REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Papers	

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Leilani Richardson
Unclassified	Unclassified	Unclassified	A		19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

62 Separate items are enclosed

C8

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FROM: PROI (TI) (STINFO) 11 October 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-192**
Hoge, B. (USC); Christe, K.O. (ERC), "A New Synthesis of Fluorine Nitrate"

Journal of Fluorine Chemistry **(Statement A)**

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A new synthesis of fluorine nitrate†

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Abstract

The reaction of $NF_4^+SbF_6^-$ with alkali metal nitrates in either CH_3CN or SO_2 solution at low temperatures, produces $FONO_2$ in quantitative yield. Attempts were unsuccessful to prepare FONO from NF_4SbF_6 and KNO_2 in an analogous manner.

Keywords: Fluorine nitrate; fluorine nitrite; tetrafluoroammonium nitrate; synthesis.

1. Introduction

Covalent hypofluorites can generally be prepared by the direct fluorination of the corresponding oxo- or oxofluoro- salts or the acids with elemental fluorine [1]:

$$MOXO_mF_n + F_2 \longrightarrow MF + FOXO_mF_n$$

(M = H or alkali metal fluoride)

An alternate method that avoids the need for handling elemental fluorine involves the metathetical synthesis of the corresponding NF_4^+ salts and their subsequent thermal decomposition to NF_3 and the desired hypofluorites [2,3]:

$$NF_4^+SbF_6^- + M^+XO_mF_n^- \xrightarrow[-78\ °C]{HF} [NF_4^+XO_mF_n^-] + MSbF_6\downarrow$$

$$[NF_4^+XO_mF_n^-] \longrightarrow NF_3 + FOXO_{(m-1)}F_n$$

This method has been successfully demonstrated for the syntheses of $FOClO_3$ [2] and $FOSO_2F$ [3]. Application of this method to $FONO_2$ had failed [2] because NO_3^- reacts with HF according to:

$$NO_3^- + 2HF \longrightarrow NO_2^+ + H_2O + 2F^-$$

In this paper it is shown that by the choice of a suitable solvent this problem can be overcome, and that the reaction of NF_4^+ with NO_3^- represents an excellent method for preparing $FONO_2$.

2. Experimental

Caution! Fluorine nitrate is shock sensitive, and the combinations of strong oxidizers, such as NF_4NO_3, with organic materials, such as CH_3CN, can be explosive.

2.1 Materials and apparatus

All reactions were carried out in ¾ inch o. d. Teflon-FEP ampoules that contained Teflon-coated magnetic stirring bars and were closed by stainless steel valves. Volatile materials were handled on a stainless steel / Teflon-FEP vacuum line [4]. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box. The CH_3CN was dried over P_2O_5 and distilled prior to its use on a grease-free Pyrex glass vacuum line. The preparation of NF_4SbF_6 has previously been described [5]. The $CsNO_3$ was prepared from aqueous Cs_2CO_3 and HNO_3 by using a pH electrode for end point detection. It was purified by recrystallization from H_2O and dried in an oven at 100 °C for 24 h.

2.2 Synthesis of $FONO_2$

In the dry box, equimolar amounts (1.00 mmol each) of NF_4SbF_6 and $CsNO_3$ were placed into a prepassivated (with ClF_3) Teflon ampoule. This ampoule was then connected to the Pyrex glass line, and dry CH_3CN (3 mL liquid) was condensed in at –196 °C. It was then connected to

the steel vacuum line, and the reaction mixture was warmed to -40 °C. Upon melting of the solvent, strong gas evolution was observed. The turbid solution was stirred for 15 min, and the volatile products were separated by fractional condensation in a dynamic vacuum through three cold traps, kept at –126 (methylcyclohexane slush bath), -183 (liquid oxygen), and –210 °C (nitrogen slush), respectively. The –126 °C trap contained the CH_3CN solvent, the –183 °C trap had 1.0 mmol of pure $FONO_2$ that was identified by its vibrational [6,7] and ^{19}F nmr [8] spectra, while the –210 °C trap contained 1.0 mmol of NF_3. The nonvolatile white solid residue in the ampoule consisted of 1.0 mmol of $CsSbF_6$ that was identified by its Raman spectrum [9].

When in the above reaction the CH_3CN solvent was replaced by SO_2 and the reaction was carried out at the melting point of SO_2 (~ -70 °C), again quantitative $FONO_2$ and NF_3 evolution was observed. However the separation of the $FONO_2$ from the SO_2 solvent was more difficult due to their more similar volatilities.

3. Results and discussion

The reaction of NF_4SbF_6 and $CsNO_3$ in a solvent that is compatible with NO_3^- offers a new synthesis for $FONO_2$ with essentially quantitative yields.

$$NF_4^+SbF_6^- + Cs^+NO_3^- \xrightarrow{SO_2 \text{ or } CH_3CN} FONO_2 + NF_3 + MSbF_6$$

The potential $NF_4^+NO_3^-$ intermediate, expected for a metathetical reaction [2,3], could not be isolated. It appears that the fluorination of the NO_3^- anion proceeds already at low temperatures in solution, thus interfering with the isolation of solid $NF_4^+NO_3^-$.

If NF_4SbF_6 is available, the new synthesis offers a convenient method for the preparation of $FONO_2$ that does not require the handling of elemental fluorine. In this study, three solvents, i. e., CH_3CN, SO_2, and SO_2ClF, were investigated. Whereas CH_3CN offers the advantage of easier

product separation, the use of SO_2 might be preferable from a safety point of view for larger scale reactions, avoiding the combination of a powerful oxidizer with an organic material. In SO_2ClF, no reaction was observed at temperatures up to 10 °C, due to the low solubility of the starting materials in this solvent.

Attempts to prepare the yet unknown FONO molecule by the analogous reaction of NF_4SbF_6 with KNO_2 in SO_2 or CH_3CN solution were unsuccessful. In SO_2, no apparent reaction took place even at –10 °C, probably due to the low solubility of KNO_2. However in CH_3CN, strong gas evolution was observed upon its melting at ~ -40 °C. The volatile products consisted of NF_3 and variable amounts of different nitrogen oxides and some FNO and $FONO_2$.

Acknowledgements

The work at USC was financially supported by the National Science Foundation, and that at the Air Force Research Laboratory by the Air Force Office of Scientific Research and the Defense Research Project Agency. One of us (B.H.) thanks the Deutsche Forschungsgemeinschaft for a stipend.

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† Dedicated to the memory of Dr. Karel Lutar, a dear friend and outstanding chemist.

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