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Report No. AFRPL-TR-66-144

(U) Synthesis of Inorganic Oxidizers

Final Summary Report

by

E. M. Garden, F. Bartoszek, et al.
Pennsalt Chemicals Corporation

June 1966

Air Force Systems Command
Research and Technology Division
Rocket Propulsion Laboratory
Edwards, California

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(U) Synthesis of Inorganic Oxidizers

Final Summary Report

by

D. M. Gardner, E. Bertoszek, et al.
Pennsalt Chemicals Corporation

June 1966

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Foreword

This report was prepared by Pennsalt Chemicals Corporation's Research and Development Department, King of Prussia, Pennsylvania, under USAF Contract No. AF 04(611)-0519. The program was initiated under Project No. 3149, Task No. 314804 and bears ARPA Order No. 352 (Amend. #4). The project engineer is Dr. William Leahy, RPCS.

This Final Summary Report covers the period August 1, 1962 to April 1, 1966.

The principal scientists who worked on the project over the whole period were E. Bartoszek, C. Mackley, E. Hillman, and O. Sprout. Analytical work was supervised by W. Clavan and J. Smith. This report was prepared by these men and D. M. Gardner, project supervisor, and was approved by W. M. Lee, Director of Contract Research.

This report references the following documents which are all classified Confidential, Group 4 (our reference numbers): 3a, 11, 16, 23, 25 and 20.

This technical report has been reviewed and is approved.

GEORGE F. BABITS, Lt. Colonel, USAF
Chief, Propellant Division
The objective of the work was to prepare new oxidizers composed of combined forms of chlorine, oxygen, and fluorine. Emphasis was placed on the use of CIF₃, CIF₅, ClO₂F, and ClO₃F as starting materials. Experimental techniques included high pressure-high temperature reactions, arc and glow discharge reactions and electrochemical reactions in interhalogens and other active fluorinating solvents.

Attempts to form salts of the alleged ClO₂F⁻ and ClO₂F₂⁻ ions by the reported interaction of chlorates and fluorides were not successful. No evidence for the existence of the salts was found after rigorous elemental, infrared and X-ray analysis of the products. It is concluded that these salts cannot be prepared by the methods reported in the literature.

The heat of combustion of NH₄ClO₄ with CO has been measured and from the data the standard heat of formation of NH₄ClO₄ is calculated to be -71.13 kcal./mole with an estimated uncertainty of 0.32 kcal. This confirms the earlier reported values of -70.74 ± 0.32 (A. A. Gilliland and W. H. Johnson, J. Research Nat'l Bur. Standards, 65A, 67 (1961) and -70.63 kcal. (M. M. Birky and L. G. Hepler, J. Phys. Chem. 64, 686 (1960)) obtained from solution-calorimetric measurements.

ClO₂F did not react with the following compounds under a variety of high pressure and temperature conditions although in many cases thermal degradation occurred: SbF₅, SF₆, BF₃, CIF₃, F₂, CsClF₄, ClF₅, ClF₄Sbf₆ and NO₂F. Additional attempts to fluorinate ClO₂F with F₂ in an electric discharge were unsuccessful.

The laboratory procedure for the safe preparation of ClO₂F, which was used as an intermediate, was developed to yield 3.0 grams per day. Liquid ClO₂F will react with metal storage vessels and decompose to ClO₂F, ClO₂ and Cl₂. Storage is best carried out at -80°C.

ClO₂F was partially fluorinated by elemental fluorine and not fluorinated by chlorine pentfluoride, chlorine trifluoride, cesium tetrafluorochlorate and cesium fluoride under a variety of temperature and pressure conditions. From the results of experiments with ClF₅-ClO₂F, it appears that ClO₂F will induce the thermal decomposition at temperatures as low as 230°. Under similar conditions ClF₅ is stable to 350°.

NO₂F reacts with ClO₂F over a period of 4 days at -78° to form a solid adduct with a melting point of -22° and a vapor pressure of 740 mm. at 0°. The solid and its melt is insoluble in CIF₃.
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Attempts to prepare novel Cl-F compounds by pyrolysis of ClF₃ and subjecting ClF₃ and mixtures of ClF₃ and F₂ to electrical discharges and gamma irradiation were unsuccessful. ClF₃ was not affected by O₂ in a spark or corona discharge and contact with ozone at -78°.

In a supporting study nitryl tetrafluorochlorate, NO₂ClF₄, was prepared by reaction of NO₂F with ClF₃ at -78°. The vapor pressure was measured from -50° (30 mm) to +25° (1360 mm) and can be expressed by the equation:

$$\log_{10} p = 7.945 - \frac{1436}{T}$$

From these data the equilibrium constant is calculated to be 0.250 atmospheres at +9.5°C.

$$\log_{10} K_p = 9.409 - \frac{2840}{T}$$

The apparent heat of dissociation to NO₂F and ClF₃ is +13 kcal/mole.

As in the case of ClF₃, attempts to prepare novel Cl-F compounds using ClF₅ as an intermediate were unsuccessful. These involved fluorination, pyrolytic, and discharge techniques and the following reactants: F₂, CsF, ClF₃. In addition ClF₅ did not react with the following oxygen-containing compounds although in many cases degradation of the ClF₅ occurred: O₂, O₃, ClO₂F, ClO₃F, KClO₃, KClO₄, and CsClO₄.

NO₂F reacted with ClF₅ at low temperatures to give a 1:1 liquid adduct possessing a vapor pressure of one atmosphere at -48°. The liquid product is not a simple solution since the vapor pressure at all temperatures is considerably lower than that predicted by Raoult's law, e.g. observed, 5 mm at -78°; predicted, 292 mm.

ClF₅ reacts with SbF₅ to produce ClF₅SbF₆, m.p. 34-35°, which is analogous to ClF₂SbF₆, m.p. 225-228°. Both materials are reactive with all but highly fluorinated materials. On storage in Kel-F containers ClF₅SbF₆ (and to a lesser extent ClF₂SbF₆) will induce extreme stress cracking of the plastic within hours.

ClF₅ did not form a complex with SF₄, SF₆, or BF₃ stable at ambient temperature.

Nitrogen trifluoride, NF₃, did not react with the following compounds at temperatures in the general range 200°-475°C and pressures of 650-2125 psig: ClF₃, ClF₅, ClO₂F, CsClF₄, ClF₂SbF₆, and ClF₄SbF₆.
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Tetrafluorohydrazine is a reductant for the series of chlorine fluorides at 25°C according to the equations

\[ \text{N}_2\text{F}_4 + \text{ClF}_5 \rightarrow 2\text{NF}_3 + \text{ClF}_3 \]
\[ \text{N}_2\text{F}_4 + \text{ClF}_3 \rightarrow 2\text{NF}_3 + \text{ClF} \]
\[ \text{N}_2\text{F}_4 + 2\text{ClF} \rightarrow 2\text{NF}_3 + \text{Cl}_2 \]

Reactions of complexes of ClF₅ and ClF₃ (ClF₄SbF₆, CsClF₄, ClF₂SbF₆) with N₂F₄ involve first a thermal decomposition of the complex followed by fluorination of N₂F₄ by the free chlorine fluoride.

N₂F₄ and ClO₂ react at 25°C in a flow system to produce NOF and Cl₂.

The trans isomer of difluorohydrazine did not react with ClO₃F or ClF₅ at temperatures from -78°C to 250°C. With ClO₂F, trans-N₂F₂ did not react in the range -78°C to 25°C but at 200°C, reaction occurred resulting in the formation of ClF₃, NF₃, N₂, and O₂.

Cis-difluorohydrazine did not react with the following compounds in the range -78°C to +150°C: ClO₂F, ClO₃F, OF₂, ClF₅, ClF₃, and ClF. At or above 150°C, thermal decomposition of N₂F₂ to N₂ and F₂ became appreciable resulting in the fluorination of the corresponding ClF₃ and ClF.

Oxygen difluoride, OF₂, did not react with the following compounds at temperatures in the general range 150°C to 250°C and pressures of 500-2950 psig: ClF₃, ClF₅, ClO₂F, ClO₃F, NF₃, SbF₅, CsF, CsClF₄, ClF₂SbF₆, ClF₅SbF₆. In most experiments, some thermal decomposition of the OF₂ to O₂ and F₂ took place and the extent of the decomposition increased with temperature. Oxygen difluoride reacted with the simple chlorides NaCl, CsCl, and CaCl₂ to form the corresponding fluorides and to liberate O₂ and Cl₂.

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

The reaction was very exothermic between CaCl₂ and OF₂ below room temperature.

Oxygen difluoride did not react with Cl₂ or ClF at 25°C; however, at 150°C, in a static system, these formed ClF and ClF₃, respectively, in addition to oxygen and a small amount of ClO₂F.

The fluorination of ClO₂ in a flow system with ClF₅, NF₃, and OF₂ was studied with the following results: ClF₅ produced ClO₂F, Cl₂, and O₂; NF₃ did not react; and OF₂ formed ClF₅, ClO₂F, and ClO₃F.

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In contrast the fluorination of Cl$_2$O with either F$_2$ or OF$_2$ in a static system at, respectively, $155^\circ$ and $130^\circ$ produced the new oxidizer, trifluorochlorine oxide, OCIF$_3$.

A study was carried out to determine the feasibility of preparing new oxidizers by electrolysis of systems containing as solvents or solutes CIF$_3$, CIF$_5$, ClO$_2$I, ClO$_3$I and other halogen fluorides. The feasibility of this approach was partially demonstrated by the preparation of CIF$_5$ by electrolysis of CIF$_3$ containing either CsF or SbF$_5$ as solutes at 0°C.

Unfortunately many of the halogen fluorides and halogenyl fluorides of interest as solvents and reactants are poor conductors, and the electrical conductivities which can be passed through a system are extremely small per unit time. The conductivities of CIF$_3$, BrF$_3$, CIF$_5$, SbF$_5$, IF$_5$, ClO$_2$I, BrF$_5$, NO$_2$F, and HF are, respectively (ohm$^{-1}$cm$^{-1}$): $4 \times 10^{-7}$ (0°), $7.53 \times 10^{-4}$ (25°), $< 2.11 \times 10^{-7}$ (-23.9°), $< 2.11 \times 10^{-7}$ (25°), $5.65 \times 10^{-5}$ (25°), $< 2.1 \times 10^{-9}$ (-51°), $2.73 \times 10^{-5}$ (25°), $< 10^{-6}$ (-78°), $< 10^{-6}$ (-12°).
Table of Contents

I. INTRODUCTION

II. RESULTS AND DISCUSSION
   A. Attempted Synthesis of Trioxofluorochlorate(V) and Dioxodifluorochlorate(V) Salts
   B. Thermochemical Measurements
      Heat of Formation of Ammonium Perchlorate
   C. Investigations of the Preparation of Derivatives of Perchloryl Fluoride
   D. Investigations of the Preparation of Derivatives of Chloryl Fluoride
   E. Investigations of the Preparation of Derivatives of Chlorine Trifluoride
   F. Investigations of the Preparation of Derivatives of Chlorine Pentfluoride
   G. Investigations of the Fluorination of Chlorine Oxides
   H. Investigations of the Chemistry of Oxygen Difluoride
   I. Investigations of the Chemistry of Nitrogen Fluorides
      Nitrogen Trifluoride
      Tetrafluorohydrazine
      Trans-Difluorodiazine
      Cis-Difluorodiazine
   J. Electrochemical Studies relating to the Preparation of New Oxidizers

III. APPENDIX
   1. Description and Layout of Adiabatic Calorimeter
   2. Synthesis of ClO₂
   3. Synthesis of ClO₃F
   4. Preparation of ClF₅

IV. REFERENCES

Tables

I. Combustion of NH₄ClO₄ with CO
II. Conductivities of Oxidizer Mixtures

CONFIDENTIAL
### Table of Contents (Cont.)

**Figures**

1. Electric Discharge Cell
2. Vapor Pressure of the NO$_2$ClO$_2$F Solid Adduct
3. Corona Electric Discharge Apparatus
4. Vapor Pressure of the NO$_2$F-CIF$_5$ System
5. Stress Cracked Kel-F Plastic. Result of Contact with CIF$_5$-SbF$_5$ Adduct
6. Electrolysis Cell
7. Layout of Calorimeter and Supporting Equipment

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
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<tbody>
<tr>
<td>1.</td>
<td>14</td>
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I. INTRODUCTION

This research was directed to the preparation of solid oxidizers composed of combined forms of chlorine, oxygen, and fluorine. In particular, we were interested in those ions or compounds in which chlorine as a central atom is coordinated with four, five, or six ligand atoms. The elements most suited and most desired for combination with chlorine are fluorine, oxygen, and nitrogen because of their relatively low atomic weight, high oxidizing potential and their suitable dimensions and electronegativities as illustrated below:

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<tr>
<th></th>
<th>O</th>
<th>F</th>
<th>N</th>
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<tr>
<td>Atomic weight</td>
<td>16</td>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>Relative electronegativity</td>
<td>3.5</td>
<td>4.0</td>
<td>3.0</td>
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<tr>
<td>Atomic covalent radius (Å)</td>
<td>0.74</td>
<td>0.72</td>
<td>0.74</td>
</tr>
<tr>
<td>Cl-X bond strength (kcal)</td>
<td>49</td>
<td>41</td>
<td>48</td>
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The similarity of the above properties implies that there may be little entropic or enthalpic objections to the substitution of one element for either of the other elements under the proper circumstances. Known species like perchloryl fluoride, ClO$_3$F, and the perchlorylamide ion, ClO$_3$NH$^+$, indicate the plausibility of seeking new oxidizers by the principal of substitution of nitrogen or fluorine for oxygen in the several oxides and ions of chlorine. Other examples are chloryl fluoride, ClO$_2$F, and the chlorylamide ion, ClO$_2$NH$^-$, and schematic relations are outlined below:

-1-
The similarity of the oxide and fluoride ions in such structures is indicated by the formation of ClO$_3^-$ and the fact that it is a stable, symmetrical molecule of nearly zero dipole moment (Ref. 1). In addition, the similarity of O and F is so close that the molecule has difficulty in distinguishing between the two and a somewhat random orientation exists in the crystal at low temperatures, resulting in a small, but measurable, zero point entropy (Ref. 2). Less is known about the equivalence of nitride and fluoride ions although ClO$_3^-$ forms many stable, but shock sensitive, salts.

By analogy, it is possible to propose a number of feasible oxidizers by application of this “substitution principle” to known compounds and ions containing chlorine in its normal valence states. Of particular interest are ClO$_3^-$, ClO$_2$F$_2^-$, OCIF$_3$, OCIF$_2^+$, CIF$_4^+$, OCIF, etc., which were considered as target oxidizers for the synthesis program.

In addition, the synthesis of chlorine pentafluoride, CIF$_5$, (Ref. 3) has indicated that a variety of novel oxidizers might be prepared using this material as an intermediate. Like BrF$_5$ (Ref. 4), CIF$_5$ is reported to have the same pyramidal configuration (Ref. 3b). Pauling suggested that in a structure of this type the bonds are directed toward the five corners of a square pyramid which, with the unshared pair, would form an octahedron (Ref. 5, page 180).

Presumably this material could function as a base toward Lewis acids more electrophilic than CIF$_5$ itself. We have been interested in forming adducts of CIF$_5$ with O, NO$_2$, NO, SbF$_5$, etc. In addition, we examined the possibility of the formation of stable salts containing the CIF$_4^+$ and CIF$_6^-$ ions.

Our studies have involved the use of CIF, CIF$_3$, CIF$_5$, ClO$_2$F, ClO$_2$, Cl$_2$O, and ClO$_3$F as starting materials and the experimental techniques being used include high pressure (ca 6000 psig), high temperature (up to 500°C), corona and arc discharges, flow reactions at ambient pressure, and electrochemical reactions in interhalogen solvents.
II. RESULTS AND DISCUSSION

A. Attempted Synthesis of Trioxofluorochlorate(V) and Dioxodifluorochlorate(V) Salts

The initial phases of this program were directed toward the preparation of trioxofluorochlorate(V), ClO₃F⁻², salts containing combustible cations. Of particular interest were (NH₄)₂ClO₃F, (N₂H₅)₂ClO₃F, [(C₂H₅)₄N]₂ClO₃F, etc. It was planned to synthesize these salts in amounts sufficient for complete physical and thermochemical evaluation including the determination of heats of combustion or reaction with appropriate gases (O₂, CO). This would permit a thorough evaluation of the theoretical performance of these salts as oxidizers in solid propellants.

The only salts reported to date presumed to contain the ClO₃F⁻² ion are the supposed soluble and hygroscopic hydrates of CuClO₃F, ZnClO₃F, NiClO₃F, and CoClO₃F and the insoluble and nonhydrated CaClO₃F and BaClO₃F (Ref. 6-11). Chemical, analytical and crystallographic data relating to and supposedly indicating these compositions and structures are given.

The metal trioxofluorochlorates were primarily of interest as useful intermediates in the preparation of combustible salts and the initial work was devoted to the preparation of pure samples of trioxofluorochlorates suitable for conversion to the (NH₄)₂ClO₃F, (N₂H₅)₂ClO₃F, etc. mentioned above.

It is reported that the preparation of the metal salts is carried out by digestion of an aqueous solution of the metal chloride with the stoichiometric amount of the sparingly-soluble metal fluoride at 85°-90°. Addition of nitric or acetic acid is required to effect solution of the fluoride.

\[ \text{M(ClO}_3\text{)}_2 + \text{MF}_2 \rightarrow 2\text{MClO}_3\text{F} \quad (\text{M} = \text{Cu, Zn, Ni, Co}) \]

The digestion is reportedly carried out in either Teflon or platinum wares and the resulting clear solution is cooled to room temperature and slowly evaporated to near dryness in a paraffin-coated desiccator using either sulfuric acid as a desiccant or vacuum drying. Crystallization of the alleged trioxofluorochlorate is supposed to begin after 75-80% of the water is evaporated.

As an alternative to the use of metal trioxofluorochlorates as intermediates, studies were conducted to determine whether concentrated aqueous solutions of HF and HClO₃ could be reacted.
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directly to produce the aqueous acid, H$_2$ClO$_3$F. Attempts were also made to prepare the free acid by passing aqueous solutions of salts believed to be trioxofluorochlorates through columns containing strong cation exchange resins (Amberlite IR-120, Rohm and Haas).

Since it is reported that the related dioxodifluorochlorate (V) salts, ClO$_2$F$_2$\(^{-1}\), can be prepared in a similar manner by the simple technique of using an excess of hydrogen fluoride during the digestion step, analogous studies were directed toward the preparation of these salts as well.

\[
\text{ClO}_3^- + 2HF \rightarrow \text{ClO}_2\text{F}_2^- + \text{H}_2\text{O}
\]

However, it is also reported that the dioxodifluorochlorate (V) salts are in equilibrium with trioxofluorochlorate (V) salts in solution and that each may be prepared from the other by a simple shift in conditions.

\[
\text{ClO}_2\text{F}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{ClO}_3\text{F}^- + \text{HF} + \text{H}^+
\]

For this reason the bulk of our experimental work was devoted to the preparation and characterization of the trioxofluorochlorates and only a minor effort was spent on studying methods for the preparation of the dioxodifluorochlorates.

In the first few months of this program crystals were obtained by using the reported procedures and elemental analyses were obtained which evidently confirmed the existence and composition of the reported trioxofluorates. Typical analyses received are given below:

<table>
<thead>
<tr>
<th></th>
<th>% Cation</th>
<th>% ClO$_3$</th>
<th>% F</th>
</tr>
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<tbody>
<tr>
<td>&quot;CuClO$_3$F$\cdot$5H$_2$O:&quot;</td>
<td>Found</td>
<td>23.9%</td>
<td>32.0</td>
</tr>
<tr>
<td></td>
<td>Theory</td>
<td>24.0</td>
<td>32.6</td>
</tr>
<tr>
<td>&quot;NiClO$_3$F$\cdot$6H$_2$O:&quot;</td>
<td>Found</td>
<td>22.0</td>
<td>31.0</td>
</tr>
<tr>
<td></td>
<td>Theory</td>
<td>21.8</td>
<td>32.5</td>
</tr>
<tr>
<td>&quot;ZnClO$_3$F$\cdot$4H$_2$O:&quot;</td>
<td>Found</td>
<td>29.2</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>Theory</td>
<td>27.3</td>
<td>34.8</td>
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Superficially, the analyses found are in reasonably good agreement with the theoretical values. However, during our studies it became apparent by qualitative tests and X-ray diffraction patterns.
that these isolated materials were actually fortuitous mixtures of chlorates with corresponding metal fluorides and/or fluosilicates. It has been demonstrated at this laboratory that the use of paraffin-coated or halocarbon wax-coated desiccators for evaporation of HF-containing solutions (the procedure used by previous workers) will result in contamination of the solutions by SiF$_6^{-2}$ ions. It is preferred to use plastic desiccators for work with HF solutions. In addition, it is to be noted that New York University personnel report that ClO$_3$F$^{-2}$ salts are isomorphous with fluosilicates and give X-ray patterns that are identical with those of the corresponding fluosilicates. It is important to note that during our work it was found that up to 10% Ba(ClO$_3$)$_2$ in BaSiF$_6$ could not be detected by using infrared absorption spectra unless the analyst was warned beforehand and used special techniques. In X-ray analysis up to 20% Ba(ClO$_3$)$_2$ could not be detected as a result of simple dilution. Consequently mixtures of BaSiF$_6$ and Ba(ClO$_3$)$_2$ could appear to be a single salt with a diffraction pattern identical with the fluosilicate but which would give strong oxidizing tests and evolve chlorine oxides on treatment with sulfuric acids as would be expected for a trioxofluorochlorate (N) salt.

A re-examination of the materials analyzed in the above table and similar products invariably showed the presence of silicon in amounts (1-2%) required for the presence of the necessary quantity of fluosilicate salt.

Our work involved the attempted preparations of the intermediates, CuClO$_3$F-5H$_2$O, NiClO$_3$F-7H$_2$O, and ZnClO$_3$F-7H$_2$O and particular trioxofluorochlorates of direct interest such as (NH$_4$)$_2$ClO$_3$F, NH

\[(\text{CH}_3)_4\text{N}_2\text{ClO}_3\text{F}, \text{ and } (\text{NH}_2\text{C}_{\text{NH}_3})_2\text{ClO}_3\text{F}.\]

However, all attempts to reproduce the preparation of ClO$_3$F$^{-2}$ and ClO$_2$F$_2^{-1}$ salts were unsuccessful and it is our conclusion that these salts cannot be prepared by the methods reported. A theoretical consideration of the valence electron configuration of the chlorine atom in the ClO$_3$F$^{-2}$ and ClO$_2$F$_2^{-1}$ ions indicates that these ions can only be formed by utilization of the available 3d orbitals in chlorine by unpairing 3p electrons and promoting one of the pair to the higher energy 3d orbital prior to bonding with oxygen and fluorine atoms. It may be possible that these ions could be formed under unusual conditions but it appears unlikely that the ClO$_3$F$^{-2}$ and ClO$_2$F$_2^{-1}$ ions can be prepared in aqueous systems below 100°C as reported.
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Our failures to prepare the materials prompted us to obtain samples from Dr. A. Ray (Visiting Fellow, New York University, 1962-63) which were reputed to be NiClO$_3$·4H$_2$O and Gu$_2$ClO$_3$F (Gu represents the guanidinium cation, NH$_2$C(NH)NH$_2$). In all, three samples were obtained of 100-200 mg. each and these are discussed below:

"NiClO$_3$·4H$_2$O" (First Sample)

A sample of allegedly pure NiClO$_3$·4H$_2$O was received from Dr. Ray and his co-workers and infrared X-ray analysis indicated the sample to be NiSiF$_6$·6H$_2$O. Since the ClO$_3$F$^-$ salts are known to be isomorphous with fluosilicates a chemical analysis for silicon was performed. Found: 9.1% Si (theoretical for NiSiF$_6$·6H$_2$O, 9.05% Si).

Qualitative analysis indicated no oxidizing power of the sample following dissolution in water.

"NiClO$_3$·4H$_2$O" (Second Sample)

Approximately 0.2 g. of a second sample of NiClO$_3$·4H$_2$O was obtained from Dr. Ray and the results of analysis are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Theory for &quot;NiClO$_3$·4H$_2$O&quot;</th>
<th>Reported by N.Y.U.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>15.2</td>
<td>15.3</td>
<td>14.2</td>
</tr>
<tr>
<td>F</td>
<td>8.1</td>
<td>9.5</td>
<td>9.2</td>
</tr>
</tbody>
</table>

An aqueous solution of the material proved to be strongly oxidizing in a qualitative test with aniline sulfate solution (indicative of a chlorate or similar oxidizing ion in solution).

An X-ray analysis of the sample as received indicated the presence of NiSiF$_6$·6H$_2$O and an unknown material.

On the assumption that the sample was a mixture of hydrated NiSiF$_6$ and Ni(ClO$_3$)$_2$ (to explain the qualitative tests reported by Dr. Ray) a mixture was formulated with the following composition based on the chemical analysis:

Ni(ClO$_3$)$_2$·4H$_2$O - 64.8% (by weight)
NiSiF$_6$·6H$_2$O - 35.2%
The nickel chlorate was a special preparation and was dehydrated below the normal hexahydrate. Formulation of the above mixture was based on the relative amounts of the Cl and F as found in the N.Y.U. sample.

An X-ray analysis of the fresh mixture showed the presence of the two components. However, on exposure to atmospheric moisture the mixture adsorbed water and an X-ray pattern of the exposed mixture was identical to that obtained for the sample from Dr. Ray and his co-workers.

The sample was thus a mixture of NiSiF₆·6H₂O and a hydrate of Ni(ClO₃)₂.

"Gu₂ClO₃F"

A sample (ca. 0.2 g) designated "Gu₂ClO₃F" was provided to Pennsalt by Dr. Ray on July 17, 1963. Elemental analysis is given below:

<table>
<thead>
<tr>
<th></th>
<th>Theory for &quot;(Gu₃F₆)₂ClO₃F&quot;</th>
<th>Reported by Ray</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>15.9</td>
<td>15.3</td>
<td>14.2</td>
</tr>
<tr>
<td>F</td>
<td>8.5</td>
<td>9.45</td>
<td>9.2</td>
</tr>
<tr>
<td>Si</td>
<td>0.0</td>
<td>---</td>
<td>0.0</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis of the Ray sample yields an unknown pattern that does not resemble the pattern of guanidinium fluosilicate that had been prepared as a reference. It is to be noted that Ray reports the ClO₃F⁻² salts are isomorphous with fluosilicates and give X-ray patterns that are identical with those of the corresponding fluosilicates.

Infrared analysis indicates a basic guanidinium structure for the cation; however, guanidinium salts show a broad infrared absorption band centering at about 6.5 μ and a weaker, sharper band at 6.4-6.5 μ. This latter band is absent in the infrared spectrum of the sample; curiously, it appears to be absent from the reported guanidinium thiocyanate spectrum also (Ref. 12). It is believed that some modification to the guanidinium cation has occurred during the supposed preparation of the trioxofluorochlorates and especially during the digestion in the hot acid oxidizing solution. It is suggested that the cation is a polybasic condensed guanidine or a higher homolog of biguanide. Unfortunately, the small sample size prevented a thorough characterization of the material.
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It is interesting to note that from the 15 attempted preparations of \( \text{Gu}_2\text{ClO}_3\text{F} \) at this laboratory and over 60 crystal fractions obtained, only three isolated crystal crops (totaling about 200 mg.) have been separated and identified as the same material as the N.Y.U. sample.

In conclusion, no evidence has been obtained for the preparation to date of either trioxofluorochlorate or dioxofluorochlorate salts based on extensive studies at this laboratory and examination of products claimed to be these materials. Therefore, all work involving preparation of these salts in aqueous solution was terminated.

It should be noted, however, that the structures of the \( \text{ClO}_2\text{F}^- \) and \( \text{ClO}_2\text{F}_2^- \) ions are reasonable and it may be assumed that salts of these ions will probably be prepared using different procedures than those reported. This work was continued in studies on the fluorinations of chlorine oxides and oxyenations of chlorine fluorides and the unsuccessful results are summarized in later sections of this report.

B. Thermochemical Measurements

Heat of Formation of Ammonium Perchlorate

A primary objective of the program was to evaluate new oxidizers as propellants and, apart from determining the stability and chemical reactivity of the new oxidizers, this is most positively accomplished by measurement of heats of combustion and/or reaction followed by calculations of heats of formation from these data.

The pilot work was carried out using \( \text{NH}_4\text{ClO}_4 \) since this was representative of the type of oxidizer to be prepared. In addition, although accurate heats of formation of \( \text{NH}_4\text{ClO}_4 \) have been determined from solution-calorimetric measurements (Ref. 13, 14) no data for the heat of combustion of \( \text{NH}_4\text{ClO}_4 \) have been reported.

Carbon monoxide was chosen as a fuel gas partially on the basis of its availability, ease of handling, and high purity and partially because a preliminary evaluation of the heat of combustion with \( \text{NH}_4\text{ClO}_4 \) indicated that the heat evolved would be comparable with that expected for hydrogen according to the following equations:

1. \( \text{NH}_4\text{ClO}_4 (s) + 2.5 \text{H}_2 (g) \rightarrow 0.5 \text{N}_2 (g) + \text{HCl (aq.)} + 4 \text{H}_2\text{O} \) (1)
   \[ \Delta H = 2.5 \text{ kcal/g, } \text{NH}_4\text{ClO}_4 \]

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2. $\text{NH}_4\text{ClO}_4(\text{s}) + 2.5 \text{CO} \rightarrow 0.5 \text{N}_2(\text{g}) + \text{HCl(\text{aq})} + 1.5 \text{H}_2\text{O(\text{l})} + 2.5 \text{CO}_2$

$\Delta H = 2.04 \text{ kcal/g. \text{NH}_4\text{ClO}_4}$

It appears that CO is a useful fuel gas and may be applicable to a variety of oxidizers (Ref. 15, 16). However, it must be noted that the combustion of oxidizers, such as $\text{NH}_4\text{ClO}_4$, containing hydrogen yields high temperature water vapor which can undergo a water-gas reaction with the excess CO present with the bomb.

3. $\text{CO(\text{g})} + \text{H}_2\text{O(\text{g})} \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ $\Delta H^{298} = -9.84 \text{ kcal.}$

In the final analysis of the combustion data for the equation 2. above, corrections must be applied for the amount of water vapor entering into the water-gas reaction, noted in eq. 3. This correction is calculated according to the following equations:

$\text{H}_2\text{O (\text{l}iq.)} \rightarrow \text{H}_2\text{O(\text{g})}$ $\Delta H^{298} = +10.520; \Delta E^{298} = +9.930 \text{ kcal.}$

$\text{CO(\text{g})} + \text{H}_2\text{O(\text{g})} \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ $\Delta H^{298} = -9.840;$

$\Delta E^{298} = -9.840 \text{ kcal.}$

$\sum \Delta E = +0.088 \text{ kcal/mole CO}_2.$

The data obtained are presented in Table 1. The $\Delta E$ of the combustion process is 2033 cal/g. $\text{NH}_4\text{ClO}_4$ or 238.87 kcal/mole $\text{NH}_4\text{ClO}_4$. This corresponds to an enthalpy of combustion, $\Delta H^{298}$, equal to $-238.57 \text{ kcal}$ with an estimated uncertainty of $\pm 0.32 \text{ kcal}.$

Using the values -38.139, -26.4157, -94.0518, -68.3174 and 57.7979 kcal, for the standard heats of formation of, respectively, aqueous HCl, CO(\text{g}), CO\text{\textsubscript{2}}(\text{g}), H\text{\textsubscript{2}}O(\text{l}iq.), and H\text{\textsubscript{2}}O (\text{g}), the standard heat of formation of $\text{NH}_4\text{ClO}_4(\text{c})$ at $25^\circ\text{C}$ is calculated to be $-71.13 \pm 0.32 \text{ kcal/mole.}$

The value $-71.13 \pm 0.32 \text{ kcal}$ is in good agreement with the reported solution-calorimetric values $-70.74 \pm 0.32$ (Ref. 13) and $-70.63 \text{ kcal.}$ (Ref. 14) for the standard heats of formation of $\text{NH}_4\text{ClO}_4$.

* The heat of formation of HCl (\text{aq.}) was graphically determined from the data presented in N.B.S. Circular 500 and for the average concentration taken to be one mole HCl per 0.19 moles water as determined by analysis.)

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## TABLE I
Combustion of NH₄ClO₄ with CO

<table>
<thead>
<tr>
<th>Wt. NH₄ClO₄ g.</th>
<th>∆T °C</th>
<th>Wt. CO₂ found, g.</th>
<th>Wt. CO₂ water-gas reaction, g.</th>
<th>Ignition Energy cal.</th>
<th>∆E&lt;sup&gt;a&lt;/sup&gt; Gross cal.</th>
<th>∆E&lt;sup&gt;b&lt;/sup&gt; water-gas reaction, cal.</th>
<th>∆E&lt;sup&gt;b&lt;/sup&gt; corrected g. NH₄ClO₄</th>
<th>∆E corr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0769</td>
<td>0.892</td>
<td>1.2222</td>
<td>0.2144</td>
<td>1.6</td>
<td>2189</td>
<td>+.43</td>
<td>2189</td>
<td>2033</td>
</tr>
<tr>
<td>0.9222</td>
<td>0.765</td>
<td>1.0824</td>
<td>0.2198</td>
<td>1.5</td>
<td>1877</td>
<td>+.44</td>
<td>1877</td>
<td>2035</td>
</tr>
<tr>
<td>1.0714</td>
<td>0.888</td>
<td>1.3339</td>
<td>0.3313</td>
<td>1.6</td>
<td>2179</td>
<td>+.66</td>
<td>2178</td>
<td>2033</td>
</tr>
<tr>
<td>1.0658</td>
<td>0.880</td>
<td>1.2329</td>
<td>0.2348</td>
<td>1.6</td>
<td>2159</td>
<td>+.47</td>
<td>2159</td>
<td>2026</td>
</tr>
<tr>
<td>1.0287</td>
<td>0.854</td>
<td>1.2091</td>
<td>0.2462</td>
<td>1.6</td>
<td>2095</td>
<td>+.49</td>
<td>2095</td>
<td>2037</td>
</tr>
</tbody>
</table>

Average: 2033 cal./g.

Standard deviation of the mean: 1.91 cal./g.

### NOTES:
- a. Calorimeter constant = 2455.5 ± 2.3 cal./°C.
- b. ∆E Gross - ∆E water gas

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It is to be noted that the heat capacity of the calorimeter, 2455 ± 2.8 cal./°C, was determined by the combustion of benzoic acid in oxygen under certificate conditions. The correction in the heat capacity of the calorimeter due to a substitution of CO for O₂ amounts to 0.025 cal./°C and was considered negligible.

C. Investigations of the Preparation of Derivatives of Perchloryl Fluoride

Perchloryl fluoride might appear to be a promising intermediate in the preparation of new oxidizers, but its symmetry and the near equivalence of the Cl-O and Cl-F bond energies are serious handicaps. To date, it is impossible to selectively activate and cleave either a Cl-O or a Cl-F bond by such physical means as heat, pressure, electric discharges, ultraviolet radiation, gamma radiation, etc. If the minimum energy is achieved, uncontrolled decomposition occurs resulting in products representing almost every stable combination of the component elements including ClO₂F, ClO₂, ClF₃, Cl⁻, Cl₂, O₂, and F₂. Chemically, it is known that unstable complexes can be formed with various bases such as phosphines, sulfides, and amines; however, these rapidly degrade with subsequent oxidation of the organic compounds to phosphine oxides, sulfoxides (and sulfones), and Schiff's bases or enamines. In several isolated instances, intermediates in the degradation processes have been found stable and have been fully characterized (Ref. 17).

\[
\begin{align*}
\hline
N\text{-perchloryl piperidine} & N\text{-fluoro-2,2,6,6-tetramethylpiperidine-4-one} \\
(\text{sensitive compound, explodes on warming to 80° C}) & \text{b.p. 60-61°/1.3 mm} \\
\hline
\end{align*}
\]

In contrast, attempts to fluorinate perchloryl fluoride with a variety of fluorinating agents under a variety of conditions have been unsuccessful. These experiments are discussed below.

Perchloryl fluoride was reacted with SbF₅ in a monel autoclave at 260° in an attempt to activate and fluorinate the ClO₃F molecule by the strong Lewis acid. On cooling it was found that no reaction had occurred. The charge was again heated at 420° for 15 hours.
and after cooling, the volatile products were identified as O₂ and Cl₂. A voluminous yellow-green solid filled the reactor and was subsequently characterized as a mixture of Sbf₅ complexes of Sbf₅ with various metal fluorides. The solid phase contained barely 1.4% chlorine. Apparently a complete decomposition of the ClO₃F occurred triggered by the presence of Sbf₅.

\[
\begin{align*}
\text{Sbf₅} + \text{ClO₃F} & \xrightarrow{420^\circ} \text{Cl₂} + 3\text{O₂} + \text{F₂} \\
\frac{1}{2}\text{F₂} + \text{M} (\text{reactor metal}) & \longrightarrow \text{MF} \\
\text{MF} + \text{Sbf₅} & \longrightarrow \text{MSbf₆}
\end{align*}
\]

With the same objective, equimolar mixtures of ClO₃F and Sbf₅ were treated with an equivalent amount of ClF₃ at temperatures up to 420°, generating autogenous pressures from 700 to 4000 psig. On cooling to 25°, the ClO₃F was recovered unchanged and the ClF₃ was found to have reacted with the Sbf₅ to form ClF₃Sbf₅. It is interesting to note that complex formation by Sbf₅ completely destroyed its catalytic effect on the decomposition of ClO₃F. There is no doubt therefore that the strong Lewis acid caused an activation or polarization of the ClO₃F molecule in the previous experiment.

Similar reactions with weaker Lewis acids than Sbf₅ were carried out in attempts to isolate either a complex of ClO₃F or to effect a more controlled fluorination without decomposition. ClO₃F did not react with either SF₆ or BF₃ at temperatures up to 330°. ClO₃F, however, did oxidize SF₄ at 375° to produce a very small amount of SF₅. When ClO₃F, ClF₃, and SF₄ were reacted together at 310°, oxidation of the SF₄ occurred and a variety of products were obtained including SF₆, SOF₄, SO₂F₂, Cl₂, O₂, and SO₂F₂.

In efforts to force a fluorination of ClO₃F with the reactive ClF₅⁺ ion, equimolar ternary mixtures of ClO₃F/ClF₃/SF₆ and ClO₃F/ClF₃/BF₃ were each heated to 310° in a monob autoclave. On cooling the reactants were essentially recovered unchanged except that in the latter system the ClF₃ had reacted with BF₃ to form the stable ClF₃BF₄. The reaction reported in the paragraphs above involving a mixture of ClO₃F, ClF₃, and Sbf₅ is also representative of this line of attack.

ClO₃F was reacted with a mixture of ClF₅ and Sbf₅ in an experiment to observe the effects of the ClF₅⁺ ion.
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\[ \text{ClF}_5 + \text{SbF}_5 \rightarrow \text{ClF}_4^+ \text{SbF}_6^- \]

Maximum conditions were 375° and a pressure of 2000 psig. The major products found were ClF$_2$SbF$_5$, ClO$_3$F, and F$_2$ indicating the following reactions:

\[ \text{ClF}_4^+ \text{SbF}_6 \rightarrow \text{ClF}_5 + \text{SbF}_5 \]

\[ \text{ClF}_5 \rightarrow \text{F}_2 + \text{ClF}_3 \]

\[ \text{ClF}_3 + \text{SbF}_5 \rightarrow \text{ClF}_2 \text{SbF}_6 \]

Since ClF$_2^+$ did not cause a fluorination of ClO$_3$F, it did not appear likely that the complementary base ClF$_4^-$ would have any effect on ClO$_3$F. However, this was investigated using CsClF$_4$ prepared from a pressure reaction of ClF$_3$ with CsF. Solid CsClF$_4$ did not react with gaseous ClO$_3$F at temperatures up to 300° and pressures up to 450 psig. The ClO$_3$F was recovered quantitatively; however, some slight decomposition of the CsClF$_4$ occurred resulting in attack of the stainless steel reaction vessel and formation of red Cs$_2$HIF$_6$ (Ref. 18, 19).

A further attempt to fluorinate the ClO$_3$F molecule was made using an electric discharge. The apparatus employed is shown in Fig. 1. The unit is a stainless steel cylinder with \( \frac{1}{2} \) in. i.d. and a total volume of about 30-35 ml. The platinum electrode (18 gauge) passes through a Kev-F gland and insulator and forms a gap of \( \frac{1}{4} \) in. A side arm to the cylinder permits charging and removal of gaseous products. The gland and nut design allows complete removal of solid products and inspection of the cell interior. All experiments were of 24 hours duration and utilized an external resistance of 37,4 megohms (unless otherwise noted) to stabilize the discharge and to permit long term operation without overloading the circuit (30 kv. and 2000 microamps). The ClO$_3$F and F$_2$ were measured out on the basis of pressure such that the total pressure was about one atmosphere and the ratio of ClO$_3$F to F$_2$ ranged from 1:1 to 2:1. With an applied voltage of 27-28 kv., the current output was 55-90 microamps. The only products found were fluorocarbons resulting from attack of the F$_2$ on the Kev-F insulator.

D. Investigations of the Preparation of Derivatives of Chloryl Fluoride

The following studies were carried out in attempts to prepare ionic derivatives of ClO$_2$F or compounds containing a higher percentage of fluorine than ClO$_2$F itself.

- 13 -

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Figure 1

Electric Discharge Cell

(Scale Full)
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In our attempts to fluorinate ClO₂F we have used elemental fluorine, chlorine pentafluoride, chlorine trifluoride, cesium tetrafluorochlorate and cesium fluoride as reagents. This work and its results are described below.

The reaction of ClO₂F with an excess of F₂ at temperatures up to 290° resulted in partial conversions (average, about 50%) of ClO₂F to ClO₃F and ClF₅. The overall reaction is considered to be the sum of several independent reactions.

a. 3ClO₂F $\xrightarrow{\Delta} 2$ ClO₃F + ClF

b. ClF + F₂ $\longrightarrow$ ClF₃
c. ClF₃ + F₂ $\longrightarrow$ ClF₅

Neither ClF nor ClF₃ was observed in the product gases and Cl₂ and O₂ were also found to be absent.

Mixtures of ClO₂F and ClF₅ when heated to 230°-430° at pressures up to 900 psig resulted in the formation of ClF, F₂, and O₂. The bulk of the ClO₂F was recovered unchanged. The primary reaction appeared to be thermal decomposition of ClF₅. It has been determined that pure ClF₅ begins to thermally dissociate at 350°-375° under the experimental conditions used, yielding ClF₃ and F₂.

\[
\begin{align*}
\text{ClF}_5 & \xrightarrow{350-375°, 1000 \text{ psig}} \text{ClF}_3 + \text{F}_2 \\
\end{align*}
\]

At higher temperatures (>425°), dissociation is virtually complete to ClF and F₂.

\[
\begin{align*}
\text{ClF}_5 & \xrightarrow{>425°} \text{ClF} + 2\text{F}_2 \\
\end{align*}
\]

From the results of the experiments with ClO₂F-ClF₅ mixtures, it appears that ClO₂F induces decomposition of ClF₅ to ClF and F₂ at a temperature lower than that required for the pure material.

A complete decomposition of the reactants and a heavy attack on the reactor walls occurred when equimolar amounts of ClO₂F and ClF₃ were reacted at 375°. The volatile products were mainly ClF, Cl₂, and O₂ and the solid residue was a mixture of metal fluorides and chlorides.

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When solid CsClF$_4$ was reacted with gaseous ClO$_2$F at temperatures up to 300°C in stainless steel cylinders, the products were oxygen, CsF, NIF$_2$, Cs$_2$NIF$_6$ (Ref. 18 and 19), Cl$_2$, and ClF. Considerable amounts of reactants were recovered unchanged.

In an experiment to attempt either a fluorination of ClO$_2$F or the formation of the hypothetical salt CsClO$_2$F$_2$, a mixture of CsF and ClO$_2$F (3:2 mole ratio) were combined in a monel cylinder and heated to 150°C for 28 hours. On cooling, the CsF and ClO$_2$F were recovered unchanged. Another charge of the CsF and ClO$_2$F mixture was heated to 300°C for 17 hours. On cooling, the gas phase contained only trace quantities of the infrared absorbers CF$_4$ and SF$_6$, and the balance of the gas phase was the infrared inactive Cl$_2$, O$_2$, and F$_2$. The recovered yellow solid was subjected to X-ray diffraction analysis, and it has been found to have a pattern similar to CsCl and isomorphous with Cs$_2$NIF$_6$.

In subsequent experiments, a number of solid ionic materials postulated to contain the ClO$_2$$^+$ ion were prepared by reacting ClO$_2$F with strong Lewis acids e.g. ClO$_2$SO$_2$F, ClO$_2$SbF$_6$, ClO$_2$AsF$_6$, ClO$_2$BF$_4$, and ClO$_2$PF$_6$ (Ref. 20 and 21) since complexes of this type offer promise as stable oxidizers providing suitable anions can be combined with the ClO$_2$$^+$ moiety. To date such an anion does not exist which forms a stable salt in conjunction with the ClO$_2$$^+$ ion.

The alleged preparation of ClO$_2$F$_2$$^-$ anions by reaction of chlorates with acid fluoride in aqueous solution has been shown to be in error (see prior discussion). However, it is expected that such an ion would be a strong oxidizer and the preparation would have to be carried out under anhydrous conditions, possibly using materials like ClO$_2$F as intermediates. Theoretically, the ion is plausible anion would involve an sp$^3$d bond hybridization which could be described as a trigonal bipyramidal configuration, with the two oxygen atoms and the unshared electron pair in the equatorial position and the two fluorine atoms at the apices.

---

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This structure has been postulated for the $\text{IO}_2\text{F}_2^-$ ion (Ref. 5, page 181) based on X-ray data for the crystal KIO$_2$F$_2$ (Ref. 22).

As indicated above unsuccessful attempts to prepare ClO$_2$F$_2$ were made using C$\text{F}_2$ and ClO$_2$F as reactants, and subsequent work was carried out using NO$_2$F and ClO$_2$F.

An adduct of NO$_2$F with ClO$_2$F was prepared by combining the gases and storing the mixture (condensed liquids) at $-78^\circ$ for 4 days. On warming the solid to 0°C the following vapor pressures were noted and plotted on the graph (Fig. 2). The apparatus was not designed for determining the melting point of the solid but it appears to be in the range $-30^\circ$ to $-20^\circ$.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>-78°</td>
<td>15 mm</td>
</tr>
<tr>
<td>-71°</td>
<td>25</td>
</tr>
<tr>
<td>-68°</td>
<td>35</td>
</tr>
<tr>
<td>-60°</td>
<td>65</td>
</tr>
<tr>
<td>-56°</td>
<td>80</td>
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<td>-45°</td>
<td>130</td>
</tr>
<tr>
<td>-43°</td>
<td>145</td>
</tr>
<tr>
<td>-40°</td>
<td>170</td>
</tr>
<tr>
<td>-35°</td>
<td>245</td>
</tr>
<tr>
<td>-25°</td>
<td>375</td>
</tr>
<tr>
<td>-15°</td>
<td>550</td>
</tr>
<tr>
<td>-10°</td>
<td>620</td>
</tr>
<tr>
<td>-5°</td>
<td>680</td>
</tr>
<tr>
<td>0°</td>
<td>740</td>
</tr>
</tbody>
</table>

The plot of the above data shows a discontinuity at $T = -22^\circ$ which may be attributed to a phase change and is in support of the observed melting point range. More exact pressure data may locate the phase transition with better accuracy.

The NO$_2$F·ClO$_2$F solid adduct was treated with C$\text{F}_3$ to determine the relative stability of the adduct and NO$_2$C$\text{F}_4$ (Ref. 23). C$\text{F}_3$ was condensed on the pale yellow solid at $-78^\circ$. On warming to about $-30^\circ$, the adduct appeared to melt and formed an oily layer above the C$\text{F}_3$. It was found that all three components could be distilled from the two phase system. It would appear that NO$_2$F·ClO$_2$F is insoluble in C$\text{F}_3$. 

- 17 -

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Fig. 2. Vapor pressure of the NO$_2$F-ClO$_2$F solid adduct (intersection at T=-22° C)
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In a second related experiment NO$_2$F·ClO$_2$F and an equimolar amount of ClF$_3$ were heated to 300°C for 10 hours in a large excess of fluorine (10%). The resulting products were primarily ClF$_5$ and some ClO$_3$F, ClO$_2$F, O$_2$ and N$_2$.

E. Investigations of the Preparation of Derivatives of Chlorine Trifluoride

1. A number of exploratory reactions were carried out to determine whether the fluorination of ClF$_3$ or a physical activation of the ClF$_3$ molecule could be used—

   a. to prepare higher fluorinated homologs; b. to effect polymolecular condensations; c. to prepare new ionic Cl–F compounds. Although qualitative considerations of possible valence bond orbital hybridizations, effective atom radii, and orbital energies tend to rule out homologs higher than ClF$_5$, serious effort was given to this work. The experiments are described below.

   Chlorine trifluoride was heated at 470°C in an attempt to pyrolyze the material and to condense it to higher homologs; however, this did not occur and the ClF$_3$ was essentially recovered unchanged.

   Continuous discharges of 27,000 volts were placed through pure ClF$_3$ held at 6–8 psig in the apparatus illustrated in Fig. 2 for periods up to 24 hours. The only products observed were various volatile fluorocarbons resulting from attack of the KeCl–F insulator by the ClF$_3$.

   In a similar experiment continuous electric discharges (25,000–30,000 volts through mixtures of ClF$_3$ and F$_2$ did not appear to cause any reaction at ambient temperature and the reaction times and reactant ratios were varied with no effect. As expected, the potential drop and current flow are dependent on the pressure which was varied in the experiments up to a maximum of 50 psig. Temperature appeared to be the most important variable. At 0° some ClF$_5$ was formed although the yield was less than 1%; however, on decreasing the temperature to −78°, the amount of ClF$_5$ is increased five-fold to about 5%.

   Apparently the chilled cell is more efficient since the formation of ClF$_5$ occurs in the liquid phase or at the gas-liquid interface by reaction of fluorine atoms with ClF$_3$. Since the ClF$_5$ is in the liquid phase, it is essentially removed from the discharge zone in the gaseous phase and the probability of dissociation is minimized. It is suggested that the mechanism may involve the following reactions:

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\[ \begin{align*}
F_2 + e & \rightarrow F^- + F \\
F^- + \text{ClF}_3 & \rightarrow \text{ClF}_4^- \\
\text{ClF}_4^- + F & \rightarrow \text{ClF}_5^- + e
\end{align*} \]

\text{ClF}_3 \text{ at a pressure of 400 mm. Hg was unaffected by a two hour exposure to a Co}^{60} \text{ gamma irradia-}

tion (240,000 roentgens/hour). 

Chlorine trifluoride was reacted with CsF at 80°C and 150 psig for 24 hours to form CsClF_4. The reactor was cooled and varying amounts of oxygen were introduced to the reactor. The gas-solid mixture was heated up to 300°C developing pressures of up to 3150 psig. The only products observed were ClF and F_2 resulting from decomposition of the CsClF_4.

2. A more intense investigation was carried out to prepare oxygenated derivatives of ClF_3. Theoretically it should be possible to prepare O=ClF_3 and O_2ClF_3 (considered to be distinct from the isomeric unstable adduct reported by Streng and Grosse (Ref. 24) which was prepared by a low temperature reaction of O_2F_2 with ClF). In fact, the former compound has been prepared in this laboratory by the fluorination of Cl_2O and also by the reaction of Cl_2O with OF_2. Rockettyn et had earlier reported the synthesis of OCIF_3 by the fluorination of Cl_2O and ClINO_3 (Ref. 25). This work will be discussed later in the section on “Chlorine Oxides”; it should be noted that all pertinent physical data have not been determined as of this date; however, it is expected that OCIF_3 will be a relatively stable liquid (extrapolated boiling point, about 30°C). Its structure will probably involve a \( \sigma^3 \) hybridization and be tetrahedral; however, since the hybridization will include the 3p and 4s orbitals (the latter has lower energy than the 3d orbital) the configuration may be that of a distorted tetrahedron with the oxygen atom located at stretched apex.

\[ \text{Cl} \]

- 20 -

CONFIDENTIAL
FIGURE 3

CORONA ELECTRIC DISCHARGE APPARATUS
(Sectional Diagram - No scale)

1. Aluminum rod 1/4" D
2. Kel-F tube 3/8" O.D. x 1/4" J.D.
4. Aluminum foil covering
5. Electrode connections
6. Annular ring, approx. 1/8" wall-to-wall
7. Threaded Teflon plug

Inlet and outlet fittings - standard flare fittings (Teflon)
Chlorine trifluoride was combined with CsF to form CsClF₄ and this solid material was treated with oxygen at 280-310°F at pressures up to 4300 psig in a monel reactor. The only reaction noted was dissociation of CsClF₄ to CsF and ClF₃ and subsequently the ClF₃ decomposed to CIF and F₂.

Other reactions which can be considered as attempts to oxidize ClF₃ with ClO₃F and ClO₂F have been described in previous sections which discuss the fluorination of the latter two compounds.

3. During the course of the work studies were made of the known complexes formed by ClF₃ for background information to similar work carried out with ClF₅ and systems investigated in the electrochemical work (see later discussion). Most of the complexes of ClF₃ are ionic and contain either the ClF₄⁺ or the ClF₄⁻ ions.

ClF₃SbF₅ was prepared by combining ClF₃ with SbF₅ (Ref. 26). The reaction is exothermic as evidenced by the warming of the Kel-F trap at the interface of the two reactants and the necessary diffusion of liquid ClF₃ through the solid ClF₃SbF₅ to contact fresh SbF₅ is a convenient rate governing phenomenon; otherwise, the exothermic reaction might have to be controlled by cooling. The density of ClF₃SbF₅ is somewhat between that of SbF₅ and ClF₃ and was tentatively taken as 2.2 g/cc. and the melting point was determined as 225-228°C.

In contrast to the reported unsuccessful attempt to prepare NO₂ClF₄ (Ref. 27) in the open literature, this compound was easily prepared by reacting NO₂F with ClF₃.

It is important to note that in contrast to NOClF₄ which is formed on contact of NOF with ClF₃, the formation of NO₂ClF₄ is a slow reaction at -78°C. Following preparation of NO₂ClF₄ the vapor pressures were redetermined.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Observed (mm.)</th>
<th>Calc'd. (mm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>30, 35</td>
<td>33</td>
</tr>
<tr>
<td>-40</td>
<td>65</td>
<td>63</td>
</tr>
<tr>
<td>-30</td>
<td>110</td>
<td>111</td>
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<tr>
<td>-20</td>
<td>180</td>
<td>188</td>
</tr>
<tr>
<td>-10</td>
<td>300</td>
<td>319</td>
</tr>
<tr>
<td>0</td>
<td>490</td>
<td>491</td>
</tr>
<tr>
<td>9.5</td>
<td>760</td>
<td>755</td>
</tr>
<tr>
<td>15</td>
<td>930, 940</td>
<td>920</td>
</tr>
<tr>
<td>20</td>
<td>1120</td>
<td>1122</td>
</tr>
<tr>
<td>25</td>
<td>1350, 1360</td>
<td>1369</td>
</tr>
</tbody>
</table>

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A least mean square treatment of the above experimental data gave the following equation which was used to determine the calculated values above.

(1) \( \log p \text{ (mm)} = 7.945 - \frac{1436}{T} \)

From these data one may calculate the temperature variation of the equilibrium constant of the dissociation reaction of the following reaction:

(2) \( \text{NO}_2\text{ClF}_4 \text{ (s) \rightleftharpoons NO}_2\text{(g)} + \text{ClF}_3 \text{ (g)} \)

\[
K_p = \frac{p_{NO_2} \cdot p_{ClF_3}}{(1/2 p_{total})^2} = 1/4 p_{total}^2
\]

\((P \text{ is expressed in atm.})\)

From the data the following values for the equilibrium constant were determined:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( K_p \text{ (atm.)} )</th>
<th>( \log K_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>5.302 \times 10^{-4}</td>
<td>-3.314</td>
</tr>
<tr>
<td>-40</td>
<td>1.828 \times 10^{-3}</td>
<td>-2.746</td>
</tr>
<tr>
<td>-30</td>
<td>5.237 \times 10^{-3}</td>
<td>-2.264</td>
</tr>
<tr>
<td>-20</td>
<td>1.402 \times 10^{-2}</td>
<td>-1.809</td>
</tr>
<tr>
<td>-10</td>
<td>3.895 \times 10^{-2}</td>
<td>-1.368</td>
</tr>
<tr>
<td>0</td>
<td>0.1039</td>
<td>-0.9855</td>
</tr>
<tr>
<td>9.5</td>
<td>0.2500</td>
<td>-0.6163</td>
</tr>
<tr>
<td>15</td>
<td>0.3824</td>
<td>-0.4459</td>
</tr>
<tr>
<td>20</td>
<td>0.5429</td>
<td>-0.2755</td>
</tr>
<tr>
<td>25</td>
<td>0.8006</td>
<td>-0.1081</td>
</tr>
</tbody>
</table>

These data may be expressed by the following equation:

(3) \( \log K_p = 9.409 - \frac{2840}{T} \)

Assuming that \( \Delta H \) is invariant with temperature and is represented by the slope of equation (3), one may obtain an approximation of the heat of dissociation of \( \text{NO}_2\text{ClF}_4 \).

- 24 -
CONFIDENTIAL

\[ \Delta H = -2840 \]
\[ 2,303 \text{R} \]

\( \Delta H \) dissociation = 13 kcal/mole

The reaction of Na\(_2\)O\(_2\) with CsClF\(_4\) was carried out in an attempt to introduce oxygen into either the tetrafluorochlorate anion or the ClF\(_3\) molecule, e.g.

\[
\begin{align*}
\text{CsClF}_4 & \quad + \quad \text{Na}_2\text{O}_2 \quad \rightarrow \quad \text{CsClO}_2\text{F}_2 & \quad + \quad 2\text{NaF} \\
2\text{CsClF}_4 & \quad + \quad 3\text{Na}_2\text{O}_2 \quad \rightarrow \quad 2\text{CsClO}_3\text{F} & \quad + \quad 6\text{NaF} \\
3\text{CsClF}_4 & \quad + \quad \text{Na}_2\text{O}_2 \quad \rightarrow \quad 3\text{CsF} & \quad + \quad 2\text{NaF} & \quad + \quad \text{ClF} & \quad + \quad 2\text{OClF}_3
\end{align*}
\]

From -78°C up to 300°C only a trace of reaction was noted with ClO\(_2\)F, ClF and O\(_2\) being the only products. When a separate mixture was programmed for a heating period at 400°C, an exothermic reaction seemed to be initiated within 30-35 minutes of the start of heating or when the temperature reached about 315°C. The reaction then appeared to be sustained and exothermic. Within the hour the reaction appeared to be finished and heating an additional 6 hrs. produced no changes. The reaction products were chiefly O\(_2\) and Cl\(_2\) plus a solid mixture containing CsF, NaF, CsClF\(_4\), and a small amount of Cs\(_2\)NiF\(_6\).

In a similar approach, the reaction of Na\(_2\)O\(_2\) with ClF\(_2\)SbF\(_5\) was carried out in an attempt to bring about the following reaction:

\[
\begin{align*}
\text{Na}_2\text{O}_2 & \quad + \quad \text{ClF}_2\text{SbF}_5 \quad \rightarrow \quad \text{ClOF} & \quad + \quad \text{NaF} & \quad + \quad \text{NaSbF}_6 & \quad + \quad 1/2\text{O}_2 \\
\text{or} & \\
\text{Na}_2\text{O}_2 & \quad + \quad \text{ClF}_2\text{SbF}_5 \quad \rightarrow \quad \text{ClOF}_3 & \quad + \quad \text{SbF}_3 & \quad + \quad 2\text{NaF} & \quad + \quad 1/2\text{O}_2
\end{align*}
\]

The Na\(_2\)O\(_2\)-ClF\(_2\)SbF\(_5\) system was less reactive than the Na\(_2\)O\(_2\)-ClF\(_4\)SbF\(_5\) system (see Section F). No appreciable reaction was noted up to 125°C and the conversion, after 24 hours, was only 2-4% at 160°-170°C. At 250°C, a sudden reaction occurred after a delay of about 30 min. at 250°C and a temperature rise of 30°C at the wall of the autoclave was noted in less than one minute. On cooling, the products were found to be ClF\(_3\), ClF, ClO\(_2\)F and O\(_2\) and the solid product was NaSbF\(_5\). At 250°C, the reaction was 90-95% complete (estimate based on recoveries). No new or unknown compounds were detected.

- 25 -

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F. Investigations of the Preparation of Derivatives of Chlorine Pentfluoride

The approach to the preparation of derivatives of ClF₅ was similar to that used for ClF₃ and broadly, can be grouped under three headings: (1) attempts to form other Cl₁-F compounds, (2) attempts to prepare Cl₁-O-F compounds and (3) attempts to incorporate the ClF₅ molecule in an adduct or salt useful as a solid oxidiser.

Two preparative methods for ClF₅ were used and their relative merits were compared. The first method involved the following separate reactions:

\[
\text{CsF} + \text{ClF}_3 \xrightarrow{80^\circ \text{C}}_{150 \text{ psi}} \text{CsClF}_4
\]

\[
\text{F}_2 + \text{CsClF}_4 \xrightarrow{150^\circ \text{C}}_{1300 \text{ psi}} \text{ClF}_5 + \text{CsF}
\]

The above sequence usually required three days per batch of ClF₅ (10-15 grams) with conversions of 60-85%. Yields based on the CsClF₄ converted were nearly 100%.

The second method was a direct fluorination of ClF₃:

\[
\text{F}_2 + \text{ClF}_3 \xrightarrow{300^\circ \text{C}}_{2500 \text{ psi}}
\]

In contrast to the first procedure, the direct fluorination is the better method for laboratory preparation since it only requires one day per batch and conversions of ClF₃ are above 90%. Yields of over 100 grams of ClF₅ are usually obtained in a single run using a conventional laboratory scale autoclave.

It was found that the latter preparative method was sensitive to the composition of the reactor metal with the best yields obtained in nickel. Under conditions producing near quantitative yields in nickel reactors, experiments carried out in stainless steel or monel reactors gave either much less ClF₅ or no ClF₅ at all.

As in the case of ClF₃, attempts to prepare novel Cl₁-F compounds using ClF₅ as an intermediate have involved pyrolysis, fluorination and electric discharge techniques.
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Pyrolyses of ClF₅ were attempted at 375° and 430° to determine whether ClF₅ could be condensed to higher homologs or to solid material. At 375° in a nickel reactor (maximum pressure, 500 psig), ClF₅ decomposed only slightly (≤ 10%) to ClF₃ and F₂. At 430° in a monel reactor, ClF₅ was quantitatively decomposed to ClF₃, ClF₇, and F₂. Note again the apparent effect of the reactor metal.

An attempt to upgrade ClF₅ with elemental fluorine was unsuccessful. A 4:1 mixture of F₂ and ClF₅ was heated to 375° for 16 hours with a maximum pressure of 2800 psig. The only observed reaction was a decomposition of ClF₅ to ClF₃. This was unexpected in view of the large excess of fluorine present in the reactor.

ClF₅ did not form an adduct with, or react with, CsF in a liquid-solid phase reaction at -78° for 8 days. The same reactants were transferred to an autoclave and the system was heated to 150°. This was followed by a reaction with a second mixture at 300°. Material balances were obtained in both cases as shown below.

<table>
<thead>
<tr>
<th>Reaction Temperature</th>
<th>150°</th>
<th>300°</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsF charged (moles)</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>ClF₅ charged</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>ClF₅ recovered</td>
<td>0.054</td>
<td>0.047</td>
</tr>
<tr>
<td>ClF₅ consumed</td>
<td>0.068</td>
<td>0.073</td>
</tr>
<tr>
<td>F₂ recovered</td>
<td>0.071</td>
<td>0.097*</td>
</tr>
</tbody>
</table>

(*probably a small quantity of air in recovered sample)

X-ray diffraction analysis indicates that the solid products are mixtures of CsClF₄ and CsF. The overall reaction can be summarized by the following equations:

a. ClF₅ → ClF₃ + F₂
b. ClF₃ + CsF → CsClF₄

In other experiments pure ClF₅ and mixtures of ClF₅ with ClF₃ were subjected to electric discharges of 19,000 to 30,000 volts at pressures of 532 mm. Hg to 20 psig in attempts to upgrade the fluorine content of the ClF₅ or to form new chlorine fluorides. No new products were observed.

- 27 -

CONFIDENTIAL
As is pointed out in the Introduction to this report, the structure of CIF$_5$ is considered to be similar to that of BrF$_5$—i.e., octahedral with the unshared electron pair occupying one corner.

Under the proper conditions, it might be expected that the electron pair could form a dative bond with certain electron deficient atoms or molecules as O, NO, NOF, etc. Typical of these would be CIF$_5$O and this compound might still retain the octahedral configuration of the original CIF$_5$.

In addition, the pyrolytic degradation of CIF$_5$ or degradation of CIF$_5$ by physical means may produce intermediates more reactive toward oxygen-containing reagents than either CIF$_5$ or CIF$_3$.

The following experiments were carried out to form novel Cl–O–F oxidizers.

Chlorine pentafluoride and O$_2$ were reacted together, in two separate experiments, at 375° and 430°. A 7:1 mixture of O$_2$ and CIF$_5$ is stable indefinitely at 25°; however, when the mixture was heated to 430° for 15 hours (maximum pressure, 2600 psig) the CIF$_5$ decomposed completely to CIF$_3$ and F$_2$. At 375°, the decomposition of CIF$_5$ was only slight under the same conditions. It appears that oxygen has no effect on the thermal stability of CIF$_5$.

Gaseous ozone, generated by a Welsbach unit, was passed through CIF$_5$ maintained at -95° to -97°C. There was no visible reaction and no new products were formed. When ozone was passed through a solution of CIF$_5$ in CCl$_2$F$_2$ at -80° the products were ClO$_2$F, ClO$_2$F, and CIF$_3$.

Equimolar mixtures of gaseous ClO$_2$F and ClF$_5$ were heated to 260°C and little or no reaction occurred. However, at 420° only residual traces of ClO$_2$F and CIF$_5$ could be detected. There were no solid products and the bulk of the gaseous products were non-absorbing in the infrared region of 2-15 microns indicating
decomposition of the reactants to the elements. This reaction was discussed in detail in the section concerned with the chemistry of ClO$_2$F. Equimolar amounts of ClF$_5$ and ClO$_3$F did not react at 300°C; therefore, the temperature was increased to 400°C. It was expected that ClF$_5$ would decompose; however, it was hoped that the ClO$_3$F might react with any transient intermediates or radicals associated with the ClF$_5$ decomposition. This was not the case and the only products observed were ClF, ClF$_3$, ClO$_3$F and F$_2$. There was no indication of the formation of the hypothetical ClO$_3$ClF$_6$ or the simpler derivative ClF$_5$O.

A similar experiment using F$_2$ as a pressurizing gas (310°C; 2600 psig) was also unsuccessful and the ClO$_3$F and ClF$_5$ were recovered unreacted.

A 20% mole excess of NO$_2$F was reacted with ClF$_5$ at -78°C for several days. The excess NO$_2$F was easily removed under vacuum (vapor pressure of NO$_2$F, 360 mm at -78°C; ClF$_5$, 23.6 mm). The residual material at -78°C was a relatively non-volatile yellow liquid with a vapor pressure of about 5 mm Hg, containing 4.1 g (0.063 moles) of NO$_2$F and 8.7 g (0.067 moles) of ClF$_5$. The mole ratio ClF$_5$/NO$_2$F is 1.06 indicating an equimolar complex.

\[ \text{NO}_2\text{F} + \text{ClF}_5 \rightarrow \text{NO}_2\text{F}\cdot\text{ClF}_5 \]

On warming the complex to -35°C (v.p. 310 mm) both NO$_2$F and ClF$_5$ can be identified in the vapor phase by infrared analysis.

It is interesting to note that the liquid material cannot be a simple solution since the vapor pressure (5 mm Hg) at -78°C is considerably less than that predicted by Raoult's Law

\[ P_T = \sum_{i=0}^{1} x_i P_i = 0.5 \times P_{\text{ClF}_5} + 0.5 \times P_{\text{NO}_2\text{F}} = \]

\[ 0.5 \times 23.6 + 0.5 \times 560 = 291.8 \text{ mm} \]

The observed vapor pressure of the adduct is given below and is presented graphically in Fig. 4.
Vapor Pressure of the NO$_2$F·ClF$_5$ System

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-105</td>
<td>5</td>
</tr>
<tr>
<td>-100</td>
<td>10</td>
</tr>
<tr>
<td>-95</td>
<td>15</td>
</tr>
<tr>
<td>-90</td>
<td>25</td>
</tr>
<tr>
<td>-85</td>
<td>35</td>
</tr>
<tr>
<td>-78</td>
<td>55</td>
</tr>
<tr>
<td>-70</td>
<td>90</td>
</tr>
<tr>
<td>-65</td>
<td>130, 135</td>
</tr>
<tr>
<td>-60</td>
<td>155</td>
</tr>
<tr>
<td>-55</td>
<td>230</td>
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<td>-50</td>
<td>275</td>
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<td>-45</td>
<td>365</td>
</tr>
<tr>
<td>-42</td>
<td>385</td>
</tr>
<tr>
<td>-40</td>
<td>420</td>
</tr>
<tr>
<td>-35</td>
<td>550, 570</td>
</tr>
<tr>
<td>-30</td>
<td>685</td>
</tr>
<tr>
<td>-28</td>
<td>760</td>
</tr>
<tr>
<td>-25</td>
<td>840, 850</td>
</tr>
<tr>
<td>-20</td>
<td>1045</td>
</tr>
<tr>
<td>-15</td>
<td>1210</td>
</tr>
<tr>
<td>-10</td>
<td>1510</td>
</tr>
</tbody>
</table>

In contrast to the solid adduct formed by NO$_2$F and ClF$_3$, the NO$_2$F·ClF$_5$ system produces a liquid which likely is a molecular adduct rather than a polar complex.

Quantities of ClF$_2$SbF$_6$ and ClF$_4$SbF$_6$ were synthesized by reactions of SbF$_5$ with ClF$_3$ and ClF$_5$. Neither solid had an appreciable vapor pressure (i.e., greater than 5 mm) at 25°. Although reactions have been carried out using excesses of both SbF$_5$ and ClF$_5$, we have found only a single well-defined combining ratio of 1 mole ClF$_5$ to 1 mole SbF$_5$. This is in contrast to data obtained by other investigators (Ref. 28) who report ratios of 2.5-1.5 SbF$_5$ to 1 ClF$_5$. This is probably associated with the difficulties of assuring complete reaction and removing unreacted starting materials. Reaction at -14° (b.p. of ClF$_5$) is complicated by the fact that SbF$_5$ (m.p. 7°C) is frozen and the ClF$_5$ must diffuse through the ClF$_4$SbF$_6$ formed before it can contact and react with the solid SbF$_5$. At ambient temperature the liquid SbF$_5$ wets the product and reaction between gaseous ClF$_5$ and liquid SbF$_5$ proceeds rapidly. Due to the low vapor pressure of SbF$_5$ (b.p. 143-145°) it is preferred to use a large excess of ClF$_5$. 
Fig. 4. Vapor pressure of the NO$_2$F-ClF$_5$ System

- 31 -
CONFIDENTIAL

The melting points were determined as 34–35° for ClF₄SbF₆ and 225–228° for ClF₃SbF₆. In charging X-ray sample tubes the ClF₄SbF₆ will melt due to the warmth of the technician's hand. Loading was easily carried out by chilling the sample beforehand and by cooling the fingers of the dry-box gloves prior to handling the sample tube.

X-ray diffraction patterns have been obtained for both ClF₃SbF₆ and ClF₄SbF₆; however, the resolution is not of high quality.

Attempts have been made to obtain infrared absorption spectra of these materials by the use of mulls with perfluorinated solvents or by pelleting the samples with inorganic diluents. These salts are so reactive that only highly fluorinated solvents are compatible and the fluorinated solvents on hand are either so volatile that poor mull results (through evaporation of the solvent and subsequent light scattering and diffraction) or the solvents have an excessive infrared absorption of their own.

Both ClF₃SbF₆ and ClF₄SbF₆ were compatible with FC-75 (Minnesota Mining and Manufacturing Company perfluorinated cyclic ether), fluorolube oils, and Halocarbon Oil 11-21. With Kel-F Oil #10, the solids turned red and some coloration was imparted to the oil. There is smoke, charring, and fire when the solids are contacted with CCl₄, 1-113 (CFCl₂CF₂Cl), CHCl₃, silicone oils, mineral oils, fluorobenzene, chlorobenzene, toluene and benzene.

The extreme reactivity of these salts is indicated in Fig. 5. The bottom sections of an electrochemical cell are shown. These are fabricated of Kel-F plastic which is inert to ClF₃, ClF₅, and SbF₅ at 25°. However, on contact with either ClF₃SbF₆ or ClF₄SbF₆ for 6-10 hours at 25° severe stress cracking results. It is emphasized that these cracks are not due to thermal strains and have been observed also in Kel-F bottles used to store the solids. It is believed that extreme fluorination of the plastic occurs locally due to the reactivity of ClF₄⁺ and ClF₃⁺ cations which causes surface stresses eventually leading to cracks. In general, the ClF₄⁺ appears to be more reactive than ClF₃⁺ and will produce the cracking phenomena in about half the time.

It was observed that when ClF₃ was added to solid ClF₄SbF₆, the material will slowly dissolve and simultaneously evolve ClF₅. It is believed that a displacement occurs according to the following equation:

- 32 -

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Stress Cracked Kcl-F Plastic. Result of Contact with ClF₅-SbF₅ Adduct. (Cracks treated with dye for contrast).
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\[
\text{ClF}_3 + \text{ClF}_4\text{SbF}_6 \rightarrow \text{ClF}_2\text{SbF}_6 + \text{ClF}_5
\]

The solid ClF₄SbF₆ dissolved in SbF₅ was heated to 375° in a stainless steel autoclave. The mixture decomposed completely and severely corroded the autoclave to produce metal fluorides and chlorides. A residual pressure of 570 mm. Hg. was due to the unexplained presence of ClF₄, C₂F₆, and SiF₄.

ClF₅ was reacted separately with SF₄, SF₆, and BF₃ at 25° and pressures up to 40 psig. There was no indication of the formation of complexes. The systems were then cooled to -78° and still no evidence for complex formation was obtained.

ClF₅ and KClO₃ reacted to a very slight extent at 150°C yielding small amounts of ClO₃F and OF₂ in the vapor phase and a detectable quantity of KF in the solid. However, at 250°C, the reaction was nearly complete since only traces of residual ClF₅ could be detected. The major components of the gaseous products were ClO₃F and ClO₂F with lesser amounts of O₂ and OF₂. The X-ray diffraction pattern of the residual solid was identical to that reported for KCIF₄ (Ref. 29).

ClF₅ and KClO₄ reacted slightly at 150° to give traces of O₂, ClO₂F, and ClO₂F and some KF in the solid. At 250°C reaction was substantially greater producing ClO₃F and O₂ as the major volatile products along with a lesser amount of ClO₂F and some residual ClF₅. X-ray powder pattern of the solid showed primarily KF and KHF₂ with additional lines which coincide with the major lines listed for KClF₄ (see ref. above).

Similar work was carried out using CsClO₄ as a reactant and the volatile products were identical to those obtained using KClO₄. The solids were CsF, CsHF₂, and some CsClF₄.

The controlled hydrolyses of ClF₃ and XeF₆ yield, respectively, ClO₂F and XeOF₄. The probable reactions may be as follows:

\[
\text{ClF}_3 + \text{H}_2\text{O} \rightarrow \{\text{ClOF}\} + 2\text{HF}
\]

\[
2\{\text{ClOF}\} \rightarrow \text{ClO}_2\text{F} + \text{ClF}
\]

\[
\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}
\]

- 34 -

CONFIDENTIAL
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By analogy, ClF₅ might react with water under moderated conditions to yield OClF₃.

\[
\text{ClF}_5 + \text{H}_2\text{O} \rightarrow \text{OClF}_3 + 2\text{HF}
\]

Since direct hydrolysis is difficult to control, the water was used in the form of a hydrate of nickel fluoride and the reaction was studied in both static and flow systems.

**Static system:**

A mixture of NiF₂·4H₂O and ClF₅ was reacted overnight with heating (200°). In addition to the unused excess ClF₅, the gaseous products obtained were primarily ClO₂F and ClO₃F, with some HF. The concentration of ClO₂F was slightly higher than that of ClO₃F. The solid phase contained NiF₂ and NiF₂·xHF. The overall reaction may be represented by two competing reactions:

\[
2\text{ClF}_5 + \text{NiF}_2·4\text{H}_2\text{O} \rightarrow 2\text{ClO}_2\text{F} + 8\text{HF} + \text{NiF}_2
\]

\[
4\text{ClF}_5 + 3\text{NiF}_2·4\text{H}_2\text{O} \rightarrow 4\text{ClO}_3\text{F} + 16\text{HF} + 3\text{NiF}_2 + 4\text{H}_2
\]

**Flow system:**

ClF₅ was passed over NiF₂·4H₂O in a mono-tube in two experiments at ambient temperature and at 190° for a total of 3.5 hours each. The only products observed were principally ClO₂F and some ClO₃F. The solid residue contained NiF₂, NiF₂·4H₂O, and some lower hydrates. These results plus those above indicate that a static system favors the formation of ClO₂F and a flow system favors ClO₃F. In addition higher temperatures in the flow system yield larger quantities of ClO₂F. These data are opposed to the expected results if one proposes the formation of ClO₃F by the thermal decomposition of ClO₂F.

In a subsequent brief exploratory reaction carried out for background information, a mixture of ClF₅ and SiO₂ was heated slowly to 250° with no sign of reaction. After 1.3 hours at 250° a sudden exothermic reaction occurred, and the pressure went from an autogeneous 600 psig to an unknown peak pressure and returned finally to 1850 psig within minutes. Considering the mass of the autoclave the heat liberated must have been appreciable to give such a fast response to the temperature rise. The thermocouple was located in the autoclave wall and is normally slow to

- 35 -

CONFIDENTIAL
The synthesis of novel Cl-O-F compounds was attempted using Na₂O₂ to introduce oxygen into the halogen fluorides and their derived ions.

Possible reactions might be:

\[
\begin{align*}
\text{Na}_2\text{O}_2 + \text{ClF}_5 & \rightarrow \text{ClO}_2\text{F}_3 + 2\text{NaF} \\
\text{Na}_2\text{O}_2 + 2\text{ClF}_5 & \rightarrow 2\text{ClO}_3\text{F} + \text{F}_2 + 2\text{NaF} \\
\text{Na}_2\text{O}_2 + 2\text{ClF}_5 & \rightarrow \text{ClO}_3\text{F} + \text{ClO}_5 + 2\text{NaF}
\end{align*}
\]

No reaction was detected at 25°C but on increasing the temperature a sudden vigorous exothermic reaction occurred at 150°C which appeared to be initiated by thermal decomposition of the Na₂O₂ followed by reaction of the Na₂O₂ and its degradation products with ClF₅ to form NaF and ClF₃. The heat was sufficiently intense to decompose most of the ClF₅ to ClF₃ and a small amount of ClF₆.

The reaction of Na₂O₂ with ClF₄SbF₆ was studied in an attempt to introduce oxygen into the ClF₄⁺ cation. The synthesis of ClOF₃ and/or ClO₂F₃ might be realized from a reaction of this type according to the equation:

\[
\text{Na}_2\text{O}_2 + \text{ClF}_4\text{SbF}_6 \rightarrow \text{ClO}_3\text{F} + \text{NaF} + \text{NaSbF}_6 + \frac{1}{2}\text{O}_2
\]

A 2:1 molar mixture of ClF₄SbF₆:Na₂O₂ was subjected to slow stepwise heating from -78°C to 250°C. The above proposed reaction did not take place; however, known compounds such as ClO₂F, ClF₅, ClF₃, ClO₂F and some O₂ were obtained as the volatile products. The solid product was NaSbF₆, as expected. The reaction was slow and the conversions, after 24 hours, were as follows: 2-4% at 75°C, 10-15% at 125°C, 30% at 160-170°C and 30% at 250°C. Additional time would undoubtedly have brought the reaction to completion.

G. Investigations of the Fluorination of Chlorine Oxides

As discussed previously, it has been proposed that compounds and ions such as OClF₃, O₂ClF₃, OCIF₅, O₂ClF₂⁻.
OCIF$_2^+$, etc., may be sufficiently stable to be isolated and studied. This phase of the work was an attempt to prepare these compounds and ions by the fluorination of the unstable, explosive, odd-electron molecule ClO$_2$ or the analogous, more stable, Cl$_2$O.

ClO$_2$, diluted with nitrogen, reacted completely with ClF$_5$ at a maximum temperature of 110° to produce ClO$_2$F and Cl$_2$ which were identified by infrared and mass spectrometric analysis. With the exception of the excess ClF$_5$, no other products were detected. The reaction might be represented by the following overall equation:

$$10 \text{ ClO}_2 + 2 \text{ ClF}_5 \rightarrow 10 \text{ ClO}_2\text{F} + \text{ Cl}_2$$

The results indicate that all of the fluorine in ClF$_5$ enters into the reaction and that ClF$_3$ and ClF (the degradation products of ClF$_5$) would probably behave in an analogous way.

No reaction occurred between NF$_3$ and ClO$_2$ under flow conditions at ambient pressure and temperature up to 110°C.

OF$_2$ is a strong oxidizer and it was considered probable that it might serve as a fluorinating agent toward ClO$_2$ under flow conditions at moderate temperatures (≤ 110°C). The product mixture contained primarily ClF$_5$, a significant amount of ClO$_2$F and a lesser amount of ClO$_3$F. It is suspected that O$_2$ was also formed; however, no specific attempt was made to trap or isolate it. The following equations probably represent only a few of the many possible reactions which occur:

a. $4\text{ ClO}_2 + 6\text{ OF}_2 \rightarrow 2\text{ ClF}_5 + 3\text{ O}_2 + 2\text{ ClO}_2\text{F}$

b. $2\text{ ClO}_2\text{F} + \text{ O}_2 \rightarrow 2\text{ ClO}_3\text{F}$

c. $2\text{ ClO}_2 + \text{ F}_2 \rightarrow 2\text{ ClO}_2\text{F}$

d. $\text{ ClO}_2 + \text{ OF}_2 \rightarrow \text{ ClO}_3\text{F} + \frac{1}{2}\text{ F}_2$

e. $2\text{ ClO}_2 + \text{ OF}_2 \rightarrow \text{ ClO}_2\text{F} + \text{ ClO}_3\text{F}$

The results would indicate that equation a. represents the general overall reaction and that equation b. occurs to a significant extent. No new or unidentified materials were detected.
The reaction of ClO$_2$ with F$_2$ is the preparative method for the synthesis of ClO$_2$F. Since N$_2$F$_4$ can be considered as a pseudohalogen, readily dissociating to NF$_2$ radicals, it is reasonable to suppose that N$_2$F$_4$ might react with the odd-molecule ClO$_2$· to form ClO$_2$· as below.

\[
\begin{align*}
\text{N}_2\text{F}_4 & \longrightarrow 2\text{NF}_2\cdot \\
\text{NF}_2\cdot + \text{ClO}_2\cdot & \rightarrow ? \text{O}_2\text{ClIF}_2
\end{align*}
\]

The reaction was smooth and the only products isolated were NOF and Cl$_2$ as well as small amounts of N$_2$ or F$_2$. There was no residual ClO$_2$ in the product mixture and no new or unknown materials were detected.

The study of the fluorination of Cl$_2$O was initiated by reacting it with F$_2$ at ambient temperature in a flow system. Cl$_2$O was freshly prepared in advance by passing a (1:1) Cl$_2$/N$_2$ mixture at about 200 cc/min. (total flow) through a 24" x 1" monel reactor packed with 31.0 g. (0.143 mole) yellow basic H$_2$C on glass wool. The Cl$_2$O was condensed at -78°C and stored at this temperature until time for use. The red-brown liquid at -78°C was predominantly Cl$_2$O containing a small amount of unconverted Cl$_2$.

The crude Cl$_2$O was warmed from -78°C to 0°C and vaporized with a stream of N$_2$ passed at a rate of about 250 cc/min. This Cl$_2$O/N$_2$ mixture was combined with F$_2$ (200 - 300 cc/min.) at ambient temperature and the entire mixture was then passed through a 4000 ml. reactor (estimated residence time; 7 min. + 1 min.).

The condensable products were caught in a trap cooled with liquid oxygen (-183°C). The products were identified as ClO$_2$F, ClF$_3$ and some ClO$_3$F.

Cl$_2$O and a large excess of F$_2$ were charged to a monel reactor and kept at 155°C for 7 hrs. at a maximum autogenous pressure of 690 psig. Aside from excess F$_2$, the product mixture contained ClO$_2$F and ClF$_3$ as the major products, ClO$_3$F and ClF$_5$ as minor products plus a novel material believed to be ClF$_3$O. The ClF$_3$O is still slightly in doubt because of the interference in its infrared absorption spectra by ClO$_2$F, ClF$_3$ and the other products and since the material was in small concentrations.

The identification of ClF$_3$O was aided by the fact that during the time this work was in progress Rocketdyne personnel reported their synthesis of this same compound and its infrared spectrum.

- 38 -

CONFIDENTIAL
In subsequent experiments, Cl2O and a large excess of OF2 were passed through a copper coil reactor at 15-20°C for several hours. No reaction occurred. In a variation of this reaction a 1:3 molar mixture of Cl2O and OF2 were heated for 5 hours at 130°C in a monel reactor and no reaction occurred.

This same 1:3 molar mixture of Cl2O and OF2 was then heated at 185°C for 20 hours (maximum pressure, 1275 psig). (Note thermal decomposition of OF2 is appreciable in the 200°C-220°C range.) After 8 hours reaction the products were condensed and pumped at -76°C to remove ClO3F, ClF5, ClF3, and ClO2F leaving residual pure ClF3O.

Further work on the preparation and properties of this new oxidizer was not possible since the contract expired.

II. Investigations of the Chemistry of Oxygen Difluoride

A number of reactions were carried out using OF2 in attempts to introduce either oxygen or the -OF group into ClFx molecule and other molecules. It was also of interest to investigate the possibility of polarizing the O-F bond and forming complexes of OF2. A few proposed reactions include:

\[
\begin{align*}
\text{OF}_2 + \text{ClF}_3 & \rightarrow \text{OCIF}_5 \text{ or FOClF}_4 \text{ (a covalent hypofluorite)} \\
\text{OF}_2 + \text{ClO}_2^\text{F} & \rightarrow \text{OF}^+\text{ClO}_2^\text{F}_2^- \\
\text{OF}_2 + \text{ClF} & \rightarrow \text{OCIF}_3 \\
& \text{etc.}
\end{align*}
\]

No reaction was detected between OF2 and ClF3 at temperatures up to 280°C (maximum pressure, 1350 psig); however, significant thermal decomposition of OF2 did occur giving O2 and F2. The fluorine formed then reacted with the ClF3 to produce ClF5. The principal reactions were:

\[
\begin{align*}
\text{OF}_2 & \rightarrow \frac{1}{2}\text{O}_2 + \text{F}_2 \\
\text{F}_2 + \text{ClF}_3 & \rightarrow \text{ClF}_5
\end{align*}
\]

No reaction occurred between OF2 and ClF5 at temperatures up to 300°C (maximum pressure, 2950 psig). A major portion of the OF2 was thermally decomposed to O2 and F2 and the ClF5 was recovered quantitatively.
An equimolar mixture of OF₂ and ClO₂F did not react at 250° (maximum pressure, 825 psig). As previously noted at these high temperatures some thermal decomposition occurs. The ClO₂F was recovered along with a small amount of ClO₃F which is believed to be a product of the reaction of oxygen with ClO₂F since CIF and its fluorinated homologs, CIF₃ and CIF₅, were absent. CIF is known to be a product of the thermal dissociation of ClO₂F.

\[ 3\text{ClO}_2\text{F} \xrightarrow{\text{heat}} 2\text{ClO}_3\text{F} + \text{CIF} \]

The overall reaction is therefore believed to be a sum of the following reactions:

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

\[ \frac{1}{2}\text{O}_2 + \text{ClO}_2\text{F} \rightarrow \text{ClO}_3\text{F} \]

Oxygen difluoride and perchloryl fluoride (ClC₃F) did not react after 20 hours at 200° (maximum observed pressure, 1110 psig). Both compounds were recovered unchanged.

Oxygen difluoride and nitrogen trifluoride did not react after 7 hours at 300° (maximum observed pressure, 1975 psig). Some thermal decomposition of the CF₂ was noted.

Oxygen difluoride and antimony pentafluoride were heated together for 16 hours at temperatures up to 200° (maximum pressure, 760 psig) in an effort to form a complex of the type CF⁺SbF₆⁻ or O⁺⁺(SbF₆)₂⁻. However, the reactants were recovered unchanged.

Similarly, OF₂ was reacted with CsF at temperatures up to 200° in the hope of forming a complex. No reaction was noted.

Oxygen difluoride and CsClF₄ were combined and heated for 20 hours at 200° (maximum pressure, 790 psig). On cooling, the product gases were found to contain small amounts of O₂, F₂, and CIF₅ which were presumably formed according to the equations.

\[ 2\text{OF}_2 \rightarrow \text{O}_2 + 2\text{F}_2 \]

\[ \text{F}_2 + \text{CsClF}_4 \rightarrow \text{CsF} + \text{ClF}_5 \]
Oxygen difluoride and ClF₄SbF₆ were heated for 18 hours at 200° (maximum pressure observed, 500 psig) and, on cooling, the product gases were found to contain ClF₅, O₂, and F₂ in addition to the residual undecomposed OF₂. Analysis of the remaining solid showed that the ClF₄SbF₆ had decomposed and the residual material was richer in the nonvolatile SbF₅.

\[
\text{ClF}_4\text{SbF}_6 \rightarrow \text{ClF}_5 + \text{SbF}_5
\]

No reaction was detected between OF₂ and ClF₄SbF₆ after 20 hours at 200°C (850 psig). As usual some decomposition of the OF₂ was obtained. Mass spectrometric analysis of the total gas phase indicated the presence of OF₂, O₂ and a small amount of Cl₂ and ClF₅.

Oxygen difluoride reacted with anhydrous CsCl at 200° to produce a mixture of gases including O₂, Cl₂, some ClF and ClO₂F and a small amount of CF₄ and SiF₄ (the latter two compounds were found to be impurities in the particular sample of OF₂ used). The major products were chlorine and oxygen. The residual solid was CsF admixed with a small amount of CsClF₄ and sufficient Cs₂NiF₆ to impart a reddish color to the solid. The principal reactions probably include the following:

\[
\text{OF}_2 + 2\text{CsCl} \rightarrow \frac{1}{2}\text{O}_2 + \text{Cl}_2 + 2\text{CsF}
\]

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

\[
\text{Cl}_2 + 3\text{F}_2 \rightarrow 2\text{ClIF}_3 \text{ (and ClIF in the presence of excess Cl}_2\text{)}
\]

\[
\text{ClIF}_3 + \text{CsF} \rightarrow \text{CsClIF}_4
\]

\[
2\text{ClIF}_3 + 2\text{CsF} + \text{reactor metal} \rightarrow \text{Cs}_2\text{NiF}_6 + \text{Cl}_2 + \text{MF}_2
\]

The ClO₂F can be accounted for by the oxidation of ClF.

In order to further explore the reaction of OF₂ with metal chlorides in search of Cl-O-F compounds, OF₂ and NaCl were heated in a monel cylinder at 200°C for 18 hours (maximum pressure, 940 psig). A reaction occurred and 94% of the oxygen in the charged OF₂ was recovered as O₂. In addition the chlorine in the NaCl used was almost quantitatively recovered as Cl₂. Other gaseous products were very small amounts of ClF and ClO₂F as well as CF₄ and SiF₄ present as impurities in the OF₂.
4NaCl + 2OF₂ → 4NaF + 2Cl₂ + O₂

Calcium chloride (anhydrous) and OF₂ were charged to a monel cylinder and, following the introduction of the OF₂ at -196°, the cylinder was allowed to warm. During the warming period, a sudden and highly exothermic reaction occurred which heated the cylinder to a high temperature. After standing 24 hours, the products in the cooled cylinder were found to be O₂ and Cl₂ with small amounts of ClF, ClF₃, ClO₂F and some unreacted OF₂. The nonvolatile solid residue was identified as CaF₂. The principal reaction was:

CaCl₂ + OF₂ → CaF₂ + 1/2 O₂ + Cl₂

The reaction of OF₂ with Cl₂ was carried out in an attempt to prepare ClOF, ClO₂F, ClOF₃ or ClO₂F₃. Streng (Ref. 30) stated that when OF₂–Cl₂ mixtures were passed through a copper tube at 300°C, small explosions occurred. In addition it was reported that on warming mixtures of OF₂ and the halogens Cl₂, Br₂ or I₂, from -196°C, explosions occurred.

The mixture of OF₂ with Cl₂ employing N₂ as a diluent, gave indications of a trace of a smooth reaction occurring. Therefore, it was decided to eliminate the N₂ and to conduct the experiment at ambient temperature or above despite Streng’s warnings of explosions. A binary mixture of OF₂ and Cl₂ was warmed to ambient temperature but no reaction was observed after 4 days under these conditions. Heating at 150°C finally resulted in the formation of ClF and O₂ as principal products. It is suggested that the following reaction occurred:

2Cl₂ + 2OF₂ → 4ClF + O₂

No reaction was detected at ambient temperature between OF₂ and ClF; however, at 150°C a slow reaction occurred as indicated by a decrease in pressure over a period of time. The main products in this reaction were ClF₃ and O₂ and a lesser amount of ClO₂F. The predominance of ClF₃ indicates that perhaps two sets of reactions occurred. Although OF₂ by itself is thermally stable to about 200°C, the decomposition to O₂ and F₂ was presumably initiated or catalyzed by ClF resulting in the following sequence of reactions:

2OF₂ → O₂ + 2F₂
2ClF + 2F₂ → 2ClF₃

-42-
CONFIDENTIAL

In addition to the ClF₃ was found a small amount of ClO₂F which probably formed through an oxidation of ClF by elemental oxygen.

\[
\text{ClF} + \text{O}_2 \rightarrow \text{ClO}_2\text{F}
\]

Another attempt was made to react OF₂ with ClF under conditions less severe than described above. The gaseous OF₂ was reacted in a flow system with ClF diluted with N₂ at a 4-6 minute residence time. In addition to the recovered reactants, the product mixture contained some O₂ and another unidentified component(s). The unknown materials were present in very small amounts and possessed infrared absorptions bands in the regions of 5.40, 6.15, 7.45, 7.8-7.9, 8.92, 9.55, and 11.8 μ. Mass spectrometric patterns of the unknown materials gave a pattern which indicated that our sample reacted with the tube walls to produce materials not present in our original mixture. The strongest infrared unknown absorptions appear in the Cl-O region with no indication of any Cl-F absorption. Further unsuccessful attempts at identification were made by submitting the fractions to gas chromatographic analysis. After several days of storage in a stainless steel cylinder, we could no longer detect the unknown infrared absorption bands indicating the material may not be very stable. We were not successful in subsequent attempts to isolate and identify this small amount of material.

I. Investigations of the Chemistry of Nitrogen Fluorides

Throughout the program reactions were studied periodically in attempts to use the nitrogen fluorides (NF₃, N₂F₄, trans-N₂F₂, cis-N₂F₂) as either fluorinating agents or as agents whereby the difluoroamino group (=NF₂) or the fluorimino group (=NF) could be substituted into oxidizer molecules. Results of these experiments are summarized below.

Nitrogen Trifluoride, NF₃

Several exploratory reactions were carried out using NF₃ in attempts to introduce the difluoroamino group into a ClFₓ molecule. A few possible reactions are:

\[
\text{NF}_3 + \text{ClF}_3 \rightarrow \text{F}_2\text{NCI}_4
\]

\[
\text{NF}_3 + \text{CsClF}_4 \rightarrow \text{CsF} + \text{F}_2\text{NCI}_4
\]

\[
\text{NF}_3 + \text{ClIF}_5 \rightarrow \text{F}_2\text{NCI}_4 + \text{F}_2
\]

etc.

- 43 -
Unfortunately, the high thermal stability of the NF$_3$ molecule precluded such reactions under the conditions of our experiments.

No reaction was detected between NF$_3$ and ClF$_3$ at temperatures up to 425°C and pressures up to 1350 psig. The reactants were recovered unchanged.

NF$_3$ and ClF$_5$ did not react after 20 hours at 325°C (maximum pressure, 2125 psig). There was, however, some thermal decomposition of the ClF$_5$ to ClF$_3$ and F$_2$. The NF$_3$ was quantitatively recovered.

No reaction occurred between NF$_3$ and ClO$_2$F at temperatures up to 475°C over a period of 18 hours (maximum pressure, 2050 psig). All of the reactants were recovered unchanged.

NF$_3$ did not react with CsClF$_4$ at temperatures up to 470°C over a period of 24 hours. The only products observed were the unreacted NF$_3$ and ClF$_3$ and CsF resulting from thermal decomposition of the CsClF$_4$.

A mixture of NF$_3$ and ClF$_4$SbF$_5$ was heated at 200°C and the products were NF$_3$, ClF$_5$, and an off-white solid containing SbF$_5$ and ClF$_5$ in a mole ratio greater than one (i.e., SbF$_5$/ClF$_5$ > 1). Since the NF$_3$ was essentially all recovered, it appears that the principal reaction was a simple decomposition of the salt.

\[ \text{ClF}_4\text{SbF}_6 \rightarrow \text{SbF}_5 + \text{ClF} \]

Nitrogen trifluoride and difluorochlorine hexafluoroantimonate (V) (ClF$_2$SbF$_6$) were combined in a mole ratio 1.3/1 and heated in a Monel vessel at several temperatures:

a. At temperatures ranging up to 250°C and for periods up to 3 hours, there were no signs of reaction and the NF$_3$ and ClF$_2$SbF$_6$ were recovered unchanged.

b. A second experiment at 350°C for 23 hours duration indicated no reaction between the NF$_3$ and ClF$_2$SbF$_6$ and the reactants were recovered unchanged.

No reaction occurred between NF$_3$ and ClO$_2$ under flow conditions at ambient pressure and temperatures up to 110°C.
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Tetrafluorohydrazine, $N_2F_4$

It has been noted that $N_2F_4$ is a source of $NF_2$ radicals, and it is conceivable that a radical induced reaction of $N_2F_4$ with halogen fluorides might lead to unusual difluoroamino-substituted halogen fluoride, e.g.

$$ClF_3 + N_2F_4 \rightarrow ClF_4NF_2 + NF_3$$

or

$$ClF_3 + N_2F_4 \rightarrow ClF_4(NF_2)_2$$

$N_2F_4$ and $ClF_3$ did not react at temperatures up to 250°. When reaction finally did occur at 250°C, $NF_3$ and $ClF_3$ were the only products suggesting a simple fluorination of $N_2F_4$ by $ClF_3$.

$$N_2F_4 + ClF_3 \rightarrow ClF_3 + 2NF_3$$

In an analogous reaction of $ClF_3$ with $N_2F_4$ an exothermic reaction occurred at 25°C resulting in fluorination of $N_2F_4$ by $ClF_3$. It is interesting to note that the temperature was similar to the initiating temperature of the $ClF_3$ system above. This suggests that the initiating step is dissociation of the Cl-F bond since $N_2F_4$ is appreciably dissociated at room temperature.

$$N_2F_4 \rightarrow 2NF_2$$

$$2NF_2 + ClF_3 \rightarrow ClF + 2NF_3$$

The reaction of $ClF$ with $N_2F_4$ was carried out to investigate the possibility of $ClF$ fluorinating $N_2F_4$ and to complete the sequence from $ClF_3$ and $ClF_3$. The reaction at 250°C did produce $NF_3$ and $Cl_2$ as expected; however, an inordinate amount of $NF_3$ was found as well as $N_2$ suggesting a simultaneous thermal decomposition of some of the $N_2F_4$.

$$N_2F_4 \rightarrow 2NF_2$$

$$2NF_2 + 2ClF \rightarrow 2NF_3 + Cl_2$$

$$3N_2F_4 \rightarrow 4NF_3 + N_2$$

$$4N_2F_4 + 2ClF \rightarrow 6NF_3 + N_2 + Cl_2$$

The heterogeneous $CsClF_4-N_2F_4$ system did not interact up to 250°C but at 350°C a rapid reaction occurred giving $ClF$, $NF_3$ and $N_2$ as gaseous products and a solid residue of $CsF.$

- 45 -

CONFIDENTIAL
CsClF₄ and some Cs₂NiF₆. From the amounts of recovered reactants and products it appears that the primary reactions were simple decompositions

\[
\begin{align*}
2N_2F_4 & \rightarrow 4NF_3 + N_2 \\
CsClF_4 & \rightarrow CsF + ClF_3 \\
ClF_3 & \rightarrow ClF + F_2
\end{align*}
\]

and a fluorination of \(N_2F_4\) by CsClF₄ according to the following equation was only secondary:

\[
CsClF_4 + N_2F_4 \rightarrow CsF + ClF + 2NF_3
\]

The reaction of ClO₂ with F₂ is the preparative method for the synthesis of ClO₂F. Since \(N_2F_4\) can be considered as a pseudohalogen, readily dissociating to \(NF_2\) radicals, it is reasonable to suppose that \(N_2F_4\) might react with the odd-molecule ClO₂⁻ to form ClO₂NF₂ as below.

\[
\begin{align*}
N_2F_4 & \rightarrow 2NF_2^- \\
NF_2^- + ClO_2^- & \rightarrow O_2ClNF_2
\end{align*}
\]

The reaction was smooth and the only products isolated were NOF and Cl₂ as well as small amounts of N₂ or F₂. The apparatus apparently contained some HF from the previous use and with the NOF formed minute amounts of solid NOF·3HF. There was no residual ClO₂ in the product mixture and no new or unknown materials were detected.

A reaction between \(N_2F_4\) and ClIF₄SbF₅ at 195°C produced NF₃, \(N_2\), ClF₃, ClIF₅, SbF₅ and a mixture (ClIF₅·SbF₅) of indeterminate composition. The amount of NF₃ recovered was greater than could be theoretically expected from a thermal decomposition of \(N_2F_4\).

\[
3N_2F_4 \rightarrow 4NF_3 + N_2
\]

The presence of ClIF₅ and SbF₅ is a result of the decomposition of ClIF₄SbF₅. The ClIF₃ in large quantities indicates that \(N_2F_4\) was fluorinated to NF₃ by the ClIF₅. The total reaction is the sum of two reactions:
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\[ \text{ClF}_4\text{SbF}_6 \rightarrow \text{ClF}_5 + \text{SbF}_5 \]

\[ \text{ClIP}_6 + \text{N}_2\text{F}_4 \rightarrow 2\text{NF}_3 + \text{ClF}_3 \]

As above, the reaction of \( \text{N}_2\text{F}_4 \) with \( \text{ClF}_2\text{SbF}_6 \) yielded \( \text{NF}_3 \), \( \text{N}_2 \), \( \text{Cl}_2 \), \( \text{SbF}_5 \) and some \( \text{ClIF}_2\text{SbF}_5 \) of indeterminate composition. From the amount of salt recovered, it was evident that the bulk of \( \text{NF}_3 \) came from the decomposition of \( \text{N}_2\text{F}_4 \); however, a lesser amount originated with the fluorination of \( \text{N}_2\text{F}_4 \) by \( \text{ClF}_3 \) and its degradation product \( \text{ClIF} \) producing ultimately \( \text{Cl}_2 \).

**Trans-Difluorodiazine, trans-\( \text{N}_2\text{F}_2 \)**

An exploratory study was begun to evaluate the feasibility of using \( \text{N}_2\text{F}_2 \) as a fluorinating agent toward \( \text{ClIO}_2\text{F} \) and \( \text{ClO}_3\text{F} \) and as a complexing agent toward \( \text{ClIO}_2\text{F} \) and \( \text{ClIF}_3 \). The first phases of this work were carried out using an isomeric mixture containing over 95 mole per cent trans- \( \text{N}_2\text{F}_2 \).

No reaction occurred between trans- \( \text{N}_2\text{F}_2 \) and \( \text{ClO}_3\text{F} \) in the temperature range -78°C to 250°C and at autogenous pressures. It is to be noted that the trans- \( \text{N}_2\text{F}_2 \) contained some cis- \( \text{N}_2\text{F}_2 \) and \( \text{NF}_3 \) initially and following exposure at 250°C there was a slight increase in the amount of \( \text{NF}_3 \) present indicating that some thermal decomposition of the difluorodiazine had occurred.

No reaction was detected between \( \text{ClIF}_5 \) and trans- \( \text{N}_2\text{F}_2 \) in the temperature range -78°C to 250°C. Again thermal decomposition of trans- \( \text{N}_2\text{F}_2 \) was indicated by the slight increase in the relative \( \text{NF}_3 \) concentration and, with this exception, a nearly quantitative recovery of the starting materials was obtained.

When equimolar amounts of trans- \( \text{N}_2\text{F}_2 \) and \( \text{ClO}_2\text{F} \) were combined at -78°C in a Kiel trap, the observed pressure was approximately that calculated for an ideal solution; however, a color change occurred immediately on contact of the reactants. The \( \text{ClO}_2\text{F} \) initially was a pale yellow liquid at -78°C and on slow addition of trans- \( \text{N}_2\text{F}_2 \) the color changed to a deep yellow-orange. No phase separation was noted. Infrared analysis of the vapor phase failed to disclose anything other than the reactants and on removing the difluorodiazine the \( \text{ClO}_2\text{F} \) again assumed its pale yellow color. Both reactants were quantitatively recovered.

In a second experiment, a similar but large charge was stored in a monel reactor at 25°C thus no color changes could be observed. Infrared analysis of the gas phase indicated only the
starting materials to be present. However, after this charge was heated at 200°C, a reaction seemed to occur. The pressure rose steadily to a maximum of 250 psig in the first 4 hours at 200°C and then dropped and leveled off at 100 psig for the balance of the heating period. Infrared analysis indicated that ClF₃ was the main product. Present also was some unreacted ClO₂F. NF₃ (in a larger amount than present in the initial N₂F₂) and no trace of any difluorodiazine. Mass spectrometric analysis confirmed the presence of N₂ and O₂. No new or unidentified materials were detected.

Cis-Difluorodiazine, cis-N₂F₂

Cis-N₂F₂ is known to form complexes with strong Lewis acids and it was of interest to study the possibility of complex formation with the Cl-O-F oxidizers. No reaction took place between cis-N₂F₂ and ClO₂F in the temperature range -78°C to 180°C. At 180°C, the thermal decomposition of cis-N₂F₂ was noted and the ClO₂F was recovered unchanged at the end of the experiment.

No reaction was observed between cis-N₂F₂ and ClO₃F in the temperature range -78°C to 180°C. Conditions were limited to the point at which the thermal decomposition of cis-N₂F₂ was detected. A quantitative recovery of ClO₂F was obtained.

No reaction was observed between cis-N₂F₂ and OF₂ in the temperature range -78°C to 180°C. At the upper temperature, the cis-N₂F₂ was almost completely decomposed and a slight decomposition of OF₂ also occurred but no new products were formed.

The reaction of cis-N₂F₂ with ClF₅ could form N₂FCIF₅ according to the equation

\[ \text{N}_2\text{F}_2 + \text{ClF}_5 \rightarrow \text{N}_2\text{F}^+\text{ClF}_6^- \]

and other possible products can be speculated. The N₂F⁺ ion is known to exist in various compounds but the ClF₅⁻ ion has yet to be synthesized. We observed no reaction, however, between
cis-N₂F₂ and ClF₅ in the temperature range -78°C to 150°C. At 150°C, thermal decomposition of the N₂F₂ occurred and also some degradation of ClF₅ to ClF₃ and F₂ took place.

The expected synthesis of N₂FCI₄ by reaction of cis-N₂F₂ with ClF₃ did not materialize. No reaction was detected between the gases at temperatures up to 150°. At the higher temperatures only the thermal decomposition of cis-N₂F₂ into N₂ and F₂ was noted in addition to some ClF₅ formed from the subsequent reaction of elemental F₂ with the ClF₃ present.

The reaction of cis-N₂F₂ with ClF did not yield N₂F²⁺ClF₂⁻. As above, no reaction occurred in the -78° to 150°C temperature range. The thermal decomposition of cis-N₂F₂ into N₂ and F₂ was detected above 150°C in addition to some ClF₃ most likely formed by a reaction of F₂ with ClF.

7. Electrochemical Studies Relating to the Preparation of New Oxidizers

This phase of the program was concerned with a study to determine the feasibility of preparing new oxidizers by electrolysis of systems containing as solvents or solutes ClF₅, ClF₃, ClO₂F, ClO₃F and other halogen fluorides or halogenyl fluorides. As indicated in several experiments below, the feasibility of this approach was partially demonstrated by the preparation of ClF₅ by electrolyses.

Unfortunately, many of the halogen fluorides and halogenyl fluorides of interest as solvents and reactants are poor conductors and the electrical equivalents which can be passed through a system are extremely small per unit time. It has been of interest therefore to screen potential systems for conductivity and to attempt to provide additives for raising the conductivity to a practical value.

The cell used performs the dual function of an electrolysis cell and a conductivity cell and the final design is given in Fig. 6. This cell was calibrated by measuring the resistance of standard KCl solutions and the cell constant was determined as 0.248.

The conductivity values determined during this phase of the work are summarized in Table II for ready reference and the discussion of the work is given in the following paragraphs.
Table II

Conductivities of Oxidizer Mixtures

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solute</th>
<th>Mole Fraction Solute</th>
<th>Temp. ('C)</th>
<th>Specific* Conductivity (ohm(^{-1}) cm(^{-1}))</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(_2)F(_3)</td>
<td>Br(_2)F(_3)</td>
<td>0(^o)</td>
<td>4 x 10(^{-7})</td>
<td>Non-conducting (NC)</td>
<td>Purer sample and lower value than that reported by Banks et al. (Ref. 31)</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>Br(_2)F(_3)</td>
<td>25(^o)</td>
<td>7.53 x 10(^{-4})</td>
<td>NC</td>
<td></td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>SbF(_5)</td>
<td>25(^o)</td>
<td>&lt;2.11 x 10(^{-7})</td>
<td>NC</td>
<td>Comparable to the value reported by Woolf and Greenwood (Ref. 35)</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>SbF(_5)</td>
<td>25(^o)</td>
<td>&lt;2.11 x 10(^{-7})</td>
<td>Commercial (99+%)</td>
<td>checks with literature (Ref. 36, 37)</td>
</tr>
<tr>
<td>IF(_5)</td>
<td></td>
<td></td>
<td>25(^o)</td>
<td>5.65 x 10(^{-5})</td>
<td>NC</td>
</tr>
<tr>
<td>ClO(_2)F</td>
<td>BrF(_5)</td>
<td>-51(^o)</td>
<td>&lt;2.1 x 10(^{-9})</td>
<td>NC</td>
<td></td>
</tr>
<tr>
<td>ClO(_2)F</td>
<td>BrF(_5)</td>
<td>-51(^o)</td>
<td>1.88 x 10(^{-6})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO(_2)F</td>
<td>HF</td>
<td>-12(^o)</td>
<td>&lt;10(^{-6})</td>
<td>NC</td>
<td></td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>CsF</td>
<td>0(^o)</td>
<td>2.3-2.9 x 10(^{-4})</td>
<td>NC</td>
<td>See also Ref. 40</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>Cl(_2)F(_2)SbF(_6)</td>
<td>0.013</td>
<td>0(^o)</td>
<td>5.1 x 10(^{-4})</td>
<td>Electrolyzed at voltages up to 20 v. D.C. to give quantitative yields of Cl(_2)F(_5)</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>BrF(_3)</td>
<td>0.098</td>
<td>0(^o)</td>
<td>7.6 x 10(^{-6})</td>
<td>NC</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>ClO(_2)F</td>
<td>0.044</td>
<td>-12(^o)</td>
<td>&lt;10(^{-6})</td>
<td>NC</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>ClO(_2)F</td>
<td>0.043</td>
<td>12(^o)</td>
<td>12.4 x 10(^{-4})</td>
<td>NC</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>CsF</td>
<td>0.019</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>IF(_5)</td>
<td>0.153</td>
<td>24(^o)</td>
<td>4.21 x 10(^{-6})</td>
<td>NC</td>
</tr>
<tr>
<td>Cl(_2)F(_3)</td>
<td>ClO(_3)F</td>
<td>0.146</td>
<td>-51(^o)</td>
<td>&lt;10(^{-6})</td>
<td>NC</td>
</tr>
<tr>
<td>SbF(_5)</td>
<td>ClF(_3)</td>
<td>0.103</td>
<td>25(^o)</td>
<td>2.64 x 10(^{-5})</td>
<td>Not homogeneous; solids</td>
</tr>
</tbody>
</table>

*Values below 10\(^{-6}\) ohm\(^{-1}\) cm\(^{-1}\) were estimated from resistances measured with a supplementary ohmmeter.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solute</th>
<th>Temp. (°C)</th>
<th>Specific Conductivity (ohm⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClF₅</td>
<td>CsF</td>
<td>0.196</td>
<td>-23*</td>
</tr>
<tr>
<td>ClO₃F₂</td>
<td>SbF₅</td>
<td>0.040</td>
<td>-51*</td>
</tr>
<tr>
<td>BrF₅</td>
<td>ClF₃</td>
<td>0.130</td>
<td>0*</td>
</tr>
<tr>
<td>NO₂F</td>
<td>ClF₃</td>
<td>0.5</td>
<td>-78*</td>
</tr>
<tr>
<td>HF</td>
<td>NO₂F</td>
<td>0.20</td>
<td>-78*</td>
</tr>
<tr>
<td>HF</td>
<td>ClF₃</td>
<td>0.20</td>
<td>-12*</td>
</tr>
<tr>
<td>HF</td>
<td>NO₂F</td>
<td>0.166</td>
<td>-12*</td>
</tr>
</tbody>
</table>

NC: Solid SbF₅ present
NC
NC
NC
NC
NC
NC: however, application of 10 v. D.C. resulted in a current flow of 1.3 amperes and formation of ClO₂F₂, ClF₅ and presumably Cl₂.
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**ClF₅/CsF System:**

Addition of CsF to ClF₅ at a mole ratio of 1 to 100 increased the conductivity from 4 x 10⁻⁷ ohm⁻¹ cm⁻¹ for the pure solvent to a solution of specific conductance of 2.3-2.8 x 10⁻⁴ ohm⁻¹ cm⁻¹. Electrolysis of this solution at 20 v. D.C. resulted in the formation of ClF₅; however, the yields were not determined.

In the work with CsF, the formation of CsClF₄ had been postulated as the contributing factor to the appreciable increase in conductivity of the ClF₅. However, on using previously prepared CsClF₄ it was found that the CsClF₄ was not soluble in ClF₅ at a mole ratio of 1:100. The specific conductance of the mixture at 0° was about 4.23 x 10⁻⁷ ohm⁻¹ cm⁻¹ and approximately equivalent to that of pure ClF₅. The mixture did not conduct appreciable current at applied potentials up to 110 v. D.C.

It is concluded that no CsClF₄ was formed in the experiment employing CsF and ClF₅. A possible explanation may be an induced ionization of the ClF₅ by CsF according to the following equation:

\[ \text{ClF}_5 + \text{CsF} \rightarrow \text{ClF}_2^+ + \text{CsF}_2^- \]

**ClF₅/SbF₅ System:**

In view of the poor conductivity of salts supposedly containing the ClF₅⁻ ion, investigations were carried out on complexes of ClF₅ with SbF₅ which are postulated to be of the type ClF₂⁺SbF₆⁻.

SbF₅ was reacted first with ClF₅ to yield the white salt and then the required ClF₅ was added to produce a mole ratio ClF₂⁺SbF₆⁻/ClF₅ of 1 to 75.8. The specific conductivity of this solution at 0° was 5.1 x 10⁻⁴ ohm⁻¹ cm⁻¹ and electrolysis was conducted for 5.25 hrs. at increasing voltages of 6, 10, and 20 v. D.C. with respective current flows of 0.005, 0.036, and 0.12 amps. A total of 8.45 milliequivalents of electricity was passed. Fractionation of the evolved gases served to separate ClF₅ in virtually quantitative yield from the Cl₂ also produced and some small amount of ClF₃ which vaporized from the cell.

**ClF₅/BrF₃ System:**

The conductivity and electrolytic properties of liquid mixtures of ClF₅ and BrF₃ were studied using proportions which were respectively high in either one of the components, or in which the proportions of the two were similar.

- 53 -

CONFIDENTIAL
The specific conductivity of BrF₃ (m.p. 9°C) was determined to be 7.53 x 10⁻⁴ ohm⁻¹ cm⁻¹ at 25°C for a material of specified 98.0% minimum purity (Matheson Co.). This was nitrogen-stripped before the conductivity measurement to remove colored material believed to be bromine, as well as any HBr.

The observed value is lower than the specific conductivity of 8 x 10⁻³ ohm⁻¹ cm⁻¹ for BrF₃ at 25°C reported by Banks, Emeleus and Woolf (Ref. 31). They had prepared BrF₃ from the elements, distilled and performed conductivity measurements in a quartz cell with platinum electrodes. Our cell was constructed of Kel-F, with nickel electrodes. In a continuation of their studies, Emeleus and Woolf (Ref. 32) demonstrated a quantitative reaction between SiO₂ and BrF₃ in accord with the reaction 3SiO₂ + 4BrF₃ → 3SiF₄ + 3O₂ + 2Br₂ from which all products should be ultimately volatile. Rather surprisingly, their experiment was conducted in silica equipment. It appears, in any event, that the difference between our observed conductivity value for BrF₃ and the previous report may be attributable to purity differences.

The conductivity of a solution of 1 mole of BrF₃ in 9.2 mole ClF₃ was 7.6 x 10⁻⁹ ohm⁻¹ cm⁻¹ (0°) and too low to attempt electrolysis. The concentration of BrF₃ was increased until it was equimolar with ClF₃. The specific conductivity of this solution was 2.4 x 10⁻⁴ ohm⁻¹ cm⁻¹ (0°) and the solution was electrolyzed at 10-11 v. D.C. with a total of 286 coulombs passed. We were not able to isolate products in order to explain the current flow in the cell although some inconclusive evidence was obtained suggesting that ClF may have been a product.

A mixture of 1 mole ClF₃ to 9.29 moles BrF₃ was electrolyzed at an average potential of 20 volts (average 0.13 amps) for 17 hours. No volatile products were noted in the traps downstream of the cell.

The residual BrF₃ solution was colored dark orange-brown. This is attributed to the presence of bromine which could be swept from the cell by nitrogen and condensed. Claassen, Weinstock and Malm (Ref. 33) noted that pure BrF₃ reacts slowly with nickel to form reddish products which may be Br₂ or Br⁺. Our nickel electrodes were tarnished although not corroded sufficiently to account for the quantity of Br₂ and it is believed the Br₂ is a direct or indirect result of electrolysis.
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During electrolysis of the ClF₅/BrF₅ solution, the conductivity decreased from $1.3 \times 10^{-4}$ to $1.2 \times 10^{-4}$ ohm⁻¹ cm⁻¹. Banks et al. (loc. cit.) observed the same phenomenon on electrolysis of pure BrF₃ and postulated the following mechanism:

$$2\text{BrF}_3 \rightarrow \text{BrF}_2^+ + \text{BrF}_4^-$$
$$2\text{BrF}_2^+ + 2e \rightarrow \text{BrF}_3 + \text{BrF} \text{ (brown, unstable)}$$
$$2\text{BrF}_4^- \rightarrow 2e + \text{BrF}_3 + \text{BrF}_5 \text{ (colorless)}$$

The formation of BrF and BrF₅ in the BrF₃ would decrease the conductance simply by dilution. The above mechanism is consistent with our observations since BrF is an unstable material forming the Br₂ observed in our cell.

$$3\text{BrF} \rightarrow \text{Br}_2 + \text{BrF}_3 \text{ (Ref. 34)}$$

It should be noted that Banks et al. proposed the above mechanism easily to explain the absence of polarization in their work. In our studies polarization was observed and could be eliminated temporarily by reversing the polarity. This may be due to some unknown influence of the dissolved ClF₅.

ClF₅/SbF₅ System:

The specific conductivity of ClF₅ prepared in this laboratory was determined to be $< 2.11 \times 10^{-7}$ ohm⁻¹ cm⁻¹ (the lower limit of our conductivity bridge) at -78°C and at -23.9°C, and is probably somewhat lower, i.e., $< 10^{-7}$ ohm⁻¹ cm⁻¹. The fact that there was no observable increase in conductivity between dry-ice temperature and -23.9°C, nearly the boiling point of ClF₅, seems to indicate that the conductivity of this substance is very low and the pure compound would be impractical as an electrolyte. This was, of course, the sole purpose of our conductivity determination.

In a separate experiment doubly-distilled SbF₅ was charged to the conductivity cell under dry-box conditions and the specific conductivity was found to be $< 2.11 \times 10^{-7}$ ohm⁻¹ cm⁻¹ at 25°C. The specific conductivity of SbF₅ has been reported as $< 10^{-9}$ ohm⁻¹ cm⁻¹ (Ref. 35). The value determined in this laboratory appears in keeping with the prior reports.

- 55 -

CONFIDENTIAL
The properties of the system mixed SbF₅-ClF₅ were then explored using a high ratio of SbF₅. Final proportions were in the mole ratio 8.72 SbF₅/ClF₅. Since SbF₅ freezes at 7°C, the reaction was initiated at 10°C and the ClF₅ was added in increments as a gas under its own vapor pressure. A slightly yellow solid was formed immediately on addition of ClF₅ to SbF₅ and persisted even though the cell was allowed to warm to 25°C. Mixing was extremely slow because of the density and viscosity of the SbF₅, coupled with the formation of a crust of complex ClF₅·SbF₅ on the surface of the liquid. Slight warming did tend to melt the complex, but this could not be carried to the point of homogeneity.

A final measurement showed the specific conductivity of the inhomogeneous liquid-solid system to be \(2.64 \times 10^{-5}\) ohm\(^{-1}\) cm\(^{-1}\) at 25-30°C. The enhanced conductivity of the system indicates that the ClF₅·SbF₅ complex is probably an ionic species such as ClF₄⁺SbF₅⁻.

During overnight storage of the cell containing SbF₅ and the complex, a severe crack developed on the interior wall of the cell (see Fig. 5). On warming slightly to dissolve the complex, further extensive cracking occurred, with leakage from the cell. The experiment, including contemplated electrolysis, was abandoned of necessity.

Subsequent studies of the ClF₅-SbF₅ system was carried out at low temperatures to minimize stress cracking of the cell. At -23°C, it was observed that a combination of ClF₅ and SbF₅ in a mole ratio of 21:5:1 consisted of supernatant liquid ClF₅ above a solid mass of frozen SbF₅ containing solid ClF₄SbF₆. The specific conductance of the non-homogeneous system was equivalent to that observed for pure ClF₅.

The presence of the ClF₄SbF₆ was indicated by a mass balance of the ClF₅ used and recovered, as well as evidence of stress cracking in the Kel-F cell due to overnight storage of non-volatile residual solids.

The non-conductivity of the liquid ClF₅ suggests that none of the complex had dissolved. Whether this was the result of inherent insolubility or poor mixing is not known. The ionic nature of the ClF₄SbF₆ complex was suggested by an experiment using a mole ratio of 1 ClF₅ to 8.72 SbF₅ in which the complex was formed and increased the conductivity of the SbF₅ from \(<2.11 \times 10^{-7}\) ohm\(^{-1}\) cm\(^{-1}\) to \(2.04 \times 10^{-5}\) ohm\(^{-1}\) cm\(^{-1}\).
**CIF₅/Metal Fluoride System:**

Since CsF was observed to increase the conductivity of CIF₃, it was of interest to investigate the conductivity of alkali metal fluorides and, for comparative reasons, that of CsF in CIF₅.

The specific conductance of a mixture containing a mole ratio of 34.1 CIF₅/CsF at -23°C was determined to be < 2 x 10⁻⁹ ohm⁻¹ cm⁻¹ by supplementary observation of resistance with a volt-ohm meter. However, the validity of the determination was questioned because a liquid product, believed to be a hydrated acid fluoride, was recovered as a final cell residue. Repetition of the experiment using CIF₅ freed of HF at a mole ratio of 50 CIF₅/CsF confirmed the specific conductance of the system to be < 10⁻⁶ ohm⁻¹ cm⁻¹. A solid product which was evidently CsF containing absorbed CIF₅ was finally obtained, but mass balance did not indicate the formation of a complex. In both experiments, CsF was insoluble in CIF₅ so that the low conductance value and failure to pass current were doubtless characteristic of CIF₅.

Anhydrous KF was insoluble in liquid CIF₅ at -23°C at a mole ratio of 26.3 CIF₅/KF. The specific conductance of the mixture was < 10⁻⁶ ohm⁻¹ cm⁻¹, which was no doubt that of CIF₅. There was no evidence of complex formation between CIF₅ and KF.

**CIF₃/ClO₂F System:**

In previous studies (Ref. 23) it had been found that ClO₂F will dissolve readily in CIF₃ to give a dense solution attractive as a mixed oxidizer. In addition the sensitivity of ClO₂F to hydrolysis by moist air seemed to be moderated by solution. Although this could be attributed to dilution, it seemed worthwhile to study the liquid system for evidence of dissolved ionic compounds. The conductivity of a solution of ClO₂F in CIF₃ was determined at -12°C, first at a mole ratio of 31.8 CIF₃/ClO₂F, then at 21.7 CIF₃/ClO₂F. The specific conductance of each system was < 10⁻⁶ ohm⁻¹ cm⁻¹. This value it of an order similar to the conductivity of CIF₃. It is concluded that ClO₂F must also have a low conductivity since addition of ClO₂F to CIF₃ did not alter conductance, even on increasing the proportion of ClO₂F.
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Since fluorination of ClO₂F is an attractive route to new oxidizers and since ClO₂F is sensitive to protic solvents, it was evident that this compound must be studied in compatible solvents such as ClF₃ containing additives such as CsF to increase the conductivity.

The ClF₃-CsF system was the conducting medium and the source of fluorine on electrolysis which could be replenished by subsequent additions of ClF₃. The ClO₂F is typical of intermediates which can be dissolved in the ClF₃-CsF mixture and, although non-conducting themselves, will be fluorinated on electrolysis. There is thus an analogy to the Simons cell and the electrolysis of hydrocarbons in KF-HF systems.

The addition of CsF to the liquid system ClF₃/ClO₂F at -12°C produced an increase in conductivity, the specific conductance being 12.4 x 10⁻⁴ ohm⁻¹ cm⁻¹ at a mole ratio of 50 ClF₃/2.3 ClO₂F/CsF. However, the CsF was incompletely soluble and in addition, flocculent material of an apparently different character formed on first storage at -78°C, persisting on warming to -12°C. Appearance of the flocculent material was accompanied by a small decrease in specific conductance to 8.43 x 10⁻⁴ ohm⁻¹ cm⁻¹. Subsequent analysis of this system indicated that the presence of ClO₂F prevented dissolution of the CsF in the ClF₃ solvent and that the observed flocculent precipitate was pure CsF.

ClF₃/IF₅ System:

The specific conductance of commercial IF₅ (99+%) was determined to be 5.65 x 10⁻⁵ ohm⁻¹ cm⁻¹ at 25°C, and 4.02 x 10⁻⁵ ohm⁻¹ cm⁻¹ in a mixed solid-liquid phase system at the freezing point of 9°C. These data compare favorably with the values reported by Woolf (Ref. 36) and by Rogers et al. (Ref. 37).

IF₅ was completely soluble at 0°C in ClF₃ and a mixture containing a mole ratio of 6.76 ClF₃/IF₅, had a specific conductance at this temperature of 2.43 x 10⁻⁵ ohm⁻¹ cm⁻¹. At 24°C and a mole ratio of approximately 5.54 ClF₃/IF₅, the specific conductance increased only slightly to 4.21 x 10⁻⁵ ohm⁻¹ cm⁻¹. Since it appeared that the conductivity values observed resulted from the dilution of IF₅ without the formation of conductive species in ClF₃, such mixtures were not explored further. There
was no indication of an induced ionization as given in the equation below and the conductivity was too low for practical electrolysis.

\[
\text{IF}_3 + \text{ClF}_3 \xrightarrow{\text{---}} \text{ClF}_2^+ + \text{IF}_3^-
\]

**ClF₃/ClO₃F System:**

The specific conductance of ClO₃F (b.p. -47°C) was determined to be \(< 2 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}\) at -51°C, in good agreement with a previously reported value (Ref. 38). The specific conductance of a ClF₃/ClO₃F mixture in the respective mole ratio 5.83/1 was observed to be \(< 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}\) at -51°C. Because both components of the mixture are poorly conductive, the low conductivity value of the mixture indicated the absence of any ionic species. ClO₃F alone or with ClF₃ did not pass current under applied potential, and electrolysis was not feasible.

\[
\text{ClO}_3\text{F} \xrightarrow{\text{---}} \text{ClO}_3^+ + \text{F}^-
\]  

\[
\text{ClO}_3\text{F} + \text{ClF}_3 \xrightarrow{\text{---}} \text{ClO}_3^+ + \text{ClF}_4^-
\]

A ternary mixture composed of a mole ratio of 29.3 ClF₃/4.86 ClO₃F/CsF contained undissolved solids at -51°C and was observed to have a specific conductivity of 1.24 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}. Electrolysis was impractical since the system did not conduct appreciable current.

The conductance of the ternary system was less than that of the initial ClF₃/CsF mixture before adding ClO₃F, indicating that the latter served mainly as a diluent and did not form ionic species with CsF. As noted above, a mixture of ClF₃ and ClO₃F was non-conductive, so that the meager conductivity detected for the ClF₃/ClO₃F/CsF system appeared to be due to a ClF₃-CsF complex, possibly ClF₂⁺CsF₂⁻ as proposed above.

**ClO₃F/SbF₅ System:**

The possible formation of complex ions by ClO₃F was explored further by observation of a mixture containing a mole ratio of 24.3 ClO₃F/SbF₅. The specific conductance of the system was \(< 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}\) at -51°C. The SbF₅ (m.p. 7°C) appeared to disperse throughout the ClO₃F as fine, white suspended particles on stirring. The mixture was non-conductive under an applied potential of 107 volts D.C., so that electrolysis was not possible. Qualitative
tests on the non-volatile material recovered showed it to be pure antimony fluoride. The conclusion that ClO$_3$F did not form an ionic complex with SbF$_5$ agrees with other studies made in this laboratory employing pressure techniques.

**ClF$_3$/BrF$_5$ System:**

The specific conductance of commercial BrF$_5$ (HF-free) was determined to be $1.88 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at -51°C (m.p. -62°C), $2.18 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 0°C and $2.73 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 25°C (b.p. 40°C). The results at -51°C and 0°C are comparable to values reported for a similar commercial material (Ref. 38); but, as expected, the value at 25°C is somewhat above the conductance of $9.1 \times 10^{-8}$ ohm$^{-1}$ cm$^{-1}$ reported for a "carefully purified" sample (Ref. 39). As noted below, some Br$_2$ may have been present in the BrF$_5$.

A homogeneous solution containing a mole ratio of 5.39 BrF$_5$/ClF$_3$ exhibited a specific conductance of $2.06 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 0°C and $2.38 \times 10^{-6}$ at 25°C. Neither the pure BrF$_5$ nor a solution with ClF$_3$ passed more than one milliampere current under an applied potential of up to 108 volts D.C. The addition of a slight amount of ClF$_3$ to the BrF$_5$ caused the color of the BrF$_5$ to change from a dark red brown to a clear faint amber. However, because no conductivity changes were noted and no solid residues were recovered, it is thought that the color change indicated the fluorination of a small amount of elemental bromine contaminant by the ClF$_3$.

**The Ternary NO$_2$F/ClF$_3$/HF System**

The conductivities of liquid mixtures containing NO$_2$F, ClF$_3$ or HF were observed while employing the constituents in various combinations, proportions and orders of addition. The specific conductances of the individual constituents were found to be $< 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at the temperatures noted below. The binary mixtures (NO$_2$F/ClF$_3$, HF/NO$_2$F, HF/ClF$_3$) and ternary mixtures were similarly non-conductive. Conductivity measurements involving NO$_2$F (b.p. -72°C) alone or with either HF or ClF$_3$ were made at -78°C because of pressure limitations, but observations of the conductivities of HF and ClF$_3$ were made at -12°C or above. The latter temperature was used in studying ternary mixtures containing excess HF, since these exhibited relatively low vapor pressure at -12°C.

However, when equimolar quantities of the three components were used, the high gas pressure which developed prevented warming much above -78°C.
An equimolar mixture of NO₂F and ClF₃ at -78° contained a small quantity of yellowish white dispersed solids identified as NO₂ClF₄. This material is insoluble in either reagent and did not increase the conductivity of the system. Addition of HF to produce an equimolar ratio of NO₂F/ClF₃/HF produced additional solids, presumably NO₂F-XHF, but the HF was insufficient to complex all the NO₂F since pressure developed on warming above -78°. The same adduct was also formed on addition of one mole of NO₂F to 4 moles of HF at -78°C. In contrast, a solution of one mole ClF₃ in 4 moles of HF was a homogeneous clear liquid. Tetra mixtures containing excess HF (mole ratio about 4HF/ClF₃/NO₂F) developed relatively little pressure at -12°, and probably contained sufficient HF to completely complex the NO₂F.

In view of the low conductance values observed, it was surprising to find that a momentarily applied potential of 10 volts D.C. resulted in a current flow as high as 1-2 amperes in ternary mixtures with excess HF at -12°. This property was shown to a limited degree by HF alone, but not by NO₂F, ClF₃, or their mixture. Action on the nickel electrodes at the higher amperages was indicated by darkening, sometimes with formation of solids.

In preparing ternary mixtures containing excess HF (mole ratio about 4HF/NO₂F/ClF₃), the order of addition appeared to have some influence on the products recovered. Addition of ClF₃ to NO₂F in HF at -196° resulted in a mixture of liquids and solids which persisted on warming to -78°. This order would have permitted preliminary formation of NO₂F·HF adducts. The ternary system passed about .05 amp. at -78° and over 1 amp. at -12°. However, when NO₂F was added to ClF₃ in HF at -196°, a pressure increase was briefly noted on warming to -78° and a liquid product resulted. If NO₂F·XHF or NO₂ClF₄ were present, they or other products were soluble. This ternary system passed about 0.6 amp. at -78° and 2 amps. at -12°.

Products from the electrolysis of the ternary NO₂F/ClF₃/HF mixtures at -12° were analyzed and were found to be ClO₂F, ClF₃ and ClF₅ but the pressure of the samples further indicated the presence of a considerable portion of a gas nonabsorbing in the infrared, presumably Cl₂. The liquid remaining in the conductivity cell after warming to 45° was also examined by infrared and several runs produced samples with consistent absorption at 4.2 μ, commonly associated with nitrogen triple bonding. This material was never identified.

- 61 -
1. Description and Layout of Adiabatic Calorimeter

The adiabatic calorimeter and temperature measuring equipment were contained within a large Flexiglass enclosure (T = 25°C ± 0.6°C) and located in a small laboratory where the room temperature was maintained at 23.5 ± 1°C. This provided a constant heat leak from the Flexiglass enclosure and easy temperature control within the enclosure. Access to instruments within the enclosure was through gum rubber "iris diaphragm" ports (cf. Fig. 7). Dials were adjustment and electrical balances were made using "poke rods" thereby eliminating thermal gradients from the human hand. This is illustrated in Fig. 7.

A platinum resistance thermometer was used to determine temperature rises in the calorimeter. The thermometer was connected to the measuring bridge (G-1 Mueller Bridge, Leeds and Northrup) through a mercury commutator (No. 8058, Leeds and Northrup) designed to permit cancellation of lead resistance differences.

A 1000-ohm resistor in series with a slow-bleed 2-volt cell (Willard DD-S-1) intentionally limited the current in the thermometer circuit to 1.5 milliamps. This current was below the 2 milliamp continuous flow used in calibration of the thermometer at the National Bureau of Standards. This limitation decreased the sensitivity of the null point galvanometer (No. 2430a, Leeds and Northrup) but essentially eliminated error due to heating of the resistance element in the thermometer.

It had been experimentally determined, by measurement of the triple point of water, that temperatures could be measured to an accuracy of ± 0.001°C with an error of ± 0.0005°C.

The linear power equation established by the National Bureau of Standards during calibration of the platinum resistance thermometer was programmed for the Bendix Model G15 computer and a print out of measured resistances versus temperature was obtained from 33°C to 30°C in intervals of 0.001°C. This permitted immediate and convenient determination of temperature in degrees Centigrade.

It is important to note that during preliminary runs with the NH₄ClO₄/CO system it was found that the use of a platinum sample cup and support and a gold-plated calorimeter were found necessary to eliminate the formation of iron carbonyl by the reaction of the bomb alloy with the excess CO at the high combustion temperature.
LAYOUT OF CALORIMETER AND SUPPORTING EQUIPMENT
For calibration a total of ten combustions were carried out using N.B.S. standard benzoic acid under certificate conditions. The final accepted heat capacity was 24.55 ± 0.0 cal/°C. Additional blank runs were carried out to determine the heating of the calorimeter due to electrical input to the ignition wire as 1.1 cal. The correction in the heat capacity of the calorimeter due to a substitution of CO for O₂ amounts to 0.025 cal/°C and was considered negligible.

The NH₄ClO₄ pellet was supported in a platinum cup within the gold-plated calorimeter and ignition was by an electrically heated platinum fuse. Prior to ignition, the loaded bomb was flushed at least three times with CO at 30 atmospheres pressure to eliminate atmospheric oxygen. The results of the experiments are summarized in Table I.

At the conclusion of the run the gases within the bomb were examined by infrared analysis for traces of nitrogen oxides indicating incomplete combustion. Vapor chromatographic analysis previously showed that the vapor phase was composed only of N₂, CO, CO₂ and water vapor.

The gaseous products were then dried by passing over MgClO₄ and adsorbed on ascarite for a direct determination of the carbon dioxide evolved. The liquid phase remaining in the bomb was quantitatively removed and analyzed for acid titter, chloride ion, and anionic and cationic nitrites. These data were used as confirmatory evidence for completeness of combustion.

2. Synthesis of ClO₂

A 1:4 molar mixture of NaClO₃ (21.2 g.) and H₂C₂O₄·2H₂O (100.0 g.) was added dry to a 500-ml. 3-necked round bottom flask. Distilled water (25 ml.) was added to the mixture and the flask was immersed in a water bath. A flow of nitrogen (75-100 cc./min.) was started and the reaction flask was slowly heated. ClO₂ generation began at 40-45°C and the nitrogen flow was increased to about 300-350 cc./min. The bulk of the ClO₂ was evolved between 45°-55°C. The temperature was slowly raised following diminution of gas evolution and was maintained in the range 65°-70°C. When generation ceased the reaction mixture was quenched with 100-150 ml. distilled water. The ClO₂, trapped out at -78°C, was purged well with nitrogen and then immersed in a -5° to -8°C salt bath to permit the ClO₂ to liquify and to disep any dissolved CO₂. After about 5 minutes under these conditions, the -78°C bath was again placed around the ClO₂ and maintained during temporary storage of the ClO₂.

2NaClO₃ + 2H₂C₂O₄·2H₂O → 2ClO₂ + 2CO₂ + 2H₂O + Na₂C₂O₄
3. (U) Synthesis of ClO$_2$F

The liquid ClO$_2$ was immersed in a 0°C salt bath and vaporized with a nitrogen flow set at about 350 cc./min. This permitted a sufficient dilution to avoid explosions and also provided a reasonable rate of consumption of the ClO$_2$. The nitrogen-diluted ClO$_2$ was led into a copper coil reactor through which F$_2$ gas was passed at a flow rate of up to 250 cc./min. The reactor was made of 3/8" copper tubing and various lengths gave reactor volumes of 11-1200 ml. (residence times of 4 seconds to 4 minutes). The most satisfactory results were obtained with a 1200-ml reactor volume and 4-min. residence time. The product gases were passed through a 1/4" copper coil of 85-ml. volume heated to 105-110°C (15-second residence time). This coil was used to effect thermal decomposition of residual ClO$_2$ to Cl$_2$ and O$_2$. The final product had been trapped out as a solid at -183°C together with solid Cl$_2$ and liquid F$_2$, N$_2$, and O$_2$. The Cl$_2$, F$_2$, N$_2$, and O$_2$ were easily removed by fractional condensation techniques. (Note: Since F$_2$ was removed at low temperatures, no reaction with solid Cl$_2$ was observed. The formation of ClF$_3$ was also not observed in the heated coil.) The water white produce following purification was stored in a stainless steel cylinder at -80°C.

4. (C) Preparation of ClF$_3$

CsF (13.4 g., 0.088 moles) was charged to a nickel autoclave. After evacuation, the autoclave was cooled to -78°C and 21.6 grams of ClF$_3$ (0.23 moles) was vacuum transferred to the autoclave. The approximate mole ratio of ClF$_3$ to CsF was 2.5:1.0. The autoclave was placed into a jacket heater and maintained at 80°C ± 2° for 24 hours, developing a maximum pressure of 80-85 psig at this temperature.

After 24 hours, the autoclave was cooled in a water bath to 20-25°C and all the volatiles were pumped off. Calculations based on ClF$_3$ recovered indicate the ClF$_3$ retained by the CsF on a 1:1 mole basis was approximately 85-90% of theoretical.

The evacuated autoclave was cooled to -196°C and 0.5 moles of fluorine was introduced to a total pressure (at 25°C) of 810 psig. The F$_2$/CsClF$_4$ mole ratio was approximately 6:1.

The autoclave was again placed in the jacket heater and maintained at 150° ± 2°C for 24 hours and then cooled to -125° to -130°C. At this temperature all the excess F$_2$ was vented off until the autoclave was at atmospheric pressure. The autoclave was then closed, warmed to ambient temperature and all the volatile products condensed at -196°C. The residual F$_2$ was removed under vacuum.

- 55 -
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The product was then fractionated through a -100°, -140°, -196°C train and CIFS was concentrated in the -140° tray.

Infrared analysis of the product indicated primarily CIFS with some slight contamination by ClO₂F, SO₂F₂ and SF₆. (The source of the sulfur compounds is the original fluorine used in the preparation.) A comparison of our observed absorption bands with those published by Rocketdyne (Ref. 3a) are given below. Our spectrum was obtained on a P-E Model 337 Grating Spectrophotometer (2-25 μm range).

<table>
<thead>
<tr>
<th>Rocketdyne</th>
<th>Our Observed Bands</th>
</tr>
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<tbody>
<tr>
<td>780 cm(^{-1})</td>
<td>780 cm(^{-1}) with a shoulder at 790 cm(^{-1})</td>
</tr>
<tr>
<td>720 cm(^{-1})</td>
<td>720 cm(^{-1})</td>
</tr>
<tr>
<td>630 cm(^{-1})</td>
<td>630 cm(^{-1})</td>
</tr>
<tr>
<td>620 cm(^{-1})</td>
<td>620 cm(^{-1}) Triplet</td>
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<tr>
<td>610 cm(^{-1})</td>
<td>610 cm(^{-1})</td>
</tr>
<tr>
<td>540 cm(^{-1})</td>
<td>545 cm(^{-1}) Doublet</td>
</tr>
<tr>
<td>495</td>
<td>535 cm(^{-1})</td>
</tr>
<tr>
<td>480</td>
<td>490 cm(^{-1}) (est. 492-493)</td>
</tr>
<tr>
<td>300</td>
<td>480 cm(^{-1}) (Beyond the range of our instrument)</td>
</tr>
</tbody>
</table>
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IV. REFERENCES


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Synthesis of Inorganic Oxidizers

Final Summary Report for Period Aug. 1, 1962 to April 1, 1966

Gardner (David M.) and Bartoszek (Edward J.) et al.

May, 1966

AF 04(611)-8518
Project No. 3148, Task No. 314804,
ARPA Order No. 352

113989 Final

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Research was carried out on the synthesis of new oxidizers composed of combined forms of chlorine, oxygen, and fluorine. Experimental techniques used included high pressure - high temperature reactions, arc and glow discharge reactions, and electrochemical reactions in interhalogens and other active fluorinating solvents (U).
### Solid Propellants
- Synthesis
- Inorganic oxidizers
- Halogen fluorides
- Chlorine oxides
- Nitrogen fluorides

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