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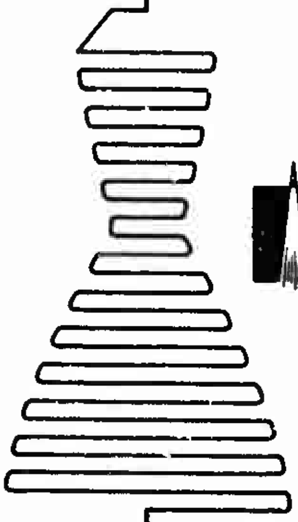

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R-7239-1

(Unclassified Title)

QUARTERLY PROGRESS REPORT, INORGANIC HALOGEN OXIDIZERS

(30 May 1967 through 31 August 1967)

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

Contract Nonr 4428(00)
G.O. 8614

Sponsored by Office of Naval Research
Power Branch
Code 429

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NO. OF PAGES 18 & iv

REVISIONS

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FOREWORD

The research reported herein was supported by 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 Navy Contract Nonr 4428(00) and covers the period 30 May 1967 through 31 August 1967. The program manager was Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The work was conducted in Oxidizer and Fluorine Chemistry with Dr. D. Pilipovich, Principal Scientist as project scientist. Full-time staff members contributing to the technical effort were Dr. C. J. Schack, Dr. C. B. Lindahl, and Mr. R. D. Wilson.

ABSTRACT

A new more powerful ultraviolet source has been employed in the ultraviolet activated reactions of chlorine oxyfluorides. This has resulted in significant reductions in the time necessary for complete reaction. Reactant systems have been limited to the $FClO_2/ClF_5$ and $FClO_3/ClF_5$ pairs. Excellent conversions and yields of ClF_3O have been realized.

Reactions of $NaClO_4$ and NO_2ClO_4 with ClF have been carried out in an effort to prepare chlorine perchlorate, $ClOClO_3$. Preliminary results are encouraging but poor yields have hampered absolute identification of the evolved reaction product.

Samples of IF_7 were prepared and converted to IF_5O. A redetermination of the sublimation pressure-temperature relationship for IF_7 was made and the derived equation is: $\log p_{mm} = 7.6939 - 1356.6/T$. Flow pyrolyses of IF_5O samples were conducted both in the presence of metal oxides and in simple straight tubes. This approach to IF_3O or IF_3O_2 was unsuccessful. Reactions of $KOCF_2NF_2$ and PF_5 were carried out with the aim of producing PF_5NF_2 through NF_2^- ion transfers from the salt. This was not achieved because one or another of the reactants was degraded by the test solvents or the PF_5 was complexed by residual KF.

(Confidential Abstract)

CONTENTS

INTRODUCTION

This program is concerned with the synthesis of new halogen fluorides and oxyfluorides. To accomplish this task, a variety of preparative techniques have been employed in both the synthesis of intermediates and also in the fluorination reactions used to give final products. Ultraviolet activated reactions of chlorine oxyfluorides in the presence of active fluorine sources have been shown to be effective in the formation of different oxyfluorides. The ultraviolet activated reactions of the present period have utilized $FClO_2$ and $FClO_3$ exclusively as F-Cl-O intermediates and ClF_5 as the fluorinating agent with resultant excellent conversions to ClF_3O.

The utility of ClF-HX condensations for synthetic reactions was demonstrated earlier in this program. Thus, reactions of ClF and HNF_2 or HNO_3 were shown to be excellent methods of preparing $ClNF_2$ or $ClNO_3$. Similar reactions of ClF and perchlorate species have been undertaken to synthesize a new chlorine oxide, chlorine perchlorate ($ClOClO_3$).

Pyrolytic studies of IF_5O were continued as a potential means of forming new covalent I-F-O materials, and an effort was made to utilize the NF_2^- ion transfer properties of the $KOCF_2NF_2$ salt in inorganic systems.

DISCUSSION

ULTRAVIOLET ACTIVATED REACTIONS

Previous work (Ref. 1) has shown that ultraviolet activated reactions involving chlorine oxyfluorides result in the formation of Florox, ClF_3O. These routes to Florox were the first demonstrations of high-yield syntheses of Florox not involving inorganic hypochlorites as intermediates. Several of the important reaction conditions were partially defined during the course of this work. For example, it was found that a low temperature ($<$-40 C) was necessary to achieve Florox formation. This investigation was continued both to define Florox synthesis parameters more precisely and also to determine the applicability of this technique as a tool for achieving the synthesis of ClF_3O_2 and ClF_5O.

The single most important variation in the more recent reactions has been the use of a new, more powerful ultraviolet source. The new lamp requires a 450-watt input as compared to the 100-watt input lamp previously employed. While the power input to the lamp is only 4.5 times as great, the resultant radiation in the 2000- to 2400-angstrom range is 75 to 150 times greater in the new lamp than in the old. It was shown earlier (Ref. 1) that the compounds of interest generally have absorption maxima in this region. The use of this new lamp was expected, therefore, to give gross changes in the course of the reactions. Thus, the radiation period required to effect complete or useful conversions of chlorine oxyfluorides was expected to be considerably shortened. It was also hoped that the tremendous increase in available radiant energy would result in different final products, the aforementioned ClF_3O_2 and ClF_5O, in addition to ClF_3O.

Reactions

The recent experimental work has been concerned exclusively with two oxyfluorides, $FClO_2$ and $FClO_3$, and only one fluorinating agent, ClF_5. The latter was chosen because of its proven superiority (Ref. 1) over other fluorinating agents in these ultraviolet activated reactions.

The same reaction cell and cooling system described previously were employed again. Results for the actual reactant combinations and conditions are presented in Table 1 and are discussed in the following paragraphs.

$\underline{FClO_2 - ClF_5}$. Because this system was the most well defined in the earlier work and gave the best conversions to Florox, it was used to test the utility of the new lamp. Irradiation of a 1:1 mixture of $FClO_2:ClF_5$ for either 1/2 or 1 hour at -40 C resulted in complete consumption of the starting materials and the clean-cut formation of ClF_3O and ClF_3 as the only condensable products. The fact that all starting materials were reacted even in the short time period under otherwise identical conditions demonstrates that even less irradiation time is needed. The excellent conversions achieved compare favorably with all but the best results from the earlier work which required significantly longer reaction times. The low yield of by-product in these short time-period reactions is the best attained to date. Overall, these results show that the basic course of the fluorination reaction producing Florox has not been altered. The reaction scheme may be considered as follows:

$$FClO_2 \xrightarrow{UV} FClO_2^*$$

$$FClO_2^* \longrightarrow [FClO] + O$$

$$FClO_2 + O \longrightarrow [FClO] + O_2$$

TABLE 1

ULTRAVIOLET ACTIVATED REACTIONS

Reaction Number	Reactants	Mole Ratio (to 1)	Temp. C	Time,* hours	Condensable Products	Percent Conversion to ClF_3O	Percent Yield to ClF_3O
1.	ClF_5, $FClO_2$	1.0	-40	1	ClF_3O, ClF_3	45	45
2.	ClF_5, $FClO_2$	1.0	-40	1/2	ClF_3O, ClF_3	45	45
3.	ClF_5, $FClO_3$	0.9	-40	1	ClF_3O, ClF_3, unreacted $FClO_3$	40	100
4.	ClF_5, $FClO_3$	1.4	-40	1/2	ClF_3O, ClF_3, unreacted $FClO_3$	30	55
5.	ClF_5, $FClO_3$	1.4	-58	1/2	ClF_3O, ClF_3, unresected $FClO_3$	30	75
6.	ClF_5, $FClO_3$	2.0	-60	1/4	Recovered Reactants		
7.	ClF_5, $FClO_3$	2.0	-60	1/2	Small amount ClF_3		
8.	ClF_5, $FClO_3$	1.0	-40	1/2	ClF_3O, ClF_3, unreacted $FClO_3$	30	55
9.	$FClO_3$	-	-60	2	Unreacted $FClO_3$, ClF, small amount $FClO_2$		
10.	$FClO_3$	-	-60	1/2	Unreacted $FClO_3$, ClF, small amount $FClO_2$		

*All reaction periods do not include a 10-minute lamp warm-up period.

$$[FClO] + O \longrightarrow ClF + O_2$$

$$[FClO] + ClF_5 \longrightarrow ClF_3O + ClF_3$$

$$ClF + ClF_5 \longrightarrow 2ClF_3$$

The observed ClF_3 is a product of ClF_5 degradation and also the fluorination of ClF.

<u>$FClO_3$ - ClF_5</u>. As shown in Table 1 several temperatures and mole ratios were utilized in the study of the ultraviolet activated $FClO_3$ - ClF_5 reactions. Only one experiment (Ref. 1) had been performed with $FClO_3$ and any fluorine source during the earlier Rocketdyne work. This revealed that $FClO_3$ is a suitable precursor to Florox. Additional experments were needed to more clearly define the reaction. Irradiation times of 0.5 to 1.0 hour and reaction temperatures of -40 to -58 C were used. The $ClF_5/FClO_3$ mole ratio was varied from 0.9 to 1.4. Consistent conversions of $FClO_3$ to ClF_3O of 30 to 40 percent were found. However, the yields varied between 55 and 100 percent. The higher yields were obtained with lower relative amounts of ClF_5 or lower temperatures. Again, the reactions were well defined and gave only ClF_3 as a condensable by-product. The experiment that resulted in a 100 percent yield of ClF_3O also gave a measured recovery of ClF_3 that quantitatively confirmed the overall reaction stoichiometry as shown:

$$FClO_3 + ClF_5 \longrightarrow ClF_3O + ClF_3 + O_2$$

While these results were well defined, the change of just one reaction parameter produced unexpected results. When the mole ratio of ClF_5 to $FClO_3$ was increased to 2, irradiation as before for 0.25 or 0.5 hour did not result in any significant reaction and the starting materials were recovered. The higher concentration of ClF_5, a much stronger ultraviolet absorber than $FClO_3$ (Ref. 1, Fig. 1), may have prevented effective excitation of the latter and thus inhibited its reaction during the short reaction time. However, the increase in ClF_5 concentration was relatively small while the effect on ClF_3O was many orders of magnitude. To ensure that an unobserved equipment malfunction had not caused these results, a 1:1 $ClF_5/FClO_3$ experiment was conducted immediately subsequent to the 2:1 mole ratio experiments. Again a good conversion (30 percent) and yield (55 percent) of ClF_3O were obtained confirming that the equipment was functioning properly. A more complete explanation of the nonreaction is desired. More experimental evidence for the reaction mechanism operative in these systems should provide an insight and fuller understanding of the process.

To aid in this determination of the reaction mechanism, two experiments were conducted with $FClO_3$ alone. A quantitative measure of the decomposition products was sought. As previously, however, the only isolated products were $FClO_2$ and ClF. Further experiments are being conducted to determine the ratio of $FClO_2$ to ClF produced.

ATTEMPTED SYNTHESIS OF CHLORINE PERCHLORATE

Condensation reactions of chlorine monofluoride have not been the subject of extensive investigations, previously. However, the synthetic utility of such reactions has been demonstrated under this program (Ref. 2 and 3). Specific examples are:

$$ClF + HNF_2 \longrightarrow HF + ClNF_2$$

$$ClF + HNO_3 \longrightarrow HF + ClONO_2$$

These equations suggest that a general condensation of this type may exist and work has been continuing to exploit this chemistry.

The present goal of these condensation reactions is the synthesis of chlorine perchlorate, $ClOClO_3$. Formation of $ClOClO_3$ would represent the first example of a chlorine oxide containing chlorine atoms in two different oxidation states, i.e., Cl(I) and Cl(VII). The comparable electronegativity of the ClO_4^- and NO_3^- groups coupled with the known stability of $ClNO_3$ makes the proposed existence of $ClOClO_3$ appear reasonable. In addition, the mild, low-temperature conditions available through ClF condensations present synthetic conditions not previously applied to chlorine oxide syntheses.

The first attempts at the preparation of $ClOClO_3$ were not conducted with anhydrous $HClO_4$. Rather, use was made of anhydrous perchlorate salts that were readily available. The desired reactions were:

$$NaClO_4 + ClF \longrightarrow NaF + ClOClO_3$$

$$NO_2ClO_4 + ClF \longrightarrow FNO_2 + ClOClO_3$$

It was hoped that the use of these materials would eliminate the need for preparing anhydrous $HClO_4$ and at the same time avoid possible complications associated with the explosive inpurity Cl_2O_7 often present in anhydrous $HClO_4$ (Ref. 4).

Several reactions of ClF and $NaClO_4$ were conducted at -78, -45, and 0 C. These reactions were of several hours to 2 weeks duration. In all cases, a volatile material was formed which could be fractionally condensed at -112 C but not at -78 C. As a solid, this material is pale yellow to colorless and on contact with moist air it is partially decomposed to $HClO_4$. The infrared spectrum of this unidentified material is simple and has the bands noted in Table 2.

TABLE 2

INFRARED BANDS OF UNKNOWN FROM $ClF-MClO_4$ REACTIONS

Band, cm^{-1}	Relative Intensity
2320	vw
1280	s
1040 (doublet)	m
750 (broad)	vw
650	s
565	w
510	vw

Comparison of these absorption with those of other covalent perchlorates (listed in Table 3) illustrates a pronounced similarity. This similarity is most noteworthy in the two bands (~1300 and 1040 cm^{-1}) assigned to the covalent $-ClO_3$ stretching vibrations (Ref. 5 through 7). This comparison indicates that the unknown formed in the $ClF-NaClO_4$ reaction may be a covalent perchlorate such as the desired $ClOClO_3$. Furthermore the remaining bands are not incompatible with a structure of the $ClOClO_3$ type. A final comparison was sought between the infrared spectra of the unknown sample and that of dichlorine hexoxide, Cl_2O_6. The infrared spectrum of the latter has not been reported and an authentic sample will be prepared (Ref. 8) to secure its spectrum. In the interim a comparison was made with unverified in-house spectra attributed to Cl_2O_6. These spectra only cover the 2 to 15 micron range. The comparison indicated that the unknown material and the "Cl_2O_6" were quite similar but not identical. In addition, the reported properties of Cl_2O_6 (dark orange-red color and low volatility) make it unlikely that Cl_2O_6 is present in the unknown.

TABLE 3

PRINCIPAL INFRARED BANDS OF COVALENT PERCHLORATES

$FClO_4$ (Ref. 5)*		$HClO_4$ (Ref. 6)		Cl_2O_7 (Ref. 7)	
Band, cm^{-1}	Relative Intensity	Band, cm^{-1}	Relative Intensity	Band, cm^{-1}	Relative Intensity
		3560	m(O-H)		
1298	s	1325	s	1310	s
1049	m	1050	m	1025	m
885	w(O-F)	725	m	690	w
666	s	580	m	600	m

*NaCl region only

A major problem is the characterization of this new unknown material is the low yield realized in the synthesis. This has generally been of the order of 5 to 10 percent with one attempt giving slightly higher results. The duration of the preparative experiment has had no significant effect on yield. Higher temperatures have so far only given slightly better yields and have also resulted in increased by-product formation (Cl_2, ClO_2, $FClO_2$, $FClO_3$).

One approach in attempting to circumvent this problem is using scaled up synthetic reactions, some of which are in progress. (The original reactions were on a small scale to minimize any potential hazard.) An alternate starting material was also chosen to find a more efficient synthesis. Thus, reactions with NO_2ClO_4 and ClF were conducted. These gave poorer yields of the desired volatile unknown and none of the expected co-product FNO_2. The failure to generate free FNO_2 may be the result of a side reaction between it and a chlorine oxide such as the reported reaction (Ref. 9):

$$FNO_2 + Cl_2O_6 \longrightarrow FClO_2 + NO_2ClO_4$$

Pending the preparation and purification of larger samples, an attempt was made to obtain a preliminary characterization of the volatile unknown by fluorination reaction. If the unknown is $ClOClO_3$, the fluorination might proceed as follows:

$$ClOClO_3 + F_2 \longrightarrow FClO_3 + ClF_3O$$

However, in an experiment completed at -45 C, it was found that fluorination yielded $FClO_2$ and $FClO_3$ in addition to some unreacted starting material. The products may have arisen from $ClOClO_3$ as follows:

$$ClOClO_3 + F_2 \longrightarrow FClO_3 + [FClO]$$
$$2\,[FClO] \longrightarrow FClO_2 + ClF$$

The amount of ClF formed would have been too small to identify spectrally. An alternate possibility is that the unknown sample is a chlorine oxide other than $ClOClO_3$. For example, the unknown Cl_2O_5 might fluorinate as follows:

$$OClOClO_3 + F_2 \longrightarrow FClO_2 + FClO_3$$

To facilitate the characterization of this unidentified material, additional preparative reactions will be employed. The use of the $CsClO_4$ salt is planned together with ClF reactions of covalent species, $HClO_4$ and Cl_2O_7:

$$HClO_4 + ClF \longrightarrow HF + ClOClO_3$$
$$Cl_2O_7 + ClF \longrightarrow FClO_3 + ClOClO_3$$

IODINE FLUORIDES AND OXYFLUORIDES

The utilization of IF_5O as a precursor to unreported IF_xO_y compositions has been of interest. Simple thermal reactions were considered as a direct approach to these materials; reactions of the following type were sought:

$$IF_5O \longrightarrow IF_3O + F_2$$

$$2IF_5O \longrightarrow IF_3O_2 + IF_7$$

Earlier pyrolysis experiments with IF_5O (Ref. 1) indicated that the predominant thermal reaction was degradation through oxygen elimination.

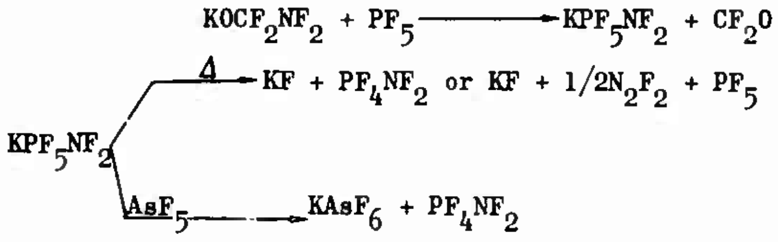
$$IF_5O \longrightarrow IF_5 + 1/2\ O_2$$

However, in some experiments conducted in the presence of CuO, the IF_5O pyrolysis was observed to result in the formation of trace quantities of an unknown volatile material.

A limited effort was made to prepare more of this material in order that it might be identified. After replenishment of the IF_5O supply, pyrolysis experiments were resumed. Duplication of the earlier reaction conditions (~350 C with CuO packing in a 1/4-inch stainless-steel tube) failed to yield any of the sample and again gave only IF_5, I_2, and noncondensables. The reaction temperature was varied between 200 and 400 C and still did not materially change the course of the reaction. Substitution of a different metal oxide, PbO_2, only resulted in lowering the temperature necessary for complete IF_5O decomposition. Finally, substitution of a Monel pyrolysis tube with a CuO packing was attempted in an effort to generate some of the previously observed material. This too was unsuccessful and the experiments were terminated. Because the only real difference between these reactions and the earlier ones was the use of a different batch of IF_5O, it is possible that the unknown previously observed arose through reaction of some impurity in the first IF_5O supply.

DIFLUORAMIDE TRANSFER REACTIONS

The use of possible "difluoramide transfer" reactions in inorganic systems has been investigated. Lewis Acids have been reacted with the perfluoroformamide - KF samples (Ref. 10) with the goal of obtaining useful intermediates such as PF_4NF_2:



$$KOCF_2NF_2 + PF_5 \longrightarrow KPF_5NF_2 + CF_2O$$

$$KPF_5NF_2 \xrightarrow{\Delta} KF + PF_4NF_2 \text{ or } KF + 1/2N_2F_2 + PF_5$$

$$KPF_5NF_2 + AsF_5 \longrightarrow KAsF_6 + PF_4NF_2$$

Experiments have been conducted using propylene carbonate, nitromethane, and acetonitrile as solvents. One sample of $KOCF_2NF_2$ was prepared in CH_3CN, redissolved in propylene carbonate and subsequently treated with PF_5. This sample deflagrated presumably through a rapid decomposition of HNF_2^- as in the $CsF \cdot HNF_2$ system. In two more reactions, $FCONF_2$ was added to a solution of KF in propylene carbonate. Upon warming from -196 C to -25 C, the material melted to a purple liquid which evolved gas and dissipated its color over a 10-minute period giving a quantitative yield of COF_2. Propylene carbonate obviously is not a suitable solvent for the desired reactions.

Reactions with CH_3NO_2 indicate that it is a relatively poor solvent for the complex formation. In several experiments, evolution of significant amounts of COF_2 has indicated that the complex (Ref. 10) goes beyond the first desired step to the second undesired steps:

$$FCONF_2 + KF \longrightarrow NF_2CF_2O^-K^+$$

$$NF_2CF_2O^-K^+ + FCONF_2 \longrightarrow (NF_2)_2CFO^-K^+ + CF_2O$$

Final solvent studies utilized the KF-$FCONF_2$ complex in CH_3CN. While it is likely that the $KOCF_2NF_2$ complex was formed in CH_3CN, addition of PF_5 to the $KOCF_2NF_2$ complex produced only small amounts of COF_2 and $FCONF_2$. It is possible that most of the PF_5 reacted with KF (present from making the $KOCF_2NF_2$ complex) or with the solvent. Because no simple direct route to the desired PF_4NF_2 was found, the effort was terminated.

EXPERIMENTAL

ULTRAVIOLET IRRADIATION

Cell and Fractionation System

A new Teflon-metal high vacuum system was constructed, passivated, and calibrated. A specially designed ultraviolet reactor was connected to the system and consisted of a stainless-steel body and a 4-inch-diameter ultraviolet-grade sapphire window. The cell temperature was automatically controlled by a circulating methanol cooling system to within 3 C of the desired temperature and within a range of -60 C to ambient temperature. The cell apparatus was modified so that a new ultraviolet lamp could be used. This modification consisted of a metal housing above the cell window to hold the new lamp and a system to supply dry nitrogen which can be blown continuously across the cell window to prevent "frosting" during low-temperature reactions. The new lamp provided a greatly increased amount of irradiation; however, it also increased the amount of heat generated and the cell housing must be cooled by a large fan.

Ultraviolet Source

Work was conducted with a Hanovia lamp No. 679-A-36 (power input 450 watts).

Materials

The $FClO_2$ was prepared by the reaction of ClF_3 and $KClO_3$. Purification of $FClO_2$ was carried out by pumping off the Cl_2 impurity while holding the $FClO_2$ at -78 C. The chromatographic purity of the colorless liquid was better than 99.9 percent. The $FClO_3$ was purchased from Pennsalt. The ClF_5 prepared at Rocketdyne, had a purity of 99+ percent.

Attempted Synthesis of $ClOClO_3$

All reactions were conducted under static conditions. Small stainless-steel bombs (10 or 30 milliliters) were passivated with ClF_3, evacuated, and then put into a nitrogen-filled dry box, where they were opened, and loaded with weighed amounts of solid perchlorate ($NaClO_4$ or NO_2ClO_4). After closing, reattaching to the vacuum line, and evacuating, measured amounts of freshly fractionated ClF were condensed into the bombs at -196 C. The quantities of reactants were in the 3 to 12 mmole range. Reactions were of several hours to several days duration and at constant temperature (-78, -45, or 0 C). At the conclusion of a reaction, the cylinder was cooled to -196 C and opened to determine if any noncondensable gas had been formed. In all experiments, only traces or no noncondensables were detected. The reactor was warmed to ambient temperature and the volatile materials were fractionated through traps cooled to -112, -142, and -196 C. The unidentified volatile product was retained at the highest temperature (it would pass a trap cooled to -78 C). By-product mixtures containing Cl_2, $FClO_2$, and $FClO_3$ were retained in the -142 C trap and unreacted ClF passed through to the -196 C trap. The amounts of unknown material formed were generally 5 to 10 percent of the starting ClF and the by-products were somewhat greater.

Preparation of IF_7

Iodine pentafluoride and excess F_2 were heated at 150 C in Monel or stainless-steel cylinders for several hours. Conversion to IF_7 was nearly quantitative. Rough purification was achieved by vacuum fractionation. Samples often contained traces of IF_5O and possibly HF. Despite the limited quantities of these impurities, it was not possible to duplicate the reported sublimation pressures for IF_7 (Ref. 11) even approximately. Therefore, when during the course of the present preparations a sample was found that contained no detectable impurities (HF or IF_5O), a redetermination of the sublimation pressure-temperature relationship was undertaken. The experimental data are presented in Table 4 and the derived equations are:

$$\log p_{mm} = 7.6939 - 1356.6/T$$

or

$$\log p_{mm} = 11.2319 - 3046.93/T + 197769/T^2$$

The derived heat of sublimation is 6.2 kcal/mole and the solid melts at 6.5 C.

TABLE 4

SUBLIMATION PRESSURE-TEMPERATURE DATA FOR IF_7

Temperature, C	Observed Pressure, mm	Calculated Pressure, mm
-79.8	6	5
-63.8	45	16
-55.5	25	29
-29.5	113	134
-11.1	316	325
0.0	567	535
8.6	822	758
17.2	1130	1050

Preparation of IF_5O

In the past, no difficulty had been encountered in the conversion of IF_7 to IF_5O with Cab-O-Sil. However, one of the recent syntheses gave no IF_5O. Instead, only SiF_4, IF_5 and O_2 were found. Apparently the heat of the reaction during its uncontrolled warm-up resulted in thermal decomposition of the IF_5O.

$$2IF_7 + SiO_2 \longrightarrow 2IF_5O + SiF_4 \longrightarrow 2IF_5 + O_2$$

Therefore, it is now evident that this synthesis does require some temperature control.

Pyrolysis of IF_5O

A cylinder containing IF_5O was attached to a straight metal tube stainless-steel or Monel; (30 inches long, 12-inch heated zone) passing through a furnace and then connected to a Teflon U-trap and the vacuum line. The tube was heated to test temperature and passivated with ClF_3 if no metal oxide packing was used. When chlorine oxides were no longer generated, the system was completely pumped down. The IF_5O cylinder was cooled to -78 C and the U-trap was cooled to -196 C. Continuous pumping was maintained and a flow of IF_5O was begun (calibrated rate = 3.5 cc/min). Separate flow experiments were of 13 to 15 minutes duration.

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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 Rockwell Corporation, 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 (30 May 1967 through 31 August 1967)

5. AUTHOR(S) *(Last name, first name, initial)*
Pilipovich, D.; Schack, C.; Lindahl, C.; Wilson, R.

6. REPORT DATE
30 September 1967

7a. TOTAL NO. OF PAGES
22

7b. NO. OF REFS
11

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

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
R-7239-1

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

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12. SPONSORING MILITARY ACTIVITY
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13. ABSTRACT

A new more powerful ultraviolet source has been employed in the ultraviolet activated reactions of chlorine oxyfluorides. This has resulted in significant reductions in the time necessary for complete reaction. Reactant systems have been limited to the $FClO_2/ClF_5$ and $FClO_3/ClF_5$ pairs. Excellent conversions and yields of ClF_3O have been realized. Reactions of $NaClO_4$ and NO_2ClO_4 with ClF have been carried out in sn effort to prepare chlorine perchlorate, $ClOClO_3$. Preliminary results are encouraging but poor yields have hampered absolute identification of the evolved reaction product. Samples of IF_7 were prepared and converted to IF_5O. A redetermination of the sublimation pressure-temperature relationship for IF_7 was made and the derived equation is: $\log p_{mm} = 7.6939 - 1356.6/T$. Flow pyrolyses of IF_5O samples were conducted both in the presence of metal oxides and in simple straight tubes. This approach to IF_3O or IF_3O_2 was unsuccessful. Reactions of $KOCF_2NF_2$ and PF_5 were csrried out with the aim of producing PF_5NF_2 through NF_2^- ion transfers from the salt. This was not achieved because one or another of the reactants was degraded by the test solvents or the PF_5 was complexed by residual KF. (C)

DD FORM 1 JAN 64 1473

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Halogen Oxidizers Chlorine Oxyfluoride						

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