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R-8037

(Unclassified Report)

SEMIANNUAL REPORT,
INORGANIC HALOGEN OXIDIZERS

(1 April 1969 through 30 September 1969)

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

Contract Nonr 4428(00)
G.O. 8614

Office of Naval Research
Power Branch
Code 429

PREPARED BY
Oxidizer and Fluorine Chemistry Group

APPROVED BY

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NO. OF PAGES 34 & vi

DATE 31 October 1969

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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 11 of Navy Contract Nonr 4428(00) and covers the period 1 April 1969 through 30 September 1969. The program manager was Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The work was conducted in the Oxidizer and Fluorine Chemistry Group with Dr. D. Pilipovich as Responsible Scientist. Staff members contributing to the technical effort include Dr. D. Pilipovich, Dr. C. J. Schack, Dr. K. O. Christe, Dr. E. C. Curtis, Dr. C. B. Lindahl, and Mr. R. D. Wilson.

ABSTRACT

The new compound chlorine perchlorate, $\text{Cl}_2\text{O}_4$, was synthesized from the action of chlorine fluorosulfate on several perchlorate salts. Characterization data, physical and chemical properties are described. The use of $\text{N}_2\text{O}$ as an oxygen source for the synthesis of $\text{ClF}_3\text{O}$ was successful but offered no advantages over oxygen. A new synthesis of nitryl chloride emerged from the studies of Ca(OCl)$_2$ as an intermediate and involved the action of nitrosyl fluoride, FNO, on calcium hypochlorite. A structural evaluation on chlorine fluorosulfate was carried out from its ir spectrum. $C_5$ symmetry for ClSO$_3$F was suggested and thermodynamic properties and force constants were computed.

(Confidential Abstract)
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INTRODUCTION

The program to be reported herein constitutes a continuation of a basic synthesis program in the area of inorganic halogen oxidizers. In the main, the program had been devoted to halogen fluorides, oxyfluorides and derivatives of both. During the past period, however, we have augmented our fluorine research with studies in the halogen oxide area. Specifically, a multifaceted program was begun in (1) studying the synthesis of halogen oxides through positive halogenation reaction, (2) evaluating positive halogenation reagents, and (3) assessing the reaction chemistry of all intermediates in synthesizing new, energetic materials. This report describes the work in preparing the new chlorine oxide, chlorine perchlorate, its characterization, and some of its reaction chemistry.
DISCUSSION

CHLORINE PERCHLORATE--PREPARATION AND PROPERTIES

In the course of developing the synthesis of chlorine fluorosulfate, CISO₃F, from CIF and SO₃ (Ref. 1) it was observed that this material exhibits an unusual degree of reactivity as a "positive" chlorinating agent. Efforts to take advantage of this property were made by attempting the chlorination of perchlorate anions.

\[
M^+ClO_4^- + CISO_3F^- \rightarrow ClO_ClO_3^- + M^+SO_3F^- \quad M=Cs, NO_2
\]

The unusual new chlorine oxide sought through this reaction was produced in high yield (75 to 95 percent) at a temperature of approximately -45 C. This oxide, chlorine perchlorate, is unusual as it represents the first example of a stable Cl-O compound containing chlorine in two different valence states.

Chlorine perchlorate had been the goal of an earlier reaction of this type in which chlorine monofluoride was used as the source of positive chlorine (Ref. 2).

\[
M^+ClO_4^- + CIF \rightarrow ClO_ClO_3^- + M^+F^-
\]

Yields from these reactions were low and irreproducible inhibiting a conclusive identification of the product, but comparison of infrared data has shown that ClO_ClO_3⁻ had been formed by the CIF reaction also.

The identification and physical characterization of chlorine perchlorate has been completed. Full details of this work is set forth in Appendix A of this report. Four reasonably stable oxides of chlorine are known and the properties of these are summarized in Table 1 as reviewed by Schmeisser.
<table>
<thead>
<tr>
<th>Oxide Property</th>
<th>Cl₂O</th>
<th>ClO₂</th>
<th>Cl₂O₆</th>
<th>Cl₂O₇</th>
<th>Cl₄ClO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>87</td>
<td>67.5</td>
<td>167</td>
<td>183</td>
<td>135</td>
</tr>
<tr>
<td>Melting Point, C</td>
<td>-116</td>
<td>-59</td>
<td>3.5</td>
<td>-91.5</td>
<td>-117</td>
</tr>
<tr>
<td>Boiling Point, C</td>
<td>2.0</td>
<td>11.0</td>
<td>203 (calc)</td>
<td>80</td>
<td>45.5</td>
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<tr>
<td>Vapor Pressure at 0°C</td>
<td>490</td>
<td>699</td>
<td>0.31</td>
<td>23.7</td>
<td>119</td>
</tr>
<tr>
<td>log Pₘₙₘ</td>
<td>7.87-1373/T</td>
<td>7.1-2070/T</td>
<td>8.03-1818/T</td>
<td>7.8156-1568.0/T</td>
<td></td>
</tr>
<tr>
<td>Trouton's Constant</td>
<td>22.5</td>
<td>23.0</td>
<td>21</td>
<td>23.4</td>
<td>22.6</td>
</tr>
<tr>
<td>Heat of Vaporization, kcal/mole</td>
<td>6.20</td>
<td>6.52</td>
<td>9.5</td>
<td>8.29</td>
<td>7.17</td>
</tr>
<tr>
<td>Heat of Formation, kcal/mole</td>
<td>21.0</td>
<td>25</td>
<td></td>
<td>63.4</td>
<td>43</td>
</tr>
<tr>
<td>Density, gm/cc</td>
<td></td>
<td>1.64 at 0 C</td>
<td>2.02 at 3.5 C</td>
<td>1.86 at 0 C</td>
<td>1.82 at 0 C</td>
</tr>
<tr>
<td>Liquid Color</td>
<td>Red-brown</td>
<td>Red-brown</td>
<td>Deep red</td>
<td>Colorless</td>
<td>Pale yellow</td>
</tr>
</tbody>
</table>
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and Brandle (Ref. 3). Supplemental data have been added and the properties of ClOClO. are noted for comparison. Recently, a fifth oxide of chlorine has been reported (Ref. 4) with the empirical formula ClO1.5 and the postulated composition OCIClO2. This compound is only marginally stable at -45°C and is very explosive (Ref. 4 and 5).

REACTIONS OF CHLORINE PERCHLORATE

In addition to the reactions of chlorine perchlorate given in Appendix A, some other reactions have been examined. The fluorination of ClOClO. was of particular interest. It was anticipated that this reaction would probably proceed by either of the following paths:

\[
\begin{align*}
\text{ClOClO}_3 + \text{F}_2 & \rightarrow \text{FCl} + \text{FOClO}_3 \\
\text{ClOClO}_3 + \text{F}_2 & \rightarrow \text{FCIO}_3 + \text{FCIO}_2
\end{align*}
\]

Chlorine oxide fluoride, FCIO, would not necessarily be found as such because its further fluorination to Florox, CIF3O, might occur readily. Using excesses of fluorine, it was observed that little or no reaction occurred at -78 or -45°C despite long reaction periods (18 and 9 days). At 0°C, however, complete consumption of the ClOClO3 was noted in 3 days. The products were FCIO3, FCIO2, and CIF. Neither fluorine perchlorate nor Florox were obtained. The conditions required for reaction and the products formed indicate that dissociation or decomposition of ClOClO3 may be necessary before fluorination can occur. Behavior of this type has been reported (Ref. 6) for the reaction of F2 with Cl2O6.

Chlorine perchlorate and chlorine trifluoride reacted smoothly and at a moderate rate. The consumed starting materials and the products formed agreed well with the overall stoichiometry shown:

\[
2\text{ClOClO}_3 + 2\text{ClF}_3 \xrightarrow{0 \degree \text{C}, 3 \text{hr}} 2\text{FCIO}_3 + \text{FCIO}_2 + 3\text{ClF}
\]
The total absence of fluorine perchlorate and the near quantitative oxygen material balance (as $\text{FCIO}_3$ and $\text{FCI}_2$) indicates that fluorination of either atom of the terminal Cl-O bond did not occur. Instead, fluorination of the central chlorine atom to give $\text{FCIO}_3$ appears certain. The remaining products would arise by disproportionation of the ClO species either before or after fluorination.

ATTEMPTED SYNTHESIS OF CHLORINE CHLORATE

Extension of the reaction of $\text{ClSO}_3\text{F}$ to other chlorine oxide anions offers a potential route to other new chlorine oxides. An initial effort in this direction was made through the following reaction:

$$\text{KCIO}_3 + \text{ClSO}_3\text{F} \rightarrow \text{KSO}_3\text{F} + \text{ClOClO}_2 \text{ or } \text{ClCIO}_3$$

Either of two structural compositions might result from this reaction and neither is the same as that postulated (Ref. 4) for the aforementioned explosive chlorine oxide of this same empirical formula, $\text{Cl}_2\text{O}_3$. When the above reaction was conducted at -45 C, only $\text{Cl}_2$, $\text{ClO}_2$, and $\text{O}_2$ were observed, indicating that the isomer, $\text{ClOClO}_2$, may have formed but decomposed. The alternate isomer would be expected to give $\text{Cl}_2$ and $\text{Cl}_2\text{O}_6$ upon decomposition. Further attempts to synthesize chlorine chlorate, using lower temperatures and other salts, are in progress.

ATTEMPTED SYNTHESIS OF NEW COVALENT HYPOCHLORITES

A convenient synthesis of chlorine nitrate was discovered (Ref. 7) through the reaction of $\text{Ca(OCl)}_2$ and $\text{NO}_2\text{F}$:

$$\text{Ca(OCl)}_2 + 2\text{NO}_2\text{F} \rightarrow \text{CaF}_2 + 2\text{ClNO}_3$$

The reaction was most successful at low temperatures ($T<0$) and the ease of reaction suggested that calcium hypochlorite may be converted to other covalent hypochlorites.
One of the more intriguing possibilities was the use of Ca(OCl)$_2$ in synthesizing the unknown chlorine nitrite, C10N0:

\[
\text{Ca(OCl)}_2 + 2\text{FNO} \rightarrow 2\text{CaF}_2 + 2\text{C10N0}
\]

We examined the reaction under a variety of conditions and found that instead of C10N0 the isomeric nitryl chloride, ClNO$_2$, was produced. Yields of ClNO$_2$ noted were 2 percent at ambient temperature, 39 percent at -112 C, 78 percent at -126 C, and 52 percent at -142 C.

The workup of all of the above reactions involved a warmup to ambient temperature prior to fractionation and ir examination. We considered the possibility that C10N0, if formed, could rearrange during the warmup period. In order to test this thesis, low-temperature ir spectra were recorded on samples which were not warmed above -78 C. These spectra showed no peaks different than those exhibited by solid ClNO$_2$ under the same conditions. Thus, C10N0 appears not to have formed at all. However, the process does offer a convenient synthesis of nitryl chloride because FNO can be made conveniently from CsF and N$_2$O$_4$ (Ref. 8).

Several attempts were made to prepare new chlorine oxides from Ca(OCl)$_2$. The reaction of ClF with Ca(OCl)$_2$ was anticipated to yield Cl$_2$O and, indeed, did so at -112 C. The less reactive perchloryl fluoride, FC1O$_3$, was then reacted with the hope that a new route to C10C10$_3$ could evolve:

\[
\text{Ca(OCl)}_2 + 2\text{FC1O}_3 \rightarrow 2\text{CaF}_2 + 2\text{C10C10}_3
\]

Not surprisingly, FC1O$_3$ did not react with Ca(OCl)$_2$ at temperatures up to 100 C. Additional reactions will be studied using Ca(OCl)$_2$ and it is anticipated that new mixed halogen oxides are highly probable as products.

PHOTOCHMICAL SYNTHESIS OF FLOROX

The synthesis of ClF$_3$0 through uv activation has been accomplished in excellent yield with a variety of reactant systems (Ref. 1 and 2) under a variety of conditions. Because it appeared that O($^1$D) formation was a

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prerequisite to the successful reaction, several experiments were conducted using N$_2$O as the oxygen source:* 

\[ \text{N}_2\text{O} + \text{ClF}_3 \rightarrow \text{N}_2 + \text{ClF}_3\text{O} \]

We were not only interested in an improved method for making ClF$_3$O but also in the formation of FCIO. The latter could arise if the photolysis of ClF-N$_2$O were rapid, thereby precluding marginally unstable materials from an excessive uv exposure.

Our experiments showed that ClF$_3$O is indeed formed during the photolysis of N$_2$O-ClF$_3$, but no significant advantage over the O$_2$-ClF$_3$ reactant system was apparent. Further, despite a slight enhancement in rate of formation, it could not be conclusively established whether O fixation occurred as a result of O$_2$ dissociation or from the direct decomposition of N$_2$O to O($^1\text{D}$). It was noted that the reaction mixture was considerably more complex in that the fluorides FNO$_2$ and FNO were formed.

*We wish to thank Dr. A. Gordon, Naval Weapons Center, China Lake, Calif. for calling our attention to the fact that N$_2$O can give O($^1\text{D}$) with medium pressure lamps and for suggesting N$_2$O as an intermediate for ClF$_3$O synthesis.
EXPERIMENTAL

FLUORINATION OF CHLORINE PERCHLORATE

A prepassivated 30-ml stainless-steel bomb was loaded with ClOClO₃ (53.1 cm³, 2.37 mmol) and approximately 1 liter of F₂ at -196 C. After 3 days at 0 C, the bomb was recooled to -196 C and the excess F₂ removed. The products were separated by fractional condensation and identified by their infrared spectra. In decreasing amount these were FC₁O₃, ClF, and FC₁O₂. Lesser quantities of SO₂F₂ and SF₆ (impurities in the F₂ supply) were also noted. No unreacted ClOClO₃ was recovered.

REACTION OF CHLORINE PERCHLORATE WITH CTF

Chlorine perchlorate (26.6 cm³, 1.19 mmol) and ClF₃ (25.9 cm³, 1.16 mmol) were condensed in a Teflon U-trap at -196 C. The reaction was allowed to proceed by warming the trap to 0 C for approximately 3 hours. Recooling to -196 C revealed only a trace of noncondensable gases had formed. Fractionation of the products through U-traps cooled to -78, -112, and -196 C indicated very minor amounts of ClOClO₃ and ClF₃ (~1 cm³ each) remained unreacted. The products found were FC₁O₃ (22.9 cm³, 1.04 mmol), FC₁O₂ (14.7 cm³, 0.65 mmol), and ClF (32.9 cm³, 1.47 mmol).

ATTEMPTED PREPARATION OF CHLORINE CHLORATE

A 1.5-g (12.2 mmol) sample of KCIO₃ was loaded into a 30-ml stainless-steel cylinder in the dry box. Chlorine fluorosulfate (106.8 cm³, 4.76 mmol) was condensed into the cylinder at -196 C which was then left at -45 C for 19 days. On recooling to -196 C, some noncondensable gases were found (~10 cm³ but not measured exactly). Vacuum fractionation was used to separate the other materials which were identified as ClO₂ (112 cm³, 5.00 mmol), Cl₂ (46.5 cm³, 2.07 mmol) and perhaps a trace of Cl₂O₆. 
PREPARATION OF NITRYL CHLORIDE

In a typical experiment calcium hypochlorite (2.34 g, 16 mmol, 95 percent, Research Inorganics Chemical Co.) was loaded into a 30-ml Hale stainless-steel cylinder in a drybox. After the cylinder was evacuated, FNO (3.75 mmol, prepared by reaction of F₂ with NO) was condensed in at -196 C. The sample was then warmed to a reaction temperature of -126 C. A reaction time of 1 hour was found to be sufficient. After reaction, volatile products were condensed at -196 C and separated by fractional condensation through traps held at -95, -126, -142, and -196 C. Small amounts of HNO₃ (0.10 mmol) were found at -95 C, ClNO₂ (2.93 mmol, 78-percent yield based on FNO) was condensed at -126 and -142 C, and Cl₂ (0.07 mmol) at -142 C.
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2. R-7547, Inorganic Halogen Oxidizers, Annual Report, Contract Nonr 4428(00), Rocketdyne, a division of North American Rockwell Corporation, Canoga Park, California, 31 July 1968, CONFIDENTIAL.


5. R-7149, Inorganic Halogen Oxidizers, Final Report, Contract Nonr 4428(00), Rocketdyne, a division of North American Rockwell Corporation, Canoga Park, California, 31 July 1967, CONFIDENTIAL.


APPENDIX A

CHLORINE PERCHLORATE

by Carl J. Schack and Don Pilipovich

Contribution from Rocketdyne,
a Division of North American Rockwell Corporation,
Canoga Park, California 91304

Abstract

The new chlorine oxide, ClOClO₃, has been prepared in high yield by the reaction of either cesium perchlorate or nitronium perchlorate with chlorine fluorosulfate at -45°. Characteristic physical data are reported for the compound together with some of its chemical reactions. Chlorine monofluoride also reacts with perchlorates to form ClOClO₃ but in low yield.

Halogen fluorosulfates and peroxydisulfuryl difluoride have been shown to be effective in oxidizing a variety of anions or in displacing halogen substituents from certain covalent species. For example, ClSO₃F can react with AgCl to generate Cl₂ or with CsF to generate CIF and the respective metal fluorosulfate. The present investigation sought to take advantage of this type of interaction using perchlorate salts as the anionic substrates. It has been found that this reaction results in the formation of the new chlorine oxide, chlorine perchlorate.

\[ \text{MClO}_4^- + \text{ClSO}_3^- \rightarrow \text{M} = \text{NO}_2, \text{Cs} \]

These reactions occur in high yield (75-95%) over a period of several days or less at approximately -45°.

Experimental

Apparatus and Materials. The equipment used in this work has been described and was supplemented with a Perkin-Elmer Infracord, Model 457. Cesium perchlorate (Matheson, Coleman and Bell) and nitronium perchlorate

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(Callery Chemical Co.) were purchased and used without further purification. Chlorine fluorosulfate was prepared from ClF and SO$_3$ as reported previously. Gaseous reactants were purified by fractional condensation. All handling of solids was performed in a dry-nitrogen filled glove box. As a routine operation, all metal or Teflon equipment was passivated with ClF$_3$ before use.

Preparation of ClOClO$_3$. In a typical experiment, a 30 ml stainless-steel cylinder was loaded with 2.45 g (10.5 mmol) of CsClO$_4$. After evacuation, ClSO$_3$F (218 cm$^3$, 9.73 mmol) was condensed into the cylinder at -196$^\circ$. The reaction was allowed to proceed by maintaining the cylinder at approximately -45$^\circ$ for several days. The products were separated by fractional condensation in U traps cooled to -78$^\circ$, -112$^\circ$, and -196$^\circ$. Little or no gases not condensable at -196$^\circ$ were found. The -196$^\circ$ fraction (8.0 cm$^3$, 0.56 mmol) was primarily Cl$_2$ with a small amount of SO$_2$F$_2$, while the -78$^\circ$ fraction was negligibly small. Pure ClOClO$_3$ (207 cm$^3$, 9.24 mmol) was retained at -112$^\circ$. The yield was 95%. A similar reaction using NO$_2$ClO$_4$ (2.0 g, 13.7 mmol) and ClSO$_3$F (200 cm$^3$, 8.93 mmol) produced ClOClO$_3$ (170 cm$^3$, 7.59 mmol) in 82% yield. The solid products from these reactions were identified as CsSO$_3$F-CsClO$_4$ and NO$_2$SO$_3$F-NO$_2$ClO$_4$ mixtures by their infrared spectra. Synthetic reactions of this scale with either salt when terminated after 3-4 days were found to be complete with no detectable ClSO$_3$F remaining. Normally, longer reaction times were used to ensure complete consumption of ClSO$_3$F since its vapor pressure and that of ClOClO$_3$ are much too close to allow separation by a fractionation procedure. For the same reason, all preparations were conducted with excess perchlorate salt.

Properties of ClOClO$_3$. Chlorine perchlorate is a pale yellow liquid and nearly white when frozen. It is stable for limited periods at room temperature in clean, dry, prepassivated stainless steel or perhalogenated plastic equipment. Storage at -45$^\circ$ in stainless-steel cylinders has resulted in <1% decomposition per week over a twelve week period. Products of this low-temperature decomposition are Cl$_2$, O$_2$ and Cl$_2$O$_6$ which are readily separated from ClOClO$_3$.
Analysis. Thermal decomposition of $\text{ClO}_3\text{Cl}$ (91.0 cm$^3$, 4.06 mmol) in a stainless-steel cylinder for 3 days at ambient temperature followed by 18 hours at 150$^\circ$ resulted in complete degradation to the elements: $\text{Cl}_2$ (90.8 cm$^3$, 4.05 mmol) identified by vapor pressure and gas chromatography and $\text{O}_2$ (181.0 cm$^3$, 8.08 mmol) identified by vapor pressure and mass spectroscopy. Therefore, the observed ratio of $\text{Cl}_2$:$\text{O}_2$ was 1.00:1.99 compared to the theoretical ratio of 1.00:2.00.

Molecular Weight. Values for the molecular weight of $\text{ClO}_3\text{Cl}$ as determined by gas density, assuming ideal gas behavior, were 133, 135, 134 (calc 135).

Vapor Pressure and Boiling Point. The vapor pressure of $\text{ClO}_3\text{Cl}$ over the temperature range -47$^\circ$ to 21$^\circ$ is $[T (^\circ C), P (mm)]$: -46.8, 8; -31.3, 21; -24.2, 18; 0.0, 119; 5.0, 150; 11.2, 202; 18.9, 283; 20.9, 305. The vapor pressure-temperature relationship is described by the equation $\log P_{mm} = 7.8156 - 1568.0/T^\circ K$. The normal boiling point calculated from the equation is 44.5$^\circ$, with a heat of vaporization of 7.17 kcal/mole and a Trouton constant of 22.6.

Melting Point. Samples of $\text{ClO}_3\text{Cl}$ frozen as a ring in the upper part of a Teflon tube were observed to melt at -117 $\pm$ 2$^\circ$.

Density. The densities measured in a Pyrex pycnometer at -78.8, 0.0, and 21.2$^\circ$ were 1.98, 1.82, and 1.75 g/ml. Over this temperature range the density $\rho$ is given by the equation: $\rho = 1.806 - 2.30 \times 10^{-3}T^\circ C$.

Infrared Spectrum. The infrared spectrum was recorded in stainless steel or Kel-F cells fitted with AgCl windows over the range 4000-400 cm$^{-1}$ at a variety of pressures. Spectra are shown in Figure 1 at two pressures. The principal bands observed are: 1282 (vs), 1041 (s), 752 (w), 661 (sh), 652 (s), 585 (sh), 574 (sh), 561 (m) and 511 (w) cm$^{-1}$.
Reactions of ClOClO₃. Hydrogen Chloride. A Pyrex ampoule was loaded with ClOClO₃ (36.2 cm³, 1.62 mmol) and HCl (42.6 cm³, 1.90 mmol) at -196⁰. After maintaining the ampoule at -78⁰ for 1 hour, separation of the products was initiated by first pumping the -78⁰ volatiles through U traps cooled to -142⁰ and -196⁰ and later changing the ampoule to -45⁰ while continuing to pump through the cold traps. The -196⁰ trap contained unreacted HCl (6.0 cm³, 0.27 mmol) while the -142⁰ trap contained only Cl₂ (36.4 cm³, 1.62 mmol). After warming the ampoule to room temperature, the weight of material retained at -45⁰ was determined and this material transferred to the vacuum line. It was identified as HClO₄ (0.155 g, 1.54 mmol) by its vapor pressure and infrared spectrum.

Reaction With AgCl. A sample of ClOClO₃ (7.9 cm³, 0.35 mmol) was loaded in a Kel-F infrared cell fitted with AgCl windows. On standing at ambient temperature for several hours, the ClOClO₃ was consumed leaving a thin deposit on the windows which was identified as ClO₄⁻ by its infrared spectrum. No other infrared absorbing material was detected. After a day, the contents of the cell were analyzed by gas chromatography and found to be pure Cl₂ (7.5 cm³, 0.33 mmol).

Decomposition in Pyrex. Chlorine perchlorate (42.6 cm³, 1.90 mmol) was condensed into a 150 cm³ Pyrex bulb (equipped with a Fischer-Porter Teflon needle valve and a metal-to-glass seal to eliminate greased closures or connections) at -196⁰. The bulb was allowed to warm to room temperature in a closed, dark, steel can and to stand for several days. At this time, the bulb was observed to contain a small puddle of a red, somewhat viscous liquid. The contents were rapidly vacuum fractionated through traps cooled to -78⁰, -112⁰, and -196⁰. An unmeasured but appreciable amount of gas not condensable at -196⁰ was observed. The other volatile products were Cl₂ (19.0 cm³, 0.85 mmol), ClO₂ (9.9 cm³, 0.44 mmol), and ClOClO₃ (~1 cm³) as identified by their vapor pressure and/or infrared spectra. The red liquid was not readily pumped out of the bulb and exhibited a low (1-2 mm) vapor pressure at ambient temperature. On standing at ambient temperature, the liquid slowly generated Cl₂, ClO₂ and...
noncondensable gases. From these observations the liquid was identified as \( \text{Cl}_2\text{O}_6 \). Based on 1 \( \text{Cl}_2\text{O}_6 \) from 2\( \text{ClO}_4 \), the \( \text{Cl}_2\text{O}_6 \) yield was approximately 80%.

A similar experiment in which the Pyrex bulb was of much smaller volume (~20 cm\(^3\)) was examined after 2 days. The charged \( \text{ClO}_4 \text{Cl}_2 \) (53.5 cm\(^3\), 2.39 mmol) was completely decomposed giving much \( \text{O}_2 \), \( \text{Cl}_2 \) (41.0 cm\(^3\), 1.83 mmol), and \( \text{ClO}_2 \) (18.6 cm\(^3\), 0.83 mmol). Only a small droplet of the red, liquid \( \text{Cl}_2\text{O}_6 \) was observed which, considering the chlorine evolved as \( \text{Cl}_2 \) and \( \text{ClO}_2 \), could not have amounted to >12% yield.

**Photolysis.** Chlorine perchlorate (35.3 cm\(^3\), 1.58 mmol) was condensed into a 200 cm\(^3\) quartz bulb at -196\(^\circ\)C. The bulb was warmed to room temperature and irradiated with uv light overnight (Hanovia 100 W Utility Lamp, Cat. No. 30620). After recooling to -196\(^\circ\)C, the noncondensable gases were measured (32.8 cm\(^3\), 1.46 mmol) and identified as \( \text{O}_2 \) by mass spectroscopy. Fractional condensation of the remaining material at -78\(^\circ\)C and -196\(^\circ\)C gave \( \text{Cl}_2 \) (24.8 cm\(^3\), 1.11 mmol) and \( \text{Cl}_2\text{O}_7 \) (10.2 cm\(^3\), 0.46 mmol) as the only detectable products. Chlorine heptoxide was identified by its vapor pressure and infrared spectrum. Based on 1 \( \text{Cl}_2\text{O}_7 \) from 2 \( \text{ClO}_4 \text{Cl}_2 \), the yield was 58%.

**Results and Discussion**

Four reasonably stable oxides of chlorine are known and have been well characterized: \( \text{Cl}_2\text{O}, \text{ClO}_2, \text{Cl}_2\text{O}_6, \) and \( \text{Cl}_2\text{O}_7 \). More recently, a fifth compound of very limited stability has been reported with the empirical formula \( \text{ClO}_{1.5} \) and the postulated composition \( \text{OCIO}_2 \). The new chlorine oxide, \( \text{ClOClO}_3 \), reported here was first obtained some time ago by the reaction of \( \text{ClF} \) and perchlorate salts at -78\(^\circ\)C or -45\(^\circ\)C.

\[
\text{MCIO}_4 + \text{ClF} \rightarrow \text{MF} + \text{ClOClO}_3 \quad M = \text{Cs}, \text{NO}_2
\]

However, the yields from these reactions were low (~5%) and somewhat irreproducible allowing only a tentative identification based on infrared data. The discovery of the present high yield synthesis confirmed the nature this low yield product and facilitated its characterization.
Caution. While no incidents were encountered during this work, chlorine perchlorate should be treated with all safety precautions appropriate to the use of any chlorine oxide. It is shock sensitive.\(^{14}\)

Chlorine perchlorate has been identified by its vapor density, elemental analysis, and infrared spectrum. A stable mass cracking pattern was not obtained but prominent m/e peaks for \(\text{ClO}_3^+\), \(\text{ClO}_2^+\), and \(\text{ClO}^+\) were found. The absence of a parent ion peak is not surprising in view of its near absence in the reported\(^{15}\) mass spectrum of \(\text{Cl}_2\text{O}_7\) for example. The basic physical and chemical properties have been determined and all data are consistent with the formulation \(\text{ClOClO}_3\).

Alternate structural formulations for the compound were ruled out on the basis of the infrared spectrum, Figure 1, and the chemical reactions discussed later. The strong bands at 1282 and 1041 cm\(^{-1}\) are readily assignable to the \(\text{ClO}_3\) antisymmetric and symmetric stretching vibrations. The position, shape, and relative intensity of these two bands are remarkably similar to those of \(\text{HOCIO}_3\) \(^{9}\) (1263 and 1050 cm\(^{-1}\)), \(\text{O}_3\text{ClOClO}_3\) \(^{11}\) (1309 and 1025 cm\(^{-1}\)), and \(\text{FOClO}_3\) \(^{16}\) (1298 and 1049 cm\(^{-1}\)) and thus are indicative of a covalent perchlorate group. Furthermore, the exact position of the strongest observed \(\text{ClO}_3\) antisymmetric stretching vibration correlates well with the electronegativity of the attached group. For the series of \(\text{XCIO}_3\) compounds, where \(X\) is \(\text{F}^-\), \(\text{O}_3\text{ClO}^-\), \(\text{FO}^-\), \(\text{HO}^-\), this band is located respectively at 1315, 1509, 1298, and 1263 cm\(^{-1}\). The position of this band for chlorine perchlorate (1282 cm\(^{-1}\)) is compatible with this correlation, further supporting the assigned structural formula. Other noteworthy bands for \(\text{ClOClO}_3\) are at 752 and 652 cm\(^{-1}\). These bands are assignable to stretching modes of the \(\text{Cl}-\text{O}-\text{Cl}\) link. Comparable terminal \(\text{Cl}-\text{O}\) absorptions are found at 720 and 703 cm\(^{-1}\) for \(\text{SF}_5\text{OCI}\) \(^{17}\) and \(\text{ClO}_2\text{SF}_2\) \(^{18}\) while \(\text{FOClO}_3\) has a strong band at 666 cm\(^{-1}\) which has been ascribed\(^{15}\) to its singly bonded chlorine-oxygen stretching vibration. A detailed analysis of the vibrational spectrum of \(\text{ClOClO}_3\) is in progress.\(^{19}\)
Reaction of ClOClO\textsubscript{3} and HCl occurred rapidly and nearly quantitatively.

\[ \text{HCl} + \text{ClOClO}_3 \rightarrow \text{Cl}_2 + \text{HClO}_4 \]

However, with AgCl large variations in the reaction rate were noted although the same final result was reached.

\[ \text{AgCl} + \text{ClOClO}_3 \rightarrow \text{Cl}_2 + \text{AgClO}_4 \]

Several factors including the surface state of the AgCl and trace impurities in the ClOClO\textsubscript{3} may account for this. In general this reaction was slower than the corresponding AgCl-ClSO\textsubscript{3}F reaction\textsuperscript{3}. The products from both of these chloride reactions conclusively support the postulated perchlorate structure derived from infrared data.

The thermal stability of ClOClO\textsubscript{3} at ambient temperature is limited with either glass or stainless-steel containers. A preparation conducted at ambient temperature in stainless steel gave no ClOClO\textsubscript{3} but a nearly quantitative yield of its elemental decomposition products. Pure ClOClO\textsubscript{3} also decomposed readily in Pyrex in the absence of light. Yields of the products of this decomposition differed greatly with the container volume and may have been influenced by other unknown variables, but a high conversion to Cl\textsubscript{2}O\textsubscript{6} (80%) was possible. The only other chlorine oxide found was ClO\textsubscript{2}, the other products being Cl\textsubscript{2} and O\textsubscript{2}. The preparation of Cl\textsubscript{2}O\textsubscript{6} by the thermal decomposition of ClOClO\textsubscript{3} may be an attractive alternate to the presently used photolysis of ClO\textsubscript{2} and O\textsubscript{3}.\textsuperscript{12}

Irradiation of ClOClO\textsubscript{3} in quartz at ambient temperature produced Cl\textsubscript{2}O\textsubscript{7} in a reaction approximating the stoichiometry:

\[ 7\text{ClOClO}_3 \rightarrow 5\text{Cl}_2 + 7\text{O}_2 + 2\text{Cl}_2\text{O}_7 \]
Formation of Cl₂O₂ directly by recombination of ClO₄ and ClO₃ radicals generated from ClOClO₃ is possible. But Cl₂O₇ can also result from irradiation of Cl₂O₆, which as noted above can be formed from ClOClO₃.

The overall stability of ClOClO₃ approaches that of the four well known chlorine oxides and is quite unlike that of the analogous compound FOClO₃, which tends to explode on freezing or during other simple operations. This behavior trend is comparable to that of FNOO₂ vs ClONO₂. However, it is the opposite of the general stability found for highly fluorinated FO- and ClO- substituted compounds, CF₃OF vs CF₃OC1 or SF₅OF vs SF₅OC1, where the ClO- derivatives are less stable.

Using the known heats of formation (kcal/mole) of FOClO₃₂₇ (+37.6) and those of the related pairs of compounds, OF₂₂₈ (+5.5) - Cl₂O₂₉ (+21.0) and FONO₂₂₇ (+2.5) - ClONO₂₃₀ (+7.0), the heat of formation of ClOClO₃ was estimated as approximately +43. This value is reasonable, in view of the heats of formation of ClO₂₂₉ (+24) and ClO₃₂₈ (+37), since the formation of the ClO-CIO₃ bond should be somewhat exothermic.

Acknowledgement. The authors wish to acknowledge sincere appreciation for support of this work by the Office of Naval Research, Power Branch. We also thank Dr. K. O. Criste for helpful discussions.
14. In a crude sensitivity test, approximately 0.15 ml of liquid ClOClO\textsubscript{3} was sealed in a small Pyrex tube. A 2-pound hammer dropped on the tube from approximately a 4 inch height resulted in a sharp explosion.
Figure 1. Infrared Spectrum of ClOClO$_3$ at 180 and 8 mm, 5 cm Path
APPENDIX B

INFRARED SPECTRUM OF ClOSO₂F

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California 91304

Abstract. The infrared spectra of gaseous and solid ClOSO₂F have been measured. Ten of the 12 fundamentals were observed and a vibrational assignment for symmetry C₅ is suggested. Some thermodynamic properties and principal force constants have been computed.

Introduction

Chlorine fluorosulfate, ClOSO₂F, was first reported by Gilbreath and Cady [1] in 1963. However, no infrared data have been reported for this interesting compound. Recently, one of us [2] has found that ClOSO₂F can be conveniently prepared by the addition of ClF to SO₂. Furthermore, it was found that ClOSO₂F rapidly attacks conventional infrared windows such as NaCl or AgCl according to:

\[ \text{AgCl} + \text{ClOSO}_2\text{F} \rightarrow \text{Cl}_2 + \text{Ag}^+\text{SO}_3\text{F}^- \]

This instantaneous attack on the windows explains the absence of infrared data in previous reports on chlorine fluorosulfate. It was also noted that this attack is catalyzed by trace impurities, possibly HF, but that carefully purified ClOSO₂F shows practically no attack on the windows. In this paper we wish to report the infrared spectrum of gaseous and solid ClOSO₂F and its assignment for symmetry C₅.
Experimental

The preparation, purification, and handling of CIOSO$_2$F has been described elsewhere [2]. The infrared spectra of gaseous and solid CIOSO$_2$F were recorded on a Beckman Model IR-7 (with CsI interchange) and Perkin Elmer Models 337 and 457 spectrophotometers in the ranges 700-250, 4000-400, and 4000-250 cm$^{-1}$, respectively. The instruments were calibrated by comparison with standard calibration points [3]. The spectrum of the gas was obtained using a 304 stainless-steel cell of 5-cm path length fitted with AgCl windows. The low-temperature spectrum of the solid was recorded by condensing the compound on the internal cold ($-196^\circ$C) window of a conventional low-temperature cell. The body of this cell was made from Pyrex glass, all windows being either AgCl or CsI.

Results and Discussion

Figure 1 shows the infrared spectrum of gaseous CIOSO$_2$F at two different pressures. Figure 2 shows the infrared spectrum of solid CIOSO$_2$F at three different concentrations. Table I lists the observed frequencies together with their assignment for pointgroup C$_s$. For comparison, the vibrational frequencies of similar molecules are also given. Pointgroup C$_s$, having a symmetry plane, was preferred over pointgroup C$_1$, having no symmetry element. This preference was based on the assumption that the F, Cl, and O ligands are all of relatively high electronegativity and hence will repel each other. Because the chlorine atom should be repelled most strongly by the most electronegative ligand, it was assumed to be located in a trans-position to the fluorine atom, thus creating a symmetry plane. However, the barrier to internal rotation is expected to be quite low. Consequently, CIOSO$_2$F might show hindered rotation only at relatively low temperature.

For a six atomic molecule of symmetry C$_s$ (or of no symmetry), a total of 12 fundamental vibrations is expected. By comparison with the known spectrum of CIONO$_2$ [4], one would expect the SOCl deformation and SOCl...
Table I. Infrared Spectrum of Cl0SO₂F (cm⁻¹) compared to those of related molecules

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torsion vibration in Cl0SO₂F to occur below 250 cm⁻¹. Hence, for Cl0SO₂F we should expect 10 fundamental vibrations in the range 4000-250 cm⁻¹. As can be seen from Table 1, the correct number of 10 fundamentals has been observed, their frequencies and intensities being in good agreement with those reported for similar molecules [5-11]. The low-temperature infrared spectrum of solid Cl0SO₂F has also been recorded to better resolve the two bands at about 850 cm⁻¹, which overlap in the gas phase, and to avoid attack on the CsI windows. The agreement between the spectrum of the gas and that of the solid is relatively good indicating little or no association in the solid state.

The assignment of the fundamental vibrations of Cl0SO₂F was made by analogy with those reported for related compounds [5-11]. Some additional support for the listed assignments can be obtained from the band shapes in the gas spectrum. Thus, the band at 572 cm⁻¹ exhibits a PQR structure and hence should be assigned to ν₅ (A'). Furthermore, the bands at 1248, 855, and 831 cm⁻¹ have a shape closer to that expected for parallel bands, whereas the 1481, 703, and 520 cm⁻¹ bands more closely resemble perpendicular bands.

The frequencies of the two SO₂ stretching vibrations show a slight dependence on the electronegativity of the O-X substituent. As in the case of P=O, C=O, or Cl=O bonds the SO₂ frequencies increase with increasing electronegativity of the remaining substituents [12]. The infrared spectrum of gaseous and solid NF₂OSO₂F has also been recorded [8] in the range 4000-250 cm⁻¹ and showed in addition to the bands listed in Table I absorptions (in cm⁻¹) at 658 w, 620 s (PQR), 425 m, 341 w, and 321 mw', which had previously [7] not been reported.

A normal coordinate analysis was made for this molecule using the reparametrization method [15], assuming the geometry to be similar to that of related molecules and using the assignments given above. There are 51 force constants in the general valence field, and little is known about the force constants of this type of molecule. Hence, additional data would be required for computing unique force constants. However, the stretching
force constants were found to be quite independent of the interaction constants and therefore should be meaningful. The computed values for the principal force constants are: \( f_{S=0} = 10.9 \), \( f_{S-F} = 4.4 \), \( f_{S-O} = 3.8 \), and \( f_{0-Cl} = 2.6 \) mdynes/Å. Because the bending force constants strongly depend on the interaction constants their values are not reported. To exactly fit the force constants to the observed frequencies, a number of interaction constants of appreciable value were required. This indicates that some of the deformation vibrations for this class of compounds may have to be reassigned. Therefore, the normal coordinate analysis adds little further credibility to the assignment and its validity rests mainly on the arguments given above.

The thermodynamic properties were computed for this molecule using the rigid-rotor-harmonic-oscillator approximation [14]. The results are given in Table II. The frequencies used are those of Table 2 and the moments of inertia used are 505, 492, and \( 153 \times 10^{-40} \) g-cm\(^2\). Free rotation was assumed (which introduces very little error if the mode is below 100 cm\(^{-1}\)) and the reduced moment of inertia was taken as \( 77 \times 10^{-40} \) g-cm\(^2\).

Acknowledgement. We are indebted to Mr. W. H. Moberly for computing the thermodynamic properties and to Dr. D. Pilipovich for continuous encouragement. This work was supported in part by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force under Contract AF49(638)-1734.
Table II. Thermodynamic Properties of ClO\textsubscript{2}F assuming an ideal gas at 1 atmosphere pressure; units for C\textsubscript{p}, S\textsubscript{o}, and -(F\textsuperscript{o} - H\textsubscript{O})/T are calories per mole-degree and H\textsubscript{O} is kilocalories per mole.

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References

* This work was supported by the Office of Naval Research, Power Branch.

2. C. J. Schack and R. D. Wilson, ibid., in press.
Figure 1. Infrared Spectrum of gaseous Cl0S0₂F.

A: P = 8 mm Hg, B: P = 30 mm Hg. Bands marked with an asterisk are probably due to background.
Figure 2. Infrared spectrum of solid ClO\textsubscript{3}F at three different concentrations.
The new compound chlorine perchlorate, \( \text{Cl}_2\text{O}_4 \), was synthesized from the action of chlorine fluorosulfate on several perchlorate salts. Characterization data, physical and chemical properties are described. The use of \( \text{N}_2\text{O} \) as an oxygen source for the synthesis of \( \text{ClF}_3 \) was successful but offered no advantages over oxygen. A new synthesis of nitryl chloride emerged from the studies of \( \text{Ca(OC1)}_2 \) as an intermediate and involved the action of nitrosyl fluoride, \( \text{FNO} \), on calcium hypochlorite. A structural evaluation on chlorine fluorosulfate was carried out from its IR spectrum. \( C_5 \) symmetry for \( \text{ClSO}_3\text{F} \) was suggested and thermodynamic properties and force constants were computed. (C)
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