Polynitrogen Chemistry: Recent Development in Pentazole and Polyazide Chemistry

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American Chemical Society Meeting (ACS) National Meeting
Anaheim, CA 28 Mar – 01 Apr 2004

20040503 192
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Inorganic Division; 227th National ACS Meeting, Anaheim-CA, April 1, 2004
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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 N₂
  - High density
  - High Iₚₚ values when compared to other monopropellants or bipropellants
  - High detonation velocity
Geometry of the $N_5^+$ cation

V-Shape Geometry

Calculated Structure

Experimental Structure

Resonance Structure

N2 makes contacts at 2.723 and 2.768 Å
N4 contacts are at 2.897 and 2.914 Å

Vij. Wilson, Vij. Tham, Shiehly & Chrisle.
C&S News, 2000, 78, 41

(In)Compatbility of $N_5^+$

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

$N_5^+N_3^-$

$N_5^+ClO_4^-$

$N_5^+NO_3^-$

$N_5^+N(NO_2)_2^-$

Our goal is the synthesis of an "aromatic" polynitrogen anion with

- A high first ionization potential
- A high activation energy barrier towards decomposition

Vij. Wilson, Vij. Tham, Shiehly & Chrisle.
C&S News, 2000, 78, 41
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.
- Free pentazole has not been isolated to date. Only aryl substituted pentazoles can be isolated and stabilized at low temperatures. These compounds rapidly decompose above 273K 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

\[ R-Si-N_2^+ \]

Aryl Diazonium Salts

\[ R-N_2^+ \]

\[ R-Si-\_
\]

Unknown

\[ R-N_2^+ \]

\[ R=\text{electron releasing group} \]

$+N_3^-$

**Formation and Stability of Silyl Diazonium Salts**

- Failed attempts to synthesize silyl diazonium salts

\[
\text{N}_2\text{F}^+\text{SbF}_6^- + \text{Me}_3\text{SiMe}_3 \rightarrow \text{Me}_3\text{SiN}_2^+\text{SbF}_6^- 
\]

- \(\text{R}_3\text{SiN}_2^+\) salts are unstable and spontaneously lose \(\text{N}_2\)

\[
\text{R}_3\text{SiN}_2^+\text{X}^- \rightarrow \text{R}_3\text{Si}^+\text{X}^- 
\]

*Theoretical calculations support this experimental observation*

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**Synthesis of Aryldiazonium Salts**

**Aqueous Media**

\[
\text{R}-\text{NH}_2 + \text{NaNO}_2/\text{HCl} < 0 \, ^\circ\text{C} \rightarrow \text{R}-\text{N}_2^+\text{Cl} \rightarrow \text{R}-\text{N}_2^+\text{BF}_4^- 
\]

**Non-aqueous Media**

\[
\text{R}-\text{NH}_2 + \text{isoamyl nitrite} \rightarrow \text{R}-\text{N}_2^+\text{CF}_3\text{COO}^- 
\]

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

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Pentazole Formation... Not a Trivial Chore !!!

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 ~ $-80$ ppm
- $^{15}$N NMR: $N_2/N_5$ at ~ $-27$ ppm and $N_3/N_4$ at ~ $-4$ 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 OH-, OR-, 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
  - Negative ion detection eliminates interference from neutral or positively charged species

MSMS of the Parent Ion Peak

- V. et al., Angew. Chem. 2002, 41, 3051
- m/z = 162
  - 10 V
    - N Labeled
    - 75 V
      - N Labeled
  - 50 V
    - N Labeled
    - -75 V
      - Unlabeled

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April 1, 2004
**Subsequent Decomposition of the Pentazole Anion**

**Pentazoles with Heterocyclic Substituents**

- Tetrazolyl system is unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N₂ gas.

\[
\text{N}_3/\text{N}_4 \quad \text{N}_2/\text{NS} \\
\text{Pentazole} \quad \text{Aryl azide}
\]

\[
\text{NH}_2 \quad \text{H} \\
\text{NH}_2
\]

i. NaNO₂/HCl

ii. -70 °C, LiN₃

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N}
\end{align*}
\]

- In comparison, the pentazole ring derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability (-30 °C)

15N NMR of 2-pentazolyl-4,5-dicyanoimidazole

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

Pentazolate Anion in Solution?

> 15N NMR shows a peak at ~-10 ppm (-30 °C) upon addition of base, which slowly decomposes to form N2 and azide ion.

> This peak is also observed upon adding a base to the solution of arylpentazoles at -30 °C.
Chronology of the Pentazole Anion

- ESIMS of para-hydroxyphenylpentazole
  Submitted: April 30, 2002; accepted July 3, 2002

- $^{15}$N NMR studies showing a peak at -10.2 ppm (-40 °C) due to the
  Pentazole anion resulting from cleavage of para-methoxyphenylpentazole
  which slowly decomposes to form N2 and azide ion. Upon standing for
  several days, all peaks disappear!
  Butler, Stephens & Burke, Chem. Commun. 2003, 1016
  Submitted: February 6, 2003; accepted February 27, 2003

- Laser Desorption Ionization (LDI) time-of-flight (TOF) mass spectrometry
  of solid para-N,N-dimethylaminophenylpentazole shows peaks at m/z: 70
  (N$_3^-$) and -42 (N$_5^-$). Peak at 70 confirmed by $^{15}$N labeling experiment.
  Ostmark, Wallin, Brinck, Carlqvist, Claridge, Hedlund & Yudina,
  Submitted: Jun. 27, 2003; accepted August 27, 2003

What are “normal” N-N distances in azides?

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Abnormalities in azide distances: Artifacts or Structural Contaminants?

- A large number of crystal structures reported in Cambridge/Inorganic CSD report unusually short \( N_\sigma-N_p \) (0.8-1.0 Å) and long \( N_p-N_\gamma \) (1.2-1.4) distances.
  According to VB theory, in covalently bonded azides, \( N_\sigma-N_p > N_p-N_\gamma \)

- In most cases, these derivatives were prepared from metal chloride salts and/or recrystallized from chlorinated solvents.

Reactivity of hexachloroantimonate (VI) with Trimethylsilylazide

\[
[\text{Ph}_4\text{M}][\text{SbCl}_6] + \text{Me}_3\text{SiN}_3 \xrightarrow{\text{CH}_3\text{CN}, 60^\circ\text{C}} [\text{Ph}_4\text{M}][\text{SbCl}_6-x(N_3)x] \quad M = P, As; x = 2-6
\]

- The substitution of all the six chlorine atoms in \( \text{SbCl}_6^- \) by the azide groups could not be accomplished in a single step, as reported in literature. The stepwise substitution gives a good insight into the substitution mechanism.

- Total substitution was achieved after four “refreshment” cycles of the reagents. During the intermediate cycles, the azide content gradually increased from two to five.
The tetraphenylarsonium antimonychloride azide case

Orthorhombic, P2₁2₁2₁:

\[ a, b, c (\text{Å}) = 7.774(14), 13.610(3), 27.094(5) \]

\[ V = 2866.8(10), Z = 4 \]

R = 3.22%, S = 1.088, highest peak = 0.58 e\(^{-}\)

Flack's parameter = 0.03(1)

Chloride contamination (%):

N\textsubscript{1}-N\textsubscript{3} × 10, N\textsubscript{4}-N\textsubscript{8} × 10: N\textsubscript{1}-N\textsubscript{4} ± 37

R = 3.22%, S = 1.088, highest peak = 0.58 e\(^{-}\)

Flack's parameter = 0.03(1)

Summary

- Synthesized aryl pentazoles: hydroxy group at the para-position on the aryl ring gives the best results as observed during this study.
- Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying \(^{15}\text{N}\) labeled pentazoles.
- Experimental detection of pentazolate anion in solution using different substrates.
- Offers potential pathway for bulk synthesis of \( \text{N}_5^{-} \) salts
- Chloride ion cause abnormalities in N-N bonds in azides
Acknowledgments

Dr. Karl Christe, Dr. William Wilson, Ms. Vandana Vij (ERC Inc.)

Dr. Gregory Drake (AFRL)

Dr. Ralf Haiges (USC)

Dr. Fook Tham (UC Riverside)

Dr. James Pavlovich (UCSB)

Dr. Robert Corley, Dr. Ronald Channell, Mr. Michael Huggins (AFRL)

 $$$

Dr. Don Woodbury, Dr. Arthur Morrisey (DARPA)

Dr. Michael Berman (AFOSR)
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

\(N_5^+\) (discovered in 1999, AFRL, Christie)

Anion

\(N_2^-\) (discovered in 1890, Curieus)

Episode I...Generation of the starting material

\[
\text{Ph}_4\text{MCl} + \text{SbCl}_5 \xrightarrow{1,2\text{-DCE}} [\text{Ph}_4\text{M}][\text{SbCl}_6]
\]

\(M = \text{P, As}\)
**Episode II...cis- or trans- disubstitution with azide groups?**

- **cis-isomer**
- **trans-isomer**

**Episode III...Substitution of 3rd chlorine... fac- or mer- isomer ???**

- **mer-SbCl$_4$(N$_3$)$_3$**
- **fac-SbCl$_4$(N$_3$)$_3$**
Episode VI... Complete substitution of chlorine atoms

No crystal structure obtained yet. However, IR and Raman spectroscopy shows that Sb-Cl bonds are absent i.e., complete substitution by the azide groups.

ESIMS of para-Phenoxypentazole

Observed peaks in the MSMS of 162

Low Collision Voltage

High Collision Voltage

m/z = 162

m/z = 134

m/z = 106

m/z = 78

m/z = 70

m/z = 42

m/z = 3051-3054
**Episode V: Synthesis of Chloropentaazidoantimonate(VI) Anion**

The Structure of $\text{Ph}_2\text{PSbCl}N_3$:  
- The crystals grown from CH$_3$CN.  
- Triclinic space group P-1.  
- Cell constants: $a = 11.134(3)$ Å, $b = 11.663(3)$ Å, $c = 13.754(4)$ Å; $\alpha = 104.314(5)^\circ$, $\beta = 97.914(5)^\circ$, $\gamma = 115.807(4)^\circ$.  
- $Z = 2$.  
- $R = 0.0762$.  
- All azide distances "normal" except N10-N11-N12.

**Reaction with Trimethylsilyl Azide**

No pentazoles were isolated !!!  
Reactions carried out in acetonitrile at -30 °C