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ADVANCED OXIDIZER RESEARCH

Report Period: 1 April 1964 to 30 June 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
DENVILLE, NEW JERSEY

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ADVANCED OXIDIZER RESEARCH

Report Period: 1 April 1964 to 30 June 1964

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

Submitted by: DONALD D. PERRY
Supervisor, Synthetic Chemical Research Section

Approved by: MURRAY S. COHEN
Manager, Chemistry Department

30 June 1964 shall be used for purposes of downgrading and/or declassification of this document.

DAVID J. MANN
Director of Research
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:

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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 six major tasks on which work has been performed are listed below, together with an abstract of each task, and are included as six separate sections of this report.

SECTION I - DIFLUORAMINE CHEMISTRY

Neither perfluoroguanidine nor isocyanic acid could be induced to add to the double bonds of 1,2-bis(fluorimino)cyclohexane. This compound was degraded by aqueous sodium hydroxide to give a quantitative yield of fluoride ion and unidentified water-soluble organic products; a possible reaction sequence is suggested.

The photolysis of 1,4-bis(fluorimino)cyclohexene-2 in cyclohexane solution resulted in rapid reaction, accompanied by darkening and precipitation. The products have not yet been identified.

The acid-catalyzed reaction of n-heptanal with difluoramine has been studied and the conditions favoring the formation of gem-bis(difluoramine) or the symmetrical ether have been defined. A mechanism for the reaction is postulated.

The dehydrofluorination of 1,1-bis(difluoramino)heptane did not yield the corresponding trifluoroamidine in a straightforward manner. Some properties of the product derived by the loss of two equivalents of hydrogen fluoride are described. Ethyldiisopropylamine, a new dehydrofluorinating agent has been successfully applied in the synthesis of 1,2-bis(fluorimino)cyclohexane.

Additional quantities of 1,2-bis(fluorimino)cyclohexene-2 and 1,2-bis(fluorimino)cyclohexene-3 have been synthesized for use in reaction studies.
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. A series of tris(difluoramino)methoxyalkanes has been synthesized by reacting C₄-C₉ alcohols with perfluoroguanidine followed by fluorination. An investigation was made of the chromatographic conditions required for obtaining adducts that are >99% pure. The main impurities in these compounds were of the following types:

\[ F = \text{NC(NF}_2\text{)}\text{OR, (F}_2\text{N)}\text{C(N}_2\text{H}_3\text{)}\text{OR (where R = alkyl or partially fluorinated alkyl group).} \]

In addition, 23.0 gm of 1,2-bis(difluoramino)cyclohexane and 6.3 gm of 1,1-bis(difluoramino)propane were synthesized, and after chromatographic purification, were submitted to the Naval Ordnance Laboratory for sensitivity measurements.

SECTION III - CHEMISTRY OF THE OXYGEN SUBFLUORIDES

The major stable reaction product of the O₂F₂-Xe reaction was identified as XeF₂ by single crystal x-ray analysis. Evidence was obtained that unstable O-Xe-F materials are also formed in the reaction but these remain unidentified.

Unsuccessful attempts were made to prepare BrF₇ by reactions of O₂F₂ with BrF₅ and with CsBrF₆. O₂F₂ reacts with CsBrF₆ to give CsBrF₅ and some BrF₅. The presence of CsF had no effect on the nature of reaction products obtained from the reaction of Cl₂ with O₂F₂.

Samples of O₃F₂ were prepared and analyzed in preparation for a study of chemical properties.

SECTION IV - STABILIZATION OF NITRONIUM PERCHLORATE BY COMPLEXATION

Attempts were made to prepare NO₂(C₅H₆N)ClO₄ by (a) direct reaction of NO₂ClO₄ with pyridine, and (b) reaction of 1(C₅H₆N)₂ClO₄ with NO₂. The reaction of NO₂ClO₄ with pyridine in Freon 113 gave a product which analysis showed to be 80% NO₂ClO₄·C₅H₆N; its x-ray pattern, however,
was almost identical to that of pure NO$_2$ClO$_4$. This product darkens slowly on standing at room temperature, and it is believed that this is due to a slow nitration of the pyridine. In the reaction of I(C$_8$H$_7$N)$_2$ClO$_4$ with NO$_2$, iodine was liberated as expected, but analysis of the residual solid has not yet been completed.

The reaction of NOCl with Ag(C$_8$H$_7$N)$_2$ClO$_4$ in chloroform gave a product which is predominantly a mixture of pyridinium perchlorate and pyridinium nitrate.

Nitronium perchlorate reacted with PCl$_3$ to give NOClO$_4$ and POCl$_3$. There was no reaction between NO$_2$ClO$_4$ and PF$_3$.

SECTION V - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

Additional experiments on the vapor pressure and thermal decomposition of anhydrous perchloric acid were carried out and evaluated in the light of recent reports from other sources.

Thermal decomposition work on hydrazine-perchlorate indicates no detectable vapor pressure for this compound below its decomposition threshold. It was discovered that the transition from solid phase to liquid phase is accompanied by an increase in thermal stability. An explanation of this phenomenon has been proposed, as well as a comparison of other reported results in the literature.

SECTION VI - CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE

cis-Difluorodiazine forms a stable 1:1 solid adduct with arsenic pentafluoride. On the basis of its infrared spectrum, $^{19}$F NMR spectrum, and x-ray diffraction pattern, this adduct has been characterized as the fluoro-diazonium salt N$_2$F$^+$AsF$_6$$^-$.

Several attempts were made to synthesize new derivatives containing the -N$_2$F group by the reduction of the N$_2$F$^+$ cation. However, cis-N$_2$F$_2$ was the only N-F containing product observed in the reactions studied. The reagents used in these studies were: NO, NO$_2$, CF$_3$NO, CF$_3$I, CF$_3$H, CF$_3$Cl, NOCl, HCl, N$_2$F$_4$, and trans-N$_2$F$_2$. 

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Task 51
DIFLUORAMINE CHEMISTRY
Section I

DIFLUORAMINE CHEMISTRY

Harry F. Smith

Report RMD 5043-Q2-64

RMD Project 5043, Task 51
Report Period: 1 April 1964
to 30 June 1964

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

This section of the quarterly project report describes research conducted from 1 April to 30 June 1964 on the synthesis and chemical reactions of organic fluoronitrogen compounds.

Technical personnel contributing to this effort were: H. F. Smith (Project Scientist), J. A. Castellano and C. B. Parisek (Synthesis), J. Creatura and A. Fremmer (Chemical Analysis) and R. Storey and D. Kates (Instrumental Analysis).
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I. INTRODUCTION

The objective of this research program is the investigation of the chemical reactions of difluoramino alkanes and related organic fluoronitrogen compounds. It is expected that information developed in the course of these studies will serve the propellant industry in several ways. Many of the known organic NF compounds promise satisfactory energy levels when incorporated into propellant compositions, but their utilization has been inhibited by sensitivity to thermal or mechanical shock. Research by a number of organizations is currently directed toward discovering means of decreasing this sensitivity; an exploration of the chemistry of organic NF compounds will assist in this effort. In addition, the utilization of NF materials in practical propellant formulations involves questions of mutual compatibility. A systematized knowledge of the chemistry of this relatively new functional group should simplify this problem. It is likely that our investigations of chemical reactions will in some cases lead to products of new structural types, some examples of which may possess an appropriate balance between stability and available energy.

During the present report period emphasis has been placed upon the definition and elucidation of the chemical reactivity of \( \text{C-NF} \) group, primarily because of the interesting and useful reactions which have been discovered involving the \( \text{C-NF} \) of PFG. Experiments with a number of model difluoramines aimed at determining the extent to which \( \text{C-NF} \) resembles olefinic or carbonyl linkages are described.

The analogy to perfluoroguanidine can be carried one step closer by the use of trifluoroarbidines as model compounds. The initial steps in the synthesis of a model compound of this type via the dehydrofluorination of a 1,1-bis(difluoramino)alkane have been undertaken.
II. DISCUSSION

A. REACTIONS OF 1,2-BIS(FLUORIMINO)CYCLOHEXANE

A number of unsuccessful attempts to bring about additions to the double bond of a fluorimino compound were described in our previous report (Ref 1). Several of these attempts have been repeated under increased forcing conditions, and some new potential addends have been investigated.

1. Diels-Alder Reactions

The conjugated unsaturated system of 1,2-bis(fluorimino)cyclohexane (I) resembles that of a 1,3-diene, and so might possibly serve as a diene in the Diels-Alder reaction. Perfluoroguanidine has been reported (Ref 2) to function as a dienophile in certain instances and the reaction of these two compounds would be expected to give a product (II) with desirable energy and stability. Initial efforts to effect this reaction have not been successful:

\[
\begin{align*}
\text{I} & \quad + \quad \text{NF} \quad \xrightleftharpoons{} \quad \text{NF} \\
& \quad \text{II}
\end{align*}
\]

Reaction conditions are limited by the thermal instability of perfluoro- guanidine, and typical temperatures for the Diels-Alder reaction could not be used.

In order to determine whether the bis(fluorimine) is capable of undergoing a 1,4-addition, reactions with two typical dienophiles have been attempted. Neither maleic anhydride nor p-benzoquinone was found to add to I in refluxing xylene; decomposition occurred on heating to 200° in the absence of solvent.
2. Other Addition Reactions

An initial unsuccessful attempt to bring about the addition of tetrafluorohydrazine to 1,2-bis(fluorimino)cyclohexane at 1000 and subatmospheric pressure was reported earlier (Ref 1). During the current quarter this experiment was repeated in a metal bomb at elevated pressure. A solution of the reactants in Freon-113 in a 75 ml reactor was heated to 60-80° for 12 hours (calculated pressure = 310 psi). No reaction occurred, and 92% of the starting materials was recovered.

\[
\begin{align*}
\text{I} & \quad \text{NF} \quad \text{NF} \\
& \quad + \quad \text{N}_2\text{F}_4 \\
& \quad \rightarrow \\
\text{III} & \quad \text{NFNF}_2 \quad \text{NFNF}_2
\end{align*}
\]

The addition of isocyanic acid to perfluoroguanidine has provided an intermediate which has made available a number of desirable compounds (Ref 3). The application to other C-NF compounds would be a logical extension of this reaction and might provide a route to new structural types such as combination vic-gem compounds. The possibility that such a reaction can be achieved is strengthened by the reported additions of isocyanic acid to carbonyl groups (Ref 4) and to olefinic linkages (Ref 5). An available Sargent Micro Combustion Unit was modified to provide a convenient apparatus for the preparation of isocyanic acid by the pyrolysis of cyanuric acid (Ref 6). The depolymerized acid was condensed with 1,2-bis(fluorimino)cyclohexane (I) in a bulb at -196°. The temperature was increased in stages, culminating in a 16-hour period at 25-28°. The acid was found to have reverted to the trimer; I was recovered unchanged.

\[
\begin{align*}
\text{I} & \quad \text{NF} \quad \text{NF} \\
& \quad + \quad \text{HNCO} \\
& \quad \rightarrow \\
\text{IV} & \quad \text{NCO} \quad \text{NFH} \quad \text{NCO} \\
& \quad \text{NCO} \quad \text{NFH}
\end{align*}
\]
3. Reaction With Base

The stability of secondary fluorimines toward base is an important consideration in the synthesis of N,N,N'-trifluoroamidines, as well as of the fluorimines themselves. The observation that aqueous sodium hydroxide was consumed by 1,2-bis(fluorimino)cyclohexane was included in our previous report (Ref 1). This experiment has been repeated on a larger scale. The fluorimino compound appeared to react rapidly with 0.5 N aqueous sodium hydroxide solution at room temperature with the system forming a single phase. After 48 hours the reaction mixture was titrated potentiometrically with standard acid; inflections occurred at pH 7.25 and 5.30 (Figure 1). The first break was probably due to unreacted sodium hydroxide and the second may be attributed to a carboxylic acid salt. According to this interpretation 85% hyrolysis occurred producing a 30% yield of carboxylate. The color of the solution interfered with the colorimetric analysis for fluoride ion so that little significance may be attached to the value obtained (113% of theory). Any organic products formed were sufficiently hydrophilic to prevent extraction with ether.

One possible interpretation of the observed results involves nucleophilic attack on nitrogen with simultaneous elimination of fluoride ion:

\[
\text{NFNOH} + \text{ZOH}^- + \text{ZF}^- \rightarrow \text{NF}_2 + \text{NOH} + 2\text{F}^- \quad (4)
\]

A base-catalyzed hydrolysis of the dioxime would probably ensue, giving cyclohexandione (VI). The diketone is subject (Ref 7) to further nucleophilic

\[
\text{NOHNOH} + 2\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{10}\text{O}_2 + 2\text{NH}_2\text{OH} \quad (5)
\]

attack, undergoing a benzilic type rearrangement with ring contraction to give a hydroxyacid salt (VII) as the final product. It is also possible that some of
Figure 1. Titration Curve, Reaction of 1,2-Bis(difluoramino)cyclohexane With Sodium Hydroxide
the sensitive diketone was oxidized by air to adipic acid. Other possible reaction courses, involving initial nucleophilic attack on carbon, cannot be ruled out at this point.

4. Metal Complexes

Considering the favorable geometry of 1,2-bis(fluorimino)cyclohexane (I), the formation of coordination complexes such as VIII with metal ions provides a significant test of the extent to which the C=NF group resembles carbonyl. Such complexes, furthermore, might serve as reactive intermediates for the synthesis of new NF compounds useful in the propellant field.

In addition to the attempted preparation of a nickel complex already reported (Ref 1), we have found that no complex is formed between I and copper, cobalt, or ferric ions in alcohol/water solution. This observation may be interpreted as an indication that substantial differences exist in the electron distributions of C=O and C=NF. The situation is further complicated by steric considerations which do not apply in the case of C-diketones. Each of the C=NF groups can theoretically exist in either syn or anti configuration, and the relative stability and rate of interconversion of the three possible forms are not yet known.

\[
\text{NF} + \text{M} \not\rightarrow \text{VIII}
\]

as an indication that substantial differences exist in the electron distributions of C=O and C=NF. The situation is further complicated by steric considerations which do not apply in the case of C-diketones. Each of the C=NF groups can theoretically exist in either syn or anti configuration, and the relative stability and rate of interconversion of the three possible forms are not yet known.

\[
\text{Ia} \quad \text{syn, syn} \\
\text{Ib} \quad \text{syn, anti} \\
\text{Ic} \quad \text{anti, anti}
\]
Steric interactions between fluorine atoms may restrict bidentate coordination to the anti,anti isomer, and may in fact prevent formation of the syn,syn form.

B. PHOTOLYSIS OF 1,4-BIS(FLUORIMINO)CYCLOHEXENE-2

The photochemical reaction of 1,4-bis(fluorimino) cyclohexene-2 (IX)

\[
\begin{array}{c}
\text{FN} = \overline{\text{NF}} \\
\text{IX}
\end{array}
\]

described previously (Ref 1) has been explored further on a preparative scale. A solution of IX in cyclohexane, approximately 0.08 molar, was exposed in a thin film at room temperature to the radiation from an immersed quartz-filtered high-pressure mercury-vapor lamp. Visible changes occurred within ten minutes. The colorless solution became yellow and an insoluble brown solid was deposited on the wall of the quartz well. Since only a small fraction of the solution was in the illuminated zone and the rate of diffusion was very low as compared to the rate of reaction, uniform exposure of the entire solution was not possible. As a consequence the final products obtained represent the results of high conversion and possible subsequent activation of primary products, even though the overall conversion of the bulk of the fluorimine was probably low. The products obtained in this experiment are being examined but greater emphasis will be placed on future experiments which will incorporate the necessary refinements to compensate for the unexpectedly rapid reaction.

C. REACTION OF HEPTANAL WITH DIFLUORAMINE

A planned extension of our study of the chemistry of the fluorimino group called for the synthesis of an N,N,N'-trifluoromamide. The n-heptyl derivative was chosen as a suitable model compound because of its low sensitivity and the ready availability of the corresponding aldehyde.

The reaction of n-heptanal (X) with difluoramine has been found to give varying yields of 1,1-bis(difluoramino)heptane (XI) and bis(1-difluoraminoheptyl) ether (XII), depending upon the relative concentrations of
reactants and the rate of addition of the aldehyde. The results of four experiments are summarized in Table I.

**TABLE I**

**REACTION OF N-HEPTANAL WITH DIFFLUORAMINE**

<table>
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<tr>
<th>Expt. No.</th>
<th>HNF₂ mmoles</th>
<th>RCHO mmoles</th>
<th>Conditions</th>
<th>gem-cpd mmoles (%)</th>
<th>Ether mmoles X₂ (%)</th>
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<tr>
<td>1</td>
<td>253</td>
<td>50</td>
<td>b</td>
<td>0</td>
<td>11</td>
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<tr>
<td>2</td>
<td>275</td>
<td>50</td>
<td>c</td>
<td>17.5</td>
<td>35</td>
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<tr>
<td>3</td>
<td>320</td>
<td>53</td>
<td>d</td>
<td>20</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>320</td>
<td>26</td>
<td>d</td>
<td>12.5</td>
<td>47</td>
</tr>
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a. All expts at 0°C in 5.0 ml 105% fuming H₂SO₄
b. RCHO added while HNF₂ was being generated
c. RCHO added during 105 min after all HNF₂ was present; refluxed 105 min
d. RCHO added after all HNF₂ was present, refluxed 4 hours.

The products were isolated by vacuum distillation and characterized by elemental analyses, infrared spectra, proton and F¹⁹NMR spectra; and in the case of XI, by comparison of physical properties with reported values (Ref 8).

\[
\text{RCHO} + \text{HNF}_2 \rightarrow \text{RC-OH} \xrightarrow{\text{H}^+} \left[ \begin{array}{c} \text{H}^+ \\ \text{RC-OH} \\ \text{H}^+ \\ \text{RC+} \\ \text{NF}_2 \end{array} \right] \xrightarrow{\text{H}_2\text{O}} \left[ \begin{array}{c} \text{H} \\ \text{RC+} \\ \text{NF}_2 \end{array} \right] \]
A large excess of difluoramine and/or the slow introduction of aldehyde would favor the reaction shown in equation 10, producing the desired gem-compound, XI. If the local concentration of aldehyde is permitted to build up, on the other hand, formation of the ether (XII) via equation 11 becomes more probable.

The $^{19}$F NMR spectrum of XII (Figure 2) consisted of an extraordinary AB quartet with J greater than $\Delta v$. The smaller splittings are due to coupling with hydrogen atoms gem to difluoramino groups. The observed resonances indicate that both difluoramino groups are identical, but that the two fluorine atoms in each group differ from each other in their environments. Such a situation requires that rotation about the carbon-nitrogen bonds be restricted, although such restriction is not clearly evident from examination of Fisher-Hirschfelder models. The problem is further complicated by the asymmetry of carbon atoms carrying the difluoramino groups; it is not known whether the compound at hand is the racemate or the meso isomer. Similar $^{19}$F NMR spectra were observed for cis (meso)- and trans (dl)-1,2-bis(difluoramino)cyclohexane (Figures 3, 4). The infrared spectra of these two compounds have been published previously (Ref 9). The infrared spectrum of XII is presented in Figure 5.
Figure 2. $^{19}$F NMR Spectrum of Bis(1-difluoramoheptyl)ether

Figure 3. $^{19}$F NMR Spectrum of cis-1,2-Bis(difluoramino)cyclohexane
Figure 4. $^{19}$F NMR Spectrum of trans-1,2-Bis(difluoramino)cyclohexane

Figure 5. Infrared Spectrum of Bis(1-difluoraminoheptyl)ether
D. DEHYDROFLUORINATION REACTIONS

1. 1,1-Bis(difluoramino)heptane

The basic ion-exchange resin (weak base type) which has proven to be an effective reagent for the dehydrofluorination of 1,2-bis(difluoramino) cyclohexane and 1,2- and 1,4-bis(difluoramino)cyclohexanes (Ref 10) was applied in the dehydrofluorination of 1,1-bis(difluoramino)heptane (XI). Using the customary two-fold excess of resin, a liquid compound containing nitrogen and fluorine was obtained. The results of elemental analysis revealed, however, that two equivalents of hydrogen fluoride had been removed. The infrared spectrum of the product (XIV) included, in addition to the expected C-H

\[
C_6H_{13}CH(NF_2)_2 + 2B \rightarrow C_6H_{13}C\overset{\text{NF}}{\text{N}}F + 2BHF + B \quad (12)
\]

and N-F absorptions, a band at 1642 cm\(^{-1}\) indicating unsaturation (C=C or C=N) and a strong sharp band at 1550 cm\(^{-1}\), probably due to a ring vibration (Figure 6).

Several plausible structures can be postulated for a compound having these features and the empirical formula C\(_7\)H\(_{12}\)N\(_2\)F\(_2\). Mass spectral evidence

\[
\begin{align*}
\text{XIV a} & \quad \text{XIV b} & \quad \text{XIV c} \\
\text{XIV d} & \quad \text{XIV e}
\end{align*}
\]
(Table II) effectively eliminates any dimeric structure such as XIV e, since no mass peaks greater than 162 were observed. The boiling point (35-38°/2.5 mm; 61-63°/20 mm) was in accord with this conclusion. The E-elimination necessary for the formation of XIV d, although favored sterically, would not have any great driving force due to electronic influences, and this structure can probably be discounted.

**TABLE II**

**PARTIAL MASS SPECTRUM OF DEHYDROFLUORINATION PRODUCT (XIV)**

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<tr>
<td>162</td>
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<td>C7H12N2F2+</td>
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</table>

The detection of unsaturated fragments in the mass spectrum tends to favor structures XIV a and XIV c. The proton NMR spectrum, on the other hand, failed to show any olefinic C-H. The F19NMR spectrum included resonance peaks at -45.9, -42.5, -16.1 and 9.8 ppm from CFC13, attributable to N-F, and a weak triplet at +138.6 ppm, possibly due to C-F. It is not possible to rationalize all of this evidence and select a single unambiguous structure at this time. Gas chromatographic analysis, in fact, indicates the possible presence of a second component; further investigation is required.

Reasonable mechanistic routes to the three plausible structures can be suggested. One may assume the initial formation of the amidine (XIII) via
normal E2 elimination, and subsequent removal of the α-proton which would
be expected to be activated by the electronegativity of the difluoramino and
fluorimino groups. The carbanion (XV) can rearrange via an internal

\[
\begin{align*}
\text{C}_2\text{H}_5\text{CH}_2\text{CH}(\text{NF}_2)_2 & \xrightarrow{-\text{HF}} \text{C}_2\text{H}_5\text{CH}_2\text{C}^\equiv\text{NF} \quad \text{(13)} \\
\text{XII} & \quad \text{XIII} \\
\text{C}_2\text{H}_5\text{CH}_2\text{C}^\equiv\text{NF} & \xrightarrow{-\text{H}^+} \text{C}_2\text{H}_5\text{CH}_2\text{C}^\equiv\text{NF} \rightarrow \text{C}_2\text{H}_5\text{CH}^\equiv\text{C}^\equiv\text{NF} \quad \text{(14)} \\
\text{XIII} & \quad \text{XV} & \quad \text{XVI}
\end{align*}
\]

nucleophilic attack (SNi) on nitrogen; subsequent elimination of fluoride ion would
result in the formation of XIV a.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{CH}_2\text{C}^\equiv\text{NF} & \xrightarrow{\text{N}^\equiv\text{F}} \text{C}_2\text{H}_5\text{CH}_2\text{C}^\equiv\text{N}^\equiv\text{F}^\equiv \quad \text{+ F}^- \quad \text{(15)} \\
\text{XV} & \quad \text{XIV a}
\end{align*}
\]

The second canonical form of the ion (XVI) might react similarly to give the
other cyclic product (XIV b). The ion XVI might also rearrange by means of
a fluoride-shift to produce the acyclic structure XIV c. The latter process,

\[
\begin{align*}
\text{C}_2\text{H}_5\text{CH}^\equiv\text{C}^\equiv\text{NF} & \xrightarrow{\text{F}^-} \text{C}_2\text{H}_5\text{CH}^\equiv\text{C}^\equiv\text{NF} \quad \text{+ F}^- \quad \text{(16)} \\
\text{XVI} & \quad \text{XIV b} \\
\text{C}_2\text{H}_5\text{CH}^\equiv\text{C}^\equiv\text{NF} & \xrightarrow{\text{F}^-} \text{C}_2\text{H}_5\text{CH}^\equiv\text{C}^\equiv\text{NF} \quad \text{+ F}^- \quad \text{(17)} \\
\text{XVI} & \quad \text{XIV e}
\end{align*}
\]
if it occurs, would be a complex one, possibly involving a nitrene intermediate.

When the reaction described above was repeated, using a single equivalent of ion exchange resin and maintaining the reaction temperature at 16-20°C, a different result was obtained. The liquid product contained N-F groups and unsaturation, but lacked the strong absorption at 1550 cm⁻¹. The presence of water, presumably introduced into the system with the ion exchange resin, made more detailed interpretation of the spectrum impossible; further work is needed in this area.

2. 1,2-Bis(difluoramino)cyclohexane

Several compounds have been dehydrohalogenated by reaction with ethyl-diisopropylamine (Ref.11) and the application of this reagent to a difluoramino compound was examined briefly during the report period. The amine did indeed prove to be useful in this connection since an 83% yield of 1,2-bis(fluorimino)-cyclohexane was obtained upon refluxing an ether solution of the amine and a cis-trans mixture of 1,2-bis(difluoramino)cyclohexane.
III. EXPERIMENTAL

A. ATTEMPTED REACTION OF 1, 2-BIS(FLUORIMINO)CYCLOHEXANE WITH PERFLUOROGUANIDINE

1. The fluorimine (1.35 gm, 9.1 mmoles), 1 gm urea, and 10 ml Freon-113 were placed, with a small magnetic stirring bar, in a glass pressure reactor (Fisher-Porter) which was cooled to -78°C and evacuated. Perfluoroguanidine (25 mmoles) was then condensed into the reactor at -115°C. The vessel was placed in a water-ice bath and allowed to warm to room temperature during a period of 20 hours. Residual pressure (at 0°C) was 375 mm.

Unreacted PFG was flushed from the system, the residue treated with water, and the layers separated. The aqueous fraction was washed with CH₂Cl₂ and the combined organic solution dried over Na₂SO₄ and evaporated. The residual liquid (1.30 gm, 95%) was identified as starting material by its infrared spectrum.

2. A similar mixture containing 1.30 gm of the fluorimine and no urea was treated in the same fashion. Recovery of starting material amounted to 1.00 gm (77%).

B. ATTEMPTED REACTION OF 1, 2-BIS(FLUORIMINO)CYCLOHEXANE WITH ISOCYANIC ACID

A Vycor tube (52.5 x 1.13 cm) was charged with 2.6 gm (0.02 mole) of cyanuric acid. The tube was placed in a Sargent Micro Combustion Apparatus and the outlet connected, by means of a ball joint, to a trap maintained at -78°C. A stream of dry N₂ was passed through the tube and the ovens were turned on. Both ovens were maintained at 500-600°C for 30 minutes. The isocyanic acid which collected in the -78°C trap was purified by trap-to-trap distillation in a vacuum system. The pure isocyanic acid was then condensed into a two liter bulb containing 1.46 gm (0.01 mole) of 1, 2-bis(fluorimino)cyclohexane. The mixture was held at -196°C for 20 minutes and then at -78°C for one hour. When the cooling bath was removed a clear homogeneous liquid phase was present in the trap but as the mixture warmed to room temperature a white solid formed. After standing overnight at room temperature, the bulb was not found to contain...
any gas. Most of the white solid was insoluble in $\text{CCl}_4$ and $\text{CH}_2\text{Cl}_2$. Infrared analysis of the liquid residue from the organic solution showed it to be the starting fluorimino compound and the white solid was identified as cyanuric acid.

C. REACTION OF 1,2-BIS(FLUORIMINO)CYCLOHEXANE WITH SODIUM HYDROXIDE

1. A mixture of 1.46 gm (0.010 mole) of 1,2-bis(fluorimino)cyclohexane and 50.00 ml of 0.4995 N sodium hydroxide solution was stirred at room temperature for 48 hours. The color changed from pale yellow to red during the first 30 minutes and the mixture became homogeneous. The mixture was titrated potentiometrically with 0.4321 N HCl and was found to have inflections at pH of 7.25 (5.185 meq) and 5.30 (8.210 meq). Thus 19.80 meq of sodium hydroxide was consumed in the reaction, 3.025 meq being used to form the salt of a carboxylic acid. The acidified solution (pH = 2.0) was extracted with ether and CH$_2$C1$_2$. The combined organic extract was dried over sodium sulfate and evaporated to dryness to yield only a small amount of Kel-F grease. The aqueous solution was diluted to 500 ml and found to contain 420 mg (113%) of fluoride ion.

2. A mixture of 0.2 gm of 1,2-bis(fluorimino)cyclohexane and 12.00 ml of 0.500 N sodium hydroxide solution was stirred at 40°C for 24 hours. The color changed from pale yellow to orange and the mixture became homogeneous. The solution was titrated with 0.4921 N hydrochloric acid solution to the phenolphthalein end point and was found to require 6.0 ml. The acidified solution was extracted with either and methylene chloride as before but only Kel-F grease was obtained. The solution was diluted to 250 ml and was found to contain 46.3 mg (90%) of fluoride ion.

D. PHOTOLYSIS OF 1,4-BIS(FLUORIMINO)CYCLOHEXENE-2

A 450 watt high-pressure mercury arc lamp (Hanovia No. 679A-36) with a water-cooled quartz immersion well having a 60/50 standard-taper joint has been obtained. A glass reactor was fabricated to fit as closely as possible (approximately 1 mm) to the sidewalls of the well. The reactor with well in place held 60 ml of liquid, about 1/3 of which was exposed to the direct rays of the lamp.

A solution of 0.72 gm (5 mmoles) of the bis(fluorimine) in 65 ml of reagent grade cyclohexane was prepared, and 5 ml was retained as a spectrophotometric reference. Upon irradiation of the remaining 60 ml at 20°C, a distinct discoloration was apparent after 5-10 minutes. The solution became yellow and a brown
solid was deposited on the walls of the quartz well. Five brief exposures were given with intermittent mixing. Evaporation of the filtered cyclohexane solution gave a pasty-solid from which colorless crystals of starting material were obtained by trituration with pentane. Identification of the insoluble brown solid and the yellow solute have not yet been completed.

E. 1,1-BIS(DIFLUORAMINO)HEPTANE

1. Difluoramine was generated in the usual manner (Ref 12) by the acid hydrolysis of 30 gm of N,N-difluorourea in aqueous solution. The difluoramine-carbon dioxide mixture was passed through a drying tube and into a flask containing 5 ml of 105% fuming sulfuric acid and equipped with a Dry-Ice condenser. After all of the difluoramine had been generated, a solution of 6.0 gm (0.053 mole) of n-heptanal in 14 ml of Freon-113 was added dropwise to the mixture with stirring at 0°C. The mixture was stirred at 0°C for four hours. After the system was flushed with nitrogen to remove unreacted difluoramine, water was added and the organic layer separated. The aqueous layer was washed with methylene chloride, the organic solution dried over anhydrous magnesium sulfate and the solvents removed by evaporation. The residue was distilled to yield 4.02 gm (0.02 mole, 38%) of 1,1-bis(difluoramino)heptane, bp 58-58.5° (12 mm); n\text{D} = 1.3830 [Lit. (ref 8) n\text{D} = 1.3824]. The distillation was continued

Anal. Calcd. for C\textsubscript{14}H\textsubscript{24}N\textsubscript{2}F\textsubscript{4}: C, 41.58; H, 6.98; N, 13.85.

Found: C, 41.69; H, 7.05; N, 13.91.

and 1.65 gm of colorless liquid, bp 86-7°C (0.1 mm); n\text{D} = 1.4133, was obtained. The infrared spectrum showed absorptions indicative of an ether-containing an N-F group. The compound was assigned the structure bis(1-difluoraminoheptyl) ether.

Anal. Calcd. for C\textsubscript{14}H\textsubscript{24}N\textsubscript{2}F\textsubscript{4}O: C, 53.15; H, 8.92; N, 8.85.

Found: C, 53.17; H, 8.85; N, 8.90.

F\textsuperscript{19}NMR spectra were taken on a Varian Associates DP-60 spectrometer at 56.4 megacycles/sec. The samples were examined in 33-50% CFC\textsubscript{13} solution containing 1-2% tetramethylsilane. The spectrum of the ether exhibited an extraordinary AB quartet with the following spectral constants: J\textsubscript{FF} = 596 cps; J\textsubscript{FB}H = 17.3 cps; J\textsubscript{FA}H = 19.7 cps; Δν = 73 cps or 1.29 ppm. The smaller splittings are due to spin-spin interaction of the fluorine atoms with the hydrogen gem to the NF\textsubscript{2} group.
2. Difluoramine was generated in the same manner as described in (1). However, only 3.0 gm (0.026 mole) of heptanal was used. The product was worked up as above and 2.50 gm (47%) of 1,1-bis(difluoramino)heptane and 0.15 gm (1%) of bis(1-difluoraminoheptyl)ether were obtained.

F. REACTION OF 1,1-BIS(DIFLUORAMINO)HEPTANE WITH AMBERLITE IR-45

1. A solution of 6.22 gm (0.031 mole) of 1,1-bis(difluoramino)heptane in 100 ml of ether was added to 12.0 gm (0.060 mole) of Amberlite IR-45 ion-exchange resin in a 300 ml flask. The ether came to a boil and the mixture was stirred under reflux for about 15 minutes. The mixture gradually cooled to room temperature and stirring was continued for 24 hours. The resin was filtered off and the ether solution evaporated to dryness. The residue was distilled to yield 1.5 gm of colorless liquid, bp 35-38°C (2.5 mm). The -78°C trap was found to contain an additional quantity of the product. This liquid was combined with the above product and distilled to yield 2.3 gm (46%) of colorless liquid, bp 61-3°C (20 mm). The compound was subjected to infrared, NMR, and mass spectral analysis

   Anal. Found: C, 49.97; H, 7.82; N, 16.51.

   Anal. Calcd. for C₁₇H₁₉N₂F₂: C, 51.84; H, 7.46; N, 17.27.
   Found: C, 50.36/49.88; H, 7.55/7.64; N, 17.02/16.18.

G. REACTION OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE WITH ETHYLDIISOPROPYLAMINE

A mixture of 1.0 gm (5.4 mmoles) of 1,2-bis(difluoramino)cyclohexane, 1.4 gm (10.8 mmoles) of ethyldiisopropylamine (Ref 10) and 25 ml of ethyl ether was refluxed for 20 hours. A viscous brown oil had separated out at the end of this time. The mixture was treated with water and the aqueous solution extracted with ether. The combined ether extracts were dried over magnesium sulfate and evaporated to dryness to yield 0.65 gm (83%) of yellow liquid. The infrared
spectrum of this product was almost identical to that of pure 1, 2-bis(fluorimino)-cyclohexene.

H. 1,4-BIS(FLUORIMINO)CYCLOHEXENE-2 AND 1,2-BIS(FLUORIMINO)CYCLOHEXENE-3

The procedure described in Reference 9 was used to effect the reaction of 25.0 gm (0.312 mole) of 1,3-cyclohexadiene with 33.3 gm (0.320 mole) of tetrafluorohydrazine in 10 runs. The crude organic difluoramino mixture (50 gm) was dissolved in 50 ml of ether and added dropwise with cooling to a mixture of 110 gm (0.55 mole) of Amberlite IR-45 ion-exchange resin in 500 ml of ether. The temperature was maintained at 10-15°C during the addition and was allowed to warm gradually to room temperature. After stirring for 24 hours the resin was filtered off and the ether evaporated. The residue was triturated with pentane to yield 7.25 gm (16.1% overall yield) of 1,4-bis(fluorimino)cyclohexene-2, mp 49.5-51°C. The pentane filtrates were combined and evaporated to dryness to yield 14.4 gm of brown liquid. Distillation of this liquid yielded 4.0 gm of un-reacted difluoramino compound and 6.1 gm (13.6%) of 1,2-bis(fluorimino)cyclohexene-2; yellow liquid; bp 103-5°C (11 mm); mp 15-7°C. The infrared spectrum was almost identical to that of the 1,4-isomer. The proton NMR spectrum has been described above.

Anal. Calcd. for C₆H₆N₂F₂: C, 50.00; H, 4.20, N, 19.44.
Found: C, 49.97; H, 4.26; N, 19.38.
IV. FUTURE WORK

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

- Identification of the product obtained by treating 1,1-bis(difluoramino)-heptane with an excess of basic ion-exchange resin.

- Synthesis of 1-difluoramino-1-fluoriminoheptane.

- Exploration of the addition reactions of the double bond in a trifluoroamidine.

- Photolysis and photochemically initiated reactions of 1,4-bis(fluorimino)-cyclohexene and related compounds.

- Preparation and purification of larger quantities of 1,1-bis(difluoramino)-heptane for study by the Naval Ordnance Laboratories and the Bureau of Mines.
V. REFERENCES


Section II

Task 52

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY
Section II

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby

D. D. Perry

Report RMD 5043-Q2-64

RMD Project 5043, Task 52
Report Period: 1 April 1964 to 30 June 1964

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

This report describes the work carried out during the period from 1 April 1964 to 30 June 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: D. D. Perry (Section Supervisor), A. P. Kotioby (Project Scientist), W. H. Wieting (Synthesis), R. N. Storey, and D. Z. Chowanec (Instrumental 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 sensitivity in 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 organodifluoramines representing a selection of structural types and functional groups is 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 sensitivity of these compounds is being measured by the thermal explosion delay test (Ref 1). Some of the data obtained on N-F materials have been described by Rose et al. (Ref 2) and presented at the Second Sensitivity Seminar (Ref 3). These results show some interesting and potentially valuable correlations between vicinally and geminally substituted organo-bis difluoramines. This work has been extended to include the study of highly energetic tris(difluoramino)methane derivatives which are produced via addition reactions of perfluoroguanidine. Our activities in the past three months have been confined to attempts to synthesize derivatives and purify them to >99% by gas-liquid chromatography.
II. DISCUSSION

A. SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

The basic considerations in the selection of compounds to be used on this program have already been discussed in the previous report (Ref 4). During the past three months work was conducted mainly on the synthesis and purification of tris(difluoramino)methoxyalkanes. In addition, several chromatographically pure vicinal and geminal bis(difluoramino)alkanes were prepared at the request of the Naval Ordnance Laboratory.

The nucleophilic addition reactions of perfluoroguanidine became known (Ref 5, 6, 7) soon after the compound was discovered (Ref 8).

\[
\begin{align*}
F_2N & \quad C = NF \\
F_2N & \quad \text{ROH} \quad \rightarrow \quad F_2N \quad C \quad \text{NHF} \\
& \quad F_2N \quad \text{OR}
\end{align*}
\]

Equation (1)

Primary and secondary alcohols have been found to add readily and in high yields to the electron-deficient double bond in perfluoroguanidine.

In Table I are listed experimental conditions and the results obtained in the synthesis of the intermediate fluoramino adducts.
### Table I

**Experimental Conditions in the Synthesis of Bis(Difluoramino)Fluoraminomethoxy Alkanes**

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Moles</th>
<th>PFG (moles)</th>
<th>Freon-113 (ml)</th>
<th>Urea (gm)</th>
<th>Time (hr)</th>
<th>Temp (°C)</th>
<th>Yield (crude) (%)</th>
<th>Remarks</th>
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<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>1.0</td>
<td>16</td>
<td>0→23</td>
<td>---</td>
<td>Not isolated; fluorinated directly</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.03</td>
<td>0.05</td>
<td>20</td>
<td>0.3</td>
<td>16</td>
<td>0→25</td>
<td>~90</td>
<td>Very shock sensitive; IR shows strong NH absorptions at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Pentanol</td>
<td>0.05</td>
<td>2x0.015</td>
<td>10</td>
<td>---</td>
<td>32</td>
<td>20</td>
<td>0</td>
<td>Starting material recovered</td>
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<tr>
<td>Pentanol</td>
<td>0.045</td>
<td>0.05</td>
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<td>1.0</td>
<td>16</td>
<td>24</td>
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</tr>
<tr>
<td>Pentanol</td>
<td>0.05</td>
<td>0.05</td>
<td>20</td>
<td>0.3</td>
<td>16</td>
<td>0→32</td>
<td>83</td>
<td>Shock sensitive; NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Pentanol</td>
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<td>0.05</td>
<td>20</td>
<td>0.3</td>
<td>16</td>
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<td>92</td>
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<td>0.05</td>
<td>10</td>
<td>0.3</td>
<td>16</td>
<td>0→25</td>
<td>90</td>
<td>Shock sensitive; NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>3-Pentanol</td>
<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>0.3</td>
<td>16</td>
<td>0→23</td>
<td>---</td>
<td>Not isolated; fluorinated directly</td>
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<tr>
<td>Hexanol</td>
<td>0.03</td>
<td>0.05</td>
<td>20</td>
<td>1.0</td>
<td>16</td>
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<td>89</td>
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<td>Hexanol</td>
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<td>0.05</td>
<td>20</td>
<td>0.3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>Glass reactor broke</td>
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<tr>
<td>Hexanol</td>
<td>0.03</td>
<td>0.05</td>
<td>20</td>
<td>0.3</td>
<td>16</td>
<td>0→28</td>
<td>82</td>
<td>Shock sensitive; strong NH absorption at 3300 cm⁻¹</td>
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<tr>
<td>2-Hexanol</td>
<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>1.0</td>
<td>16</td>
<td>0→21</td>
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<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>0.3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>Explosion during condensation of PFG</td>
</tr>
<tr>
<td>3-Hexanol</td>
<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>0.3</td>
<td>16</td>
<td>0→19</td>
<td>---</td>
<td>Shock sensitive; strong NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Heptanol</td>
<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>1.0</td>
<td>16</td>
<td>0→26</td>
<td>---</td>
<td>Borderline sensitivity; strong NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Heptanol</td>
<td>0.03</td>
<td>0.05</td>
<td>20</td>
<td>0.3</td>
<td>32</td>
<td>0→29</td>
<td>99</td>
<td>Borderline sensitivity; strong NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Heptanol</td>
<td>0.03</td>
<td>0.05</td>
<td>20</td>
<td>0.3</td>
<td>16</td>
<td>0→28</td>
<td>---</td>
<td>Borderline sensitivity; strong NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Octanol</td>
<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>1.0</td>
<td>16</td>
<td>0→28</td>
<td>100</td>
<td>No fire under hammer; NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Octanol</td>
<td>0.03</td>
<td>0.06</td>
<td>20</td>
<td>1.0</td>
<td>16</td>
<td>0→23</td>
<td>90</td>
<td>No fire under hammer; NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Octanol</td>
<td>0.03</td>
<td>0.05</td>
<td>20</td>
<td>1.0</td>
<td>16</td>
<td>0→22</td>
<td>86</td>
<td>No fire under hammer; NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Nonanol</td>
<td>0.04</td>
<td>0.05</td>
<td>---</td>
<td>1.0</td>
<td>---</td>
<td>25</td>
<td>---</td>
<td>Acetonitrile (10 ml) used instead of Freon-113; explosion soon after reaction started</td>
</tr>
<tr>
<td>Nonanol</td>
<td>0.04</td>
<td>0.06</td>
<td>10</td>
<td>1.0</td>
<td>16</td>
<td>0→29</td>
<td>---</td>
<td>No fire under hammer; NH absorption at 3300 cm⁻¹</td>
</tr>
<tr>
<td>Nonanol</td>
<td>0.03</td>
<td>0.05</td>
<td>10</td>
<td>1.0</td>
<td>16</td>
<td>0→30</td>
<td>95</td>
<td>No fire under hammer; NH absorption at 3300 cm⁻¹</td>
</tr>
</tbody>
</table>
The uptake of perfluoroguanidine in these reactions was nearly quantitative. The infrared spectral analysis of the residual gas at the end of the reaction period showed it to be unreacted perfluoroguanidine contaminated with traces of Freon-113 which was used as a solvent. The amount of perfluoroguanidine remaining corresponded approximately to its excess over the quantity theoretically required by the stoichiometry of the reaction.

The addition of urea is known to facilitate this reaction (e.g., Ref 6). Although no optimum concentrations have been determined, the addition of 0.3 gm urea per 0.03 mole of alcohol proved to be sufficient. In one case where no urea was added, the starting materials were recovered at the end of 32-hours.

The fluoramino adducts from alcohols up to C₈ were sensitive to impact and could be detonated in a crude hammer test; those made from C₉ - C₁₂ alcohols did not fire. The adducts could be distilled without decomposition under reduced pressure, but they had only a limited stability when stored at 0 - 5°C in glass containers. The infrared spectrum of freshly prepared materials showed, in addition to N-F absorptions (10.3, 11.1, 11.6 μ), strong absorptions at 3.04 μ corresponding to the N-H stretching. A partly decomposed sample showed the presence of the C = N bond at 5.96 - 6.10 μ, indicating the elimination of the difluoramine from the molecule as shown in equation 2:

\[
\text{NF}_2 \quad \text{OR} \quad \text{HNF} \quad \text{OR} \quad \text{NF}_2
\]

The bis(difluoramino)fluoraminomethoxy derivatives were fluorinated by bubbling fluorine, diluted to 2% by volume with nitrogen, into the solution at 0°C. Table II presents the data obtained in the fluorination reactions.
| TABLE II |

EXPERIMENTAL CONDITIONS IN THE SYNTHESIS OF TRIS[(DIFLUORAMINO)METHOXALKANES]

<table>
<thead>
<tr>
<th>R</th>
<th>BP (°C/mm Hg)</th>
<th>Frenn-113 (ml)</th>
<th>Acetonitrile (ml)</th>
<th>NaF (g)</th>
<th>Total (%)</th>
<th>BP (°C/mm Hg)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>-(CH₂)₂CH₃</td>
<td>52-53/4.2</td>
<td>20</td>
<td>68</td>
<td>44/49/4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₃CH₃</td>
<td>46/1.0</td>
<td>20</td>
<td>49</td>
<td>40/4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₄CH₄</td>
<td>38-49/1.4</td>
<td>20</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₅CH₅</td>
<td>59-61/5.6</td>
<td>20</td>
<td>52-53/4.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₆CH₆</td>
<td>10</td>
<td>95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₇CH₇</td>
<td>10</td>
<td>42-46/6.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₈CH₈</td>
<td>10</td>
<td>46-52/0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₉CH₉</td>
<td>58-60/0.4</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₁₀CH₁₀</td>
<td>50-52/0.2</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₁₁CH₁₁</td>
<td>10</td>
<td>54</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₁₂CH₁₂</td>
<td>62-66/0.5</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₁₃CH₁₃</td>
<td>58-56/0.7</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₁₄CH₁₄</td>
<td>77-78/0.45</td>
<td>48-70/0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-(CH₂)₁₅CH₁₅</td>
<td>10</td>
<td>70-78/0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: F₂ adduct (mole ratio) is 5 in all cases except as noted in Remarks.

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There was no significant difference in results obtained whether Freon-113 or acetonitrile was used as solvent, although the presence of NaF (as an HF scavenger) in the reaction mixture in many instances resulted in the loss of HNF₃ from the molecule. If NaF was added at room temperature to the solution of the fluoramino adduct, an exothermic reaction began immediately accompanied by HNF₃ evolution. The infrared spectrum showed the disappearance of the N-H stretching (3.04μ) in the spectrum of the starting material and the appearance of a strong absorption of 5.96 - 6.10μ (C=N). The elimination of NaF from the reaction did not completely prevent the formation of the fluorimino derivative.

In addition to the starting material and the fluorimino compound, the other main byproducts in this synthesis were the tris(difluoramino)methoxyalkanes in which the alkyl chain of the molecule was partially fluorinated. No separation of these impurities could be effected by simple vacuum distillation. Because the objective of this program is to obtain products of >99% purity, a preparative gas chromatograph was purchased solely for use on this project. Since then efforts have been concentrated on the search for the optimum conditions for purifying the tris-compounds. The conditions (see Table III) are being worked out for a single compound, tris(difluoramino)methoxypentane.

**TABLE III**

<table>
<thead>
<tr>
<th>Liquid Phase (%)</th>
<th>Solid Phase (mesh)</th>
<th>Column material</th>
<th>Column Temp. (°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF-96 Methyl Silicone Fluid 20</td>
<td>Chromosorb P, regular 30-60</td>
<td>Al 1</td>
<td>110</td>
<td>Decomposition, no separation</td>
</tr>
<tr>
<td>SF-96 Methyl Silicone Fluid 20</td>
<td>Chromosorb P, regular 30-60</td>
<td>Cu</td>
<td>110</td>
<td>Too long retention time, no resolution, possible decomposition</td>
</tr>
<tr>
<td>Kel-F Oil No. 10 20</td>
<td>Chromosorb P, acid washed</td>
<td>Cu</td>
<td>75</td>
<td>Poor resolution</td>
</tr>
<tr>
<td>SF-96 Methyl Silicone Fluid 20</td>
<td>Chromosorb P, acid washed</td>
<td>Cu</td>
<td>75</td>
<td>Two major components; long retention time</td>
</tr>
<tr>
<td>SF-96 Methyl Silicone Fluid 20</td>
<td>Chromosorb P, acid washed</td>
<td>Cu</td>
<td>75</td>
<td>Two major components; total retention time of ca. 70 min. Infrared spectra of both fractions indicate need for further purification</td>
</tr>
</tbody>
</table>
As may be seen from the summary in Table III, the best separation was obtained so far with a 3 ft. x 1/4 in. Cu column filled with acid-washed Chromosorb P coated with SF-96 Silicone Oil. Copper tubing, prior to being charged with chromatographic material, was pressurized with fluorine and left overnight. The passivated column produced less decomposition of the tris-compound. At present a quantity of the two fractions is being accumulated for a second pass through the chromatographic column. The pure fractions will then be identified by the NMR or infrared spectral analysis.

B. SYNTHESIS OF BIS(DIFLUORAMINO)ALKANES

In addition to the main work on the synthesis and purification of tris-compounds, work was carried out on the synthesis of some additional bis-difluoramines which had been requested by the Naval Ordnance Laboratory. These compounds are listed in Table IV.

TABLE IV

BIS(DIFLUORAMINO)ALKANES

<table>
<thead>
<tr>
<th>Compound</th>
<th>BP</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Bis(difluoramino)cyclohexane</td>
<td>41.0/50</td>
<td>23 gm separated on SF-96 Chromosorb P column to give 15 gm of chromatographically pure cis- and trans-mixture.</td>
</tr>
<tr>
<td>1,1-Bis(difluoramino)propane</td>
<td>31.0/160</td>
<td>6.3 gm chromatographically purified to give 0.5 gm of ( \geq 99% ) pure cpd.</td>
</tr>
<tr>
<td>Ethyl 2,3-Bis(difluoramino)-butyrate</td>
<td>50.0/6</td>
<td>Purification by g.c. resulted in loss of NF(_2) groups.</td>
</tr>
<tr>
<td>1,1-Bis(difluoramino)hexane</td>
<td>53.0/25</td>
<td>Insufficient quantity—synthesis will be repeated.</td>
</tr>
</tbody>
</table>

The experimental procedure used in the preparation of these compounds has been described earlier in this program (Ref 9). Both compounds, after purification on a regular fire brick column (30/60 mesh) with Methyl Silicone Oil SF-96 (20%) as the liquid phase (column temperature 95\(^\circ\)O) were submitted to the Naval Ordnance Laboratory for sensitivity measurements.
III. EXPERIMENTAL

A. MATERIALS

The perfluoroguanidine used in our work was obtained from the American Cyanamid Company. The compound was stored in a low-carbon steel cylinder at ambient temperature under 200-300 mm Hg pressure. After about three months of storage the gas mixture in the cylinder, according to its mass spectrum, had the following composition: perfluoroguanidine 81.6%, tris(difluoramino) fluoromethane 4.3%, SiF$_4$ 0.6%, NO 2.3%, CO$_2$ 2.2%, unknown 9.0%. Before each experiment the mixture, after purification by trap-to-trap distillation at -120$^\circ$C, consisted of 94-98% perfluoroguanidine and traces of tris(difluoramino)fluoromethane. No decomposition of purified perfluoroguanidine was observed when the gas was stored at ambient temperature in Pyrex glass bulbs for 2-3 days.

Eastman reagent grade alcohols were used without further purification.

B. SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

Onto a twice-degassed solution of an alcohol (0.03 mole) in 20 ml Freon-113 containing 0.3 gm of urea cooled to -120$^\circ$C (Freon-113/liquid N$_2$ slush bath) was condensed 0.05 mole of perfluoroguanidine (94-98% pure). The reactor was cooled and allowed to gradually come to 0$^\circ$C while being stirred with a Teflon-coated magnetic bar; after about an hour the reactants were brought to room temperature and kept so overnight. The uptake of perfluoroguanidine was nearly quantitative. The small excess of perfluoroguanidine was then removed, the solution flushed with dry nitrogen and the pressure in the reactor was brought to atmospheric. The solution was filtered, Freon-113 was stripped off, and the product diluted with 20 ml acetonitrile. Through the solution kept overnight at 0$^\circ$C was passed dilute fluorine (2% by vol. in N$_2$, 0.04 mole of F$_2$). The solution of crude tris(difluoramino)methoxyalkane was flushed with nitrogen, stripped of the solvent under 10-20 mm Hg pressure and distilled through a 10-inch glass column under reduced pressure.
IV. FUTURE WORK

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

- To continue the synthesis of tris(difluoramino)methoxyalkanes
- Vapor phase chromatographic purification of the tris-adducts
- The preparation of vicinal or geminal bis(difluoramino)alkanes as may be requested by the Naval Ordnance Laboratory
V. REFERENCES


Section III

Task 53

CHEMISTRY OF THE OXYGEN SUBFLUORIDES
Section III

CHEMISTRY OF THE OXYGEN SUBFLUORIDES

S. I. Morrow
A. R. Young

Report RMD 5043-Q2-64

RMD Project 5043, Task 53
Report Period: 1 April 1964
to 30 June 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 April 1964 to 30 June 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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Task 53
Report RMD 5043-Q2-64
I. INTRODUCTION

The chemistry of dioxygen difluoride has been extensively explored for routes to new inorganic oxidizers. The most significant accomplishment of this research program was the discovery that reactions of dioxygen difluoride with arsenic pentafluoride and with antimony pentafluoride produce thermally stable salts of the dioxygenyl cation ($O_2^+$). It was thought that this discovery had opened a route to a new class of high-energy, solid oxidizers. However, attempts to prepare dioxygenyl salts of anions such as $\text{ClF}_4^-$, $\text{ClO}_4^-$, $\text{NO}_3^-$, and $\text{C(NO}_2)_3^-$, either by direct reactions of $O_2F_2$ or by metathetical conversion of $O_2\text{AsF}_6$, have been unsuccessful. Since this approach to new high energy oxidizers appears to be unpromising, we have abandoned our studies of dioxygenyl salts and are seeking new reactions of the oxygen subfluorides that might lead us to high energy oxidizers. We have recently initiated a study of the chemistry of trioxygen difluoride in the hopes that this paramagnetic compound will exhibit a chemistry quite different from that of dioxygen difluoride.
We have reported a reaction of xenon with dioxygen difluoride leading to unidentified products which were believed to contain oxygen as well as xenon and fluorine (Ref 1). During the past quarter we carried out additional studies on this reaction and ascertained that the major stable product is xenon difluoride. It is possible that the $\text{XeF}_2$ (as well as $\text{XeF}_4$) is obtained by the decomposition of an initial F-Xe-O species such as $\text{XeO}_2\text{F}_2$. In addition to the $\text{Xe-O}_2\text{F}_2$ reaction, unsuccessful efforts were made to induce reactions of $\text{O}_2\text{F}_2$ with krypton and with argon.

We studied reactions of $\text{O}_2\text{F}_2$ with $\text{BrF}_5$ and with CsBrF$_6$ in an effort to prepare BrF$_7$ at reduced temperatures and briefly studied the effect of the presence of CsF on reactions of $\text{O}_2\text{F}_2$. We have also initiated a study of the reactions of $\text{O}_2\text{F}_2$.

A. REACTIONS OF DIOXYGEN DIFLUORIDE WITH NOBLE GASES

1. Reaction of Xenon with $\text{O}_2\text{F}_2$

The reaction of $\text{O}_2\text{F}_2$ with xenon at $-117^\circ \text{C}$ has been reported to result in virtually complete conversion of xenon to a mixture of products which liberate oxygen, xenon, and fluorine both below and at room temperature (Ref 1). During this report period we determined that the stable solid products of this reaction are $\text{XeF}_2$ and $\text{XeF}_4$, with the former being predominant. Oxygen containing products are undoubtedly produced in the initial reaction but are unstable and evolve oxygen over the range from $-78^\circ \text{C}$ to room temperature. The overall reaction may be represented by the scheme outlined (equation 1):

$$\text{O}_2\text{F}_2(\text{xs}) + \text{Xe} \xrightarrow{-117^\circ \text{C}, 3 \text{ hr}} \text{Yellow solid} \xrightarrow{-78^\circ \text{C}} \text{White solid} \xrightarrow{25^\circ \text{C}} \text{Unidentified liquid} + \text{XeF}_2 \text{ (major)} + \text{XeF}_4$$

+ $\text{Xe} + \text{O}_2 + \text{F}_2$

\[\text{(1)}\]
Large transparent crystals of XeF$_2$ were obtained from the white solid (equation 1) by heating it to 50°C in a vacuum; the crystals condensed onto the cooler, upper surfaces of the Kel-F reactor. These crystals were identified as XeF$_2$ by means of single crystal x-ray analysis performed by Drs. W. Hamilton and J. Ibers of Brookhaven National Laboratories.

Although we were unable to isolate a significant amount of the liquid product (equation 1) for characterization, we did determine that it contains oxygen as well as xenon and fluorine. The reaction tube, which contains predominantly XeF$_2$ at room temperature, slowly evolves Xe, O$_2$, and F$_2$ on standing. Since XeF$_2$ and XeF$_4$ are thermally stable, we thought it possible to deduce the composition of the unstable component from an analysis of the gas phase. The results of several such analyses were not reproducible and empirical formulas ranging from Xe$_{1.3}$OF to Xe$_{2.7}$O$_2$F were obtained. This variation could have been caused by the presence of two or more unstable compounds which were not always present in the same ratio.

2. Attempted Reaction of Krypton with O$_2$F$_2$

Since the ionization potential of krypton is less than 20% higher than that of xenon, we anticipated that O$_2$F$_2$ might be capable of oxidizing it to fluorides or oxyfluorides, as was the case with xenon. However, when the reaction of krypton and O$_2$F$_2$ was attempted under conditions similar to those used for xenon, the krypton was completely recovered. Since VonGrosse et al. have reported the synthesis of KrF$_2$ by passing Kr and F$_2$ through a discharge tube at -80°C (Ref 2), it is felt that O$_2$F$_2$ (a discharge product) should be capable of fluorinating krypton. It is possible that we failed to obtain sufficient contact of the reagents.

3. Attempted Reaction of Argon with O$_2$F$_2$

Although it was questionable whether O$_2$F$_2$ would react with argon (ionization potential almost 50% greater than xenon), this reaction was of sufficient interest, because of the low atomic weight of argon, to make it worthwhile evaluating. Argon and O$_2$F$_2$ were kept in contact with each other at -118°C for two hours. No evidence of reaction was detected.

B. REACTIONS of O$_2$F$_2$ WITH HALOGEN COMPOUNDS

In our efforts to uncover reactions of O$_2$F$_2$ leading to new oxidizers we investigated the reactions of O$_2$F$_2$ with BrF$_3$, CsBrF$_6$, and with Cl$_2$ in the
presence of CsF. The objectives of these reactions were to prepare new inter-
halogens, dioxygenyl salts, or oxyfluorides as shown in equations 2 through 4.

\[
\begin{align*}
\text{O}_2\text{F}_2 + \text{BrF}_7 & \rightarrow \text{O}_2 + \text{BrF}_7 \quad (2) \\
\text{O}_2\text{F}_2 + \text{CsBrF}_6 & \rightarrow \text{CsF} + \text{BrF}_7 + \text{O}_2 \quad (3) \\
\text{O}_2\text{F}_2 + \text{CsF} & \rightarrow [\text{CsOF}] + \text{Cl}_2 + \text{CsCl} + \text{ClOF} \quad (4)
\end{align*}
\]

1. Attempted Reaction of O\textsubscript{2}F\textsubscript{2} with BrF\textsubscript{7}

Bromine pentafluoride was treated with dioxygen difluoride at -78°C. It was hoped that the low temperature at which O\textsubscript{2}F\textsubscript{2} acts as a fluorinating agent would permit isolation of BrF\textsubscript{7}, which up to now has never been observed in high temperature Br\textsubscript{2}-F\textsubscript{2} systems. The mixture was allowed to stand overnight at -78°C. After F\textsubscript{2}, O\textsubscript{2}, and unreacted O\textsubscript{2}F\textsubscript{2} were removed from the system, the liquid residue was analyzed by nuclear magnetic resonance spectroscopy. The only constituents were BrF\textsubscript{7} and traces of HF. After the BrF\textsubscript{7} was pumped out of the reactor there was a trace of white solid left which evolved BrF\textsubscript{3} and oxides of nitrogen on heating. The solid was probably the known compound, NO\textsubscript{2}BrF\textsubscript{4}. Traces of NO\textsubscript{2} and/or NO are often present in samples of O\textsubscript{2}F\textsubscript{2}.

2. Attempted Reaction of CsBrF\textsubscript{6} with O\textsubscript{2}F\textsubscript{2}

An alternate approach to BrF\textsubscript{7} might be to fluorinate a BrF\textsubscript{6}\textsuperscript{-} salt. Again we thought that the low temperatures at which O\textsubscript{2}F\textsubscript{2} releases active fluorine should make this an ideal reagent for the preparation of BrF\textsubscript{7}. The preparation of CsBrF\textsubscript{6} was attempted by heating CsF and BrF\textsubscript{5} to 140°C in a Monel cylinder for several hours. Since the loss of BrF\textsubscript{5} indicated conversion to the desired product, a sample of the solid recovered from the cylinder was treated with O\textsubscript{2}F\textsubscript{2} at -78°C. However, x-ray analysis of the solid used in the O\textsubscript{2}F\textsubscript{2} reaction showed that it was not, in fact, CsBrF\textsubscript{6}. The material obtained after reaction of the BrF\textsubscript{5}-CsF product with O\textsubscript{2}F\textsubscript{2} was identified by x-ray analysis as CsBrF\textsubscript{6}. 

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It is believed that the initial product of the high temperature CsF-BrF₅ reaction was CsBrF₄ which was converted to CsBrF₆ as shown in equation 5.

\[ \text{O}_2\text{F}_2 + \text{CsBrF}_4 \rightarrow \text{CsBrF}_6 + \text{O}_2 \]  

(5)

The CsBrF₆ was subjected to repeated contact with freshly prepared O₂F₂ at -78°C without any evidence of further reaction.

3. Reaction of Cl₂ with O₂F₂ in the Presence of CsF

Since various reactor materials as well as the conditions of their surfaces are known to significantly alter the rate of decomposition of O₂F₂, it was thought possible that certain solid compounds might also alter the mechanism of decomposition of O₂F₂ in such a way as to provide -OF groups. For example, a metal fluoride might interact with O₂F₂ as shown in equation 6. A reaction of

\[ \text{MF} + \text{O}_2\text{F}_2 \rightarrow \text{[MOF]} + \text{OF}_2 \rightarrow \text{MF} + \frac{1}{2} \text{O}_2 \]  

(6)

Cl₂ with O₂F₂ was carried out in the presence of CsF in the hope that a CsOF species would form and interact with Cl₂ to produce ClOF and CsCl₂. The only volatile products observed in the quartz system were SiF₄, ClOF, and O₂. X-ray analysis of the residual solid has not been completed.

C. CHEMISTRY OF TRIOXYGEN DIFLUORIDE, O₃F₂

Studies of the reactions of O₃F₂ have not been undertaken on this program because of the difficulty anticipated in handling O₃F₂, which is even more unstable than O₂F₂. However, there are two excellent reasons for anticipating significant differences in the product obtainable from O₃F₂ and O₂F₂ reactions. In the first place, O₃F₂ is paramagnetic and, therefore, may undergo combination reactions with other odd electron molecules that do not occur with O₂F₂, a diamagnetic molecule. Examples of possible combination reactions of O₃F₂ are shown in equations 7 and 8.

\[ \text{O}_3\text{F}_2 + \text{N}_2\text{O}_4 \rightarrow \text{O}_3\text{F}_2 \cdot 2\text{NO}_2 \]  

(7)

\[ \text{O}_3\text{F}_2 + \text{N}_2\text{F}_4 \rightarrow \text{O}_3\text{F}_2 \cdot 2\text{NF}_2 \]  

(8)
Second, the mode of decomposition of \( \text{O}_3\text{F}_2 \) \( \text{O}_2\text{F}_2 \rightarrow \text{O}^- + \text{O}_2\text{F}_2 \) suggests that it may tend to act as an oxyfluorinating agent rather than primarily as a fluorinating agent, as is the case with \( \text{O}_2\text{F}_2 \) \( \text{O}_2\text{F}_2 \rightarrow \text{O}_2 + 2\text{F}^- \). For example, a reaction of \( \text{O}_3\text{F}_2 \) with \( \text{Cl}_2 \) may yield \( \text{ClOF} \) or \( \text{OCIF}_3 \) as shown in equation \( \text{9} \):

\[
2\text{O}_3\text{F}_2 + \text{Cl}_2 \rightarrow 2\text{ClO} + 2\text{O}_2\text{F}_2 \\
\text{OCIF}_3 + \text{ClO}_2\text{F} + \text{O}_2
\]

(9)

In view of these interesting possibilities, we have carried out a study of the preparation and analysis of \( \text{O}_3\text{F}_2 \) samples during this report period as a preliminary step in the investigation of its chemical properties. We plan to devote our efforts during the next quarter almost exclusively to this end.

We prepared trioxygen difluoride in a U-shaped quartz discharge tube similar to that used in some of our \( \text{O}_2\text{F}_2 \) preparations. We anticipate, however, that many of the reactions that we wish to study will yield products that are incompatible with quartz. In these cases we will either attempt to fashion Kel-F discharge tubes or distill the \( \text{O}_3\text{F}_2 \) from the quartz generator to a Kel-F reactor.

Samples of a mixture of oxygen and fluorine of nominally \( 3:2 \) molar ratio were analyzed by absorption of the fluorine in mercury and measuring the residual oxygen. In this way a reproducible value of \( 2.84:2.00 \) was obtained for the \( \text{O}_2\text{F}_2 \) molar ratio. Additional samples of this mixture were subjected to a high voltage discharge at \(-196^\circ\text{C}\) until the pressure (initially \( 10^{-20} \) min) in the discharge tube was reduced to a minimal value. A blood red condensate was observed in the discharge tube. This condensate melted almost at the instant the liquid nitrogen bath was removed, and shortly thereafter pressure began to build up in the reactor. When decomposition was complete, the gases were sampled and absorbed in mercury. An average composition of \( 58.7\% \text{O}_2 \) and \( 41.3\% \text{F}_2 \) was obtained for the blood red condensate by analyses of the decomposition gases from several preparations. Theory for \( \text{O}_3\text{F}_2 \) is \( 60\% \text{O}_2 \).
III. EXPERIMENTAL

A. REACTIONS OF DIOXYGEN DIFLUORIDE WITH NOBLE GASES

1. Reaction of $O_2F_2$ with Xenon

Two representative experiments with xenon are described below. Of the five performed there was little variation in the observed results except that an unidentified liquid produce fraction appeared in some of the runs. A number of different methods of analysis were tried in an effort to isolate and identify the constituents. These procedures are schematically summarized in Figure 1.

In the first experiment 2.04 millimoles of xenon were allowed to react with excess $O_2F_2$ at $-117^\circ C$ for two hours. The yellow solid obtained turned white when it was stored overnight at $-78^\circ C$. The product was pumped at $-78^\circ C$, thereby removing 0.694 millimoles of gases composed of COF$_2$, CF$_4$, C$_2$F$_6$, SiF$_4$, CO$_2$, SF$_6$, and a trace of xenon. Then the product was pumped at $-21^\circ C$ for several additional hours. This treatment produced 0.252 millimoles of gas composed of SiF$_4$ and a small amount of moisture. The sample was then stored at $-78^\circ C$.

Prior to carrying out analytical procedures, the temperature of the sample was raised in stages from $-196^\circ C$ to $0^\circ C$ and the gases evolved at each temperature were monitored by means of a Time-of-Flight mass spectrometer. At $-78^\circ C$, O$_2^+$ and XeF$^+$ were detected. There were also small amounts of BF$_3$, CO$_2$, HF, SiF$_4$, and C$_2$F$_6$ which may have resulted from reactions occurring within the sampling system of the mass spectrometer. When the temperature was raised to $-21^\circ C$, O$_2^+$ and the fragmentation pattern of XeF$_4$ were observed. At $0^\circ C$ the XeF$_4$ pattern disappeared and only O$_2^+$ and Xe$^+$ peaks were observed. After recooling the sample to $-21^\circ C$, XeF$_2^+$ and XeF$^+$ peaks reappeared along with Xe$^+$ and O$_2^+$. Recoiling to $-78^\circ C$ resulted in the disappearance of all Xe-F peaks and again O$_2^+$ and Xe$^+$ were present. The mass spectral observations might be explained by the presence of an O-Xe-F compound or compounds, the cracking pattern of which contain O$_2^+$ and Xe$^+$ as the most intense ion fragments. As the temperature is raised, and hence the concentration of the species in
Figure 1. Reaction of $O_2F_2$-Xe (Metal, Kie-F System)
the vapor phase, XeF$_n^+$ ion peaks appear in the pattern. At 0°C extensive decomposition occurs in the vapor phase leaving only O$_2^+$ and Xe$^+$ mass fragments.

The product remaining after the mass spectrometric analysis was completed was vacuum distilled from room temperature to a trap held at -196°C. The solid condensate exhibited white, yellow, and slightly pinkish bands at -196°C. When this material was warmed to room temperature both a white solid and a liquid were present. The gas present over the solid and liquid was sampled and analyzed by mercury absorption. The fluorine content was 20.8%. The gas fraction remaining after treatment with mercury was shown by mass spectrometric analysis to contain 90% Xe, 3% O$_2$, 7% air and CO$_2$. Calculation of the Xe:O:F ratio gave 1.7:0.1:1.0. The solid and liquid mixture in the reactor was heated to 48°C causing further decomposition and vaporization. The vapor phase at this temperature was analyzed by mercury absorption and was found to contain 24.9% F$_2$. The residual gas after fluorine removal was composed of xenon and oxygen in a ratio of 4:1. Although there was some interfering SiF$_4$ present, the approximate Xe:O:F ratio of the vapor phase deduced from these data was 2:1:5. Decomposition of the sample appeared to be incomplete since small amounts of solid and liquid remained on cooling the reactor to room temperature.

In the second experiment 2.06 millimoles of xenon were allowed to react with excess xenon at -117°C for 2.5 hours. The product, a yellow/orange solid, was stored overnight at -78°C. Then it was pumped at 21°C for three hours. The material collected at -196°C was slightly orange in color. The fraction retained at -2°C was a white solid. When this was pumped on at room temperature part of it distilled over to a -196°C trap, and part was left as a white solid. The portion collected at -196°C was a white solid at room temperature. It was heated with a water bath at 50°C in a vacuum to induce decomposition so that the resultant gases could be analyzed. It was hoped that the composition of the solid material could be deduced from the composition of the gaseous break-down products. When the Kel-F trap was cooled, small transparent crystals formed on the wall at spots where water drops were left behind by the water bath. These were identified as XeF$_2$ by single crystal x-ray analysis.

The gases collected on heating the white sublimate were shown to contain 10.5% F$_2$. The gases left after the removal of fluorine contained 63% xenon, 26% oxygen, and 11% air. The Xe:O:F ratio derived from these data was 2.7:2.0:1.0.
The white solid that remained when the product was pumped originally at room temperature was stored under nitrogen at -78°C for a week. Then it was transferred to another Kel-F tube, pumped at -78°C (to remove xenon) and heated to 49°C for about 15 minutes. Crystals of XeF₂ were formed as before. Analysis of the gases produced by decomposition of an unstable component in the solid showed a Xe:O:F ratio of 1.33:1.00:1.04. This is not too far from the ratio required for XeOF.

A mass spectrometric study of a sample of XeF₄ obtained from Argonne National Laboratories was made. The results were compared to those obtained under similar conditions with the white solid product from the reaction of O₂F₂ with xenon. It was particularly desirable to determine whether oxygen would be evolved when XeF₄ was introduced into the mass spectrometer, as was the case when the products from xenon and dioxygen difluoride were analyzed in this instrument.

When XeF₄ was held at -78°C and the vapor analyzed by the mass spectrometer, only background peaks were evident. At -23°C the reported fragmentation pattern of XeF₄ was observed (Ref 3), although the relative intensities of the ions were not identical to those reported. No oxygen was observed. The same results were obtained at room temperature.

A comparison of the cracking patterns at -23°C of XeF₄ and of the Xe-O₂F₂ product (excluding the O₂⁺ peaks observed in the latter cracking pattern) is given in Table I.

### TABLE I

**MASS SPECTRA OF XeF₄ AND SOLID FROM Xe + O₂F₂ REACTION**

<table>
<thead>
<tr>
<th>M/E</th>
<th>Ionic Species</th>
<th>XeF₄</th>
<th>Xe + O₂F₂ (solid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td>Xe(132)⁺</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>151</td>
<td>Xe(132)F⁺</td>
<td>47.5</td>
<td>50.8</td>
</tr>
<tr>
<td>170</td>
<td>Xe(132)F₂⁺</td>
<td>43.0</td>
<td>27.7</td>
</tr>
<tr>
<td>189</td>
<td>Xe(132)F₃⁺</td>
<td>64.0</td>
<td>1.2</td>
</tr>
<tr>
<td>208</td>
<td>Xe(132)F₄⁺</td>
<td>9.0</td>
<td>0.17</td>
</tr>
</tbody>
</table>

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These data show that the O₂F₂-Xe product contains XeF₄ at -23°C. The presence of XeF₄ is indicated by the ratio of m/e 189 to m/e 208 which is 7:1 in both spectra.

However, after the ion peaks due to XeF₄ were subtracted from those of the experimental solid, the intensity ratios of the residual peaks did not agree well with those reported for XeF₂ in the literature (Ref 3). It is concluded (from this and the observation of a high intensity oxygen peak in the cracking pattern of the Xe-O₂F₂ product at -78 and at -23°C) that a xenon-oxygen species was present which undoubtedly also contained fluorine. It may have been XeO₂F₂ although no Xe-O ion fragments were observed.

2. Reaction of O₂F₂ with Argon

Dioxygen difluoride was prepared at -196°C in a quartz U-trap. The trap was warmed to -118°C and pressurized with an atmosphere of argon. The pressure in the system did not decrease as might be expected if a reaction were taking place between the two reagents. No evidence of a reaction of argon with O₂F₂ was detected.

3. Reaction of O₂F₂ with Krypton

This experiment was performed in the same manner as the one with argon. Oxygen difluoride was pressurized at -118°C with 332 mm of krypton. The 42 mm pressure rise over a three-hour period was attributed to the decomposition of O₂F₂. The only materials recovered other than krypton were NO₂ and SiF₄.

B. REACTIONS OF O₂F₂ WITH HALOGEN COMPOUNDS

1. Reaction of BrF₅ with O₂F₂

An attempt was made to prepare BrF₇ by allowing O₂F₂ to act upon BrF₅ at -78°C in a vacuum. The BrF₅ used in this reaction was purified by passing it over a bed of NaF pellets at 100°C to remove HF and BrF₃. The material so obtained was light amber in color. When such a sample was vacuum-distilled at room temperature in a Kel-F trap the residue became almost colorless. However, when the colorless material was passed through the vacuum system, it too became colored. The only way the BrF₅ could be maintained colorless in the liquid state was to avoid transferring it from trap to trap in the vacuum system. Whenever a sample of colorless BrF₅ was
exposed to a previously unpassivated section of the vacuum system, it became dark brown and evolved a brown gas (probably Br₂) at room temperature.

A 1.0 cc liquid sample of BrF₅, which was pale straw colored (high purity), was transferred to a Kel-F trap. The sample became slightly darker in color but still appeared to be a reasonably pure sample of BrF₅. Excess O₂F₂ was transferred to the reactor and the mixture was allowed to stand overnight in a vacuum.

The next day a brown liquid and a yellow solid were observed in the trap at -78°C. This mixture was pumped on at -78°C, and the gases removed in this way were found to be composed of COF₂, SiF₄, SF₆, fluorocarbon materials, and an unidentified material that exhibited an infrared absorption at 730 cm⁻¹. After the mixture had been pumped on at -78°C, a white solid remained. When the cold bath was removed this solid slowly melted to a slushy, clear liquid. There was a small amount of white solid left after all of the volatile material had been pumped off at room temperature to a trap held at -196°C. As the material condensed at -196°C was warmed to room temperature, it turned into a light yellow liquid. Distillation of this material to a Kel-F tube for nuclear magnetic resonance spectroscopic analysis resulted in its becoming blood red in color. Analysis showed only the presence of BrF₅ and traces of HF. The latter was presumably derived from impurities in the vacuum system used for the experiment.

The small amount of white solid residue left in the reactor was still present several days later when it was submitted for analysis. Decomposition of the solid at 75°C into a mass spectrometer showed the presence of BrF₅ or BrF₄, NF⁺, NO², N₂O, Cl₂ (trace), SiF₄, and fluorocarbon materials from the Kel-F container.

2. Reaction of CsBrF₆ with O₂F₂

The preparation of CsBrF₆ was undertaken by heating 9.65 gm of CsF and 10.5 cc of BrF₅ in a stainless steel bomb overnight at 100°C. A 6.0 cc quantity of BrF₅ was recovered from the bomb. The bomb was recharged with the same BrF₅ and reheated overnight at 140°C. Again 6.00 cc of BrF₅ was recovered and it was concluded that the reaction had gone to completion. The consumption of 4.5 cc of BrF₅ was exactly equal to that expected for 100% conversion of CsF to CsBrF₆. A sample of the solid CsF·BrF₅ product was treated with O₂F₂.
Quite unexpectedly the x-ray pattern of the product was different than that of CsBrF₆. (This was not learned until after we had reacted the product with O₂F₂, as described in the next paragraph.)

A 2.92 gm sample of CsF-BrF₅ product was loaded into a Kel-F reactor. Over a period of several days successive batches of O₂F₂ were prepared and transferred to the reactor. At first the O₂F₂ was allowed to react with this material at -107°C. Then a -78°C bath was placed around the reactor. After treatment with an excess of O₂F₂ in this way, the solid became gray in color. When it was pumped at -78°C, a small amount of volatile material was collected at -196°C. This produced a noncondensable gas at room temperature. No identification of this unstable material could be accomplished.

When the solid product was pumped on at room temperature, the principal volatile material obtained was BrF₅, with lesser amounts of CO₂, COF₂, SiF₄, and fluorocarbon materials. Although we had some difficulty with leaks in the system during work-up of the product, there was some evidence that a component may have been present which gives off oxygen at room temperature. The x-ray pattern of the solid obtained matched that of the known pattern for CsBrF₆. Although the x-ray pattern of CsBrF₄ is not available, we suspect that this was undoubtedly the composition of the original product we obtained from the thermal treatment of CsF and BrF₅. This CsBrF₆ was treated further with O₂F₂ at -107°C and then at -78°C without further change in its composition and with no evidence of BrF₇ formation.

3. Reaction of O₂F₂ with Cl₂ and CsF

Two mmoles of Cl₂ were condensed on CsF at -196°C in the discharge trap. Approximately 2 mmoles of O₂F₂ were then generated and condensed on the Cl₂ and CsF. Some purple color formation was noted. After warming to room temperature the gaseous products were found to be CF₄, SiF₄, Cl₂, ClO₂ and O₂.
IV. FUTURE WORK

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

- Studies of the reactions of $\text{O}_3\text{F}_2$ with odd electron molecules will be initiated.

- Further studies will be made of the decomposition of $\text{O}_2\text{F}_2$ over metal fluoride catalysts.

- The reaction of $\text{O}_2\text{F}_2$ with CsCl$_2$ will be examined as an approach to the anion, ClO$_2$F$_2^-$.

- The reaction of BrF$_5$ with O$_2$F$_2$ will be attempted under high pressure conditions.
V. REFERENCES


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-Q2-64

RMD Project 5043, Task 54
Report Period: 1 April 1964
to 30 June 1964

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

This section of the advanced oxidizer report summarizes work carried out during the period from 1 April 1964 to 30 June 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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Task 54
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I. INTRODUCTION

This research program is concerned with improving the physical and chemical properties of nitronium perchlorate via complexation of the nitronium cation. It is believed that such complexes, by virtue of the increased size of the cation, would have greater ionic character and hence, lower reactivity than nitronium perchlorate.

During this report period attempts were made to prepare complexes of nitronium perchlorate with pyridine, $\text{PCl}_3$, and $\text{PF}_3$. 
II. DISCUSSION.

Pyridine forms numerous complexes with metallic and nonmetallic perchlorates (Refs 1, 2, 3). Moreover, complex salts containing non-metal cations such as I(py)$_2$ClO$_4$ and Cl(py)NO$_3$ are less hygroscopic and more thermally stable than their respective parent salts. It was believed, therefore, that a pyridine complex of the nitronium cation might be stable. Such a complex could be a useful intermediate in the synthesis of more energetic complexes of nitronium perchlorate, as shown in equation 1.

\[
\text{NO}_2(C_5H_5N)_x\text{ClO}_4 \quad \text{+} \quad x\text{NH}_3 \rightarrow \text{NO}_2(\text{NH}_3)_x\text{ClO}_4 \quad \text{+} \quad xC_5H_5N
\]  

The following approaches were explored as routes to NO$_2$(py)$_x$ClO$_4$:

- The direct interaction of NO$_2$ClO$_4$ with pyridine (eq. 2);

\[
\text{NO}_2\text{ClO}_4 \quad \text{+} \quad xC_5H_5N \rightarrow \text{NO}_2(C_5H_5N)_x\text{ClO}_4
\]  

- The reaction of nitryl chloride with silver bis-pyridine perchlorate (eq. 3);

\[
\text{NO}_2\text{Cl} \quad \text{+} \quad \text{Ag(C}_5\text{H}_5\text{N})_2\text{ClO}_4 \rightarrow \text{AgCl} \quad \text{+} \quad \text{NO}_2(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4
\]  

- The reaction of iodinium bis-pyridine perchlorate with nitrogen dioxide (eq. 4);

\[
2\text{I(C}_5\text{H}_5\text{N})_2\text{ClO}_4 \quad \text{+} \quad \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4 \quad \text{+} \quad \text{I}_2
\]

These experiments gave some indication that a pyridine complex of NO$_2$ClO$_4$ may be prepared, although isolation of a complex in high purity has not yet been achieved.
Attempts to form complexes of NO₂ClO₄ with PF₃ and PCl₃ were totally unsuccessful.

A. REACTION OF NO₂ClO₄ WITH PYRIDINE

Since the direct interaction of NO₂ClO₄ with pyridine at ambient temperatures was expected to result in considerable degradation of the reactants, preliminary experiments were conducted at low temperatures and in the presence of diluents such as acetonitrile and Freon-113. The results of these experiments have been reported (Ref 4). It was noted that the solid product obtained when equimolar amounts of NO₂ClO₄ and pyridine were allowed to react in Freon-113 had an x-ray powder pattern consistent with that of NO₂ClO₄. The infrared spectrum of the solid product, however, did show absorptions attributable to pyridine; elemental analysis suggested that the product was not homogeneous. In order to determine whether a reaction of pyridine with NO₂ClO₄ could be driven to completion, a three-fold excess of pyridine was added to a suspension of nitronium perchlorate in Freon-113. The solid recovered upon removal of the Freon-113 and excess pyridine again produced an x-ray pattern (Figure 1) almost identical to that of pure NO₂ClO₄, although chemical analysis of the solid is consistent with a monopyridine complex of about 80% purity (Table 1).

TABLE I

ANALYSIS OF NITRONIUM PERCHLORATE-PYRIDINE PRODUCT

<table>
<thead>
<tr>
<th>Element</th>
<th>Found (%)</th>
<th>Calcd. for NO₂(C₅H₅N)ClO₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>20.07</td>
<td>26.78</td>
</tr>
<tr>
<td>H</td>
<td>2.02</td>
<td>2.23</td>
</tr>
<tr>
<td>N</td>
<td>10.03</td>
<td>12.47</td>
</tr>
</tbody>
</table>

The solid gradually darkens in color on storage at ambient temperatures. This color change may be indicative of a slow nitration of the pyridine ring.
Figure 1. X-ray Diffraction Patterns of NO$_2$ClO$_4$-$C_3$H$_5$N Reaction Products
When NO₂ClO₄ was allowed to react with a large excess of pyridine in the absence of a solvent, different results were obtained. The infrared spectrum of the solid product shows absorptions attributable to a pyridinium (C₅H₅NH⁺) salt such as C₅H₅NHClO₄; the x-ray powder pattern of the product is unlike that of NO₂ClO₄ (Figure 1). A possible reaction of nitronium perchlorate with pyridine which would lead to the formation of pyridinium salts is shown in equation 5.

\[
\text{NO}_2\text{ClO}_4 + \text{C}_5\text{H}_5\text{N} \rightarrow \text{O}_2\text{NC}_5\text{H}_4\text{N} + \text{HClO}_4 \\
\text{C}_5\text{H}_5\text{N} \quad \text{C}_5\text{H}_5\text{NHClO}_4
\]

\[\text{NO}_2\text{ClO}_4 \rightarrow \text{O}_2\text{NC}_5\text{H}_4\text{NHClO}_4\]

\[\text{C}_5\text{H}_5\text{NHClO}_4\]

**B. REACTION OF Ag(C₅H₅N)₂ClO₄ WITH NO₂Cl**

A possible alternative method for preparing a pyridine complex of nitronium perchlorate is by means of a reaction of NO₂Cl with Ag(C₅H₅N)₂ClO₄ (equation 6). The feasibility of this approach was pursued initially using commercially available NOCl (equation 7), rather than NO₂Cl, which is difficult to prepare in high purity.

\[
\text{Ag(C}_5\text{H}_5\text{N})_2\text{ClO}_4 + \text{NO}_2\text{Cl} \rightarrow \text{AgCl} + \text{NO}_2(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4
\]

\[
\text{Ag(C}_5\text{H}_5\text{N})_2\text{ClO}_4 + \text{NOCl} \rightarrow \text{AgCl} + \text{NO}(\text{C}_5\text{H}_5\text{N})_2\text{ClO}_4
\]

When NOCl was added to a nitromethane solution of AgClO₄ and pyridine, AgCl precipitated as predicted by equation 7, but nitric oxide was simultaneously liberated. Removal of the solvent in vacuo yielded a solid product having an x-ray diffraction pattern (Figure 2) similar to that obtained when NO₂ClO₄ is allowed to react with excess pyridine. This indicated that the product consisted of pyridinium salts. Upon hydrolysis the solid gave a negative test for NO₂⁻ and a positive test for ClO₄⁻. The infrared spectrum showed absorptions attributable to NO₃⁻, ClO₄⁻, and C₅H₅NH⁺. Chemical analysis (Table II) indicated that the product was a mixture of C₅H₅NHNO₃ and C₅H₅NHClO₄.
TABLE II
ANALYSIS OF Ag(CsHsN)2ClO4-NOCl REACTION PRODUCT  
(IN NITROMETHANE)

<table>
<thead>
<tr>
<th>Element or Group</th>
<th>Calcd. for 1:1 Mixture of C5H5NHNO3/C5H5NHClO4 (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>37.32</td>
<td>37.75, 36.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.79, 4.03</td>
</tr>
<tr>
<td>H</td>
<td>30.94</td>
<td>3.79, 4.03</td>
</tr>
<tr>
<td>ClO4^-</td>
<td>13.06</td>
<td>34.1</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td>8.67</td>
</tr>
</tbody>
</table>

When NOCl was added to a chloroform solution of Ag(CsHsN)2ClO4, AgCl precipitated without evolution of nitric oxide. After the AgCl was separated by filtration, the filtrate was evaporated in vacuo. The residual solid contained NO+, although considerably less than the theoretical amount (Table III). The x-ray powder pattern of the solid product is also comparable to that of the product of the reaction of excess pyridine with NO2ClO4 (Figure 2), which has been tentatively identified as predominantly pyridinium perchlorate. The infrared spectrum shows absorptions attributable to NO3-, ClO4- and the pyridinium ion. The product evidently contains only a small amount of the desired complex, NO(C5H5N)2ClO4,

TABLE III
ANALYSIS OF Ag(CsHsN)2ClO4-NOCl REACTION PRODUCT  
(IN CHLOROFORM)

<table>
<thead>
<tr>
<th>Element or Group</th>
<th>Calcd. for NO(C5H5N)2ClO4 (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>41.73</td>
<td>36.33, 36.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.59, 4.05</td>
</tr>
<tr>
<td>H</td>
<td>34.60</td>
<td>53.2</td>
</tr>
<tr>
<td>ClO4^-</td>
<td>14.60</td>
<td>7.6</td>
</tr>
<tr>
<td>N</td>
<td>10.43</td>
<td>1.63</td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In a similar reaction NOCl was added to a chloroform solution of Ag(C₅H₅N)₂ClO₄ and the precipitated AgCl was separated by filtration. The filtrate was added to an equal volume of ether which yielded an insoluble white solid. The solid has infrared absorptions attributable to NO₃⁻, ClO₄⁻ and pyridine. Its x-ray powder pattern (Figure 2) is not similar to those of previous products. Chemical analysis which is not yet complete fails to show more than a trace of ClO₄⁻. These results are not presently understood.

C. REACTION OF I(C₅H₅N)₂ClO₄ WITH NO₂

A preliminary investigation into the preparation and reactivity of I(C₅H₅N)₂ClO₄ has been reported (Ref 4). It has since been determined that I(C₅H₅N)₂ClO₄ is readily obtained by the reaction of I₂ with Ag(C₅H₅N)₂ClO₄ in chloroform (equation 8). It is a white solid that discolors on standing several days at room temperature. Chemical analysis of the product is given in Table IV.

\[
\text{CHCl₃} \quad \text{Ag(C₅H₅N)₂ClO₄} + \text{I₂} \rightarrow \text{AgI} + \text{I(C₅H₅N)₂ClO₄} \quad (8)
\]

**TABLE IV**

ANALYSIS OF Ag(C₅H₅N)₂ClO₄-I₂ REACTION PRODUCT

<table>
<thead>
<tr>
<th>Element or Group</th>
<th>Found (%)</th>
<th>Calcd. for I(C₅H₅N)₂ClO₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>32.87</td>
<td>31.25</td>
</tr>
<tr>
<td>H</td>
<td>3.19</td>
<td>2.66</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>27.4</td>
<td>26.28</td>
</tr>
<tr>
<td>I</td>
<td>25.3</td>
<td>33.04</td>
</tr>
</tbody>
</table>

The infrared spectrum and x-ray diffraction pattern are given in Figures 3 and 4, respectively.

An investigation was conducted of the usefulness of I(C₅H₅N)₂ClO₄ as an intermediate in the preparation of the complex perchlorate, NO₂(C₅H₅N)₂ClO₄ (equation 9). When NO₂ was added to a chloroform solution of I(C₅H₅N)₂ClO₄, a solid precipitated and the solution became intensely violet, indicating that
Figure 3. Infrared Spectrum of $\text{I(C}_2\text{H}_5\text{N)}_2\text{ClO}_4$

Figure 4. X-ray Diffraction Patterns of $\text{I(C}_2\text{H}_5\text{N)}_2\text{ClO}_4$ Reaction Product
iodine had been liberated. The x-ray powder pattern of the reaction product was quite different from that of I(C₅H₅N)ClO₄ (Figure 4). Chemical analysis of the product is pending.

\[ 2I(C₅H₅N)₂ClO₄ + N₂O₄ \rightarrow NO₂(C₅H₅N)₂ClO₄ + I₂ \]  

(9)

D. REACTION OF I(C₅H₅N)₂ClO₄ WITH AMMONIA

The reaction of I(C₅H₅N)₂ClO₄ with ammonia was investigated in an attempt to determine whether pyridine could be displaced from the complex salt (equation 10).

\[ I(C₅H₅N)₂ClO₄ + 2NH₃ \rightarrow I(NH₃)₂ClO₄ + 2C₅H₅N \]  

(10)

When ammonia was added to a chloroform solution of I(C₅H₅N)₂ClO₄, a black precipitate formed which turned pale yellow after the reaction mixture was stirred at room temperature for several hours. The solution became orange/brown and was found to contain free iodine. Since pyridine solutions of iodine are brown, the orange/brown color is indicative of liberated pyridine, as well as iodine. However, the x-ray and infrared patterns produced by the pale yellow precipitate indicated that it was predominantly ammonium perchlorate.

E. REACTION OF NO₂ClO₄ WITH PF₃ AND WITH PCl₃

In order to determine whether a phosphorous donor might complex with NO₂ClO₄, reactions of PF₃ and of PCl₃ with NO₂ClO₄ were examined. No reaction occurred between NO₂ClO₄ and PF₃, but PCl₃ was found to react with NO₂ClO₄ to yield NOClO₄ and POCI₃ (equation 11). The solid product was characterized by its x-ray diffraction pattern; the volatile reaction product was identified as POCI₃ by its mass spectrum.

\[ NO₂ClO₄ + PCl₃ \rightarrow NOClO₄ + POCI₃ \]  

(11)
III. EXPERIMENTAL*

A. REACTION OF NO$_2$ClO$_4$ WITH PYRIDINE

1. In Freon-113

To a mixture of 0.4994 g (3.43 mmole) of NO$_2$ClO$_4$ and 25 ml of Freon-113 at -196°C was added 0.83 cc (10.29 mmoles) of pyridine. The reaction mixture was stirred and allowed to warm slowly to -20°C. After stirring several hours the solvent was removed in vacuo. The residual solid was sampled for x-ray and infrared analysis and then stirred at -78°C. The x-ray powder pattern (Figure 1) was consistent with that of NO$_2$ClO$_4$. Chemical analysis is given in Table I.

2. In Excess Pyridine

To 0.3957 g (2.72 mmoles) of NO$_2$ClO$_4$ at -196°C was slowly added approximately 25 ml of pyridine. The reaction mixture was then allowed to slowly warm to -20°C. After stirring for several hours at -20°C the solvent was removed in vacuo. The x-ray powder pattern of the product is given in Figure 1.

B. REACTION OF Ag(C$_2$H$_4$N)$_2$ClO$_4$ WITH NOCl

1. In Nitromethane

To 12.8 mmoles of pyridine in 20 ml of CH$_3$NO$_2$ was slowly added 1.3447 g (6.4 mmoles of AgClO$_4$). The resultant solution was cooled to -196°C and 7 mmoles of NOCl was introduced. The reaction mixture was allowed to warm to room temperature. The head vapor was sampled for mass spectroscopic analysis and found to contain NO. The precipitated AgCl was separated by filtration. The filtrate was evaporated. Chemical analysis of the residual solid is given in Table II.

2. In Chloroform

To 4.5715 g (0.022 moles) of AgClO$_4$ at -196°C was added 3.63 cc (0.45 moles) of pyridine. This mixture was allowed to warm to room temperature and stirred for several hours; 25 cc of chloroform was then added while

* All solid reagents were handled in a dry box.
stirring. When all the Ag(C$_5$H$_5$N)$_2$ClO$_4$ dissolved, the reaction mixture was cooled to -196°C and 0.022 moles of NOCl introduced. The reaction mixture was allowed to warm to room temperature and the AgCl separated by filtration. The chloroform filtrate was evaporated. Chemical analysis of the residual solid is given in Table III and its x-ray powder pattern is given in Figure 2.

3. In Chloroform With Ether Precipitation

The reaction was conducted as described in subparagraph 2 except that the chloroform filtrate was added to an equal volume of diethyl ether and allowed to stand several hours. The precipitated solid was separated by filtration and dried in vacuo. Chemical analysis is pending. The x-ray powder pattern is given in Figure 2.

C. PREPARATION OF I(C$_5$H$_5$N)$_2$ClO$_4$

To 1.6786 g (8.1 mmoles) of AgClO$_4$ at -196°C was added 1.31 cc (16.2 mmoles) of pyridine. After warming the system to room temperature and stirring for several hours, 25 cc of chloroform was added. When the resultant solution became clear, 2.0558 g (8.1 mmoles) of I$_2$ was slowly added. Vigorous stirring was maintained. When the reaction was complete the mixture was filtered and the filtrate added to an equal volume of ether. The precipitated I(C$_5$H$_5$N)$_2$ClO$_4$ was separated and dried in vacuo; chemical analysis appears in Table IV. The infrared spectrum and x-ray diffraction pattern of the reaction product are given in Figures 3 and 4, respectively.

D. REACTION OF I(C$_5$H$_5$N)$_2$ClO$_4$ WITH NO$_2$

A chloroform solution of I(C$_5$H$_5$N)$_2$ClO$_4$ was prepared from Ag(C$_5$H$_5$N)$_2$ClO$_4$ and NO$_2$ as described in paragraph B and cooled to -196°C. A calculated amount of NO$_2$ was then added. The mole ratio of NO$_2$ to I(C$_5$H$_5$N)$_2$ClO$_4$ was 1:1 based on the amount of AgClO$_4$ used. After warming to room temperature, the resultant precipitate was separated by filtration and dried. Chemical analysis is pending. The x-ray diffraction pattern is given in Figure 4.

E. REACTION OF I(C$_5$H$_5$N)$_2$ClO$_4$ WITH NH$_3$

To a chloroform solution of 5.4 mmoles of I(C$_5$H$_5$N)$_2$ClO$_4$ (based on the amount of AgClO$_4$ used) was added 10.8 mmoles of anhydrous NH$_3$ at -196°C. The reaction mixture was allowed to warm to room temperature and stirred for several hours. The solid which precipitated was found to be predominantly NH$_4$ClO$_4$. 
F. REACTION OF PF₃ WITH NO₂ClO₄

To 0.4780 g (3.3 mmoles) of NO₂ClO₄ at -196°C was added 10 mmoles of PF₃. The reaction mixture was stirred at -150°C for several hours. It was then allowed to warm to room temperature. The gas was recondensed on the solid several times. Both PF₃ and NO₂ClO₄ were recovered.

G. REACTION OF PCl₃ WITH NO₂ClO₄

To 0.3827 g (2.63 mmoles) of NO₂ClO₄ at -196°C was added 3.00 mmoles PCl₃. After warming to room temperature the volatile materials were collected and found to be POCl₃. The solid residue was found to be NOClO₄.
IV. FUTURE WORK

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

- Attempts will be made to prepare and evaluate addition compounds of perchloric acid with NO$_2$ClO$_4$, HONH$_2$ClO$_4$, and NOF.

- Attempts will be made to prepare and evaluate substituted ammonium perchlorates such as; NH$_3$ClO$_4^+ClO_4^-$ and H$_3$NONO$_2^+ClO_4^-$. 
V. REFERENCES


Section V
Task 55

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS
Section V

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki
W. Cruice

Report RMD 5043-Q2-64

RMD Project 5043, Task 55
Report Period: 1 April 1964 to 30 June 1964

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

This section of the advanced oxidizer report summarizes work carried out during the period from 1 April 1964 to 30 June 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. Gruice (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. Work previously reported included highlights of a preliminary literature search and results of experimental work on the vapor pressure of anhydrous HClO₄.

Additional work on the vapor pressure and thermal decomposition of anhydrous HClO₄ has been performed. Thermal decomposition studies on high purity HP have been initiated and the results are compared with other work in the field. Other solid amino-perchlorate oxidizers are being prepared and purified for experimentation.

This report includes a summary of experimental work done in the second quarter and a brief summary of projected experiments for the following quarter.
II. SUMMARY

During this report period vapor pressure and thermal decomposition studies on anhydrous HClO₄ were continued and thermal decomposition studies on hydrazine perchlorate have been initiated.

The vapor pressure of anhydrous HClO₄ was found to be 71 mm Hg at 41°C which is in excellent agreement with work previously reported. The presence of chlorine oxides in a second sample of anhydrous HClO₄ reduced the vapor pressure at 55°C considerably from the value expected in view of previous work. The qualitative aspects of the decomposition reaction are as indicated by previous published papers. Computation of the activation energy of decomposition gives values of 23.1 kcal/mole and 22.4 kcal/mole (two different methods) in excellent agreement with the value of 22.2 kcal/mole reported in recent Soviet papers. Results of a vapor decomposition run on HClO₄ indicated that the vapor decomposes very slowly at 139°C.

Hydrazine perchlorate has been synthesized in high purity for experimental work. A DTA thermogram is included in the report. Hydroxylammine perchlorate has also been synthesized, but the purity is not yet high enough for good experimental work.

High purity hydrazine perchlorate has been found to undergo measurable thermal decomposition at 140°C. The pressure vs time curve follows the theoretical plot for nucleation according to a power law and normal growth thereafter. The expressions describing the curve are $P = 2.29 \times 10^{-4}t^2$ up to 1100 min and $P = 0.491t - 270$ to over 2000 min. A second run performed at 150°C showed a marked increase in stability following the plot of $P = 0.085t + 30$ after 250 min to atmospheric pressure at about 8500 min. The marked difference in thermal decomposition characteristics through the fusion point is assumed to be a result of the disappearance of high-energy strain areas and reactant product concentration gradients present in the crystalline form.
III. EXPERIMENTAL

A. PROCEDURES

1. Vapor Pressure and Thermal Stability of Anhydrous Perchloric Acid

Thermal decomposition of anhydrous perchloric acid was studied in an all glass reactor with a pressure sensitive glass diaphragm. The apparatus is described in detail in the first quarterly report. The anhydrous acid was introduced into this Sickle gage reactor, degassed and then the loading arm was sealed under vacuum. Pressure readings were taken at frequent intervals until the rate of pressure rise was too great for accurate measurement and the sensitive glass diaphragm was in danger of rupture. Extrapolation of the pressure-time plot to \( t = 0 \) yields the vapor pressure of the anhydrous acid at the temperature of the experiment.

2. Thermal Decomposition of Hydrazinium Perchlorate

A slightly modified version of the sickle gage has been adopted for use in solid phase decomposition experiments (Figure 1). The use of the spherical bottom removes the possible effects of packing, excessive contact with the glass, reduced thermal conductivity, etc. A further modification, i.e., addition of a break seal arm for gas sampling, has been adopted for future use in both liquid decomposition cells and solid decomposition cells.

High purity HP was placed into a sickle gage and degassed for 30 minutes prior to seal-off in the usual manner. The gage was then immersed in a bath of Cellolube-220 at a specified temperature and pressure was monitored as a function of exposure time.

B. MATERIALS

1. Anhydrous Perchloric Acid

The method of preparation and purification of anhydrous perchloric acid was described in detail in the first quarterly report.
Figure 1. Modified Version of the Sickle Gage Decomposition Apparatus
2. Hydrazinium Perchlorate

Hydrazinium perchlorate (HP) has been produced according to the method of Barlot and Marsaule (1) in limited quantities suitable for our research purposes. The method as stated, however, appears to allow a considerable amount of water of hydration to remain in the salt. Material dried for two hours under a vacuum of < 1 mm Hg at 70°C assayed 99.94% and 99.83% by potentiometric titration (two separate batches). The DTA curves of this material are extremely sharp and well-defined, showing the melt endotherm beginning at 139°C and the deflagration exotherm beginning at 220°C. The extremely small quantity of water present is visible as a slight endothermic peak at 95°C (see Figure 2).

3. Hydroxylammonium Perchlorate

Hydroxylammonium perchlorate (HAP) has been synthesized by using the method of Robson (2) which is completely non-aqueous; the initial reaction is:

\[
2\text{HONH}_3\text{Cl} + \text{Ba(ClO}_4\text{)}_2 \xrightarrow{\text{EtOH}} 2\text{HONH}_3\text{ClO}_4 + \text{BaCl}_2
\]

The absolute alcohol is removed by flash evaporation. The crude HAP is redissolved in diethyl ether and reprecipitated by the slow addition of anhydrous benzene. The material is then dried at moderate temperature for an extended period. The drying procedure has been thoroughly investigated at Thiokol Chemical Corp., Elkton Division, (3), but batches produced to date at Thiokol -RMD have not been sufficiently pure for experimental purposes. This disparity is probably a result of using considerably different drying apparatus. Further study of the purification process is currently under way.

4. Guanidinium Perchlorate

A quantity of guanidinium perchlorate (GP) on hand is being prepared for experimentation. A study is being made to determine methods of purification and criteria of purity.
Figure 2. DTA Curve of High Purity Hydrazinium Perchlorate
IV. RESULTS AND DISCUSSION

A. DECOMPOSITION OF PERCHLORIC ACID

The pressure vs time curve for the decomposition of liquid anhydrous perchloric acid at 41°C is shown in Figure 3. The pressure increased gradually until t = 129 min; from this point on the slope of the curve increased rapidly until it was nearly vertical. The acceleration was accompanied by a progressive color change beginning shortly after introduction of the reactor into the bath. The pure acid was clear and colorless; it became pale yellow (scarcely detectable), then amber, orange, red, and deep reddish brown. Extrapolation of the pressure-time plot to t = 0 gave a vapor pressure of 71 mm Hg at 41°C, which is in excellent agreement with our first quarter report (RMD 5034 Q2-64). The slope of the straight line portion of the curve is 0.533 mm Hg/min (t = 0 to t = 129).

A subsequent run at 55°C performed in the same manner was very similar in the shape of the pressure-time curve (Figure 3) and in color characteristics. When the curve was extrapolated to t = 0, however, the vapor pressure reading was 120 mm Hg, a value which is lower than previously reported. The acid assayed at 104.6% by titration, indicating the presence of some oxide of chlorine. Since the initial material was colorless, the oxide was probably ClO₇ produced by excessive dehydration of the 70-72% acid used in the production step.

In order to calculate temperature coefficients from this data, the assumption was made that the concentration of all reactants was the same after an equivalent amount of reaction had occurred. Then the time to a fixed amount of decomposition is inversely proportional to the specific rate constant. Rates were compared at two degrees of reaction. First, a point corresponding to a relatively rapid dP/dt was selected to minimize the error caused by the difference in initial assays. This corresponds to 59 minutes at 55°C and 285 minutes at 41°C. Combining the Arrhenius equation at T₁ = 41°C and T₂ = 55°C, gives:

\[ \ln \frac{t₁}{t₂} = \frac{E}{R} \left[ \frac{T₂-T₁}{T₂ T₁} \right] \]
Figure 3. Pressure versus time curves for anhydrous HClO₄.
The activation energy thus calculated is 23.1 kcal/mole, substantially in agreement (~5% deviation) with the value of 22.2 kcal/mole reported by Soviet investigators (4). The second method was to obtain the time at which the linear portion of the curve terminates (induction period) which is also inversely proportional to the rate constant. The induction period at 41°C is 129 min, at 55°C is 28 min. Using the same expression, an activation energy of 22.4 kcal/mole was obtained. This is in excellent agreement with the Soviet report previously mentioned.

A single experiment was performed on the thermal decomposition of anhydrous HClO₄ in the vapor state at 139°C. The initial pressure of the vapor at 139°C was 67 mm Hg. After almost 65 hours at 139°C the pressure had risen to 85 mm Hg. Assuming a linear pressure-time relationship, this corresponds to 4.65x10⁻³ mm/min.

If the reaction is assumed to be first order, and following the stoichiometry:

\[ \text{HClO}_4 \rightarrow 0.5 \text{H}_2\text{O} + 0.5 \text{Cl}_2 + 1.75 \text{O}_2 \]

as proposed by Levy (5), the first order constant can be calculated from:

\[ \log \left( \frac{1.75 P_0}{2.75 P_0 - P} \right) = \frac{k t}{2.3} \]

The value of k thus obtained (1.16x10⁻⁴) is approximately within the range predicted by extrapolation of Levy's plot of first order rate constants versus temperature, but the scatter in points obtained at the lower temperatures of his experiments make such an extrapolation almost insignificant.

B. DECOMPOSITION OF HYDRAZINIUM PERCHLORATE

The initial experiment with hydrazinium perchlorate was an exploratory one designed to determine the temperature at which it decomposes at a measurable rate. The sample was first heated for five hours at 90°C and there was no detectable pressure rise. No detectable pressure was observed after subsequent heating at 100°C for five hours, 110°C for eight hours, 120°C for three hours and 130°C for three hours. At 140°C no pressure was evident after 60 min, but after 135 min a pressure of 56 mm Hg was observed. Thereafter the pressure rose linearly with time to over 500 mm Hg at 500 min, when the run was discontinued. The fact that the material had been subjected to extended preheating makes the data inaccurate from the point of view of a kinetic study; the primary objective (i.e. to discover the "threshold" of thermal decomposition detectable in our system) was accomplished.
A new sample of the same high purity HP was run at 140°C. The total duration of the run was over 50 hours with no sign of sudden acceleration of the type characteristic in hydrazine diperchlorate (HP-2). The pressure-time curve (Figure 4) is classical in solid-phase decompositions, corresponding to nucleation according to a power law and normal growth of nuclei thereafter to over 2000 min. The curve is very closely approximated by:

\[ P = 2.29 \times 10^{-4} t^2 \text{ up to 1000 min, thereafter following } P = 0.491t - 270 \text{ to over atmospheric pressure.} \]

The residue (solid) was still white and crystalline, showing no evidence of having melted during the run.

Another sample of high purity HP was run at 150°C for over 7500 min (125 hours) before atmospheric pressure was attained. The earliest reading obeyed the power law \( (P = C t^n) \) with \( n = 2 \) and a value of \( C \) approximately double that found at 140°C. A decline in rate was then observed and the plot from that point (~250 min) follows a linear relationship with a slope of 0.085 mm Hg/min, a much lower rate than that observed for the upper (linear) portion of the run at 140°C (Figure 5). For a more accurate comparison, \( N/No \) was calculated for each run: where \( N = \) moles of gaseous products and \( No = \) initial moles of HP. The combined plot is shown in Figure 6. The material was quite definitely molten during the run; upon removal from the bath it congealed in a fraction of a second to a single solid mass.

These experiments, while not yet sufficiently extended to allow computation of activation energies, are in accord with work done recently at Aerojet-General (6) where activation energies for three temperatures regions were calculated on the basis of thermogravimetric experiments. For the region from 124°C to 142°C, \( E_A = 22 \text{ kcal/mole; for the region from 142°C to 160°C, } E_A = 96 \text{ kcal/mole; for the region from 160°C to 180°C, } E_A = 24 \text{ kcal/mole. These experimentors found the melting point to be 142°C. A rather recent Soviet paper (7) lists percent weight loss per six minute period at varying temperatures in the 180°C-240°C region. Assuming the percent weight loss to be directly proportional to the rate constant, activation energy may be calculated using the expression}

\[
\log \left( \frac{\text{loss at } T_2}{\text{loss at } T_1} \right) = \frac{E_A}{R} \left( \frac{T_2 - T_1}{T_2 T_1} \right)
\]

Values of \( E_A \) obtained by this means are inconsistent, but the average value is approximately 24.5 kcal/mole, in very good agreement with Aerojet-General's value above 160°C.
Figure 4. Pressure Versus Time Curve for Hydrazinium Perchlorate at 140° C
Figure 5. Pressure Versus Time Curve for Hydrazinium Perchlorate at 150°C.
Figure 6. Fraction of Hydrazinium Perchlorate Decomposed as a Function of Time
This peculiar increase in stability from 140°C to 150°C may be a result of the fusion of the solid at 141-142°C. Disappearance of decomposition nuclei which exist in the solid state would tend to slow the reaction somewhat by removing high-energy crystal dislocations. However, even in the light of the sudden increase in $E_A$ at 142°C reported by Aerojet-General, the reaction would be expected to proceed more rapidly at the higher temperature. Therefore, these experiments should be regarded as preliminary and additional experiments will be performed in order to clarify the nature of the reaction in this temperature region.

It is of interest to note that the activation energies of HP and HP-2 are quite similar in the solid state reaction (22 kcal/mole and 23 kcal/mole, respectively), and that these compare remarkably well with the value of $E_A$ for the decomposition of liquid anhydrous HClO$_4$ (22-23 kcal/mole). This lends additional weight to the proposition that HClO$_4$ is the effective decomposing agent in all cases and indeed suggests the strong possibility that the rate-determining step is the same in these cases at least.
V. FUTURE WORK

During the next period extensive efforts will be made to establish the activation energies, stoichiometry, and mechanisms of the thermal decomposition of HP. It is hoped that elucidation of the characteristics of the HP reaction will provide information leading to a full understanding of the decomposition of HP-Z and other amino-perchlorate oxidizers.

Additional work is scheduled on anhydrous $\text{HClO}_4$. The determination of vapor pressures at temperatures above the range already covered, and confirmation of pressures already reported, as well as stoichiometry studies, are considered critically important to the goals of the program.

Purification of HAP and determination of its vapor pressure and thermal decomposition characteristics are also scheduled for the coming quarter.

Specific experiments planned for the future include:

- Extension of thermal decomposition studies of HP to both higher and lower temperatures.
- Determination of the vapor pressures of HAP.
- Determination of the thermal decomposition characteristics of HAP.
- Extension of vapor pressure measurements on anhydrous $\text{HClO}_4$ to higher temperatures.
- Determination of thermal decomposition characteristics of anhydrous $\text{HClO}_4$. 
VI. REFERENCES


Section VI

Task 56

CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE
Section VI

CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE

A. R. Young
D. Moy

Report RMD 5043-Q2-64

RMD Project 5043, Task 56
Report Period: 1 April 1964 to 30 June 1964

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

This section of the Advanced Oxidizer Research report summarizes work carried out on a new task (Task 56) which was added to Project 5043 on April 1, 1964. This task is directed toward the synthesis of inorganic N-F oxidizers from difluorodiazine and from nitrosyl fluoride.

Contributors to the studies conducted during the period from 1 April 1964 to 30 June 1964 were: A. R. Young (Project Supervisor), D. Moy (Principal Investigator), J. Crothamel, D. Kates, and E. Egbert.
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ILLUSTRATIONS

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<td>IV</td>
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1. INTRODUCTION

This research program is concerned with the chemistry of difluorodiazine and nitrosyl fluoride, the ultimate objective being the synthesis of N-F containing solid oxidizers from these reagents.

Cis-difluorodiazine has been observed to form a solid compound with arsenic pentafluoride. The studies made on this compound to date indicate that it is ionic and contains the fluorodiazonium cation \((N_2F^+)\). We have, therefore, initiated studies directed toward the utilization of \(N_2FA_{2}F_6\) as a precursor to new solid N-F oxidizers.
II. DISCUSSION

This report describes in detail the synthesis of a 1:1 solid adduct of cis-difluorodiazine with arsenic pentafluoride, and its characterization as fluorodiazonium hexafluoroarsenate, \( \text{N}_2\text{FAsF}_6 \). It also describes attempts to trap \( \text{N}_2\text{F} \) radicals generated from \( \text{N}_2\text{FAsF}_6 \) by reduction of the \( \text{N}_2\text{F}^+ \) cation.

A. REACTION OF cis-DIFLUORODIAZINE WITH ARSENIC PENTAFLUORIDE

During the first year of this program considerable effort was expended in attempts to carry out the addition of radicals to the N=N bond of difluorodiazine (Ref 1). As an extension of this study we decided to examine the possibility that Lewis acids, such as AsF_5, might promote addition to the N=N bond of difluorodiazine. In our initial attempt to utilize arsenic pentafluoride as an addition catalyst it was observed that this reagent reacted rapidly with cis-\( \text{N}_2\text{F}_2 \) to form a white solid which is stable to above 100°C.

By studying the formation of this solid adduct when the proportions of the starting reagents were varied, it was established that the product is a 1:1 adduct (equation 1). The data leading to this conclusion are summarized in Table I. The study also showed that only the cis-isomer of \( \text{N}_2\text{F}_2 \) forms an adduct with AsF_5, and that impurities in the arsenic pentafluoride, such as SiF_4 and BF_3, do not react with cis-\( \text{N}_2\text{F}_2 \) under the conditions which are effective in the formation of cis-\( \text{N}_2\text{F}_2\cdot\text{AsF}_5 \).

\[
\text{N}_2\text{F}_2 + \text{AsF}_5 \rightarrow \text{N}_2\text{F}_2\cdot\text{AsF}_5 \text{ (white solid)} \tag{1}
\]

B. CHARACTERIZATION OF cis-\( \text{N}_2\text{F}_2\cdot\text{AsF}_5 \) PRODUCT

The formation of a solid 1:1 adduct from \( \text{N}_2\text{F}_2 \) and AsF_5 was of interest because of the possibilities that (a) it might be conic, or (b) it might undergo addition reactions more readily than gaseous \( \text{N}_2\text{F}_2 \). A thorough characterization of the product was therefore carried out.

The white solid adduct of AsF_5 and cis-\( \text{N}_2\text{F}_2 \) is stable in glass in an inert atmosphere at room temperature. It decomposes without melting at
approximately 200°C. It has essentially no vapor pressure at room temperature. The adduct is readily soluble in anhydrous HF at room temperatures, but insoluble in nonpolar solvents such as CHF₃, CF₃Cl, C₂F₆, and C₄F₈. It decomposes rapidly at room temperature in AsF₅, forming AsF₅ and N₂.

1. Stoichiometry

In addition to the evidence presented in Table I, the stoichiometry of the white solid can be inferred from quantitative studies of its reactions with water and with sodium fluoride in anhydrous hydrogen fluoride. Reactions of the adduct with water consistently gave nitrous oxide in quantities which were in excellent agreement with the calculated yields predicted by the reaction shown in equation 2. The fact that difluorodiazine does not react readily with water suggested that the adduct was probably not a molecular complex.

The reaction of the adduct with sodium fluoride in HF also serves to confirm the 1:1 stoichiometry. The total nitrogen was recovered in excess of 98% of theoretical according to equation 3 as cis-difluorodiazine with a small nitrous oxide impurity. A small amount of water in the sodium fluoride reagent can account for the formation of some nitrous oxide.

Finally, elemental analysis of a sample of the adduct gave the following results:

| Found      | As, 31.6;  F, 56.8;  N, 11.8 |
| Theory for N₂FAsF₆ | As, 31.8;  F, 56.4;  N, 11.8 |

2. Mass Spectrum

A mass spectrum of N₂FAsF₆ was obtained at 150°C (Table II). It shows only peaks which are identifiable with the compound N₂FAsF₆, or a mixture consisting predominantly of the cis-isomer of N₂F₂ and AsF₅, formed by
TABLE I

PREPARATION OF $N_2F_2AsF_5$

$$cis-N_2F_2 + AsF_5 \rightarrow N_2F_2AsF_5 \text{ (white solid)}$$

<table>
<thead>
<tr>
<th>$N_2F_2$ (mmole)</th>
<th>AsF$_5$ (mmole)</th>
<th>Volatile Products</th>
</tr>
</thead>
</table>
| 1                | 1               | $< 0.2 \text{ mmole}$ $trans-N_2F_2$
|                  |                 | $SiF_4, BF_3$    |
| 2                | 1               | $\sim 1 \text{ mmole}$ $cis-N_2F_2, trans-N_2F_2$
|                  |                 | $SiF_4, BF_3$    |
| 1                | 2               | $\sim 1 \text{ mmole}$ $AsF_5$
|                  |                 | $SiF_4, BF_3, trans-N_2F_2$ |
| $trans-N_2F_2 + AsF_5 \rightarrow$ No Reaction |

TABLE II

MASS SPECTRUM $N_2F.AsF_6$ AT $150^\circ C$

<table>
<thead>
<tr>
<th>M/e</th>
<th>Ion</th>
<th>Relative Intensity</th>
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</thead>
<tbody>
<tr>
<td>19</td>
<td>$F^+$</td>
<td>8.9</td>
</tr>
<tr>
<td>28</td>
<td>$N_2^+$</td>
<td>93.0</td>
</tr>
<tr>
<td>33</td>
<td>NF$^+$</td>
<td>5.2</td>
</tr>
<tr>
<td>47</td>
<td>$N_2F^+$</td>
<td>93.0</td>
</tr>
<tr>
<td>66</td>
<td>$N_2F_2^+$</td>
<td>3.1</td>
</tr>
<tr>
<td>75</td>
<td>As$^+$</td>
<td>6.0</td>
</tr>
<tr>
<td>94</td>
<td>AsF$^+$</td>
<td>6.2</td>
</tr>
<tr>
<td>113</td>
<td>AsF$_2^+$</td>
<td>8.6</td>
</tr>
<tr>
<td>132</td>
<td>AsF$_3^+$</td>
<td>14.2</td>
</tr>
<tr>
<td>151</td>
<td>AsF$_4^+$</td>
<td>100.0</td>
</tr>
</tbody>
</table>

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3. Fluorodiazonium Ion, $N_2F^+$

The data obtained up to this point offered no conclusive evidence concerning the ionic or covalent nature of the $cis-N_2F_2-AsF_6$ adduct. The fact that the reaction of $N_2FAsF_6$ with NaF in HF liberated only the $cis$-isomer of $N_2F_2$ suggested that the solid was a molecular complex. On the other hand, the rapid conversion of the adduct to $N_2O$ by water seemed to be evidence for proposing an ionic structure since $cis-N_2F_2$ does not react readily with water. The results subsequently obtained from studies of the infrared spectrum, $F^{19}$NMR spectrum, and x-ray powder diffraction pattern of the solid strongly supported the ionic structure $N_2F^+AsF_6^-$. 

4. Infrared Spectrum of $N_2FAsF_6$

The infrared spectrum of a thin film of $N_2FAsF_6$ (Figure 1) definitely shows the presence of the hexafluoroarsenate anion by the intense band at 700 cm$^{-1}$. The characteristic absorption bands due to $AsF_6$ (Ref 2) and $cis-N_2F_2$ (Ref 3) are absent. The band at 1050 cm$^{-1}$ is in the region normally assigned to N-F stretching vibrations, and is believed to be characteristic of the fluorodiazonium ion $NF^+$. 

5. $F^{19}$NMR Spectrum

Additional evidence that $N_2FAsF_6$ is a fluorodiazonium salt was obtained from the $F^{19}$NMR spectrum of an HF solution at room temperature (Figure 2). The spectrum shows a fluorine on nitrogen triplet at a chemical shift of -179 ppm from trifluoroacetic acid (TFA) which was used as an external reference. The N-F coupling constant is 328 cps. A comparison of these values with the corresponding chemical shifts and coupling constants of $cis$- and trans-difluorodiazine (Ref 4) shows the chemical shift of the fluorodiazonium ion to be 29 ppm upfield of $cis$-difluorodiazine and 12.4 ppm downfield of the trans-isomer (Table III). The magnitude of the N-F coupling rules out the presence of $cis$- or trans-difluorodiazine. Moreover, the large increase in the N-F coupling constant in the adduct relative to that of $cis-N_2F_2$ suggests an increase in the "s" character of the nitrogen bonding orbital as would be the case in going from $N_2F_2$ ($sp^2$) to $:N^2NF^+ (sp)$. 

---

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Figure 1. Infrared Spectrum of $\text{N}_2\text{F}^+\text{AsF}_6^-$ Film on AgCl
Figure 2. F$^{19}$NMR Spectrum of N$_2$FAsF$_6$ in Anhydrous HF

**TABLE III**

F$^{19}$ CHEMICAL SHIFTS OF N-F COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (Ppm from CF$_3$COOH)</th>
<th>$J_{N-F}$ (Cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-N$_2$F$_2$</td>
<td>-208</td>
<td>145</td>
</tr>
<tr>
<td>trans-N$_2$F$_2$</td>
<td>-167</td>
<td>136</td>
</tr>
<tr>
<td>N$_2$FAsF$_6$</td>
<td>-179.4</td>
<td>328</td>
</tr>
</tbody>
</table>

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There is no $^{19}$F resonance peak assignable to the $\text{AsF}_6^-$ ion in this spectrum. The HF peak is displaced by approximately 10 ppm upfield relative to pure HF and these are conditions indicative of rapid fluoride exchange between HF and the $\text{AsF}_6^-$ ion (Ref 4).

6. X-Ray Diffraction Pattern

The powder diffraction lines of $\text{N}_2\text{FAsF}_6$ were indexed on a rhombohedral unit cell (Table IV) having the following cell constants: $a = 11.49$ Å and $\alpha = 103^\circ$. All of the hexafluoroarsenate salts of the larger univalent metal cations crystallize in the rhombohedral system (Ref 5). The volume of a rhombohedral unit cell having the dimensions given above is 1369 Å$^3$. If one assumes that there are 10 molecules per unit cell, a molecular volume is obtained for $\text{N}_2\text{FAsF}_6$ (136.9 Å$^3$) which is slightly larger than that of $\text{CsAsF}_6$ (Table V). On this basis, a crystal density of 2.8 gm/cc is predicted for $\text{N}_2\text{FAsF}_6$. The observed density of 2.6 gm/cc is in quite good agreement with this value.

C. REACTIONS OF $\text{N}_2\text{FAsF}_6$

The initial product of the reduction of the $\text{N}_2\text{F}^+$ cation should be an $\cdot\text{N}_2\text{F}$ radical (equation 4). It was thought, therefore, that the reduction

$$\text{N}_2\text{F}^+ + e^- \rightarrow \cdot\text{N}_2\text{F} \quad 1/2 \text{N}_2 + 1/2 \text{F}_2 \quad (4)$$

of $\text{N}_2\text{FAsF}_6$ might lead to new compounds containing the fluorazine group (-N=N=NF), as shown in the reactions proposed below (equations 5 through 9).

$$2\cdot\text{N}_2\text{F} \rightarrow \text{FN=N-N=NF} \quad (5)$$

$$\cdot\text{N}_2\text{F} + \cdot\text{CF}_3 \rightarrow \text{CF}_3\cdot\text{N=N=NF} \quad (6)$$

$$\cdot\text{N}_2\text{F} + \cdot\text{Cl} \rightarrow \text{Cl-N=N=NF} \quad (7)$$

$$\cdot\text{N}_2\text{F} + \cdot\text{NF}_2 \rightarrow \text{FN=N-NF}_2 \quad (8)$$

$$\cdot\text{N}_2\text{F} + \text{trans-}\text{N}_2\text{F}_2 \rightarrow \text{F-N=N(NF-NF)N=NF} \quad (9)$$

However, to date we have been unable to produce any fluorazine derivatives other than cis-$\text{N}_2\text{F}_2$ by this approach.

* A single crystal study of $\text{N}_2\text{FAsF}_6$ is presently being conducted at Shell Development Laboratories, Emeryville, California.
TABLE IV
DIFFRACTION PATTERN OF N\textsubscript{2}FAsF\textsubscript{6}

Rhombohedral Unit Cell: \(a = 11.49\ \text{Å}, \alpha = 103^\circ, \rho_{\text{obs}} = 2.6\ \text{gm/cc}, Z = 10\)

<table>
<thead>
<tr>
<th>(h, k, l)</th>
<th>(d) (calc Å)</th>
<th>(d) (obs Å)</th>
<th>(I/I_0) (rel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 1, (\bar{2})</td>
<td>5.18</td>
<td>5.18</td>
<td>40</td>
</tr>
<tr>
<td>1, 1, 1</td>
<td>4.92</td>
<td>4.92</td>
<td>60</td>
</tr>
<tr>
<td>1, 2, (\bar{1})</td>
<td>4.58</td>
<td>4.56</td>
<td>50</td>
</tr>
<tr>
<td>2, 2, (\bar{1}); 1, 2, 1</td>
<td>3.57</td>
<td>3.57</td>
<td>100</td>
</tr>
<tr>
<td>1, 2, (\bar{3})</td>
<td>3.41</td>
<td>3.41</td>
<td>20</td>
</tr>
<tr>
<td>2, 2, 1</td>
<td>2.93</td>
<td>2.90</td>
<td>20</td>
</tr>
<tr>
<td>3, 3, 0; 1, 1, 4; 4, 2, (\bar{3})</td>
<td>2.24</td>
<td>2.23</td>
<td>30</td>
</tr>
<tr>
<td>2, 2, 4; 4, 2, 2</td>
<td>1.79</td>
<td>1.79</td>
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TABLE V
LATTICE CONSTANTS OF HEXAFLUOROARSENNATES

<table>
<thead>
<tr>
<th>Compound</th>
<th>(r^+) (Å)</th>
<th>Lattice Type</th>
<th>Constants</th>
<th>Molecular Vol. ((\text{Å}^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAsF\textsubscript{6}</td>
<td>1.33</td>
<td>Rhombohedral</td>
<td>(a = 4.92\ \text{Å}, \alpha = 97.2^\circ)</td>
<td>120.9</td>
</tr>
<tr>
<td>RbAsF\textsubscript{6}</td>
<td>1.48</td>
<td>Rhombohedral</td>
<td>(a = 5.00\ \text{Å}, \alpha = 96.1^\circ)</td>
<td>124.6</td>
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<tr>
<td>CsAsF\textsubscript{6}</td>
<td>1.69</td>
<td>Rhombohedral</td>
<td>(a = 5.20\ \text{Å}, \alpha = 96.0^\circ)</td>
<td>131.2</td>
</tr>
<tr>
<td>N\textsubscript{2}FAsF\textsubscript{6}</td>
<td>1.84</td>
<td>Rhombohedral</td>
<td>(a = 11.49\ \text{Å}, \alpha = 103^\circ)</td>
<td>136.9</td>
</tr>
</tbody>
</table>
1. Reaction of NO With $N_2FAsF_6$

NO was oxidized on standing with $N_2FAsF_6$ at room temperature with the formation of NOAsF$_6$. The gaseous fraction consisted only of unreacted NO, cis-$N_2F_2$ and $N_2$.

$$2NO + 2N_2FAsF_6 \rightarrow 2NOAsF_6 + \text{cis-}N_2F_2 + N_2$$ (10)

2. Reaction of NO$_2$ With $N_2FAsF_6$

NO$_2$ was easily and rapidly oxidized by $N_2FAsF_6$ at room temperature as evidenced by the rapid disappearance of its brown color. Analysis of the gases showed only $N_2$, cis-$N_2F_2$ and $N_2O$. The solid residue was identified as a mixture of NOAsF$_6$ and NO$_2$AsF$_6$ by x-ray analysis.

$$NO_2 + N_2FAsF_6 \rightarrow N_2O + \text{cis-}N_2F_2 + N_2 + NOAsF_6 + NO_2AsF_6$$ (11)

3. Reaction of $CF_3NO$ With $N_2FAsF_6$

Attempts were made to prepare $CF_3N_2F$ by the following reaction:

$$CF_3NO + N_2FAsF_6 \rightarrow NOAsF_6 + CF_3N_2F$$ (12)

$CF_3NO$ and $N_2FAsF_6$ reacted rapidly below room temperature to give a complex mixture of compounds. Fluorocarbons, $(CF_3)_2NONO$, $CF_3NO_2$ and $(CF_3)_2N$-NO were identified. There was also a small amount of unidentified material present but no evidence was obtained by mass spectral or infrared analysis for N-F bonding. The solid residue was identified as NOAsF$_6$. The desired compound, $CF_3N_2F$ was not detected.

The appearance of the mixture of fluorocarbons $(CF_3)_2NONO$, $CF_3NO_2$ and $(CF_3)_2N$-NO can be accounted for by the reaction of $CF_3^+$ (equation 13) and NO$^-$ radicals (present in $CF_3NO$) with $CF_3NO$ and subsequent reaction products according to the reactions shown in equations 14-17.

$$CF_3NO + N_2FAsF_6 \rightarrow CF_3^+ + NOAsF_6 + \text{cis-}N_2F_2 + N_2$$ (13)

$$CF_3^+ + CF_3NO + NO \rightarrow (CF_3)_2NONO$$ (14)

$$(CF_3)_2NONO \leftrightarrow NO_2 + (CF_3)_2N$$ (15)

$$NO_2^- + CF_3^+ \rightarrow CF_3NO_2$$ (16)
(CF₃)₂N' + NO' → (CF₃)₂N-NO

4. Reaction of CF₃I With N₂FAsF₆

N₂FAsF₆ and CF₃I reacted very vigorously below -80°C to give a mixture of fluorocarbons and noncondensable gases. A red solid residue was left which slowly decomposed to give iodine.

5. Attempted reaction of HCF₃ and ClCF₃ With N₂FAsF₆

Neither HCF₃ nor ClCF₃ appeared to undergo any reaction with N₂FAsF₆ at temperatures from -196°C to room temperature.

6. Reactions of NOCl and HCl With N₂FAsF₆

Attempts were made to prepare ClN₂F by the reaction of N₂FAsF₆ with NOCl and HCl. Excess NOCl reacted rapidly with N₂FAsF₆ on warming the cold mixture to room temperature. cis-N₂F₂, Cl₂, N₂O and N₂ were identified as gaseous products of this reaction. The solid residue was NOAsF₆.

A reaction of N₂FAsF₆ with HCl produced Cl₂, cis-N₂F₂, N₂ and AsF₅.

7. Attempted Reactions of N₂F₄ and trans-N₂F₂ With N₂F' Radical

The N₂F' radical was liberated by the reaction of NO with N₂FAsF₆. No apparent coupling of the N₂F' radical with either NF₂ or trans-N₂F₂ was observed, however, when N₂FAsF₆ was reacted with mixtures of NO and N₂F₄, and NO and trans-N₂F₂.

8. Attempted Reaction of N₂F' Radicals With Perfluoro-olefins

C₃F₆ and C₄F₈ were recovered intact from reaction mixtures of N₂FAsF₆ with C₃F₆ and NO, and C₄F₈ and NO. N₂FAsF₆ reacted violently with C₂F₄ below -80°C to give a mixture of fluorocarbons, AsF₅, and N₂. Addition of Freon solvents had no moderating effect on the reaction.
III. EXPERIMENTAL

A. REACTION OF cis-DIFLUORODIAZINE WITH ARSENIC PENTAFLUORIDE

Arsenic pentafluoride (Peninsular Chem Research) contained small amounts of SiF₄ and BF₃ as impurities. cis-Difluorodiazine (Air Products) contained small amounts of trans-N₂F₂ as the principal impurity. The reagents were used without further purification.

Quantities of cis-N₂F₂ and AsF₅ were measured separately in a calibrated Monel bulb then condensed into a Kel-F reaction tube at -196°C. The tube was allowed to warm to room temperature. After 1-2 hours the residual pressure in the tube was measured and gas samples taken for infrared analysis.

Less than 10% of the original reactants were recovered on mixing a 1:1 ratio of cis-N₂F₂ and AsF₅. The residual gas was identified as SiF₄, BF₃, and trans-N₂F₂, all known impurities in the starting materials. When a two-fold excess of one reagent or the other was used, a complete recovery of the excess reagent was obtained at the end of the preparative run.

In a separate experiment, trans-N₂F₂ and AsF₅ did not react to form a stable product.

B. HYDROLYSIS OF N₂FAsF₆

Two samples of N₂FAsF₆ (0.73 mmole and 1.14 mmole) produced 0.67 mmole (93% of theoretical) and 1.12 mmole (98.5% of theoretical) respectively of N₂O on hydrolysis in a closed Kel-F tube. N₂O was distilled from the hydrolysis tube at -80°C and identified by its IR spectrum.

C. REACTION OF N₂FAsF₆ WITH NaF IN HF

Anhydrous HF was obtained by reacting water-contaminated HF with N₂FAsF₆ until N₂O was no longer evolved. The anhydrous HF was recovered and used in subsequent experiments.
To a solution of 0.87 mmole of N\textsubscript{2}FAsF\textsubscript{6} in approximately 5 ml of anhydrous HF was added excess NaF. After shaking for several minutes the gaseous evolution ceased. The reactor was cooled to -80°C and 0.85 mmole (98% theoretical) of gas (>95% cis-N\textsubscript{2}F\textsubscript{2}, balance N\textsubscript{2}O) was obtained. These were identified by their IR spectra.

D. MASS SPECTRUM

A sample of N\textsubscript{2}FAsF\textsubscript{6} in a small Monel tube was attached to a Bendix Time-of-Flight mass spectrometer. It was evacuated and heated to 150°C in vacuo while open to the mass spectrometer.

E. INFRARED SPECTRUM

A 1:1 mole ration of AsF\textsubscript{5} and cis-N\textsubscript{2}F\textsubscript{2} were condensed on a silver chloride window at -196°C. The window was warmed to room temperature and the residual gases removed. By this procedure a thin film of N\textsubscript{2}FAsF\textsubscript{6} was formed on the window. The film was then scanned on a Perkin-Elmer 21 Spectrometer from 2 to 15μ.

F. F\textsuperscript{19}NMR SPECTRUM

The F\textsuperscript{19}NMR spectrum of N\textsubscript{2}FAsF\textsubscript{6} in anhydrous HF (approximately 40% solution) was obtained on a Varian HR-60 Spectrometer at room temperature. Trifluoroacetic acid (TFA) was used as an external reference. Approximate chemical shift (uncorrected for bulk susceptibility effects) and N-F coupling constants were obtained from the location of TFA side bands with an accuracy of ± 10 cps. Sample tubes were made by fitting a 6" x 0.5" Teflon tube to a valve and ball joint by means of Swagelok connections. The TFA reference capillary was taped to the outside of the tube.

G. X-RAY POWDER DIFFRACTION PATTERN

X-ray powder patterns were obtained on samples of N\textsubscript{2}FAsF\textsubscript{6} from separate preparative runs and a sample recovered from HF solution. All of the patterns were identical. The powder diffraction patterns were photographed with CuK\textalpha radiation from a nickel filter. The x-ray samples were sealed under nitrogen in Pyrex capillaries.

H. DENSITY OF N\textsubscript{2}FAsF\textsubscript{6}

The density of FC-75 \* (d\textsubscript{25} = 1.77 gm/cc) was determined with a 2 ml pycnometer. The density of N\textsubscript{2}FAsF\textsubscript{6} was determined to be 2.6 gm/cc by displacement of FC-75.

\*Minnesota Mining and Manufacturing Co.

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Report RMD 5043-Q2-64
I. REACTIONS OF N₂FA₇F₆

1. With Nitric Oxide

2.3 mmole N₂FA₇F₆ and 1.1 mmole NO were mixed at -196°C and allowed to warm to room temperature. After standing for several hours, the gases were analyzed by mass spectral and IR methods. The principal components were cis-N₂F₂ and N₂ (in roughly equivalent amounts). The solid residue was analyzed by IR and x-ray analysis and found to be NOAsF₆. Varying the ratio of N₂FA₇F₆:NO did not change the reaction product.

2. With Nitrogen Dioxide

1.25 mmole each of N₂FA₇F₆ and NO₂ were mixed at -196°C. On warming, the brown color of NO₂ quickly disappeared. Analysis of the bases by IR showed predominantly N₂O, with much smaller amounts of N₂ and cis-N₂F₂. The solid was determined to be a mixture of NOAsF₆ and NO₂AsF₆.

3. With CF₃NO

1:1 and 1:2 mole ratio mixtures of N₂FA₇F₆ and CF₃NO gave essentially identical results. The materials were mixed together at -196°C and allowed to warm slowly. Rapid evolution of gas occurred well below room temperature with a gradual disappearance of the blue color of CF₃NO. The mixture of gases was fractionated at -80°C, -120°C and -196°C and analyzed by IR and mass spectral methods. (CF₃)₂NONO, CF₃NO₂, CF₃N-NO and unreacted CF₃NO were identified. A small fraction collecting at -80°C had unidentified IR bonds at the 6.15 μ, 10.3 μ and 7-8 μ regions, but mass spectral analysis failed to detect any N-F mass fragments. The solid residue was identified as NOAsF₆.

4. With CF₃I

0.8 mmole CF₃I was condensed on 0.8 mmole N₂FA₇F₆ at -196°C. On warming to -80°C a rapid reaction occurred leaving an unstable red residue and a mixture of fluorocarbons and noncondensable gases. The red residue liberated iodine on standing.

5. With HCF₃ and ClCF₃

Equimolar amounts of HCF₃ and N₂FA₇F₆ and ClCF₃ and N₂FA₇F₆ appeared to undergo no reaction at temperatures from -196°C to room temperature.
6. With Nitrosyl Chloride

0.5 mmole \( \text{N}_2\text{FAsF}_6 \) and 3 mmole NOCl were mixed at \(-196^\circ\text{C}\) and underwent a rapid reaction at temperatures below room temperature. On fractionation, approximately 50% \( \text{N}_2 \) was obtained. The condensable fraction consisted mainly of \( \text{Cl}_2 \) with a smaller amount of cis-\( \text{N}_2\text{F}_2 \).

7. With HCl

1.2 mmole of HCl and 1.2 mmole \( \text{N}_2\text{FAsF}_6 \) reacted below room temperature to give predominantly noncondensable gases. The condensable fraction contained mostly \( \text{Cl}_2 \) with only traces of cis-\( \text{N}_2\text{F}_2 \).

8. With \( \text{N}_2\text{F}_4 \)

A mixture of 0.8 mmole of \( \text{N}_2\text{FAsF}_6 \) and 0.8 mmole \( \text{N}_2\text{F}_4 \) gave no reaction on standing for 24 hours. To the mixture was added 0.8 mmole NO. After reacting at room temperature for several hours the gases were fractionated at \(-196^\circ\text{C}\) and \(-160^\circ\text{C}\). Approximately 95% of the original amount of \( \text{N}_2\text{F}_4 \) was recovered unchanged. Traces of \( \text{N}_2\text{O} \) and \( \text{NF}_3 \) were observed in the \(-196^\circ\text{C}\) trap. Noncondensables made up the balance of the gaseous fraction.

9. With trans-\( \text{N}_2\text{F}_2 \)

No evidence of an addition of \( \text{N}_2\text{F}^- \) radicals was observed in mixing equimolar amounts of \( \text{N}_2\text{FAsF}_6 \), trans-\( \text{N}_2\text{F}_2 \) and NO.

10. With \( \text{C}_2\text{F}_4 \)

An equimolar mixture of \( \text{C}_2\text{F}_4 \) and \( \text{N}_2\text{FAsF}_6 \) reacted below \(-80^\circ\text{C}\). Fractionation of the gases gave approximately 35% \( \text{N}_2 \), 60% \( \text{CF}_4 \), 5% of \( \text{C}_2\text{F}_6 \), \( \text{COF}_2 \) and \( \text{AsF}_5 \).
IV. FUTURE WORK

During the next quarter work will consist of attempts to synthesize energetic fluorodiazonium salts by further reactions of cis-$N_2F_2$ and by metathesis from $N_2F^+AsF_6^-$. 
V. REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division,
   Advanced Oxidizer Research (U) RMD-AOR-ATS-63,
   (annual summary report) Contract No. 4079(00), February 1964.


5. G. A. Olah, S. J. Kuhn, W. S. Tolomeo and E. B. Boher,

   1963, 4408.