UNCLASSIFIED

AD NUMBER

AD367137

CLASSIFICATION CHANGES

TO: **unclassified**

FROM: **confidential**

LIMITATION CHANGES

TO:

Approved for public release, distribution unlimited

FROM:

Controlling DoD Organization. Director, Advanced Research Projects Agency, 1400 Wilson Blvd., Arlington, VA 22209-2308.

AUTHORITY

30 Sep 1977, Group-4, DoDD 5200.10; 30 Sep 1977, DoDD 5230.24

THIS PAGE IS UNCLASSIFIED

AD 367 137

ROCKETDYNE
A DIVISION OF NORTH AMERICAN AVIATION INC
6633 CANOGA AVENUE CANOGA PARK CALIFORNIA

R-5883-4

(Unclassified Title)

QUARTERLY PROGRESS REPORT, INORGANIC HALOGEN OXIDIZERS

(29 May 1965 through 28 August 1965)

Group 4
Downgraded at 3-Year Intervals
Declassified After 12 Years

Contract Nonr 4428(00)

Sponsored by Advanced Research Projects Agency
Washington 25, D. C.
ARPA Order No. 23

PREPARED BY

D. Pilipovich
C. B. Lindahl
H. F. Bauer
C. J. Schack

Reproduction in whole or in part is permitted for any purpose of the United States Government

APPROVED BY

Best Available Copy

J. Silverman
J. Silverman
Section Chief
Chemistry
Research Department

NO OF PAGES 22 & vi

REVISIONS

DATE 30 Sept 1965

DATE	REV. BY	PAGES AFFECTED	REMARKS

SECURITY MARKING

The classified or limited status of this report applies to each page, unless otherwise marked. Separate page printouts MUST be marked accordingly.

CONFIDENTIAL

ROCKETDYNE
A DIVISION OF NORTH AMERICAN AVIATION INC
6633 CANOGA AVENUE CANOGA PARK CALIFORNIA

R-5883-4

(Unclassified Title)

QUARTERLY PROGRESS REPORT, INORGANIC HALOGEN OXIDIZERS

(29 May 1965 through 28 August 1965)

Group 4
Downgraded at 3-Year Intervals
Declassified After 12 Years

Contract Nonr 4428(00)

Sponsored by Advanced Research Projects Agency
Washington 25, D. C.
ARPA Order No. 23

PREPARED BY
D. Pilipovich
C. B. Lindahl
H. F. Bauer
C. J. Schack

Reproduction in whole or in part is permitted for any purpose of the United States Government

APPROVED BY

J Silverman
J. Silverman
Section Chief
Chemistry
Research Department

NO OF PAGES 22 & vi

REVISIONS

DATE 30 Sept 1965

DATE	REV BY	PAGES AFFECTED	REMARKS

CONFIDENTIAL

NOTICE

UNITED STATES PATENT OFFICE SECRECY ORDER

A patent application has been filed in the U. S. Patent Office by North American Aviation, Inc. based upon subject matter included herein or related hereto, and the Secrecy Order appended hereto has been issued thereon pursuant to Title 35, United States Code (1952) Sections 181-188. Further dissemination of said subject matter is prohibited except in strict compliance with said order. The recipient of this document is requested to notify all persons who will have access to this material of the Secrecy Order. Penalties for violation of a Secrecy Order include a fine of up to $10,000 or imprisonment for not more than two years, or both.

DEPARTMENT OF COMMERCE
United States Patent Office
Washington

SECRECY ORDER

NOTICE: To the applicant above named, his heirs, and any and all his assignees, attorneys and agents, hereinafter designated principals:

You are hereby notified that your application as above identified has been found to contain subject matter, the unauthorized disclosure of which might be detrimental to the public safety or defense, and you are ordered in nowise to publish or disclose the invention or any material information with respect thereto, including hitherto unpublished details of the subject matter of said application, in any way to any person not cognizant of the invention prior to the date of the order, including any employee of the principals, but to keep the same secret except by written permission first obtained of the Commissioner of Patents, under the penalties of 35 U. S. C. (1952) 182, 186.

Any other application which contains any significant part of the subject matter of the above identified application falls within the scope of this order. If such other application does not stand under a secrecy order, it and the common subject matter should be brought to the attention of the Patent Security Division, Patent Office.

If prior to the issuance of the secrecy order any significant part of the subject matter has been revealed to any person, the principals shall promptly inform such person of the secrecy order and the penalties for improper disclosure.

This order should not be construed in any way to mean that the Government has adopted or contemplates adoption of the alleged invention disclosed in this application; nor is it any indication of the value of such invention.

DEPARTMENT OF COMMERCE
United States Patent Office
Washington

PERMIT FOR PATENT APPLICATION CLASSIFIED BY GOVERNMENT CONTRACT

This permit authorizes the principals, as designated in the secrecy order, to take any action with regard to the subject matter of the application, to the extent authorized by the security requirements of the Government contract which imposes the highest security classification on the subject matter of this application, except that this permit does not authorize export of this application or the subject matter thereof, whether for the foreign filing of corresponding applications or otherwise. Permission for such export must be specifically obtained from the Patent Office.

FOREWORD

The research reported herein was supported by the Advanced Research Projects Agency through the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Nonr 4428(00) under ARPA Order No. 23, and covers the period 29 May 1965 through 28 August 1965. This work was carried out in the Synthetic Chemistry Group with Dr. D. Pilipovich, Principal Scientist of the Fluorine Chemistry Unit, as the Responsible Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, Dr. C. J. Schack, and Dr. C. B. Lindahl.

ABSTRACT

The new oxidizer oxychlorine trifluoride, ClF_3O, has been prepared by the fluorination of cesium fluoride complexes of both chlorine monoxide and chlorine nitrate. The density of ClF_3O is 1.90 ±0.05 g/cc at 25.5 C; it melts at -66 C and boils at 29.4 C. The vapor pressure/temperature equation for ClF_3O has been obtained from -22 to 32 C: $\log_{10} p\ (mm) = 8.433 - 1680/T$. The molar heat of vaporization is 7.7 kcal. Oxychlorine trifluoride was found to be thermally stable to 284 C, although reactivity with metal containers was noted. Elemental analyses confirm the empirical formula ClF_3O.

Several members of a new class of complexes have been formed: $Cl_2O \cdot CsF$, $Br_2O \cdot CsF$, and $ClONO_2 \cdot CsF$. Fluorination of these materials has led to solid oxyhalogen fluoride complexes. Evidence for another new oxychlorine fluoride candidate has been obtained during this study.

Reactions of ClF_3O with Lewis acids and bases gave the complexes $NO_2^+ClF_4O^-$, $Cs^+ClF_4O^-$, $ClF_2O^+BF_4^-$, and $ClF_2O^+AsF_6^-$, indicating a pronounced amphoteric behavior. No reaction of ClF_3O was observed with either F_2 or N_2F_4.

A new, convenient synthesis of Cl_2O has yielded a product of improved purity. The reaction of BrF_5 with $FOClO_3$ failed to give $BrF_6^+ClO_4^-$ while the reaction of Cl_2O and N_2F_4 gave no new products.

(Confidential Abstract)

CONTENTS

TABLES

INTRODUCTION

During a search for new inorganic halogen oxidizers several avenues of interest have been explored, particularly those leading to new compounds containing fluorinated nitrogen, oxynitrogen, halogen, and oxyhalogen moieties. One of the primary objectives of this program, oxychlorine trifluoride, was achieved during last year's effort. This eagerly sought compound is the first known chlorine oxyfluoride containing but one chlorine-oxygen bond.

During the past quarter, effort has been directed primarily toward the elucidation of the synthesis and properties of oxychlorine trifluoride, ClF_3O. An understanding of the chemistry of this new compound has aided materially in the improvement of its synthesis as well as suggesting syntheses for the unknown, related compounds ClFO and ClF_5O.

Various aspects of the chemistry of chlorine monoxide, the principal source of ClF_3O to date, were fruitfully investigated. As a precursor to new BrF_xO oxidizers, bromine monoxide was studied in a parallel manner.

DISCUSSION

OXYCHLORINE TRIFLUORIDE (ClF_3O)

The characterization of oxychlorine trifluoride has continued and satisfactory elemental analyses have been obtained. This new Cl, F, O compound has been studied with regard to new synthetic methods, improvement of the existing synthesis, thermal stability, and other physical characteristics. The physical properties presented in Table 1 are a summary of the best available data.

TABLE 1

PROPERTIES OF OXYCHLORINE TRIFLUORIDE

Melting Point, C (corrected)	-66 ±1
Boiling Point, C	29.4 ±1.0
Molecular Weight	
Found (vapor density)	105
Calculated	108.5
Molar Heat of Vaporization, kcal	7.7
Trouton Constant	25.4
Density, g/cc at 25.5 C	1.90 ±0.05

The properties were measured from samples of oxychlorine trifluoride which was analyzed as follows: Cl, 30.8 percent; F, 49.5 percent; and O, 2.3 percent. The theorized analysis was Cl, 32.7 percent; F, 52.5 percent; and O, 14.7 percent.

Physical Properties of ClF_3O

Vapor Pressure/Temperature Relation. The vapor pressure/temperature equation of oxychlorine trifluoride was determined from -22 C to 32 C at nine temperatures. A least-squares fit yielded the equation $\log_{10} p(\mathrm{mm}) = 8.433 - 1680/T$. The normal boiling point is 29.4 C and the heat of vaporization is 7.7 kcal/mole indicating a fairly associated liquid.

Density Measurements. The density of oxychlorine trifluoride was determined in two ways using a Kel-F pycnometer. A known volume of liquid was weighed and gave densities of 1.89 and 1.91 g/cc at 25.5 ±1.0 C. The quantity of gas from a known liquid volume was determined and converted to ClF_3O weight, using 108.5 as the molecular weight. This weight corresponded to a liquid density of 1.95 g/cc at 23 C and 2.06 g/cc at 18 C. The direct method not only gave more reproducible data than the gas volume method but allowed calculation of the sample purity by molecular weight as well (105 vs 108.5 theory). Insufficient data were obtained to establish a quantitative dependence of density on temperature.

Thermal Stability of Oxychlorine Trifluoride. Samples of ClF_3O were heated in stainless steel and Monel for periods of 16 hours. Cesium fluoride was added to the stainless-steel cylinders. The runs in Monel were carried out in the presence and absence of fluorine. The data presented in Table 2 show the percent of ClF_3O recovered.

TABLE 2

THERMAL STABILITY OF ClF_3O

Container	Duration, hours	Temperature, C	Other Material Present	Recovery of ClF_3O, percent
Stainless Steel (five runs)	16	200	CsF	0
Monel	16	70	F_2	41
Monel	16	100	F_2	87
Monel	16	200	F_2	63
Monel	16	200	F_2	66
Monel	16	284	F_2	70
Monel	16	200	None	63
Monel	16	200	None	67

The absence of monotonic results indicates reaction with the container to be more important than thermal degradation. There was no evidence for equilibrium reactions involving ClF_3O.

Elemental Analysis of Oxychlorine Trifluoride

The combustion of ClF_3O and anhydrous ammonia in glass gave nonreproducible results. Metal-Teflon reactors were more successful and the following analytical results were obtained: Calculated for ClF_3O: Cl, 32.7 percent; F, 52.5 percent; found: Cl, 30.8 percent; F, 49.5 percent. The low results were attributed to 88- and 94-percent material recovery based on initial ClF_3O gas volumes. The fluorine-to-chlorine ratios for the recovered material were 2.97 and 2.99, respectively.

The determination of oxygen in ClF_3O was attempted directly by the reaction:

$$4Hg + 2ClF_3O = HgCl_2 + 3HgF_2 + O_2 \qquad (1)$$

Incomplete oxygen release was observed so an indirect method was tried using sodium chloride:

$$2ClF_3O + 6NaCl = 6NaF + O_2 + 4Cl_2 \qquad (2)$$

Although the theoretical ratio of chlorine to oxygen was four, ratios from two to eight were obtained by gas/liquid chromatography. More satisfactory results were obtained when NaCl was reacted at 200 C and the oxygen volume was obtained by pumping the oxygen gas at -196 C with a Toepler pump. The following analytical results were obtained: calculated for ClF_3O: O, 14.7 percent; found: O, 12.3 percent.

Another method of chlorine and oxygen analysis became available when it was observed that oxychlorine trifluoride reacts with the inside surface of a stainless-steel cylinder at 200 C to give a gas mixture containing only chlorine and oxygen:

$$2ClF_3O + nM \xrightarrow[\text{16 hours}]{\text{200 C}} Cl_2 + O_2 + nMF_{6/n} \qquad (3)$$

During four runs, ClF_3O was heated to 200 C in the presence of CsF for a minimum of 16 hours. The condensible gas was measured and compared to the amount of reacted ClF_3O on a molar basis.

The following analytical results were obtained: calculated for Cl_2/ClF_3O: 0.50 percent; found: 0.50, 0.49, 0.48, and 0.49 mole percent.

The nature of the reaction was confirmed by mass spectrometric analysis of the volatile products of a fifth reaction: Cl_2, 59.9 m/o; O_2, 40.1 m/o. The relatively low oxygen content was not unexpected due to the possibility of oxide formation from ClF_3O at 200 C.

New Syntheses of Oxychlorine Trifluoride

Fluorination of Chlorine Nitrate. There are few well-characterized singly bonded chlorine-oxygen compounds represented by the structure XOCl. Because one of these, chlorine monoxide, proved successful in the preparation of ClF_3O, the possible utility of chlorine nitrate, $ClONO_2$, was examined. Low-temperature fluorinations of the cesium fluoride-chlorine nitrate complex were carried out in a fashion similar to the preparation of ClF_3O from Cl_2O. Chlorine nitrate was prepared by the reactions of Cl_2O with N_2O_4 and with N_2O_5 (Ref. 1).

On exposure of chlorine nitrate to cesium fluoride at -80 C, a slow lowering of vapor pressure was observed indicating some complex formation. The reaction was reversible because chlorine nitrate could be removed by warming and pumping. The $CsF-ClONO_2$ complex was treated with excess fluorine at -80 C for several days.

After removal of excess fluorine at -196 C, the products volatile at ambient temperature were principally FNO_2 and less $FClO_2$ with one case of HNO_3 and N_2O_5 contamination. No further volatiles were evolved even after 4 weeks. Because not all of the starting material was accounted for, the residues were heated to drive off any complexed ClF compounds in a manner analogous to that used for obtaining pure ClF_3 from KF-$KClF_4$ (Ref. 2). Colorless gases were evolved, containing 60- to 80-percent ClF_3O with FNO_2, $FClO_2$, and ClF_3 comprising the remainder. The yield of ClF_3O based on chlorine nitrate was 36 percent. Because the total product gases did not correspond to the initial amount of chlorine nitrate, additional unrecovered ClF_3O may have been tied up in the solid, indicating the need for more drastic pyrolysis conditions. When the chlorine nitrate-cesium fluoride complex was formed at -18 C and treated similarly, a 22-percent yield of ClF_3O was obtained.

The following reaction sequence is proposed:

$$ClONO_2 + CsF \xrightarrow{-80\ C} CsF\cdot ClONO_2 \qquad (4)$$

$$CsF\cdot ClONO_2 + 2F_2 \xrightarrow{-80\ C} CsF\cdot ClF_3O + FNO_2 \qquad (5)$$

$$CsF\cdot ClF_3O \xrightarrow{\Delta} ClF_3O + CsF \qquad (6)$$

Fluorination of Mercury Salt-Cl_2O Complexes. The static method used for preparing Cl_2O (discussed later in this report) indicated the formation of a complex between Cl_2O and the residual mercury salts. A decrease in the vapor pressure of Cl_2O was observed as well as incomplete Cl_2O removal from the salts at -80 C. Proceeding by broad analogy with the $CsF\cdot Cl_2O$ complex, the preparation of ClF_3O or other new F, Cl, O moieties was attempted by fluorination.

Two reactions of this type were conducted at -80 C, but did not yield ClF_3O:

$$(HgO \cdot HgCl_2 \cdot Cl_2O) + F_2 \not\longrightarrow ClF_3O \tag{7}$$

Among the products obtained, however, were $FClO_2$, ClF_3, and ClF_5. The observation of ClF_3, and ClF_5 in particular, at this low temperature suggested a highly active form of chlorine because ClF_5 had not been previously produced under such mild conditions. In addition, the infrared spectrum of the products contained several unidentified peaks. Attempts to separate and identify these products were unsuccessful.

A New Synthesis of Cl_2O

Because of the increased requirements for Cl_2O as an intermediate in several preparations essential to this work, an improved synthetic route was desired. The presently accepted, and indeed the only proved method of preparing Cl_2O is via the ambient temperature flow reaction of nitrogen-diluted chlorine and freshly prepared yellow HgO (Ref. 3). This procedure is rather tedious and generally gives 85-percent Cl_2O (15-percent Cl_2) with 60- to 70-percent conversion of the HgO according to the following literature reaction.

$$2HgO + 2Cl_2 \longrightarrow Cl_2O + HgO \cdot HgCl_2 \tag{8}$$

It has been found that the static reaction of HgO and Cl_2 at -80 C, using either the above stoichiometry or excess HgO, produces high-purity

Cl_2O in good yield with minimal effort. Furthermore, it has been established that under these conditions at least, the stoichiometry of the reactions approaches:

$$HgO + 2Cl_2 \longrightarrow Cl_2O + HgCl_2 \qquad (9)$$

when the Cl_2:HgO ratio exceeds 2:1. The results from some representative preparations are presented in Tables 3 and 4. The Cl_2O yields are for purified material after removal of the Cl_2 impurity.

TABLE 3

CONVERSION OF Cl_2 TO Cl_2O BASED ON $2HgO + 2Cl_2 = Cl_2O + HgO \cdot HgCl_2$

(HgO IN EXCESS)

HgO:Cl_2, mole ratio	HgO, millimoles	Cl_2, millimoles	Cl_2O Yield, percent
1:1	9.1	9.06	100
1.08:1	281.6	260.8	79
1.5:1	127.4	84.3	79
2:1	18.2	9.06	77
2:1	18.7	9.33	80
4:1	37.4	9.33	70

TABLE 4

CONVERSION OF HgO TO Cl_2O BASED ON $HgO + 2Cl_2 = Cl_2O + HgCl_2$ (Cl_2 IN EXCESS)

HgO, millimoles	Cl_2O, millimoles	Cl_2O Yield, percent
169	119	70.4
229	129	56.3
277	225	81.2
233	187	80.2
193	184	95.5

Thus, the technique using excess chlorine gave maximum utilization of the HgO and achieved nearly quantitative conversion of the oxygen of HgO to Cl_2O. Other pertinent advantages of this method were its simplicity and safer handling for gross quantities of the explosive Cl_2O. Because the dispersed Cl_2O was drawn off as required from the mercury salt-Cl_2O reactor, the need to handle large volumes of liquid Cl_2O was eliminated.

The exact mechanism by which Cl_2O is formed from HgO and Cl_2 is not completely understood. It is known, however, that Cl_2O was not all present as free material when in contact with the mercury salts at -80 C. This was demonstrated by the lower vapor pressure (2 millimeters) exhibited under these conditions than that shown by pure Cl_2O (6 to 8 millimeters). Moreover, it was not possible to remove all the Cl_2O by pumping on the mixture at -80 C. Only 50- to 60-percent was evolved at that temperature, the remainder being obtained on warming the reactor to ambient temperature. The possibility of a Cl_2O-$HgCl_2$ complex is therefore being investigated.

When part or all of the HgO was converted to $HgCl_2$ by chlorine, an active form of $HgCl_2$ was formed. Exposure of $HgCl_2$ so formed to moist air resulted in a partial conversion to chlorine, mercuric oxide, and mercury.

Effect of Experimental Conditions on Oxychlorine Trifluoride Synthesis

One of the reaction sequences postulated for the conversion of Cl_2O to ClF_3O is:

$$Cl_2O + CsF \longrightarrow Cl_2O \cdot CsF \qquad (10)$$

$$Cl_2O \cdot CsF + nF_2 \longrightarrow ClF_3O + ClF_{2n-3} \cdot CsF \qquad (11)$$

$$ClF_3O + CsF \rightleftharpoons ClF_3O \cdot CsF \qquad (12)$$

The main goals of this effort were to optimize the conversion of Cl_2O to ClF_3O and to understand the fluorination process by which the conversion is effected. Several parameters were examined: Cl_2O-metal fluoride complex formation, fluorination temperature, sample size, reaction time, and product recovery temperature.

Because the addition of alkali metal fluorides to Cl_2O has been essential to ClF_3O synthesis, conditions leading to effective CsF-Cl_2O and KF-Cl_2O complexes were examined. Formation of the CsF-Cl_2O complex was complete at -80 C after 6 hours (disappearance of Cl_2O color), while at -22 C, Cl_2O vapor in contact with excess CsF was only one-third complexed after 11 hours. This observation was attributed to enhanced solid/liquid contact at -78 C. Once formed, the CsF complex was stable to dissociation at -22 C but showed a pressure of at least 6 mm Hg at 0 C. The potassium fluoride complex, however, formed only slowly at -80 C and was not stable at -45 C. The optimum temperature for fluorination was considered the maximum temperature at which the Cl_2O complex is intact and reacts smoothly. A tabulation of Cl_2O-CsF fluorinations at several temperatures is presented in Table 5. Variations in the quantity of Cl_2O used and the reaction time were also examined. Only ClF_3O that was evolved at ambient temperature was considered in Table 5. Subsequent evidence for $ClF_3O \cdot CsF$ complex formation suggested that several low yields and variations in yield from run to run were due, in part at least, to ClF_3O containing solids which could be heated to give additional ClF_3O. Although no clear-cut correlations between yield and experimental parameters are evident, several satisfactory conversions to ClF_3O have been obtained after several days at Dry Ice temperature.

Solid Products From Fluorination of Cl_2O-CsF Complexes

The low-temperature fluorination of the Cl_2O-CsF complex might be expected to yield complexes of $ClOClF_2$, ClF_2OClF_2, ClF_2OClF_4, and possibly ClF_4OClF_4 as well as complexes of ClF, ClF_3, $FClO_2$, and ClF_3O. Products removed by pumping at ambient temperature were $FClO_2$, ClF_3O, and occasionally ClF_3. Pyrolysis of the remaining solid products yielded additional ClF_3O as well as ClF and an unknown species. The unknown partially passed through a -160 C trap and showed infrared absorptions in the ClO and ClF regions. This new compound may be a new F, Cl, O compound. The products ClF_3O and ClF_3 could have arisen from either degradation of $ClF_4OClF_2 \cdot CsF$ or from $Cs^+ClF_4O^-$ and Cs^+ClF_4. Chlorine monofluoride and any new F, Cl, O species could similarly have arisen from either their CsF complexes or CsF complexes of the fluorinated Cl_2O structure.

TABLE 5

CONVERSION OF CsF - Cl_2O COMPLEX TO ClF_3O

Temperature, C	Time		Cl_2O Used, millimoles	Yield, percent
	Days	Hours		
0		0.5	8.7	0
		1	13	11
		2	15	0
		3	6.1	62
-22		2.5	32	11
		3	13	10
		3	24	26
		4	11	22
-45		9.5	32	46
-78	3.5		3.9	82
	6		11	79
	8		5.2	22
	9		11	21
	10		3.6	26
	10		333	2.4
	11		129	76
	12		1.1	11
	13		5.2	22
	13		8.6	41
	19		75	14
	20		35	3.2
	22		8.6	5.1
	26		7.8	43

emical Studies of ClF_3O

chemistry of ClF_3O was expected to parallel that of ClF_3 with regard
its behavior with strong Lewis acid and bases. That is, reactions in-
lving either the addition or loss of fluoride were considered likely.
rination reactions involving the loss of two fluorine atoms are also
isidered possible, although less likely.

l-Base Reactions. The pentavalent ion ClF_4O^- was initially sought
ng FNO as a donor:

$$FNO + ClF_3O \xrightarrow{?} NO^+ClF_4O^- \qquad (13)$$

siderıng the predicted enhanced acidity of ClF_3O over that of ClF_5
e is a high expectation of preparing the complexes $NO_2^+ClF_4O^-$ and
ClF_4O^-. Two reactions were carried out using FNO and ClF_3O. No con-
ions could be drawn inasmuch as hydrogen nitrate was observed as a
luct, signifying an air leak in the system. A mixture of FNO_2 and
$_3O$ showed a marked vapor pressure decrease indicating complex forma-
. Experiments to more completely define the complexes of ClF_3O with
and FNO_2 are now in progress.

ution of ClF_3O from CsF-containing solids was achieved by pyrolysis
suggested the presence of the salt $Cs^+ClF_4O^-$. The complex $CsF \cdot ClF_3O$
e formulated as $Cs^+ClF_4O^-$ by virtue of its relative thermal stability
analogy with other alkali metal fluoride-interhalogen fluoride salts
. 2 and 5). salt represents the first example of a stable penta-
nt fluorinated chloro-centro anion. Previous work with CsF and ClF_3O

gave little indication of complex formation at -80 C, an observation which may have been due to solidification of ClF_3O at -66 C before sufficient contact with CsF was achieved. While the formation of the $CsF \cdot ClF_3O$ complex in situ was established during the course of the reaction of $ClONO_2$, it was not known whether it could be produced directly from ClF_3O and CsF. Exposure of ClF_3O to fused and freshly powdered CsF at ambient temperature overnight resulted in only small amounts of ClF_3O remaining in the gas phase. Pyrolysis of the residual solids led to the evolution of ClF_3O of good purity, demonstrating the reversible reaction:

$$ClF_3O + CsF \rightleftharpoons Cs^+ClF_4O^- \tag{14}$$

Separation of ClF_3O from ClF_3 and $FClO_2$, the usual contaminants, was attempted with BF_3 in the hope that ClF_3O would be a weaker Lewis base than either impurity. A sample of impure ClF_3O was treated with a lesser volume of BF_3 for 20 minutes at -80 C. ClF_3, $FClO_2$, and excess ClF_3O were volatile at this temperature, but BF_3 was not. No additional pressure was observed at room temperature indicating the absence of $ClF_2{}^+BF_4{}^-$ and $ClO_2{}^+BF_4{}^-$ in the remaining solids.

Oxychlorine trifluoride exhibited a relatively strong basic behavior and reacted preferentially while most if not all of the $FClO_2$ and ClF_3 remained free. The BF_3 complex of ClF_3O is a white solid which can be sublimed only slowly at 100 C and 10^{-3} mm Hg.

The reaction of ClF_3O as a Lewis base toward AsF_5 resulted in the formation of a white solid, nonvolatile at 50 C. Such a complex was expected to be $ClF_2O^+AsF_6{}^-$. However, it was not determined whether a side reaction may have occurred to give $ClO_2{}^+AsF_6{}^-$, which behaves similarly (Ref. 1).

Oxychlorine trifluoride therefore exhibits a pronounced amphoteric character similar to chlorine trifluoride, reacting both as an acid and a base (Eq. 14):

$$ClF_3O + FNO_2 \longrightarrow NO_2^+ClF_4O^- \tag{15}$$

$$ClF_3O + BF_3 \longrightarrow ClF_2O^+BF_4^- \tag{16}$$

$$ClF_3O + AsF_5 \longrightarrow ClF_2O^+AsF_6^- \tag{17}$$

Reaction of ClF_3O and F_2. A series of fluorination experiments in the same Monel reactor with different samples of ClF_3O was conducted consecutively in hopes of forming ClF_5O. Five runs from 70 to 284 C yielded no new species. Fluorination of fluorinated Cl_2O-metal fluoride complexes at various temperatures as a possible route to ClF_5O are in progress.

Reaction of ClF_3O and N_2F_4. The reaction of ClF_3O with N_2F_4 was examined as a possible route to FClO as in the following equation:

$$ClF_3O + N_2F_4 \not\longrightarrow 2NF_3 + FClO \tag{18}$$

The vapor or gas pressures of the system ClF_3O-N_2F_4 showed no appreciable deviations from calculated pressures over the temperature range -80 to 60 C. Under the conditions used, ClF_3O was compatible with N_2F_4; i.e., no reaction was observed. There is a good possibility of arriving at FClO by the alternate fluorination of AsF_3 owing to the additional driving force of complex formation:

$$ClF_3O + AsF_3 \xrightarrow{?} FClO\cdot AsF_5 \rightleftharpoons FClO + AsF_5 \tag{19}$$

MISCELLANEOUS REACTIONS

Attempted Synthesis of NF_2ONF_2

During the recent investigations of reactions of the HNF_2-KF complex and OF_2, nonreproducible infrared indications for a new compound, possibly NF_2ONF_2, were obtained. An alternate route to NF_2ONF_2, namely the reaction of Cl_2O and N_2F_4, was examined at -112 C in Pyrex. When an excess of N_2F_4 was used, the products were FNO, $ClNF_2$, and Cl_2; when Cl_2O was in excess, $ClONO_2$, ClO_2, and Cl_2 were found. Solids believed to be $(NO)_2SiF_6$ were observed in each case. No further studies are planned in this direction.

Reactions of Fluorine Perchlorate

The synthesis of the BrF_6^+ cation was attempted to provide a model for the ClF_6^+ cation. Bromine pentafluoride and fluorine perchlorate were combined in hopes of forming hexafluorobromine (VII) perchlorate:

$$BrF_5 + FOClO_3 \longrightarrow BrF_6^+ClO_4^- \qquad (20)$$

The only detectable reaction was a 10-percent decomposition of $FOClO_3$ to $FClO_3$ and noncondensible gas.

Synthesis of New Br, F, O Compounds by Fluorination of Br_2O

Samples of Br_2O were prepared from yellow HgO and bromine in Freon 11 at -45 to -80 C. The formation of Br_2O was deduced on the basis of the same meager information that is in the literature (Ref. 6). This included the black color, low volatility, and decomposition of the sample above -40 C giving bromine and noncondensible gas (oxygen).

The CsF complex of this material was formed from the Freon 11 solution at low temperature. After removing the solvent, the complex was fluorinated with the expectation of forming BrF_3O and/or BrF_5O. After several days, the reaction yielded room temperature volatile gases composed of BrF_5 with lesser amounts of FNO_2, SOF_2, and SF_6. In addition, several weak, unidentified absorptions were present in the infrared spectrum of the mixture. Too little sample was obtained to permit isolation of the components producing these absorptions. The CsF used in this reaction had become a fused mass, which on hydrolysis gave large amounts of Br_2 vapor. In view of more recent Rocketdyne findings regarding the course of the $Cl_2O \cdot CsF$ fluorinations, wherein it was observed that some of the ClF_3O formed remained in the reactor as a stable complex, it is probable that BrF_3O or possibly BrF_5O would be similarly complexed with CsF. Pyrolysis of the solids from the $Br_2O \cdot CsF$ fluorination is in progress to free any complexed F, Br, O species.

$$Br_2O + CsF \longrightarrow CsF \cdot Br_2O \qquad (21)$$

$$CsF \cdot Br_2O \xrightarrow{F_2} CsBrF_xO + BrF_5 \qquad x = 4, 6 \qquad (22)$$

$$CsBrF_xO \xrightarrow{\Delta} CsF + BrF_{x-1}O \qquad (23)$$

EXPERIMENTAL EFFORT

PREPARATION OF Cl_2O

Yellow HgO was freshly prepared by the reaction of mercuric chloride and sodium hydroxide solutions. After drying and powdering, HgO was loaded into small glass ampoules together with appropriate amounts of chlorine. The closed, evacuated ampoule was kept at Dry Ice temperature at least overnight, although longer reaction periods were beneficial rather than detrimental to Cl_2O formation. Very pure Cl_2O was obtained if HgO was in excess, while better utilization of the oxygen of HgO was achieved if chlorine was in excess. Impure Cl_2O was upgraded by trap-to-trap distillation using carbon disulfide slush (-112 C) and liquid nitrogen baths. The purity and identity of the product was established by its infrared spectrum (Ref. 7), vapor phase chromatography and vapor pressure.

PREPARATION OF Br_2O

The synthesis of Br_2O was accomplished in much the same manner as that of Cl_2O. The reactants Br_2 and HgO were mixed in Freon 11 solvent to provide contact while maintaining low temperatures. The reaction was conducted over several days at -45 to -80 C with occasional agitation. Bromine monoxide was obtained in reasonably good purity by subsequent vacuum fractionation. Usually this was not necessary as the Br_2O-Freon 11 solution was used to form the $Br_2O \cdot CsF$ complex directly. The bromine and Freon 11 were then stripped off.

PREPARATION OF $ClNO_3$

Chlorine nitrate was prepared by allowing roughly equimolar quantities of Cl_2O and N_2O_4 or N_2O_5 to react in evacuated glass ampoules at -80 C overnight or longer. Residual Cl_2O indicated by its red color was consumed by allowing the reaction to proceed briefly in the vacuum line at ambient temperature. The $ClNO_3$ produced was purified by vacuum fractionation and identified by its infrared spectrum (Ref. 8) and vapor pressure (Ref. 9).

FLUORINATION OF HYPOHALITE-ALKALI METAL FLUORIDE COMPLEXES

Regardless of the material being fluorinated, before the introduction of fluorine into the metal cylinder, at least 16 hours were allowed to perform the complex substrate, usually at -80 C. After cooling to -196 C, a twenty-fold molar excess of fluorine was condensed into the cylinder. The reactor temperature was generally maintained at -80 C for several days before removing the excess fluorine at -196 C. Volatile products were then separated, trapped, and examined.

PREPARATION OF OXYCHLORINE TRIFLUORIDE

Oxychlorine trifluoride was prepared by the fluorination of an alkali metal-Cl_2O complex. In a typical preparation the alkali-metal fluoride was first dried by fusion and then transferred to a dry box for grinding. The powdered fluoride was placed in a 300-milliliter stainless-steel cylinder. Chlorine monoxide was distilled into the reactor in vacuo. The cylinder was maintained at -78 C at least overnight to allow complex formation. Then fluorine was added and allowed to warm to the desired reactor temperature. After reaction, the products which were volatile at ambient temperature were separated by fractionation using a -95 C slush bath which condensed most of the ClF_3O. Any unreacted Cl_2O, other products, and impurities passed through. Additional ClF_3O was evolved by heating the residual solid in the reactor with a heat gun.

REFERENCES

1. Schmeisser, M. and K. Brandle in Advances in Inorganic Chemistry and Radiochemistry, Vol. V, Academic Press, New York City, 1963.
2. R-5883-2, Inorganic Halogen Oxidizers, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, 30 November 1964, CONFIDENTIAL.
3. Cady, G. H., Inorganic Synthesis, Vol. V, McGraw Hill, New York City, p. 156, 1957.
4. Cady, G. H., Inorganic Synthesis, Vol. V, McGraw Hill, New York City, p. 161, 1957.
5. Whitney, E. D., R. O. MacLaren, C. E. Fogle, and T. J. Hurly, J. Am. Chem. Soc., 86, 2583 (1964).
6. Schwarz, R. and H. Wiele, J. prakt. Chem., 152, 157 (1939).
7. Hedberg, K., J. Chem. Phys., 19, 509 (1951).
8. Brandle, K., M. Schmeisser, and W. Luttke, Ber., 93, 2300 (1960).
9. Martin, H., Angew. Chem., 70, 97 (1958).

CONFIDENTIAL

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Rocketdyne, a Division of North American Aviation, Inc., 6633 Canoga Avenue, Canoga Park, California

2a. REPORT SECURITY CLASSIFICATION
CONFIDENTIAL

2b. GROUP
4

3. REPORT TITLE
Inorganic Halogen Oxidizers

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Quarterly Report (29 May 1965 through 28 August 1965)

5. AUTHOR(S) (Last name, first name, initial)
Pilipovich, D., Lindahl, C. B., Bauer, H. F., Schack, C. J.

6. REPORT DATE
30 September 1965

7a. TOTAL NO OF PAGES
28

7b. NO OF REFS
9

8a. CONTRACT OR GRANT NO.
Nonr 4428(00)

b. PROJECT NO
ARPA Order No. 23

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
R-5883-4

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Advanced Research Projects Agency
Washington 25, D.C.

13. ABSTRACT

The new oxidizer oxychlorine trifluoride, ClF_3O, has been prepared by the fluorination of cesium fluoride complexes of both chlorine monoxide and chlorine nitrate. The density of ClF_3O is 1.90 ±0.05 g/cc at 25.5 C; it melts at -66 C and boils at 29.4 C. The vapor pressure/temperature equation for ClF_3O has been obtained from -22 to 32 C: $\log_{10}P$ (mm) = 8.433 - 1680/T. The molar heat of vaporization is 7.7 kcal. Oxychlorine trifluoride was found to be thermally stable to 284 C, although reactivity with metal containers was noted. Elemental analyses confirm the empirical formula ClF_3O. Several members of a new class of complexes have been formed: $Cl_2O \cdot CsF$, $Br_2O \cdot CsF$, and $ClONO_2 \cdot CsF$. Fluorination of these materials has led to solid oxyhalogen fluoride complexes. Evidence for another new oxychlorine fluoride candidate has been obtained during this study. Reactions of ClF_3O with Lewis acids and bases gave the complexes $NO_2^+ClF_4O^-$, $Cs^+ClF_4O^-$, $ClF_2O^+BF_4^-$, and $ClF_2O^+AsF_6^-$, indicating a pronounced amphoteric behavior. No reaction of ClF_3O was observed with either F_2 or N_2F_4. A new, convenient synthesis of Cl_2O has yielded a product of improved purity. The reaction of BrF_5 with $FOClO_3$ failed to give $BrF_6^+ClO_4^-$ while the reaction of Cl_2O and N_2F_4 gave no new products. (C)

DD FORM 1 JAN 64 1473

CONFIDENTIAL

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Oxidizers Fluorides Halogens Chlorines						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
_______________________________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
_______________________________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
_______________________________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (*TS*), (*S*), (*C*), or (*U*).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.