proved unsuccessful, anhydrous HClO₄ was produced according to the method of G. Frederick Smith (Ref 23). Thirty milliliters of fuming sulfuric acid was added to 10 milliliters of 72% HClO₄ in a flask at 0°C, the flask was connected through an all-glass transmission line to a cold trap at Dry Ice temperature, and the trap was connected to a vacuum line as stated above. The flask and contents were permitted to warm to ambient temperature, stirred constantly with a magnetic stirrer, and pure anhydrous HClO₄ was evolved at a reasonable rate (2 to 4 cc/hr). A sample was taken with a Teflon syringe tube for titration, dissolved in distilled water and weighed by difference. Assay was determined by titration with standard 0.1 N NaOH to the phenolphthalien end point. Another sample was spot-tested for SO₄⁻ with BaCl₂. The lowest assay of any sample was 99.28%; more common assays range from 99.50-99.95%. No sample of HClO₄ is used that fails to give a negative SO₄⁻ test.

B. VAPOR PRESSURE OF ANHYDROUS HClO₄

The vapor pressure of anhydrous perchloric acid is being determined in an all-glass system. A glass diaphragm Sickie-type gauge is used for pressure measurements. The apparatus is shown in Figure 1.

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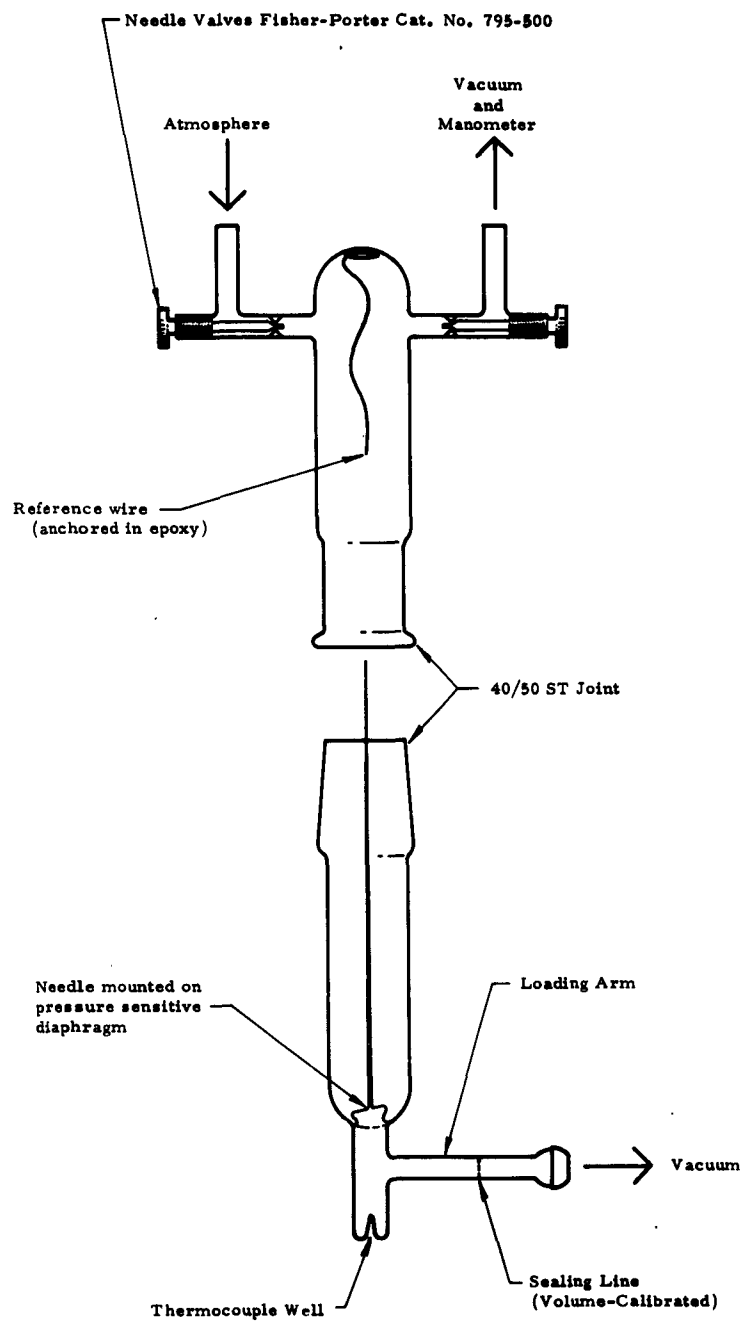


Figure 1. Sickle Gauge Apparatus

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About 0.5 cc of anhydrous HClO_4 is introduced into the sample reservoir with a Teflon syringe tube. The gauge assembly is then evacuated on the sample and reference sides of the diaphragm to a pressure of about 0.1 mm (the acid being held at Dry Ice temperature) and the loading arm sealed with a torch. A zero-point reading is taken, the slush bath is removed, and a Nujol bath is raised around the gauge so that the entire Sickie chamber is submerged. Temperature is observed with a thermocouple inserted into the well on the bottom of the vessel and read on an L and N "H" Azar recorder to an accuracy of $\pm 0.5^\circ\text{C}$. The gauge is back-pressured to the zero-point and the pressure in the reference chamber is read on a mercury manometer as soon as a constant temperature is reached. Readings at the same temperature are repeated after a period of about 30 to 45 min to ensure equilibrium.

The probability of some decomposition occurring at even ambient temperature is such that only a few points may be taken in any one run, but confining each run to a small range of temperature provides reasonably good results. The results of several experiments are compiled in Table III and presented graphically in Figure 2.

TABLE III

VAPOR PRESSURE OF ANHYDROUS PERCHLORIC ACID

<u>T</u> <u>(°C)</u>	<u>P</u> <u>(mm Hg)</u>	<u>T</u> <u>(°C)</u>	<u>P</u> <u>(mm Hg)</u>
16.6	10	40	62
20	12	46	82
25	18	51	102
29	26	61.5	146*
35	41	--	--

* Decomposition set in at an extreme rate

The deviation of the latter three points from the expected straight line of $\log P$ vs $1/T^\circ\text{K}$ is presumed to be a result of partial dissociation yielding water and Cl_2O_7 , both reducing the vapor pressure of the liquid. The linear plot from 20°C to 40°C yields a ΔH vaporization of 15.03 kcal/mole.

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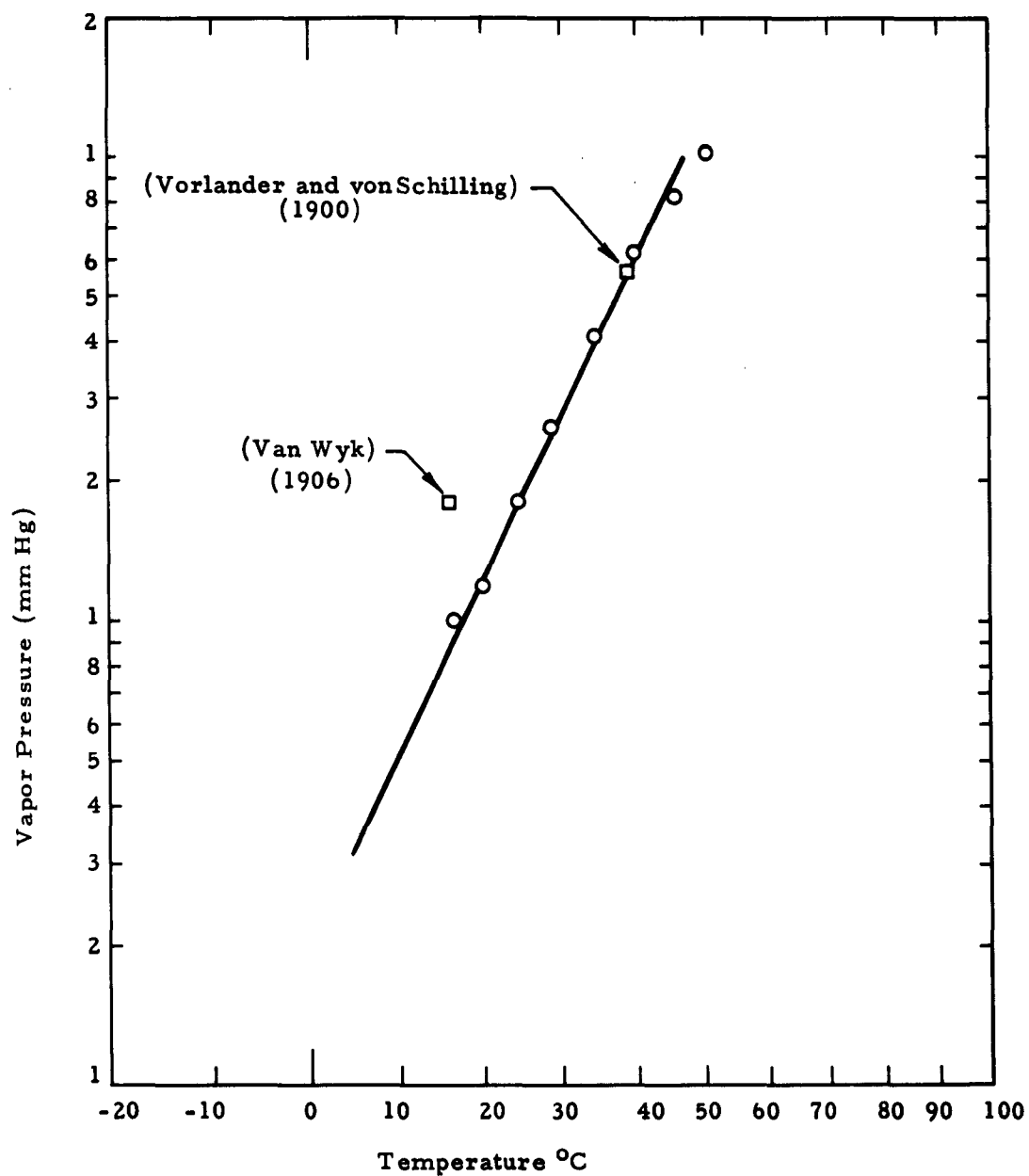


Figure 2. Vapor Pressure of Anhydrous Perchloric Acid

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IV. FUTURE WORK

During the next period an attempt will be made to extend the vapor pressure studies of anhydrous perchloric acid to its boiling point. The reaction of anhydrous perchloric acid will also be studied in the temperature region up to its normal boiling.

Data on the dissociation constants of many of the salts are lacking and these will be determined in the all-glass apparatus. Research samples of guanidinium perchlorate and hydrazinium diperchlorate are available and hydroxylammonium perchlorate and hydrazinium monopерchlorate will be prepared. Specific experiments planned for the next period include:

- Extend vapor pressure measurements of HClO_4 to higher temperatures
- Determine the stoichiometry and rate of thermal decomposition of HClO_4 .
- Determine the dissociation pressure of hydroxylammonium perchlorate
- Determine the stoichiometry and rate of thermal decomposition of hydroxylammonium perchlorate.
- Attempt to correlate thermodynamic data with thermal stabilities of amino-type perchlorates.

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