15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

a. REPORT
   Unclassified

b. ABSTRACT
   Unclassified

c. THIS PAGE
   Unclassified

17. LIMITATION OF ABSTRACT

18. NUMBER OF PAGES
   A

19a. NAME OF RESPONSIBLE PERSON
    Leilani Richardson

19b. TELEPHONE NUMBER
    (661) 275-5015

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 229.18
MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)  

30 Apr 98


Christe (Raytheon) Boatz, Sheehy  “Theory and Synthesis of New High Energy Density Materials”

HEDM Conference Presentation  (Statement A)

(Approved for distribution)
THEORY AND SYNTHESIS OF NEW HIGH ENERGY DENSITY MATERIALS

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Efforts are described to combine the NF$_4^+$ cation with highly energetic anions, such as NO$_2^-$, NO$_3^-$, and N(NO$_2$)$_2^-$.$^1$ In the case of NO$_3^-$, the NO$_3^-$ anion was fluorinated already at very low temperatures by NF$_4^+$ to give fluorine nitrate in high yield. In the case of NO$_2^-$, the reaction with NF$_4^+$ yielded an unknown unstable decomposition product in low yield, but the reaction was very difficult to control and consistently exploded. In the case of N(NO$_2$)$_2^-$, again no stable salt was formed, and a thermally unstable decomposition product, probably FN(NO$_2$)$_2^-$, was observed by $^{19}$F NMR spectroscopy.

In search for new difluoroaminating agents, attempts were made to prepare SO$_2$(NF$_2$)$_2$ from N$_2$F$_4$ and either SO$_2$ or SO$_2$Cl$_2$ using thermal or photolytic methods. Only the previously known compounds, FSO$_2$NF$_2$ and CISO$_2$NF$_2$, were obtained. The possibility of stabilizing ozone by protonation in superacid solution was investigated. It was found that ozone does not form a stable O$_3$H$^+$ cation at temperatures as low as -78°C.

The synthesis and reactions of oxidative oxygenators, which might lead to the novel oxidizer ClF$_3$O, were explored. It was found that HOF does not oxygenate ClF$_3$, ClF$_3$O, BrF$_5$ or IF$_5$. Attempts to repeat a previously reported synthesis of H$_2$OF$^+$ salts from XeF$_2$ and water, which had been claimed to be cabable of oxygenating ClF$_3$ to ClF$_3$O, revealed that the previous claims are incorrect. No evidence for the existence of H$_2$OF$^+$ salts was found. Instead a novel oxygen bridged water adduct of XeF$_2$ is formed in these systems. When reacted with ClF$_3$, this adduct forms ClO$_2^+$ salts and not ClF$_2$O$^+$ salts, as previously claimed.

The ClF$_4^+$SbF$_6^-$ and O$_2^+$SbF$_6^-$ salts were prepared and their crystal structure were determined.

In the area of high coordination number compounds, our studies of the pentagonal planar IF$_5^-$ anion and the pentagonal bipyramidal SbF$_7^-$ and BiF$_7^-$ anions were completed and written up in manuscript form. Extensive use of electronic structure calculations was made in these studies to determine the geometries, stabilities, vibrational and NMR spectra of these molecules.

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20021121 045
THEORY AND SYNTHESIS OF NEW HIGH ENERGY DENSITY MATERIALS


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NF$_4^+$ CHEMISTRY

- NF$_4^+$ CATION FIRST PREPARED IN 1965 BY US AT STAUFFER AS NF$_4^+\text{AsF}_6^-$ SALT
- HIGHLY ENERGETIC CATION WHICH IS STABLE UP TO 250°C
- NF$_4^+\text{BF}_4^-$ HAS BEEN USED FOR DEVELOPMENT OF SOLID PROPELLANT NF$_3/\text{F}_2$ GAS GENERATORS FOR CHEMICAL HF/DF LASERS
- FOR ROCKET PROPULSION OR EXPLOSIVES APPLICATIONS, AN ENERGETIC COUNTERION IS REQUIRED
- THE ONLY ENERGETIC NF$_4^+$ SALT PREPARED SO FAR: NF$_4^+\text{CO}_2\text{O}_4^-$ (CHRISTE, WILSON, INORG. CHEM. 1980) BUT IS THERMALLY UNSTABLE
NF₄⁺ Chemistry

- Energetic NF₄⁺ Salts of Interest
  - NF₄⁺ NO₃⁻
  - NF₄⁺ NO₂⁻
  - NF₄⁺ N(NO₂)₂

- Synthesis by Metathesis
  \[ \text{NF}_4^+ \text{SbF}_6^- + \text{CsNO}_3^- \xrightarrow{\text{SOLVENT}} \text{CsSbF}_6 \downarrow + \text{NF}_4^+ \text{NO}_3^- \]

- Problem: HF Solvent Reacts with NO₃⁻
  \[ \text{NO}_3^- + 4\text{HF} \xrightarrow{\text{HF}} \text{NO}_2^+ + 2\text{HF}_2^- + \text{H}_2\text{O} \]

- Answer: Use SO₂ or CH₃CN as Solvents
\[
NF_4^+ \text{SbF}_6^- + \text{Gd}^+ \text{NO}_3^- \xrightarrow{-78^\circ\text{C}} \text{GdSbF}_6^- + [NF_4^+ \text{NO}_3^-]
\]

\[
[NF_4^+ \text{NO}_3^-] \xrightarrow{-78^\circ\text{C}} NF_3 + \text{FONO}_2
\]

- \text{NF}_4 \text{NO}_3 \text{ is thermally very unstable}
- \text{New synthesis of FONO}_2 \text{ in quantitative yield}
NF$_4^+$ / NO$_2^-$ SYSTEM

- REACTION OF NF$_4^+$SO$_6^-$ + K$^+$NO$_2^-$ IN CH$_3$CN SOLUTION IS VIOLENT

- OBSERVED A NEW, UNSTABLE COMPOUND WITH STRONG IR BANDS AT

  1971 cm$^{-1}$ TERMINAL N=O STRETCH

  1185 cm$^{-1}$ N=O STRETCH OR V$_{asy}$m F-O-N

  832 cm$^{-1}$ O-F STRETCH OR V$_{sym}$ F-O-N

- MOST LIKELY COMPOUND: "FONO", HOWEVER:

  PREVIOUS MATRIX ISOLATION STUDY BY SMARDEWSKI (1974) PROPOSED 1716, 1199, 702 cm$^{-1}$ FOR FONO

  AB INITIO CALCULATIONS (SHEEHY, LEE, DIXON, SORENSON) DO NOT FIT WELL FOR EITHER DATA SET (PROBLEM CASE !)
\[ \text{NF}_4^+ / \text{N}(\text{NO}_2)_2 \] \text{SYSTEM}

- Low temperature \(^{19}\)NMR study of

\[
\text{NF}_4^+ \text{SbF}_6^- + \text{K}^+ \text{N}(\text{NO}_2)_2 \xrightarrow{\text{SO}_2, -75 \text{ to } 25^\circ \text{C}} \text{K}_2 \text{SbF}_6 + \text{NF}_4^+ \text{N}(\text{NO}_2)_2^-
\]

- Showed \(\text{NF}_4^+ \text{N}(\text{NO}_2)_2^-\) to be stable below -50\(^\circ\)C.

- Above -50\(^\circ\)C, \(\text{NF}_3\) evolution and formation of a thermally unstable compound with \(S = 53.3\).

- Ab initio calculations for \(\text{FN}(\text{NO}_2)_2\) give

\[ S = 53.9 \text{ (IGLO II, B3LYP/6-31G*)} \]

- FT-IR study of gaseous decomposition products from \(\text{NF}_4^+ \text{SbF}_6^- + \text{K}^+ \text{N}(\text{NO}_2)_2\) reaction in HF at -78\(^\circ\)C.

- Show new bands at 1711, 1324, 1301, 878, 803, 458 \text{ cm}^{-1}.

- In accord with expectations for \(\text{FN}(\text{NO}_2)_2\).

- More complete characterization and theoretical calculations are in progress.
WORK IN PROGRESS ON NOVEL NF<sub>2</sub> HEDM COMPOUNDS

\[ \text{NF}_2\text{O}_3\text{O}_3 \]
\[ \text{NF}_2\text{OSO}_2\text{F} + \text{CO}_2\text{CO}_4^- \rightarrow \text{CO}^+\text{SO}_3\text{F}^- + \text{NF}_2\text{O}_3\text{O}_3 \]

- \( \text{SO}_2(\text{NF}_2)_2 \) ("BAUM REAGENT")
  \[ \text{SO}_2 + \text{N}_2\text{F}_4 \xrightarrow{\text{UV or } \Delta T} \text{FSO}_2\text{NF}_2 \], but NOT \( \text{SO}_2(\text{NF}_2)_2 \)
  \[ \text{SO}_2\text{Cl}_2 + \text{N}_2\text{F}_4 \xrightarrow{\text{UV or } \Delta T} \text{ClSO}_2\text{NF}_2 \], but NOT \( \text{SO}_2(\text{NF}_2)_2 \)
  \[ \text{SF}_5\text{NF}_2 + \text{K}^+\text{N}(\text{NO}_2)_2^- \rightarrow \text{FSO}_2\text{NF}_2 \]
  \[ \left( \text{SF}_4(\text{NF}_2)_2 \rightarrow \text{SO}_2(\text{NF}_2)_2 \right) \]

- BAUM REAGENT IS NOT \( \text{SO}_2(\text{NF}_2)_2 \)
- VIBRATIONAL SPECTRA AND PHYSICAL PROPERTIES SUGGEST
  \[ \text{NF}_2\text{SO}_2\text{-O-SO}_2\text{NF}_2 \cdot m\text{SO}_3 \]
STABILIZATION OF OZONE

- $O_3$ is 34.1 kcal/mol endothermic
- TIP of $O_3/H_2$ is 39 sec higher than $O_2/H_2$
- $O_3H^+$ has been observed by ion cyclotron resonance spectroscopy (CACACE, 1994)
- Shock sensitive $O_3$ might be stabilized by protonation

$$O_3 + HF + SF_5 \xrightarrow{-78^\circ C} \text{HF}$$

Little solubility of $O_3$ in liquid phase, resulting in separate pure $O_3$ phase at -196
CHEMISTRY AT THE LIMITS OF COORDINATION

WORK ON PENTAGONAL PLANAR $\text{IF}_2^-$ WAS COMPLETED

AND PUBLISHED IN JACS (MAY 8)

$\text{XeF}_5^-$ AND $\text{IF}_5^-$ ARE THE ONLY KNOWN PENTAGONAL PLANAR SPECIES

WORK ON $\text{SbF}_6^2-$ AND $\text{BiF}_3^2-$ WAS ALSO COMPLETED AND IS IN PRESS (JACS)

ALTHOUGH $\text{SbF}_6^2-$ AND $\text{BiF}_3^2-$ HAD BEEN KNOWN FOR A VERY LONG TIME, $\text{SbF}_6^2-$ AND $\text{BiF}_3^2-$ HAD BEEN UNKNOW
CRYSTAL STRUCTURE DETERMINATION.
COFs

- COFs would be highest performing, earth-storable oxidizer with an Isp being 10 sec higher than that of O2.
- Theoretical calculations show that it is vibrationally stable.
- All previous attempts to oxidatively fluorinate C2F3O or C2F4O− failed due to oxidative attack on oxygen.
  
  Example: C2F3O + K2F → C2F4 + \(\frac{1}{2}\)O2

- Alternate potential route to COF5
  
  Oxidative oxygenation of COF5
  
  C2F5 + “Magic Oxygenator” → COF5
MINKWITZ, NOWICKI (ANGEW. CHEMIE, 1990)

$\text{XeF}^+ \text{MF}_6^- + \text{H}_2\text{O} \xrightarrow{\text{HF} \text{60}^\circ\text{C}} \text{HOF}^+ \text{MF}_6^-$

(M = Aq, Sb)

$\text{HOF}^+ \text{MF}_6^- + \text{CeF}_6^- \xrightarrow{\text{HF}} \text{CeO}^+ \text{MF}_6^- + 2 \text{HF}$

OUR RESULTS
- $\text{XeF}^+ / \text{H}_2\text{O}$ SYSTEM IS EXTREMELY COMPLEX, BUT DOES NOT GIVE $\text{HOF}^+$ SALTS.
- $\text{XeF}^+ / \text{H}_2\text{O}$ REACTION PRODUCT DOES NOT OXYGENATE $\text{CeF}_6^-$, BUT HYDROLYSES IT TO $\text{CeO}^+$
- WORK IN PROGRESS TO FULLY CHARACTERIZE THIS SYSTEM BY:
  - VIBRATIONAL AND MULTINUCLEAR NMR SPECTROSCOPY
  - SINGLE CRYSTAL X-RAY DIFFRACTION
  - COMPUTATIONAL CHEMISTRY
\[ \text{XeF}^+\text{AOF}_6^- / \text{H}_2\text{O} \text{ SYSTEM} \]

\[ 4 \text{XeF}^+\text{AOF}_6^- + \text{H}_3\text{O}^+\text{AOF}_6^- \]

\[ \rightarrow \]

\[ 2 \text{Xe}_2\text{F}_3^+\text{AOF}_6^- + 2 \text{H}_3\text{O}^+\text{AOF}_6^- + 2\text{H}_2\text{O} + 2\text{HF} \]

\[ + \text{AOF}_6^- \rightarrow \text{B} + \text{F}^- \]

\[ -64 \degree \text{C} \]

\[ 4 \text{XeF}^+\text{AOF}_6^- \rightarrow 4 \text{H}_3\text{O}^+\text{AOF}_6^- + 4 \text{XeF}_2 \]

\[ -64 \degree \text{C} \]

\[ + \text{HF} \rightarrow 4 \text{H}_2\text{O} \cdot \text{XeF}^+\text{AOF}_6^- + 4 \text{HF} \]

\[ + \text{HF} \rightarrow -64 \degree \text{C} \]

\[ 20 \degree \text{C} \]

\[ -\text{HF} \]

\[ \text{blue-green} \]

\[ 2 \text{Xe}_2^+\text{AOF}_6^- + \text{Xe}_2\text{F}_3^+\text{AOF}_6^- \]

\[ \leftarrow \]

\[ 2 \text{XeF}^+\text{AOF}_6^- (\text{s}) + 2 \text{H}_3\text{O}^+\text{AOF}_6^- (\text{s}) + 2 \text{Xe} + \text{O}_2 + 2\text{HF} \]

\[ -78 \degree \text{C} \]

\[ 20 \degree \text{C} \]

\[ \text{vac} \]

\[ -3 \text{ A} \]

\[ \text{Xe}_2\text{F}_3^+\text{AOF}_6^- (\text{s}) + 2 \text{H}_3\text{O}^+\text{AOF}_6^- (\text{s}) + \text{AOF}_5^- \]

\[ \text{FXe}^+\text{OH}_2^- + \text{XeF}_2 \]

\[ \rightarrow [\text{FXe-O-XeF}]^+ \]

\[ \rightarrow \text{FXe-O-XeF} \]

\[ -\text{HF} \rightarrow -\text{AOF}_5^- \]
HOF REACTIONS

- PREPARATION

\[ \text{F}_2 + \text{H}_2\text{O} \xrightarrow{-45^\circ\text{C}} \text{HOF} + \text{HF} \]

- PROTONATION

\[ \text{HOF} + \text{HF} + \text{SbF}_5 \xrightarrow{\text{HF}, -78^\circ\text{C}} \text{DOES NOT GIVE} \quad \text{H}_2\text{OF}^+\text{SbF}_6^- \]

- REACTION CHEMISTRY

- REACTIONS OF HOF WITH COF$_3$, COF$_4$, COF$_5$, BF$_5$ OR IF$_5$

  WERE STUDIED IN GAS-PHASE BY FT IR SPECTROSCOPY.

- NO EVIDENCE FOR OXIDATIVE OXYGENATIONS
1) NAKED FLUORIDE ION SOURCES (JACS)
2) TETRAFLUOROPHOSPHATE ANION, POF$_4^-$ (JACS)
3) DISORDER AND POLYMORPHISM IN N(CH$_3$)$_4$I$_2$ (INORG. CHEM)
4) PREPARATION, NMR, RAMAN AND DFT/IQGO/AIO-MP2 STUDY OF MONO-, DI-, AND TRI-PROTONATED THIOUREA (JACS)
5) $^{17}$O AND $^{13}$C NMR/AB INITIO STUDY OF OXONIUM AND CARBOXONIUM IONS (JACS)
6) DIRECT SYNTHESSES OF N(CH$_3$)$_4^+$ SALTS OF COMPLEX FLUOROANIONS (J. FLUOR. CHEM.)
7) NOVEL HEDM MATERIALS: SYNTHESIS AND CHARACTERIZATION OF C(N$_2$)$_4^+$ SALTS OF N(NO)$_2^-$, CO$_3^-$ AND Bi$_4^-$ (JACS)
8) TRIMETHYL PEROXONIUM ION, CH$_3$OOOC(CH$_3$)$_2^+$ (JACS)
9) THEORETICAL STUDY OF NO$_4^+$ (J. PHYS. CHEM)
10) PENTAGONAL PLANAR AX$_5$ SPECIES, IF$_5^-$ (JACS)
11) PREPARATION AND VIBRATIONAL SPECTRA OF N(CH$_3$)$_4^+$IF$_2^-$ AND ELECTRONIC STRUCTURE CALCULATIONS OF IF$_2^-$, BF$_5^-$, COF$_2^-$, XeF$_2$, AND KrF (J. FLU.
THE COMBINATION OF NF₄⁺ WITH NO₃⁻, NO₂⁻ AND N(NO₂)₂ YIELDS THERMALLY INSTABLE MATERIALS WHICH DECOMPOSE TO FON₂ AND INTERESTING NEW COMPOUNDS, TENTATIVELY IDENTIFIED AS FOND AND FN(NO₂)₂.

IN SEARCH FOR NOVEL NF₂ SUBSTITUTED OXIDIZERS AND DIFLUOROADAMANTATING REAGENTS, THE SYNTHESSES OF NF0000₃ AND SO₂(NF₂)₂ WERE PURSUED.

OZONE CANNOT BE STABILIZED THROUGH PROTONATION IN PURSUIT OF (OF₅)³⁻, A NEW LIQUID EARTH-STORABLE OXIDIZER, THE PREVIOUSLY REPORTED H₂OF⁺ CATION AND ITS ALLEGED OXYDATIVE OXYGENATING POWER COULD NOT BE CONFIRMED. THE REPORTED H₂OF⁺ SALTS ARE ACTUALLY ([FX₆-OH]⁺ ADDUCTS. THE CRYSTAL STRUCTURES OF NUMEROUS HEDM COMPOUNDS WERE DETERMINED.

WORK WAS COMPLETED ON THE PENTAGONAL D Planar IF₅²⁻ AND PENTAGONAL Bipyramidal SF₅²⁻ AND BiF₇²⁻ ANIONS.

THIS PROGRAM CONTINUES TO BE A SHOWCASE FOR THE SYNERGISM BETWEEN THEORY AND SYNTHESIS AND HAS PRODUCED 11 HIGH QUALITY PUBLICATIONS DURING THE LAST YEAR.