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11/21 087
MEMORANDUM FOR PRR (Contractor Publication)

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0045A

K.O. Christe, D.A. Dixon et al. (RSTX) and J.A. Sheehy, "A Quantitative Scale for the Strength of Lewis Acids"
and "On the Reaction of N$_2$F$^*$ with HN$_3$ and the Synthesis and Characterization of N$_5$AsF$_6$"

Presentation (Statement A)
A QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS

KARL O. CHRISTE, DAVID A. DIXON, DOUGLAS McLEMORE

ON THE REACTION OF $\text{N}_2\text{F}^+$ WITH HN$_3$ AND
THE SYNTHESIS AND CHARACTERIZATION OF N$_5^+$AsF$_6^-$

KARL O. CHRISTE, WILLIAM W. WILSON, JEFFREY A. SHEEHY

Approved for public release; distribution unlimited
QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS

TWO TYPES OF ACIDS

• BRONSTED OR PROTIC ACIDS (PROTON DONORS)

\[ \text{HA} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ \text{(solv)} + \text{A}^- \text{(solv)} \]

QUANTITATIVE SCALES ARE KNOWN: pH AND pK SCALES

IONIC PRODUCT OF H₂O

\[ K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14} \quad \text{pH} = -\log [\text{H}_3\text{O}^+] \]

\[ \text{pK}_\alpha = -\log K_\alpha = [\text{H}^+] [\text{A}^-]/[\text{HA}] \]

• LEWIS ACIDS (ELECTRON ACCEPTORS)

DONOR \rightarrow ACCEPTOR INTERACTION

(LEWIS BASE) \quad (LEWIS ACID)

STRENGTH IS DIFFICULT TO MEASURE

NO QUANTITATIVE SCALE KNOWN
PROPOSED LEWIS ACID STRENGTH SCALE

- F⁻ ion is a very strong Lewis base
  has a small diameter
  interacts with most Lewis acids
  is well suited for theoretical calculations

- F⁻ affinity (FA) increases with Lewis acid strength and, therefore, can serve as a basis for a quantitative Lewis acidity scale

- Only few F⁻ affinity data were available especially for inorganics; many were only qualitative (cyclotron resonance bracketing and equilibrium measurements)
  large errors and different methods gave different results

- Needed
  a quantitative, internally consistent set of FA's for any desired Lewis acid
METHODS FOR CONSTRUCTION OF QUANTITATIVE $F^-$ AFFINITY SCALE

- THEORETICAL CALCULATIONS, USING POLARIZED DOUBLE-ZETA BASIS SETS, WERE PERFORMED AT THE FOLLOWING LEVELS
  
  LDF
  
  NLDF
  
  MP2

- TO SIMPLIFY THE CALCULATIONS, BECAUSE THE ELECTRON AFFINITY OF F IS HARD TO CALCULATE, COF$_2$ WAS USED AS A REFERENCE COMPOUND

  $\text{F}_3\text{CO}^- + B \rightarrow \text{COF}_2 + \text{BF}^-$

- TO CONVERT TO ABSOLUTE VALUES, THE EXPERIMENTALLY KNOWN FA OF COF$_2$ (49.9 kcal/mol) WAS ADDED TO THE RELATIVE FA VALUES
PROPOSAL OF A pF SCALE FOR LEWIS ACIDITY

- $F^-$ affinities were calculated for 106 Lewis acids and range from 0 - 120 kcal/mol on the absolute scale giving a value of $FA (AIF_3) = 115$ kcal/mol, the same as determined by thermodynamic experiment.

- To obtain a Lewis acidity scale range comparable to the familiar pH scale range of 0-14, the following convention is proposed:

\[
pF = \frac{F^- \text{ affinity (kcal/mol)}}{10}
\]

Giving a pF range of 0-12, with 12 being the value for the strongest known Lewis acid ($SbF_5$).
## ABBREVIATED pF SCALE

*(CHRISTE, DIXON, McLEMORE)*

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>pF</th>
<th>COMPOUND</th>
<th>pF</th>
<th>COMPOUND</th>
<th>pF</th>
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<tbody>
<tr>
<td>SbF$_5$</td>
<td>12.03</td>
<td>cis-IO$_2$F$_3$</td>
<td>9.66</td>
<td>SOF$_4$</td>
<td>6.60</td>
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<tr>
<td>AlF$_3$</td>
<td>11.50</td>
<td>PF$_5$</td>
<td>9.49</td>
<td>XeOF$_4$</td>
<td>6.37</td>
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<tr>
<td>AlFCl$_2$</td>
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<td>InF$_3$</td>
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<td>ClF$_5$</td>
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<td>COF$_2$</td>
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<td>BrF$_3$</td>
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<td>PF$_3$</td>
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<td>AsF$_5$</td>
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<td>SiF$_4$</td>
<td>7.35</td>
<td>HF</td>
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<td>SnF$_4$</td>
<td>9.82</td>
<td>SeF$_4$</td>
<td>7.12</td>
<td>NO$_2$F</td>
<td>1.92</td>
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<tr>
<td></td>
<td></td>
<td>NOF</td>
<td>1.74</td>
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SPECIAL COMMENTS ABOUT THE pF SCALE

- pF VALUES ARE FOR THE FREE ISOLATED MOLECULES

- VALUES FOR ASSOCIATED SOLIDS MUST BE CORRECTED

- FORMATION OF COMPLEX FLUORO ANIONS CAN BE CORRELATED WITH THE pF SCALE AND BECOMES DIFFICULT BELOW pF ~ 3.5

- PREPRINTS OF PAPER SHOULD BECOME AVAILABLE WITHIN 4-8 WEEKS
$N_2F^+$ CHEMISTRY AND SYNTHESIS OF $N_5^+AsF_6^-$

- HOMOLEPTIC POLYNITROGEN COMPOUNDS ARE OF GREAT INTEREST FOR HIGH ENERGY DENSITY MATERIALS (HEDM)

- MANY THEORETICAL STUDIES DURING THE PAST 15 YEARS HAVE BEEN DONE, BUT NO SUCCESSFUL SYNTHESIS OF A HOMOLEPTIC POLYNITROGEN HEDM HAS BEEN REPORTED

- ONLY TWO HOMOLEPTIC POLYNITROGEN COMPOUNDS ARE KNOWN WHICH CAN BE PREPARED IN SUBSTANCE

  $N_2$  1772  RUTHERFORD, SCHEELE, CAVENDISH

  $N_3^-$  1890  CURTIUS
PROBLEMS WITH SYNTHESIS OF POLYNITROGEN HEDM

- ALL THE ENERGY MUST COME FROM ENDOOTHERMICITY WHICH MAKES
  POLYNITROGEN HEDM EXTREMELY DANGEROUS
  (SENSITIVITY INCREASES WITH INCREASING ENERGY)
- BASIS FOR HIGH ENERGY CONTENT ARE THE LARGE DIFFERENCES IN BOND
  ENERGIES FOR N-N BONDS

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<tr>
<th>Bond</th>
<th>Energy (kcal/mol)</th>
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<tr>
<td>N-N</td>
<td>38</td>
</tr>
<tr>
<td>N=N</td>
<td>100</td>
</tr>
<tr>
<td>N≡N</td>
<td>228</td>
</tr>
<tr>
<td>C-C</td>
<td>85</td>
</tr>
<tr>
<td>C≡C</td>
<td>143</td>
</tr>
<tr>
<td>C≡C</td>
<td>194</td>
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</table>

\[-(N=\text{N})_n \rightarrow \mid N=\text{N} \mid \\
38 + 100 \rightarrow 228\]

\[-(\text{C}=\text{C})_n \rightarrow \text{CH}=\text{CH} \\
85 + 143 \rightarrow 194\]

EXCEPTIONS: $N_2$, $O_2$

NORMAL CASE:

STABLE MONOMERS
UNSTABLE POLYMERS

STABLE POLYMERS
UNSTABLE MONOMERS
GENERAL CONCEPT FOR POLYNITROGEN HEDM SYNTHESIS

• ALL POLYNITROGEN COMPOUNDS ARE UNSTABLE WITH RESPECT TO N₂

• ACTIVATION ENERGY BARRIER TOWARD N₂ ELIMINATION IS DETERMINED BY THE WEAKEST BOND IN POLYNITROGEN COMPOUND

• THE BARRIER AND METAStABILITY OF POLYNITROGEN COMPOUNDS MUST BE INCREASED BY SUITABLE RESONANCE STRUCTURES

  \[ \begin{array}{c}
  [ | N\cdot N\equiv N \rangle ]^- \quad \longleftrightarrow \quad [ \langle N\equiv N\equiv N \rangle ]^- \quad \longleftrightarrow \quad [ | N\equiv N\cdot N \rangle ]^- \\
  \end{array} \]

• DOUBLE BOND CHARACTER OF N-N BONDS IN AZIDE ION EXPLAINS ITS EXCEPTIONAL STABILITY

• HOW CAN THIS STABILIZATION EFFECT BE TAKEN ADVANTAGE OF?
EXPANSION OF THE AZIDE STRUCTURE

- ADDITION OF \([ \mathrm{N}\] \)^+ UNITS TO \(N_3^-\)

\[
[\langle\text{N=N=N}\rangle^-] + [\mathrm{N}]^+ \rightarrow \langle\text{N=N=N=N}\rangle \quad \text{\(N_4\)}
\]

\[
\langle\text{N=N=N=N}\rangle + [\mathrm{N}]^+ \rightarrow \langle\text{N=N=N=N=N}\rangle^+ \quad \text{\(N_5^+\)}
\]

- HOWEVER, THEORETICAL CALCULATIONS SHOW THAT \(D_{\infty h} \text{\(N_4\)}\) IS NOT STABLE

\[
\langle\text{N=N=N=N}\rangle \quad \text{NEIGHBORING CHARGES OF EQUAL SIGN MUST BE AVOIDED}
\]

\[
(-) (+) (+) (-)
\]

- NO PLAUSIBLE RESONANCE STRUCTURES CAN BE WRITTEN FOR \(N_4\) WHICH RETAIN DOUBLE BOND CHARACTER WHILE AVOIDING NEIGHBORING CHARGES OF EQUAL SIGN
EXPANSION OF THE AZIDE STRUCTURE TO $N_5^+$

- THE SAME PROBLEM EXISTS FOR $N_5^+$ WITH NEIGHBORING POSITIVE CHARGES

\[
\begin{align*}
\left[ &N=N=N=N=N \right]^+ \\
\text{(-)(+)(+)(+)(-)}
\end{align*}
\]

- RESONANCE STRUCTURES, HOWEVER, CAN BE WRITTEN WHICH AVOID THIS PROBLEM

![Resonance Structure Diagram]

- AB INITIO CALCULATIONS (CCSD(T) AND B3LYP) CONFIRM THE STABILITY OF THIS $C_{2v}$ STRUCTURE
SELECTION OF SUITABLE STARTING MATERIALS FOR $N_5^+$ SYNTHESIS

- REQUIREMENTS

STARTING FRAGMENTS MUST HAVE ALREADY BUILT IN WEAKENED BONDS

MUST HAVE A FORMAL POSITIVE CHARGE (IP OF $N_2 = 359$ kcal/mol)

COUPLING REACTION MUST BE EXOTHERMIC

CHOICE OF SUITABLE SOLVENT (HEAT SINK, STABILIZATION, SAFETY)

- IDEAL CANDIDATE SYSTEM

\[
\begin{align*}
&\text{AsF}_6^-+\text{N}_2+\text{H}-\text{N}^+\text{F}^-\rightarrow \\
&\text{N}≡\text{N}^-\text{AsF}_6^-\text{N}≡\text{N}^-\rightarrow \\
&\text{N}≡\text{N}^+\text{N}=\text{N}^- + \text{AsF}_6^-
\end{align*}
\]
ACTUAL SYNTHESIS OF $N_5^+ \text{AsF}_6^-$

- SYSTEM WORKED AS PLANNED

$$N_2F^+\text{AsF}_6^- + HN_3 \xrightarrow{HF \text{ at } -78^\circ C} N_5^+\text{AsF}_6^- + HF$$

HIGH YIELD

ONLY OTHER BYPRODUCT 20-40% $H_2N^+_3\text{AsF}_6^-$

2 MMOL (0.5 G SCALE)

- PROPERTIES OF $N_5^+\text{AsF}_6^-$

WHITE SOLID

SPARINGLY SOLUBLE IN HF

MARGINALY STABLE AT 22 ºC

HIGHLY ENERGETIC

REACTS VIOLENTLY WITH WATER AND ORGANICS

CALCULATED $\Delta H_f^\circ \ N_5^+ (g) = 353 \text{ kcal/mol}$
SYNTHESIS OF $^{15}$N LABELED $N_5^+AsF_6^-$

$$
\begin{align*}
2 \text{NaN}^+\text{NN} & + 2 \text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H} \quad \xrightarrow{80^\circ\text{C}} \quad \text{HN}^+\text{NN} + \text{HNNN}^+ + 2 \text{NaO}_2\text{C(CH}_2)_{16}\text{CH}_3 \\
2 \text{N}_2\text{F}^+\text{AsF}_6^- & + \text{HN}^+\text{NN} + \text{HNNN}^+ \quad \xrightarrow{} \quad [\text{N}^+\text{NNNN}]^+\text{AsF}_6^- + [\text{NNN}^+\text{NN}]^+\text{AsF}_6^- + 2 \text{HF}
\end{align*}
$$

$^{15}$N LABELED $N_5\text{AsF}_6$ NEEDED FOR POSITIVE IDENTIFICATION OF $N_5^+$ BY SPECTROSCOPIC METHODS
CHARACTERIZATION OF $\text{N}_5^+ \text{AsF}_6^-$

- $^{14}\text{N}$ AND $^{15}\text{N}$ NMR SPECTRA
- LOW-TEMPERATURE RAMAN AND INFRARED SPECTRA OF NORMAL AND ISOTOPICALLY LABELED $\text{N}_5^+$
- NORMAL COORDINATE ANALYSIS
- MASS SPECTROSCOPY
- THEORETICAL CALCULATIONS
  - OPTIMIZED GEOMETRY
  - VIBRATIONAL SPECTRA
  - ISOTOPIC SHIFTS
  - NMR SHIFTS
  - HEAT OF FORMATION
PHOTOGRAPH OF $N_5AsF_6$ IN QUARTZ TUBE
OPTIMIZED GEOMETRIES FOR N$_5^+$ CCSD(T) (B3LYP) VALUES
\[ \text{[}^{14}\text{N}^{14}\text{N}^{14}\text{N}^{14}\text{N}^{14}]^{+} \text{AsF}_{6}^{-} \]

LOW-TEMPERATURE RAMAN SPECTRUM

\[ \begin{array}{lcccc}
\text{*} &=& \text{AsF}_{6}^{-} \\
\text{N}_{5}^{+} & \text{Obsd} & \text{CCSD(T)} & \text{B3LYP} \\
\text{v}_{1} (\text{A1}) & 2271 & 2229 & 2336 \\
\text{v}_{7} (\text{B2}) & 2211 & 2175 & 2282 \\
\text{v}_{2} (\text{A1}) & 871 & 818 & 850 \\
\text{v}_{4} (\text{A1}) & 209 & 181 & 193 \\
\end{array} \]

Frequency, \text{cm}^{-1}
\[ ^{15}N-N^{14}N-^{14}N-N^{14}N-^{14}N^+ \text{AsF}_6^- \]

\[ ^{14}N-N^{14}N-^{15}N-N^{14}N-^{14}N^+ \text{AsF}_6^- \]

LOW-TEMPERATURE RAMAN SPECTRUM

14N-15N SHIFTS (cm\(^{-1}\))

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<th>CALCD</th>
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<td>21.4</td>
</tr>
<tr>
<td>(V_2)</td>
<td>14</td>
<td>14.1</td>
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Frequency, cm\(^{-1}\)
NITROGEN NMR SPECTRA OF

$[^{15}N-^{14}N-^{14}N-^{14}N-^{14}N]^+$ AND $[^{14}N-^{14}N-^{15}N-^{14}N-^{14}N]^+$

$N_3$

$N_2$

$N_1$

$\ast = [H_2N-N-N]^+$

NMR SHIFTS (ppm)

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<th>CALCD</th>
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<tr>
<td>$N_1$</td>
<td>-237.3</td>
<td>-235</td>
</tr>
<tr>
<td>$N_2$</td>
<td>-165.3</td>
<td>-166</td>
</tr>
<tr>
<td>$N_3$</td>
<td>-100.4</td>
<td>-95</td>
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WORK IN PROGRESS

- SYNTHESIS OF $\text{N}_5^+\text{SbF}_6^-$

- SENSITIVITY AND SAFETY DATA

- COMBINATION OF $\text{N}_5^+$ WITH POLYNITROGEN ANIONS
  TO PREPARE FIRST ALLOTROPE OF $\text{N}_2$

- SYNTHESIS OF $\text{XeN}_3^+$
SUMMARY

- A QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS WAS DEVELOPED

- $\text{N}_5^+\text{AsF}_6^-$, THE ONLY HOMOLEPTIC POLYNITROGEN COMPOUND BESIDES $\text{N}_2$ AND $\text{N}_3^-$ WHICH CAN BE MADE IN BULK, WAS PREPARED FROM $\text{N}_2\text{F}^+\text{AsF}_6^-$ AND $\text{HN}_3$ AND WAS CHARACTERIZED

- $\text{N}_5^+$ HAS A V-SHAPED CHAIN STRUCTURE AND IS MARGINALLY STABLE AT ROOM TEMPERATURE
ACKNOWLEDGEMENT

- COWORKERS

- JERRY BOATZ
  MARIO FAJARDO
  ALAN KERSHAW
  JOHN STANTON

- DARPA
  AFOSR
  NSF