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Journal of Fluorine Chemistry (Statement A)

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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 \( \text{CH}_3\text{CN} \) 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.

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]:

\[
\text{MOXO}_m\text{F}_n + \text{F}_2 \rightarrow \text{MF} + \text{FOXO}_m\text{F}_n
\]

\(( \text{M} = \text{H} \text{ or alkali metal fluoride })\)

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]:

\[
\begin{align*}
\text{NF}_4^+\text{SbF}_6^- + \text{M}^+\text{XO}_m\text{F}_n^- & \xrightarrow{\text{HF} \ -78^\circ C} [\text{NF}_4^+\text{XO}_m\text{F}_n^-] + \text{MSbF}_6^- \\
[\text{NF}_4^+\text{XO}_m\text{F}_n^-] & \rightarrow \text{NF}_3 + \text{FOXO}_{(m-1)}\text{F}_n
\end{align*}
\]
This method has been successfully demonstrated for the syntheses of FOCIO₃ [2] and FOSO₂F [3]. Application of this method to FONO₂ had failed [2] because NO₃⁻ reacts with HF according to:

\[
\text{NO}_3^- + 2\text{HF} \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + 2\text{F}^-
\]

In this paper it is shown that by the choice of a suitable solvent this problem can be overcome, and that the reaction of NF₄⁺ with NO₃⁻ represents an excellent method for preparing FONO₂.

2. Experimental

_Caution!_ Fluorine nitrate is shock sensitive, and the combinations of strong oxidizers, such as NF₄NO₃, with organic materials, such as CH₃CN, can be explosive.

2.1. Materials and apparatus

All reactions were carried out in \( \frac{1}{4} \) 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 CH₃CN was dried over P₂O₅ and distilled prior to its use on a grease-free Pyrex glass vacuum line. The preparation of NF₄SbF₆ has previously been described [5]. The CsNO₃ was prepared from aqueous Cs₂CO₃ and HNO₃ by using a pH electrode for endpoint detection. It was purified by recrystallization from H₂O and dried in an oven at 100 °C for 24 h.

2.2. Synthesis of FONO₂

In the dry box, equimolar amounts (1.00 mmol each) of NF₄SbF₆ and CsNO₃ were placed into a prepassivated (with ClF₃) Teflon ampoule. This ampoule was then connected to the Pyrex glass line, and dry CH₃CN (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 CH₃CN solvent, the -183 °C trap had 1.0 mmol of pure FONO₂ that was identified by its vibrational [6,7] and ¹⁹F nmr [8] spectra, while the -210 °C trap contained 1.0 mmol of NF₃. The nonvolatile white solid residue in the ampoule consisted of 1.0 mmol of CsSbF₆ that was identified by its Raman spectrum [9].

When in the above reaction the CH₃CN solvent was replaced by SO₂ and the reaction was carried out at the melting point of SO₂ (~ -70 °C), again quantitative FONO₂ and NF₃ evolution was observed. However, the separation of the FONO₂ from the SO₂ solvent was more difficult due to their more similar volatilities.

3. Results and discussion

The reaction of NF₄SbF₆ and CsNO₃ in a solvent that is compatible with NO₃⁻ offers a new synthesis for FONO₂ with essentially quantitative yields.

\[
\text{SO}_2 \text{ or CH}_3\text{CN} \quad \text{NF}_4^+\text{SbF}_6^- + \text{Cs}^+\text{NO}_3^- \rightarrow \text{FONO}_2 + \text{NF}_3 + \text{MSbF}_6^-.
\]

The potential NF₄⁺NO₃⁻ intermediate, expected for a metathetical reaction [2,3], could not be isolated. It appears that the fluorination of the NO₃⁻ anion proceeds already at low temperatures in solution, thus interfering with the isolation of solid NF₄⁺NO₃⁻.

If NF₄SbF₆ is available, the new synthesis offers a convenient method for the preparation of FONO₂ that does not require the handling of elemental fluorine. In this study, three solvents, i.e., CH₃CN, SO₂, and SO₂ClF, were investigated. Whereas CH₃CN 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$_2$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$_4$SbF$_6$ with KNO$_2$ in SO$_2$ or CH$_3$CN 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$_3$CN, 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$_2$.

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References

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