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On the stability of $NF_4^+NO_3^-$ and 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. © 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]:

$$MOXO_mF_n + F_2 \rightarrow MF + FOXO_mF_n$$
$$(M = H\,\text{or alkali metal})$$

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]:

$$NF_4^+SbF_6^- + M^+XO_mF_n^- \xrightarrow[-78^\circ C]{HF} [NF_4^+XO_mF_n^-] + MSbF_{6\downarrow}$$

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

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

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

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. 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.

$$NF_4^+SbF_6^- + Cs^+NO_3^- \xrightarrow{SO_2\,\text{or}\,CH_3CN} FONO_2 + NF_3 + CsSbF_{6\downarrow}$$

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. 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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