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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<sup>†</sup>

B. Hoge<sup>a1</sup>, K. O. Christe<sup>a,b,\*</sup>

<sup>a</sup>Loker Hydrocarbon Research Institute, University of Southern California, University Park, Los Angeles, California 90089-1661, USA, and <sup>b</sup>Air Force Research Laboratory, Edwards Air Force Base, California 93524, USA

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## Abstract

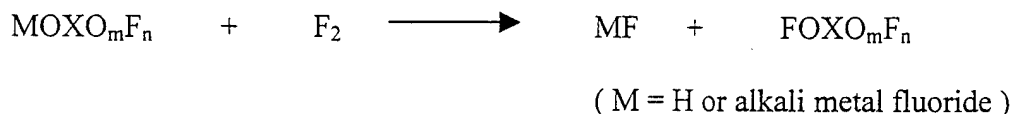
The reaction of  $\text{NF}_4^+\text{SbF}_6^-$  with alkali metal nitrates in either  $\text{CH}_3\text{CN}$  or  $\text{SO}_2$  solution at low temperatures, produces  $\text{FONO}_2$  in quantitative yield. Attempts were unsuccessful to prepare  $\text{FONO}$  from  $\text{NF}_4\text{SbF}_6$  and  $\text{KNO}_2$  in an analogous manner.

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

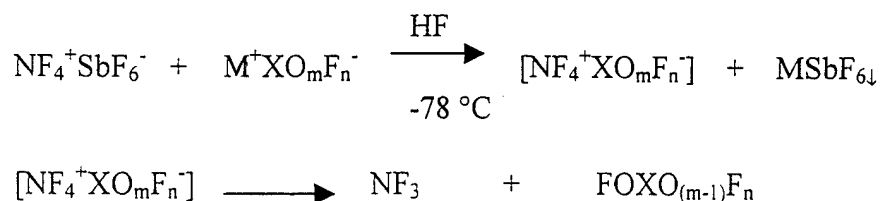
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## 1. Introduction

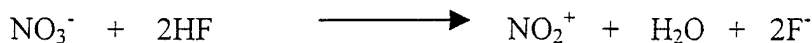
Covalent hypofluorites can generally be prepared by the direct fluorination of the corresponding oxo- or oxofluoro- salts or the acids with elemental fluorine [1]:



An alternate method that avoids the need for handling elemental fluorine involves the metathetical synthesis of the corresponding  $\text{NF}_4^+$  salts and their subsequent thermal decomposition to  $\text{NF}_3$  and the desired hypofluorites [2,3]:



This method has been successfully demonstrated for the syntheses of  $\text{FOClO}_3$  [2] and  $\text{FOSO}_2\text{F}$  [3]. Application of this method to  $\text{FONO}_2$  had failed [2] because  $\text{NO}_3^-$  reacts with HF according to:



In this paper it is shown that by the choice of a suitable solvent this problem can be overcome, and that the reaction of  $\text{NF}_4^+$  with  $\text{NO}_3^-$  represents an excellent method for preparing  $\text{FONO}_2$ .

## 2. Experimental

*Caution!* Fluorine nitrate is shock sensitive, and the combinations of strong oxidizers, such as  $\text{NF}_4\text{NO}_3$ , with organic materials, such as  $\text{CH}_3\text{CN}$ , can be explosive.

### 2.1 Materials and apparatus

All reactions were carried out in  $\frac{3}{4}$  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  $\text{CH}_3\text{CN}$  was dried over  $\text{P}_2\text{O}_5$  and distilled prior to its use on a grease-free Pyrex glass vacuum line. The preparation of  $\text{NF}_4\text{SbF}_6$  has previously been described [5]. The  $\text{CsNO}_3$  was prepared from aqueous  $\text{Cs}_2\text{CO}_3$  and  $\text{HNO}_3$  by using a pH electrode for end point detection. It was purified by recrystallization from  $\text{H}_2\text{O}$  and dried in an oven at  $100^\circ\text{C}$  for 24 h.

### 2.2 Synthesis of $\text{FONO}_2$

In the dry box, equimolar amounts (1.00 mmol each) of  $\text{NF}_4\text{SbF}_6$  and  $\text{CsNO}_3$  were placed into a prepassivated (with  $\text{ClF}_3$ ) Teflon ampoule. This ampoule was then connected to the Pyrex glass line, and dry  $\text{CH}_3\text{CN}$  (3 mL liquid) was condensed in at  $-196^\circ\text{C}$ . It was then connected to

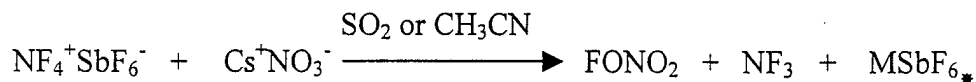
the steel vacuum line, and the reaction mixture was warmed to  $-40\text{ }^{\circ}\text{C}$ . Upon melting of the solvent, strong gas evolution was observed. The turbid solution was stirred for 15 min, and the volatile products were separated by fractional condensation in a dynamic vacuum through three cold traps, kept at  $-126$  (methylcyclohexane slush bath),  $-183$  (liquid oxygen), and  $-210\text{ }^{\circ}\text{C}$  (nitrogen slush), respectively. The  $-126\text{ }^{\circ}\text{C}$  trap contained the  $\text{CH}_3\text{CN}$  solvent, the  $-183\text{ }^{\circ}\text{C}$  trap had 1.0 mmol of pure  $\text{FONO}_2$  that was identified by its vibrational [6,7] and  $^{19}\text{F}$  <sup>NMR</sup> nmr [8] spectra, while the  $-210\text{ }^{\circ}\text{C}$  trap contained 1.0 mmol of  $\text{NF}_3$ . The nonvolatile white solid residue in the ampoule consisted of 1.0 mmol of  $\text{CsSbF}_6$  that was identified by its Raman spectrum [9].

Capitalize  
- NMR

When in the above reaction the  $\text{CH}_3\text{CN}$  solvent was replaced by  $\text{SO}_2$  and the reaction was carried out at the melting point of  $\text{SO}_2$  ( $\sim -70\text{ }^{\circ}\text{C}$ ), again quantitative  $\text{FONO}_2$  and  $\text{NF}_3$  evolution was observed. However the separation of the  $\text{FONO}_2$  from the  $\text{SO}_2$  solvent was more difficult due to their more similar volatilities.

### 3. Results and discussion

The reaction of  $\text{NF}_4\text{SbF}_6$  and  $\text{CsNO}_3$  in a solvent that is compatible with  $\text{NO}_3^-$  offers a new synthesis for  $\text{FONO}_2$  with essentially quantitative yields.



The potential  $\text{NF}_4^+\text{NO}_3^-$  intermediate, expected for a metathetical reaction [2,3], could not be isolated. It appears that the fluorination of the  $\text{NO}_3^-$  anion proceeds already at low temperatures in solution, thus interfering with the isolation of solid  $\text{NF}_4^+\text{NO}_3^-$ .

If  $\text{NF}_4\text{SbF}_6$  is available, the new synthesis offers a convenient method for the preparation of  $\text{FONO}_2$  that does not require the handling of elemental fluorine. In this study, three solvents, i. e.,  $\text{CH}_3\text{CN}$ ,  $\text{SO}_2$ , and  $\text{SO}_2\text{ClF}$ , were investigated. Whereas  $\text{CH}_3\text{CN}$  offers the advantage of easier

product separation, the use of SO<sub>2</sub> 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<sub>2</sub>ClF, 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<sub>4</sub>SbF<sub>6</sub> with KNO<sub>2</sub> in SO<sub>2</sub> or CH<sub>3</sub>CN solution were unsuccessful. In SO<sub>2</sub>, no apparent reaction took place even at -10 °C, probably due to the low solubility of KNO<sub>2</sub>. However in CH<sub>3</sub>CN, strong gas evolution was observed upon its melting at ~ -40 °C. The volatile products consisted of NF<sub>3</sub> and variable amounts of different nitrogen oxides and some FNO and FONO<sub>2</sub>.

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### References

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

\* Corresponding author. *E-mail address*: karl.christe@ple.af.mil (K.O.Christe)

<sup>1</sup> Current address: Institute of Inorganic Chemistry, University of Cologne, Germany.

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