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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER Technical Report A	2. GOVT ACCESSION NO. AD-A243697	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Some Interesting Observations in Chlorine Oxyfluoride Chemistry		5. TYPE OF REPORT & PERIOD COVERED Technical Report	
		6. PERFORMING ORG. REPORT NUMBER RI/RD84-186	
7. AUTHOR(s) Karl O. Christe and William W. Wilson		8. CONTRACT OR GRANT NUMBER(s) N00014-83-C-0531	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rocketdyne 6633 Canoga Avenue Canoga Park, CA 91306		10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-840	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE July 23, 1984	
		13. NUMBER OF PAGES 6	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC ELECTED JUL 26 1984			
18. SUPPLEMENTARY NOTES To be published in <u>Journal of Fluorine Chemistry</u>			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Fluorine perchlorate Cesium tetrafluoroxychlorate (V) Hexafluorochlorine (VII) perchlorate Synthesis fluorine fluorosulfate Reactions			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A new synthesis of FOClO_3 was discovered involving the fluorination of ClO_4^- with ClF_6^+ . An unexpected oxygen abstraction from ClF_4O^- was observed when CsClF_4O was reacted with FOSO_2F .			

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Contract N00014-83-C-0531

Task No. NR 053-840

TECHNICAL REPORT NO. 4

Some Interesting Observations in Chlorine
Oxyfluoride Chemistry

by

Karl O. Christe and William W. Wilson

Rocketdyne
A Division of Rockwell International
Canoga Park, CA 91304

July 23, 1984

Prepared for publication in Journal of Fluorine Chemistry

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SOME INTERESTING OBSERVATIONS IN CHLORINE OXYFLUORIDE CHEMISTRY

KARL O. CHRISTE AND WILLIAM W. WILSON

Rocketdyne, A Division of Rockwell International Corporation,
Canoga Park, California 91304 (U.S.A.)

SUMMARY

A new synthesis of FOClO_3 was discovered involving the fluorination of ClO_4^- with ClF_6^+ . An unexpected oxygen abstraction from ClF_4O was observed when CsClF_4O was reacted with FOSO_2F .

ClO_4^- with ClF_6^+ .

ClF_4O

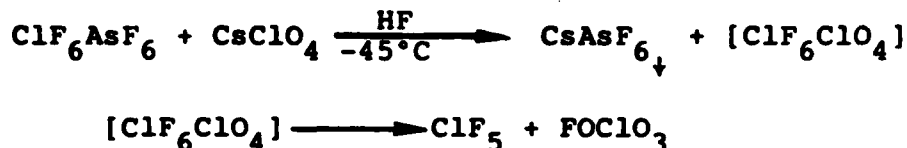
INTRODUCTION

We would like to report two interesting reactions observed during our studies in the area of chlorine oxyfluorides. The first reaction involved the low-temperature metathesis of ClF_6AsF_6 with CsClO_4 in anhydrous HF solution. In view of the known NF_4^+ reaction [1]



it was interesting to study whether ClF_6^+ is also capable of

oxidizing ClO_4^- to FOClO_3 . The thermal stability of ClF_6ClO_4 was found to be lower than that of NF_4ClO_4 [1] and did not permit the isolation of solid ClF_6ClO_4 even at temperatures as low as -45°C . However, the corresponding decomposition products, FOClO_3 and ClF_5 , were observed in good yield.



Although this presents an alternative synthetic path to FOClO_3 , the NF_4^+ reaction is preferred from a synthetic point of view since the NF_4SbF_6 starting material is more readily accessible [2].

The second reaction involved CsClF_4O and FOSO_2F . Fluorine fluorosulfate is known to be a useful reagent for the synthesis of hypofluorites [3], such as



For CsClF_4O , however, the major reaction was not the formation of either the unknown ClF_4OF or its expected decomposition products, but oxygen abstraction accompanied by SO_2F_2 elimination according to the following reaction.

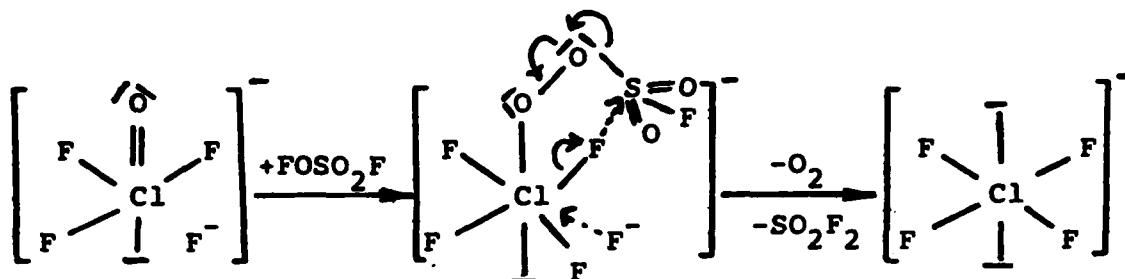


This unexpected reaction path might be rationalized in terms of an addition of FOSO_2F to the $\text{Cl}=\text{O}$ bond in one of the favored resonance structures of ClF_4O^- [4], followed by an intramolecular



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nucleophilic substitution (S_N^1) reaction accompanied by O_2 and SO_2F_2 elimination:



To our knowledge, this is the first example of a reaction in which $FOSO_2F$ acts as a deoxygenating agent.

EXPERIMENTAL

Apparatus. Volatile materials were handled in a stainless steel-Teflon FEP vacuum line [5]. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution using a previously described apparatus [6].

Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer. Spectra of solids were obtained using dry powders pressed between AgCl windows. Spectra of gases were obtained by using a Teflon cell of 5 cm path length equipped with AgCl windows. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the $4880\text{-}\overset{\circ}{A}$ exciting line of an Ar-ion laser.

Materials. Literature methods were used for the syntheses of ClF_6AsF_6 [7], $CsClF_4O$ [8] and $FOSO_2F$ [9] and for the drying of

the HF solvent [10]. The CsClO_4 (ROC/RIC) was used as received.

Reaction of ClF_6AsF_6 with CsClO_4 . In the drybox ClF_6AsF_6 (0.318 mmol) and CsClO_4 (0.304 mmol) were placed into the bottom U-tube of the metathesis apparatus [6]. On the vacuum line, dry HF (1.1 ml of liquid) was added at -78°C . The resulting mixture was agitated at -45°C for 1.5 hr and then filtered at -78°C through a porous Teflon filter while the filtrate was collected at -45°C . All material volatile at -45° was pumped off for 2.5 hr and separated by fractional condensation through a series of traps kept at -126 , -142 and -196°C . The -126° trap contained the HF solvent and a small amount of FClO_2 , the -142° trap contained a mixture of FOClO_3 and ClF_5 (0.445 mmol), and the -196° trap contained FClO_3 (0.128 mmol). Essentially no filtrate residue was left behind. The white solid filter cake (106 mg, weight calcd for 0.304 mmol of CsAsF_6 98 mg) was identified by infrared and Raman spectroscopy as CsAsF_6 . The FClO_3 formed in the above reaction is attributed to decomposition of a small amount of FOClO_3 . For a larger scale reaction, the percentage of FClO_3 in the product is expected to decrease significantly.

Caution! Fluorine perchlorate is highly shock sensitive [11] and proper safety precautions must be taken when working with this material.

Reaction of CsClF_4O with FOSO_2F . In the dry box CsClF_4O (2.24 mmol) was placed into a 10 ml stainless steel cylinder. On the vacuum line FOSO_2F (4.97 mmol) was added to the cylinder at -196°C . The cylinder was kept at 0°C for 3 days, then cooled

to -196°C . Oxygen (2.23 mmol) was pumped off at -196°C , and all material volatile at ambient temperature was separated by fractional condensation through traps kept at -112 , -142 , and -196°C . The -112° trap contained small amounts of ClF_3O , FClO_2 and ClF_3 . The -142° trap contained FOSO_2F (2.6 mmol) and SO_2F_2 (1.7 mmol), and the -196° trap showed SO_2F_2 (0.52 mmol). The white solid residue showed a weight loss of 39 mg (calcd weight loss for 1.12 mmol of O_2 36 mg) and was identified by infrared and Raman spectroscopy as CsClF_4 [12] containing a small amount of CsSO_3F .

ACKNOWLEDGEMENTS

The authors are grateful to Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson for their help and to the Army Research Office and the Office of Naval Research for financial support.

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