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Matchmaking in Polynitrogen Chemistry: Search for prospective anions for combination with N$_5^+$

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Award Symposium for Karl Christe, March 25-26, 2003
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Why Polynitrogen Compounds?

- Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are:
  - *High endothermicity*
  - "Green" propellant
    "combustion" product is only gaseous $N_2$
  - *High density*
  - *High $I_{sp}$ values when compared to other monopropropellants or bipropellants*
  - *High detonation velocity*
Predicted Specific Impulse (s) Values for Neutral Polynitrogen Compounds

Synthesis and Properties of $N_5^+$

- First compound made was $N_5^+\text{AsF}_6^-$
  - $-78\,^\circ\text{C}$, 5 days, 60% purity, 50 mg scale
  - Unstable at room temperature
  - Exploded in low-temperature Raman spectrometer

- Second compound made was $N_5^+\text{SbF}_6^-$

\[ \text{N}_2\text{F}^+\text{SbF}_6^- + \text{HN}_3 \rightarrow N_5^+\text{SbF}_6^- \]

  - First run: $-64\,^\circ\text{C}$, 5 days, 80% purity, 300 mg scale
  - Present method: Room temp., $\frac{1}{2}$ day, 100% purity, 4 g scale

- Properties of $N_5^+\text{SbF}_6^-$:
  - White solid
  - Thermally stable to $70\,^\circ\text{C}$
  - Survives impact sensitivity test (drop weight) at 150 kg/cm

Geometry of the $N_5^+$ Cation
Predicted versus Experimental

Resonance Structure

Calculated Structure

Experimental Structure

Structure of the $N_5^+$ Cation

The Structure of $N_5^+\text{Sb}_2\text{F}_{11}^-$

- The crystals grown from a mixture of $\text{SO}_2$ and $\text{SO}_2\text{ClF}$
- Crystal belong to the Monoclinic space group $C2/c$.
- Cell constants: $a = 10.913 \text{ Å}$, $b = 12.654 \text{ Å}$, $c = 16.675 \text{ Å}$; $\beta = 104.72^\circ$
- $Z = 8$
- $R = 0.0678$

Inter-ionic Clipping!!

The $N_5^+$ cation fits into the $\text{Sb}_2\text{F}_{11}^-$ bend thus locking it, thereby precluding any possibilities of twisting

Crystal Packing Effects

The N...F Contacts support the resonace structure, where the N2 and N4 nitrogen atoms have a positive charge.

N2 makes contacts at 2.723 and 2.768 Å; N4 contacts are at 2.887 and 2.814 Å

(In)Compatibility of $N_5^+$

Attempts to couple $N_5^+$ with energetic anions can result in explosive reactions !!!

$N_5^+N_3^-$

$N_5^+\text{ClO}_4^-$

$N_5^+\text{NO}_3^-$

$N_5^+\text{N(NO}_2)_2^-$

Recipe for Synthesizing Neutral Polynitrogen Compounds

- Combine a polynitrogen cation with a polynitrogen anion to form a neutral polynitrogen compound.

\[ N_x^+ + N_y^- \rightarrow N_{x+y} \]

ONLY TWO STABLE POLYNITROGEN IONS KNOWN TO EXIST IN BULK

Cation \( N_5^+ \) cation

(Discovered in 1999, AFRL, Christe)

Anion \( N_3^- \) anion

(Discovered in 1890, Curtius)

What Determines the Stability of a Polynitrogen Species?

Stability of a Polynitrogen Salt is Determined by Thermodynamic and Kinetic Factors

Thermodynamic Factors

1. Electron Affinity of the Cation
   - A fixed value, if we aim for a $N_5^+$ salt, i.e., 10.5-11.5 eV

2. First Ionization Potential of the Anion
   - The azide ion has a very low value of about 2.1 eV, which is the main reason for the instability of $N_5^+N_3^-$
   - New polynitrogen anions are needed with higher first IP values. $N_5^-$ and $N_7^-$ anions are most promising candidates

What Determines the Stability of a Neutral Polynitrogen Species?

3. Lattice Energy of the Crystal

- $U_L$ fixed by the molar volumes of cation and anion. Born-Haber cycle calculations for the lattice energy estimated for $N_5^+N_3^-$ are 50 kcal/mole lower than the requirement for the stabilization of an ionic salt

Kinetic Factor

- Activation Energy Barriers of the Ions Towards Decomposition

- These energy values determine the stability of the individual ions
Polynitrogen for *Dummies I*

What has Thermodynamics and Kinetics got to do with it??

**Kinetics**
Low Barrier towards catastrophic downfall

**Thermodynamics**
It is an uphill battle!!

Polynitrogen for Dummies II

- Metastability requires a delicate balancing act!!
Polynitrogen for *Dummies III*

Avoid a domino effect !!!

Assembling a polynitrogen chain is like assembling metastable dominos with perfect spacing, without prematurely triggering an unwanted collapse

New Polynitrogen Anions as Counterparts for $N_5^+$

Pentazole anion ($N_5^-$)

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to $N_3^-$ and $N_2$ is only 11 kcal/mol exothermic.

- Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and $N_2$ gas.

Synthetic Challenge – How do we make These New Anions??

Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N$_5^-$)

- Silyl Diazonium Salts
- Aryl Diazonium Salts

R = electron releasing group

Unknown

Known

Formation and Stability of Silyl Diazonium Salts

- Failed attempts to synthesize silyl diazonium salts

\[
N_2F^+\text{SbF}_6^- + \text{Me}_3\text{SiSiMe}_3 \rightarrow \text{Me}_3\text{SiN}_2^+\text{SbF}_6^-
\]

- \( R_3\text{SiN}_2^+ \) salts are unstable and spontaneously lose \( N_2 \)

\[
R_3\text{SiN}_2^+ X^- \rightarrow \text{N}_2 \rightarrow \left[ R_3\text{Si}^+ X^- \right]
\]

Theoretical calculations support this experimental observation

Use of Aryl Diazonium Salts – A Better Bet!

- R must be an electron releasing group, i.e., -NMe₂, -OH, -OCH₃.
- Some of these substituted aryldiazonium salts have been known for about four decades but no success had been achieved to cleave the N₅ ring from the ary group.

Aryl Pentazoles can rapidly lose N₂ at room temperature

I. Ugi, Angew Chem., 1961, 73, 172 and references therein
Synthesis of Aryldiazonium Salts

Aqueous Media

\[
\begin{align*}
R & \rightarrow \text{NH}_2 \quad \text{NaNO}_2/\text{HCl} \\ & \quad \text{(0 °C)} \\
R & \rightarrow \text{N}_2^+\text{Cl}^- \\
 & \rightarrow \text{N}_2^+\text{BF}_4^-
\end{align*}
\]

\[R = \text{H, OH, OCH}_3, \text{OC}_6\text{H}_5, \text{OC}_6\text{H}_4\text{N}_2^+, \text{N(CH}_3)_2\]

Non-aqueous Media

\[
\begin{align*}
R & \rightarrow \text{NH}_2 \\
 & \rightarrow \text{isoamyl nitrate} \\
 & \rightarrow \text{CF}_3\text{COOH} \\
 & \rightarrow \text{CH}_2\text{Cl}_2 \\
 & \rightarrow \text{N}_2^+\text{CF}_3\text{COO}^-
\end{align*}
\]

Colas and Goeldner, *Eur. J. Org. Chem.* 1999, 1357-1366 reported the p-phenoxy diazonium salt to be a double salt. However, X-ray crystallography reveals no such stoichiometry.
Role of the Lone Pair at Para Position

\[
\text{Me}_2\text{N} - \text{NH}_2 \xrightarrow{\text{i. xs NaNO}_2/\text{HCl}} \xrightarrow{< 0 \degree \text{C}, \text{ii. NaN}_3} \begin{array}{c}
\text{Me}_2\text{N} \\
\text{N} \\
\text{NO}_3 \\
\text{N} \\
\text{N}
\end{array} \xrightarrow{- \text{N}_2} \begin{array}{c}
\text{Me}_2\text{N} \\
\text{N} \\
\text{NO}_3 \\
\text{N}_3
\end{array}
\]

\[
\text{NaNO}_2 + \text{HCl} \xrightarrow{< 0 \degree \text{C}} \text{NaCl} + \text{HONO}
\]

\[
3 \text{HONO (aq)} \leftrightarrow \text{H}_3\text{O}^+ + \text{NO}_3^- + 2\text{NO}
\]

Reaction with Trimethylsilyl Azide

\[
\begin{align*}
\text{N}_2^+\text{BF}_4^- + (\text{CH}_3)_3\text{SiN}_3 & \rightarrow (\text{CH}_3)_3\text{SiF} - \text{BF}_3 - \text{N}_2 \\
\text{X} & \rightarrow \text{X} \\
\text{R} & \rightarrow \text{R} \\
\end{align*}
\]

\[
\begin{align*}
\text{X} &= \text{N, O} \\
\text{No pentazole were isolated}!!! \\
\text{Reactions carried out in acetonitrile at -30 °C}
\end{align*}
\]

Identification of Arylpentazoles

Pentazoles can be characterized by low temperature NMR spectral studies using $^{15}$N labeled samples.

- $^1$H NMR: $AB$-type spectrum with $H_a$ and $H_b$ at 8.0 and 7.0 ppm
- $^{14}$N NMR: $N_1$ at $\sim -80$ ppm
- $^{15}$N NMR: $N_2/N_5$ at $\sim -27$ ppm and $N_3/N_4$ at $\sim 4$ ppm

Note: Qualitative evidence for the presence of a pentazole ring: $N_2$ gas evolution in solution

Cleavage of the Aryl-Pentazole Bond with Retention of the Pentazole Ring

- **Chemical Methods**
  - Ozonolysis does not work! (Ugi, Radziszewski)
    
  - Nucleophilic substitution using strong nucleophiles such as the $\text{OH}^-$, $\text{OR}^-$, $\text{F}^-$ etc.

- **Collisional Fragmentation** (*Electrospray Ion Mass Spectroscopy – ESIMS*)
  - Electrospray is very gentle and produces high concentration of the parent anion which can be mass selected
  - Collisional fragmentation of the mass selected anions with variable collisional energies allow tailoring of fragmentation
  - Negative ion detection eliminates interference from neutral or positively charged species

ESIMS of para-Phenoxypentazole

Observed peaks in the MSMS of 162

Low Collision Voltage

ES

MSMS

m/z = 162

NNN

NNN

m/z = 134

-N₂

m/z = 106

-N₂

m/z = 78

CO

m/z = 42

$^{15}$N Labeling of the Pentazole Ring

$R-N_a \equiv N_b^+$ + $^*N\equiv N\equiv N^-^-$

Net Structure

$R-N_a N N_b$ + $N \equiv N N_a N_b$

Is the Peak at m/e 70 indeed due to the Pentazole Anion??

**15N Labeled Pentazole**

- Observed peaks in the MSMS of 163
  - m/z = 135/134
  - m/z = 106
  - m/z = 78
  - Labeling experiment shows that CO is lost in the last step

**Definitive proof for the pentazole anion**

- m/z = 71

**15N statistically distributed over N₂, N₃, N₄ & N₅**

Chemical Cleavage of the C-N Bond

Formation of azide from decomposition of $N_5^-$

Crystal Structure of Residue

1.172(1) Å

1.172(1) Å
Pentazoles with Heterocyclic Substituents

- These systems are unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N₂ gas.


- Pentazole derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability

\textsuperscript{15}N NMR of 2-amino-4,5-dicyanoimidazolyl pentazole

\textsuperscript{15}N NMR recorded in a mixture of methanol and acetonitrile at -30 °C, nitromethane used as an external reference (0 ppm)

Summary

• Synthesized aryl pentazoles: hydroxy group at the para-position on the aryl ring gives the best results.

• Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying $^{15}$N labeled pentazoles.

• First experimental detection of pentazole anion

• Synthesis of pentazoles with a heterocyclic substitutents

• Offers potential pathway for bulk synthesis of N$_5^-$ salts