

On the stability of $\text{NF}_4^+\text{NO}_3^-$ and a new synthesis of fluorine nitrate

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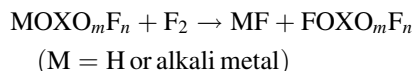
Abstract

The reaction of $\text{NF}_4^+\text{SbF}_6^-$ 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. © 2001 Elsevier Science B.V. All rights reserved.

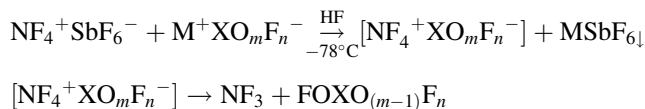
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1. Introduction

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 NF_4^+ salts and their subsequent thermal decomposition to NF_3 and the desired hypofluorites [2,3]:



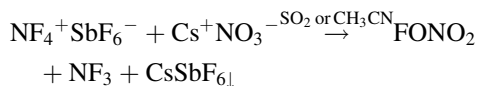
This method has been successfully demonstrated for the syntheses of FOClO_3 [2] and FOSO_2F [3]. Application of this method to FONO_2 had failed [2] because NO_3^- reacts with HF according to



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. 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.



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 NO_3^- anion proceeds already at low temperatures in solution, thus interfering with the isolation of solid $\text{NF}_4^+\text{NO}_3^-$.

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. For the separation of the FONO_2 from the NF_3 , the liquid oxygen trap can be replaced by a liquid argon (-186°C) trap if argon is available.

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

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evolution was observed upon its melting at approx. -40°C . The volatile products consisted of NF_3 and variable amounts of different nitrogen oxides and some FNO and FONO_2 .

3. 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.

3.1. Materials and apparatus

All reactions were carried out in 3/4 in. 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.

3.2. 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 (approx. -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.

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