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SOME INTERESTING OBSERVATIONS IN CHLORINE OXYFLUORIDE CHEMISTRY

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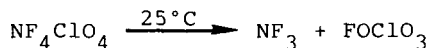
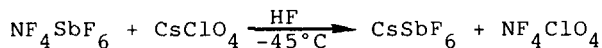
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SUMMARY

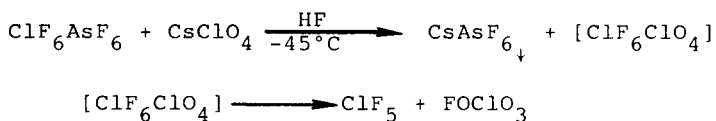
A new synthesis of FOClO_3 was discovered involving the fluorination of ClO_4^- with ClF_6^+ . An unexpected oxygen abstraction from ClF_4O^- was observed when CsClF_4O was reacted with FOSO_2F .

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.

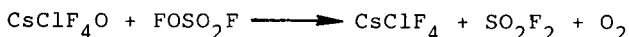


Although this presents an alternative synthetic path to FOClO_3 , the NF_4^+ reaction is preferred from a synthetic point of view since the NF_4SbF_6 starting material is more readily accessible [2].

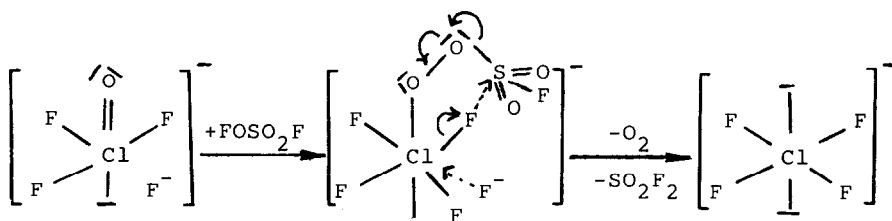
The second reaction involved CsClF_4O and FOSO_2F . Fluorine fluorosulfate is known to be a useful reagent for the synthesis of hypofluorites [3], such as



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 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 $4880\text{-}\overset{\circ}{\text{A}}$ 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 CsClF₄O with FOSO₂F In the dry box CsClF₄O (2.24 mmol) was placed into a 10 ml stainless steel cylinder. On the vacuum line FOSO₂F (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 ClF₃O, FC1O₂ and ClF₃. The -142° trap contained FOSO₂F (2.6 mmol) and SO₂F₂ (1.7 mmol), and the -196° trap showed SO₂F₂ (0.52 mmol). The white solid residue showed a weight loss of 39 mg (calcd weight loss for 1.12 mmol of O₂ 36 mg) and was identified by infrared and Raman spectroscopy as CsClF₄ [12] containing a small amount of CsSO₃F.

ACKNOWLEDGEMENTS

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