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ADVANCED OXIDIZER RESEARCH (U)

SEMIANNUAL REPORT RMD-5043-SA-2

Report Period: 1 July 1966 to 31 December 1966

Office of Naval Research Contract No. N00r 4364(00)

January 31, 1967

Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

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Report RMD-5043-SA-2
FOREWORD

This report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of oxidizer chemistry conducted over the period from July 1, 1966 to December 31, 1966. This research was sponsored by the Office of Naval Research with Mr. Richard L. Hanson serving as Scientific Officer.

Contributors to the work described in this report are as follows:

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Dr. Josephine Readio, N.M.R. Analysis

Mr. Boyd Fagan, X-ray Analysis
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ABSTRACT

The existence of trifluorodiazyl ions in BrF₅ and in IF₅ was established by F⁴¹ n.m.r. and infrared analyses. Solutions of N₂F₃AsF₆ in IF₅ treated with perchlorates showed absorptions of N₂F₃⁺ and ClO₄⁻ in the infrared.

Attempts to isolate trifluorodiazyl perchlorate from solution were not successful.

An attempt to prepare N₂F₅ by reaction of N₂F₃AsF₆ with C₅CNF₂ at -70 resulted in the formation of N₂F₄ and trans-N₂F₂.

Attempts to prepare new interhalogen oxides by the fluorination of Cl₂O₂AsF₆ and NOCl·O₂AsF₆ were unsuccessful.
INTRODUCTION

This research effort is directed toward the synthesis of new inorganic oxidizers with potential application as liquid or solid propellants. The scope of our synthesis research includes the chemistry of nitrogen fluorides, oxygen fluorides, and interhalogen compounds. During this report period emphasis has been placed on attempts to prepare trifluorodiazyl perchlorate (N$_2$F$_3$ClO$_4$).

Evidence of the coexistence of trifluorodiazyl and perchlorate ions in iodine pentafluoride was established, however, efforts to isolate the salt were not successful.
DISCUSSION

A. Reactions of Trifluorodiazyl (N₂F₃⁺) Salts

A number of stable salts containing cationic N-F species have been reported in recent years. Salts of N₂F⁺ (Refs 1, 2, 3), N₂F₃⁺ (Refs 4, 5), and ONF₂⁺ (Refs 6, 7) are prepared by reactions of covalent nitrogen fluorides with fluorides of Group V elements, as shown in equation 1. Salts of NF₄⁺ (Refs 8, 9, 10) are obtained in reactions involving elemental fluorine, as shown in equations 2 and 3. Finally, NH₃F⁺ (Ref 4) salts are obtained by reactions of N-fluorocarbamates with strong protonic acids (equation 4).

\[ \text{N}_x\text{F}_y + \text{MF}_5 \rightarrow \text{N}_x\text{F}_{y-1}\text{MF}_6^- \quad (M = \text{P, As, Sb}) \]  
(1)

\[ \text{NF}_3 + \text{F}_2 + \text{MF}_5 \rightarrow \text{NF}_4^+\text{MF}_6^- \quad (M = \text{As, Sb}) \]  
(2)

\[ \text{N}_2\text{F}_3^+\text{AsF}_6^- + 2\text{F}_2 \rightarrow \text{NF}_4^+\text{AsF}_6^- + \text{NF}_3 \]  
(3)

\[ \text{FNHCOOR} + 2\text{HClO}_4 \rightarrow \text{H}_2\text{NFClO}_4 + \text{CO}_2 + \text{RCIO}_4 \]  
(4)

The fluorammonium (NH₃F⁺) cation is the only N-F cation which has been demonstrated to form stable salts with oxygen-containing anions. Our
most recent work in this area of N-F chemistry has been directed toward the

synthesis of a perchlorate of the trifluorodiazyl (N₂F₃⁺) ion.

1. Reaction of N₂F₃AsF₆ with Perchlorates

   We have previously reported attempts to react N₂F₃AsF₆ with
   perchlorates in hydrogen fluoride (Ref 12), and in sulfur dioxide at subambient
temperatures (Ref 13). We found that the addition of soluble perchlorates to
solutions of N₂F₃AsF₆ in hydrogen fluoride results in the evolution of tetra-
fluorohydrazine. Similarly, because of a slow reaction of the trifluorodiazyl
ion with sulfur dioxide, we obtained NOClO₄ from mixtures of N₂F₃AsF₆ and
(CH₃)₄ClO₄ in that solvent.

   The behavior of N₂F₃AsF₆ in other liquids has now been briefly
investigated in the hopes of uncovering a suitable medium for the desired
metathesis. The results of these tests are presented in Table I.
Table I

N₂F₃AsF₆ Solubility Study

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO₃F</td>
<td>ambient</td>
<td>Soluble with rapid decomposition</td>
</tr>
<tr>
<td>CF₃OF</td>
<td>-95°</td>
<td>Insoluble</td>
</tr>
<tr>
<td>SF₄</td>
<td>-78° → -40°</td>
<td>Insoluble</td>
</tr>
<tr>
<td>CF₃Cl</td>
<td>ambient</td>
<td>Insoluble, slight gassing</td>
</tr>
<tr>
<td>(CF₃)₂CO</td>
<td>-28°</td>
<td>Insoluble</td>
</tr>
<tr>
<td>BrF₅</td>
<td>-60° → ambient</td>
<td>Soluble</td>
</tr>
<tr>
<td>IF₅</td>
<td>ambient</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

Confirmation of the existence of trifluorodiazyl ions in BrF₅

and in IF₅ was obtained by F¹⁹ n.m.r. (Figure 1) and liquid phase infrared analyses (Figure 2).

Efforts to achieve an exchange reaction between N₂F₃AsF₆

and perchlorates were resumed using IF₅ as a solvent medium. Because of the low volatility of IF₅, it was convenient to carry out most of the operations involved in these experiments in a glove box.

Equimolar Mixtures of N₂F₃AsF₆ and CsClO₄ in IF₅

When IF₅ solutions containing equimolar quantities of N₂F₃AsF₆ and CsClO₄ were mixed in an open tube (under dry nitrogen in a
Figure 1. A. $^{19}F$ n.m.r. of Trifluorodiazyl Ion in BrF$_5$ at -60°

B. $^{19}F$ n.m.r. of Trifluorodiazyl Ion in IF$_5$ at Room Temperature
Figure 2. Infrared Spectrum of NaF$_2$As$_2$F$_6$ in IF$_5$

( NaCl Liquid Cell )

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glove box) vigorous gas evolution was observed. In spite of this indication
of decomposition of trifluorodiazyl ions, the infrared spectrum of the residual
solution shows a small peak at 920 cm\(^{-1}\), characteristic of \(\text{N}_2\text{F}_3^+\), and a very strong
perchlorate absorption at 1150-1040 cm\(^{-1}\) (Figure 3). The higher frequency
absorptions of \(\text{N}_2\text{F}_3^+\) (Figure 2) are not apparent in Figure 3, but they may well
be masked by the perchlorate and window absorptions. Other features of the
spectrum (Figure 3) include an increase (see Figure 2) in the absorption at
2300 cm\(^{-1}\), which is probably due to nitrosonium ion (\(\text{NO}^+\)), and a new ab-
sorption at 1240 cm\(^{-1}\) (8 µ) in the nitrite ion region.

Although there was obviously some loss of \(\text{N}_2\text{F}_3^+\) in this run,
the results were encouraging. The strong concentration of perchlorate in the
residual solution seemed to rule out any conclusion that the loss was due to
instability of trifluorodiazyl perchlorate.

The equimolar reaction of \(\text{N}_2\text{F}_3\text{AsF}_6\) with \(\text{CaClO}_4\) in \(\text{IF}_5\)
was repeated in a closed Kel-F apparatus, in order to determine the composition
and approximate quantity of gas liberated on mixing the reagents. In this experiment, one millimole each of the reagents were observed to produce approximately 0.3 millimoles of gas. The gas was identified as $\text{N}_2\text{F}_4$ with a trace of $\text{ClO}_2\text{F}$ (Figure 4). Since the $\text{N}_2\text{F}_4$ liberated on initial mixing of the reagents was significantly less than the $\text{N}_2\text{F}_3\text{AsF}_6$ charged, there was reason to assume that $\text{N}_2\text{F}_3^+$ and $\text{ClO}_4^-$ ions were still present in solution. The solvent was removed by vacuum distillation at room temperature and the residual solid was examined by infrared analysis (Figure 5). It exhibited only $\text{ClO}_4^-$ and $\text{AsF}_6^-$ absorptions. One must conclude, therefore, that the residual $\text{N}_2\text{F}_3^+$ was discharged as $\text{N}_2\text{F}_4$ during the distillation of the IF$_5$.

Reaction of CsClO$_4$ with Excess $\text{N}_2\text{F}_3\text{AsF}_6$

An IF$_5$ solution containing approximately 2 millimoles of $\text{N}_2\text{F}_3\text{AsF}_6$ was mixed with a solution of 1 millimole CsClO$_4$. The solutions were mixed in a closed Kel-F apparatus under an atmosphere of nitrogen.

A rapid exothermic reaction ensued, and a suspension of needle-like white
Figure 4. Gaseous Products from Equimolar Reaction of $\text{N}_2\text{F}_3\text{AsF}_7$ with $\text{CsClO}_4$ in $\text{IF}_5$
crystals appeared. After 24 hours the crystals settled to the top of the

solvent, because of the design of the apparatus however, it was not possible

to separate the fine crystals from the liquid. A sample of the liquid (24 hours

after mixing the reagents) was withdrawn for infrared analysis. As in the case

of the equimolar reaction, it showed a strong perchlorate absorption and an

N-F absorption at 920 cm\(^{-1}\) (Figure 6). After removal of the solvent, an

infrared of the residual solid showed no N-F absorptions. Thus, even though

a two-fold excess of \(\text{N}_2\text{F}_3^+\) to perchlorate had been present initially, only per-

chlorate (and \(\text{AsF}_6^-\)) was recovered in the residual solid.

Reaction of \(\text{N}_2\text{F}_3\text{AsF}_6\) with \(\text{KClO}_4\)

The reaction of \(\text{N}_2\text{F}_3\text{AsF}_6\) with \(\text{KClO}_4\) (equimolar) bears men-
tioning because \(\text{KClO}_4\) was observed to be only sparingly soluble in \(\text{IF}_5\), thus

the concentration of \(\text{N}_2\text{F}_3^+\) in solution was initially far greater than that of

perchlorate. Indeed, the infrared spectrum of the solution (Figure 7) obtained

immediately after the addition of \(\text{KClO}_4\) shows no trace of perchlorate. After
twelve hours, the solution still showed no significant absorption in the perchlorate region (9-10 μ), yet the N$_2$F$_3^+$ absorptions at 900 cm$^{-1}$, 1100 cm$^{-1}$, 1300 cm$^{-1}$, and 1500 cm$^{-1}$ had decreased considerably (Figure 8). After two days, a sample of the gas phase was examined by infrared analysis. It contained approximately equivalent amounts of ClO$_4^-$ and NF$_3$, along with a smaller quantity of trans-N$_2$F$_2$ (Figure 4).

Although these results suggest the possibility of a reaction between N$_2$F$_3^+$ and perchlorate, the residual solid (Figure 10) showed a strong perchlorate absorption.

Summary of Results of IF$_3$ Studies

The results obtained in our studies of the behavior of IF$_3$ solutions of the trifluorodiazyl ion in the presence of perchlorate, do not lead themselves to simple interpretation. Infrared evidence was obtained that N$_2$F$_3^+$ and ClO$_4^-$ may coexist in solution, yet no N$_2$F$_3^+$ salt could be recovered from such solutions. There was also evidence of decomposition of perchlorate
Figure 8. Solution Phase. Equimolar Mixture of KClO₃ and N₂H₄ in 72 Hours.
via the formation of ClO$_3$F, yet even when an excess of N$_2$F$_3$AsF$_6$ was used,

most of the perchlorate was recovered. An additional confusing fact is that

the trifluorodiazyl ion in some runs was converted to N$_2$F$_4$ and in others to a

mixture of N$_2$F$_3$ and trans-N$_2$F$_2$. We do not have the experimental data necessary

to completely describe the processes that occur in N$_2$F$_3$AsF$_6$-MClO$_4$-IF$_5$ systems.

We are fairly certain, however, that the IF$_5$ plays an active role via a reaction

with perchlorate ions. For this reason we plan to investigate the behavior of

tetrafluoroperchlorate (ClF$_4^-$) salts with solutions of N$_2$F$_3$AsF$_6$ in IF$_5$. 
2. Reactions of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ with Perchlorates

An alternate approach to the synthesis of trifluorodiazyl perchlorate involves the use of the low melting (74-78°) tetrafluorohydrazine-antimony pentafluoride adduct (Ref 4) as a solvent and as a source of the trifluorodiazyl cation (equation 5).

$$
\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11} + \text{CsClO}_4 \xrightarrow{80-90^\circ\text{C}} \text{N}_2\text{F}_3\text{ClO}_4 + \text{CsSb}_2\text{F}_{11}
$$

Equation 5

Compatibility of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ with $\text{CsClO}_4$

When approximately equimolar amounts of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ and $\text{CsClO}_4$ were ground together in an agate mortar, no visual indication of reaction was observed. However, a more recently prepared sample of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ did deflagrate upon mixing with $\text{CsClO}_4$. For reasons to be discussed later, this result is believed to be anomalous. Additional confirmation that the materials are compatible is being sought.

Compatibility of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ with $\text{CsClO}_4$ at 90°C

When a mixture of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ and $\text{CsClO}_4$ was heated to 90°C,
well above the melting point of the antimony complex, a small amount of gas

was liberated which contained ClO₃⁻F and NF₃. However, the bulk of the solid

material charged was recovered and the presence of ClO₄⁻, SbF₆⁻ and N₂F₃⁺ was

established by infrared analysis. The results of X-ray analysis of the residual

solid mixture cannot be interpreted unambiguously (Table II). The diffraction

patterns of N₂F₃Sb₂F₁₁ and CsSbF₆ are quite similar and one might expect the

same to hold true for N₂F₃ClO₄ and CsClO₄.

| Table II |
| Comparison of Diffraction Patterns (Principal Lines) |

<table>
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<th>N₂F₃Sb₂F₁₁</th>
<th>CsSbF₆ (CsSb₂F₁₁?)</th>
<th>CsClO₄</th>
<th>Reaction Product</th>
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<td>I/I₀</td>
<td>d, Å</td>
<td>I/I₀</td>
</tr>
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<td>60</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>3.89</td>
<td>100</td>
<td>3.95</td>
<td>100</td>
</tr>
<tr>
<td>3.56</td>
<td>100</td>
<td>3.53</td>
<td>70</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>2.18</td>
<td>1</td>
<td>2.19</td>
<td>35</td>
</tr>
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</table>

However, extraction of the reaction product at low temperatures with SO₂

yielded an insoluble solid which showed only SbF₆⁻ and ClO₄⁻ in the infrared.
A small unidentified SO₂ soluble fraction was presumed to be unreacted

\[ \text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11} \].

In a similar experiment CsClO₄ was added to molten

\[ \text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11} \] at 80°C. Upon addition of the CsClO₄, a vigorous reaction ensued, accompanied by a pressure surge. Although the evolved gases were not completely trapped, a portion was identified by infrared analysis as NF₃ and ClO₃F. The solid residue has an infrared absorption attributable to SbF₆⁻ (Sb₂F₁₁⁻), and is apparently pure CsSbF₆ or CsSb₂F₁₁ (equation 6).

\[ \text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11} + \text{CsClO}_4 \xrightarrow{?} [\text{N}_2\text{F}_3\text{ClO}_4] \rightarrow \text{NF}_3 + \text{ClO}_3\text{F} + \text{CsSb}_2\text{F}_{11} \] (6)

Since \( \text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11} \) and CsClO₄ react vigorously at elevated temperatures, an attempt was made to prepare \( \text{N}_2\text{F}_3\text{ClO}_4 \) by suspending CsClO₄ in SbF₆ and subsequently adding \( \text{N}_2\text{F}_4 \). In this manner a white amorphous solid (1) was obtained which contained \( \text{N}_2\text{F}_3^+ \), \( \text{SbF}_6^- \) and \( \text{ClO}_4^- \) by infrared. Heating a portion of 1 to 80°C resulted in the liberation of NF₃ and ClO₃F, and left a residue of CsSbF₆. Extraction of 1 with SO₂ at low temperatures resulted in the
isolation of $N_2F_3Sb_2F_{11}$. The insoluble fraction contained $ClO_4^-$ and $SbF_6^-$ absorptions in the infrared. This indicates that the reaction product (I) is simply a mixture of $N_2F_3Sb_2F_{11}$ and $CsClO_4$ (equation 7). It is also additional evidence that the two salts are compatible at room temperature.

$$2SbF_5 + CsClO_4 + N_2F_4 \rightarrow N_2F_3Sb_2F_{11} + CsClO_4 \xrightarrow{\Delta} ClO_4^-F + NF_3 + CsSb_2F_{11}$$ (7)

SO$_2$ extraction

$$N_2F_3Sb_2F_{11} \rightarrow CsClO_4$$

Compatibility of $N_2F_3Sb_2F_{11}$ with $CsClO_4$ by Differential Thermal Analysis

Since $N_2F_3Sb_2F_{11}$ and $CsClO_4$ appear to be compatible at room temperature but extremely reactive at elevated temperatures, an attempt is currently being made to determine by differential thermal analysis whether the desired perchlorate is being formed at some intermediate temperature and subsequently decomposing (equation 8). It was during the initiation of these studies that difficulty was encountered in preparing mixtures of $N_2F_3Sb_2F_{11}$ and $CsClO_4$. When freshly prepared $N_2F_3Sb_2F_{11}$ was mixed with $CsClO_4$ on an agate
mortar deflagration occurred. Pre-grinding the materials and then mixing
them resulted in a delayed ignition. Although the infrared spectrum of the
$\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ is consistent with prior samples, the salt appeared to undergo
several transformations near room temperature in the differential thermal
analysis apparatus. Since these results appear to be anomalous we believe that
the difficulty is associated with one particular sample of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ and plan
to pursue this investigation further, after preparing a new supply of $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$.

3. Reaction of $\text{N}_2\text{F}_3\text{AsF}_6$ with $\text{O}_3\text{CNF}_2$

An attempt was made to isolate $\text{N}_2\text{F}_5$ via the reaction of
$\text{N}_2\text{F}_3\text{AsF}_6$ with $\text{O}_3\text{CNF}_2$ (equation 9). Since the solid reactants deflagrate upon
$\text{N}_2\text{F}_3\text{AsF}_6 + \text{O}_3\text{CNF}_2 \rightarrow \text{N}_2\text{F}_5 + \text{O}_3\text{CA}_{2}\text{F}_6$ (9)
contact, $\text{O}_3\text{CNF}_2$ was added to a solution of $\text{N}_2\text{F}_3\text{AsF}_6$ in liquid $\text{SO}_2$ at $-70^\circ\text{C}$.

An immediate reaction took place and a gaseous product was obtained which con-
tained $\text{N}_2\text{F}_4$ and possibly $\text{N}_2\text{F}_3$. Removal of the solvent at $-50^\circ\text{C}$ gave a solid
residue which was shown to be $O_3CAsF_6$. The reaction probably proceeds

as shown in equation 10.

$$N_2F_3AsF_6 + O_2CNF_2 \xrightarrow{-70^\circ C/SO_2} O_3CAsF_6 + [N_3F_3] \xrightarrow{} N_2F_4 + 1/2 N_2F_2$$ (10)

B. Fluorination Studies

In addition to pursuing the synthesis of new solid oxidizers from the

Group V pentafluoride adducts of simple N-F compounds, we have initiated a

study of the fluorination and oxyfluorination of chlorine-containing compounds

with the view of obtaining new interhalogen compounds. Thus we have investigated

the fluorination of $Cl_2NF$ as a possible route to $F_3ClNF$ and the fluorination of

$"Cl_2\cdot OAsF_6"$ as a route to interhalogen oxides (Ref 13). Additional work was
done in this area during this report period.

1. Reaction of $"Cl_2\cdot OAsF_6"$ with Fluorine

Chlorine forms an uncharacterized purple complex with $O_2AsF_6$

which is stable at $-78^\circ C$ (Ref 14). An investigation of the fluorination of this
complex had been initiated with the purpose of preparing new interhalogen oxides. In a previously reported experiment (Ref 13), the fluorination of Cl₂·O₂AsF₆ produced a mixture of gaseous products including Cl₂, O₂, ClO₂, and an unidentified minor product. The reaction has since been repeated at a higher fluorine pressure in an attempt to increase the amount of the minor constituent for identification. However, the only gaseous products obtained were O₂, Cl₂, ClO₂ and ClO₃F.

2. Reaction of NOCl with O₂AsF₆

The possibility of preparing a complex between NOCl and O₂AsF₆ was investigated, also with the view of preparing new interhalogen compounds (equations 11, 12).

\[
\text{NOCl} + \text{O₂AsF₆} \rightarrow \text{NOCl·O₂AsF₆} \quad (11)
\]

\[
\text{NOCl·O₂AsF₆} + \text{F₂} \rightarrow \text{F₂ClO₇} + \text{NOAsF₆} + \ldots \quad (12)
\]

In an initial experiment NOCl was condensed on O₂AsF₆ and the reaction mixture was allowed to warm to room temperature. No complex
was formed and the reactants were substantially recovered with only a trace
of NO₃F being formed. When the reaction was repeated and the reagents
brought in contact for a longer period of time, only two thirds of the NOCl
charged was recovered and a non-condensable gas, presumably oxygen, was
liberated. Upon hydrolysis, the white solid product gave a positive test for
NO₂⁻ indicating the presence of NO⁺. Since the overall reaction appears to be
the formation of NOAsF₆ with the liberation of O₂ rather than the formation of
the desired complex, we do not intend to pursue this reaction further.
EXPERIMENTAL

Reaction of $N_2F_3Sb_2F_{11}$ and CsClO$_4$

A Kel-F reactor was charged with a mixture of 0.296 g (0.4 mmole) of $N_2F_3Sb_2F_{11}$ and 0.696 g (0.3 mmole) of CsClO$_4$ and heated to 70°C when a yellow gas was evolved. The reactor was pumped on and heating continued to 90°C. The evolved gas was found to contain ClO$_3$F and NF$_3$. The infrared spectrum of the residual solid (0.83 g) showed the presence of $N_2F_3^+$, ClO$_4^-$ and SbF$_6^{2-}$. Extraction of the reaction product at low temperatures with SO$_2$ yielded an insoluble solid which showed only SbF$_6^{2-}$ and ClO$_4^-$ in the infrared.

A small SO$_2$ soluble fraction was presumed to be unreacted $N_2F_3Sb_2F_{11}$.

In a similar experiment 0.7559 (1.4 mmole) of $N_2F_3Sb_2F_{11}$ was heated to 80°C and then 0.696 g (0.3 mmole) of CsClO$_4$ was added. A vigorous reaction ensued with the evolution of NF$_3$ and ClO$_3$F. The residual solid has an infrared absorption attributable to SbF$_6^{2-}$ and is apparently pure CsSbF$_6$.
Reaction of $\text{N}_2\text{F}_4\text{Sb}_2\text{F}_{11}$ with CsClO$_4$ in Excess SbF$_5$

To a suspension of 0.696 g (13 mmole) of CsClO$_4$ in 2 ml of SbF$_5$ was added $\text{N}_2\text{F}_4$. The pressure of $\text{N}_2\text{F}_4$ in the system was kept below 100 mm. The reaction mixture turned yellow and finally orange. After standing overnight the reaction mixture was pumped on in vacuo at 40°C for several hours to yield an amorphous solid (I) which contained $\text{N}_2\text{F}_4^+$, SbF$_6^-$ and ClO$_4^-$ by infrared analysis. Extraction of I with SO$_2$ resulted in the isolation of $\text{N}_2\text{F}_4\text{Sb}_2\text{F}_{11}$. The insoluble fraction contained SbF$_6^-$ and ClO$_4^-$ absorptions in the infrared.

Reaction of $\text{N}_2\text{F}_4\text{AsF}_5$ with $\text{CsCNF}_2$

To 0.274 g (1 mmole) of $\text{N}_2\text{F}_4\text{AsF}_5$ in approximately 10 ml of SO$_2$ at -70°C was added 0.295 g (1 mmole) of $\text{CsCNF}_2$. The reaction mixture immediately turned brown and then yellow. The reaction mixture was pumped on at -70°C and $\text{N}_2\text{F}_4$ was collected in a -196°C trap. The reactor was then allowed to warm slowly to room temperature while being pumped on. The

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materials collected in this way contained SO₂ and N₂F₄. The residual solid
was identified as G₂CA₃F₆.

Reaction of NOCl with O₂AsF₆

To 0.276 g (0.8 mmole) of O₂AsF₆ at -196°C was added 1.75 mmole
of NOCl. The reaction mixture was allowed to warm slowly to room temperature
with stirring. The NOCl was recondensed on the solid several times. Finally
the reaction mixture was stirred at -6°C for an hour. No evidence for the
formation of a complex was obtained. In addition to recovering two thirds of the
NOCl, a non-condensable gas, presumably O₂ was liberated. The residual solid
upon hydrolysis gave a positive test for NO₃⁻ indicating the presence of NO⁺.
The overall reaction appears to be the formation of NOAsF₆ and oxygen.

IF₅ Studies

The IF₅ used in the attempts to achieve a metathesis between N₂F₃AsF₆
and perchlorates was obtained from Mathieson Co. The commercial material
contains colored impurities (I₂ and lower fluorides) which were removed by
bubbling fluorine through the liquid at room temperature. The colorless

IF₅ was then distilled in an all glass apparatus. The distillate was stored

under dry nitrogen in a Kel-F tube having a tightly fitting Teflon cap.

N₂F₃AsF₆ dissolves readily in IF₅, treated as described above, with no evidence

of gassing.

All of the operations performed in the studies of the behavior of IF₅

solutions of N₂F₃AsF₆ with perchlorates were carried out in a dry nitrogen
glove box, with the exceptions of gas collection and solvent distillation pro-
cedures.

A Teflon-glass syringe was used to introduce samples of IF₅ into NaCl

liquid cells for infrared analysis. The NaCl cell was attacked somewhat by

the IF₅ solutions, giving rise to absorptions at 4.7μ, 5.8-6.5μ, and 8.4μ.

In spite of this, it was possible to identify the presence of N₂F₅⁺ in the infrared
even after repeated use of the cell.
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10. E. Lawless and G. Hannon, Midwest Research Institute, Report

11. Aerojet-General Corporation, Report 3132, October, 1965,
Contract NOnr 2655(00).

12. Thiokol Chemical Corporation, Reaction Motors Division, Report
RMD-5043-65F, January, 1966, Contract NOnr 4364(00).

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14. Thiokol Chemical Corporation, Reaction Motors Division, Report
RMD-5043-64F, January, 1965, Contract NOnr 4364(00).
The existence of trifluorodiazyl ions in BrF₅ and in IF₅ was established by F¹⁹ n.m.r. and infrared analyses. Solutions of N₂F₃AsF₆ in 143° treated with perchlorates showed absorptions of N₂F₃⁺ and ClO₄⁻ in the infrared. Attempts to isolate trifluorodiazyl perchlorate from solution were not successful.

An attempt to prepare N₂F₅ by reaction of N₂F₃AsF₆ with O₃CNF₂ at -70° resulted in the formation of N₂F₄ and trans-N₂F₂.

Attempts to prepare new interhalogen oxides by the fluorination of Cl₂·O₂AsF₆ and NOCl·O₂AsF₆ were unsuccessful.
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