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Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 2. REPORT TYPE
Technical Papers 3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE 5a. CONTRACT NUMBER
In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62500P

6. AUTHOR(S) 5d. PROJECT NUMBER
3058

5e. TASK NUMBER
00E7

5f. WORK UNIT NUMBER
549983

Please see attached

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-TP-FY99-0119


12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030312 053

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT 	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5015

TP-FY99-0119

E1

ERC# E99-013

✓ Spreadsheet
✓ OTS

MEMORANDUM FOR PRR (Contractor/In-House Publication)

27 May 1999

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0119
Christe and Wilson (ERC) and Sheehy and Boatz, "On a quantitative scale for Lewis acidity and recent progress
in polynitrogen chemistry"

Proceedings to be published in J. Fluorine Chemistry

(Public Release)

On a quantitative scale for Lewis acidity and recent progress in polynitrogen chemistry

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Abstract

A quantitative scale for Lewis acidities based on fluoride ion affinities is discussed. It uses pF^- values which represent the fluoride ion affinities in kcal/mol divided by 10. These values were obtained for 106 Lewis acids in a self-consistent manner using ab initio calculations at the MP2/PDZ level of theory. In the area of polynitrogen chemistry, the synthesis and characterization of the novel N_5^+ cation from N_2F^+ and HN_3 is described.

Keywords: Lewis acidity scale; Ab initio calculations; Fluoride affinity calculations; High energy density materials; Polynitrogen compounds; Synthesis

1. Introduction

This paper describes two major developments from our laboratories in the field of Lewis acids and high energy density materials (HEDM).

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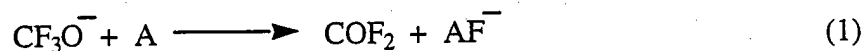
§ Pacific Northwest National Laboratory

Whereas quantitative scales for the strength of Brønsted-Lowry or protic acids are well established and are being taught in high school chemistry classes, surprisingly, no quantitative scale for the measurement of Lewis acidity strength exists at the present time.

In the area of polynitrogen chemistry, recent interest in new HEDM compounds based on all nitrogen compounds has produced dozens of theoretical papers [1] but, except for the discovery of the azides by Curtius in 1890 [2], no homoleptic polynitrogen species were known that can be prepared in bulk.

2. Quantitative scale for Lewis acidity

Due to its high basicity and small size, the fluoride ion readily reacts with essentially all Lewis acids. The reaction enthalpy of this interaction, i.e., the fluoride ion affinity, serves as a good measure for the strength of a Lewis acid. Since only a small number of fluoride ion affinities had been estimated experimentally and often with relatively large uncertainties and discrepancies due to the use of different techniques [3-10], it was important to create a self-consistent set of fluoride ion affinities containing essentially all of the important Lewis acids. This was achieved with the help of theoretical fluoride affinity calculations at the correlated MP2/PDZ level of theory [11,12] using effective core potentials [13] for the heavier elements. Because the electron affinity of F is hard to calculate, COF_2 was used as a reference compound to simplify the calculations, as shown in (1).



The resulting relative fluoride ion affinities were converted to an absolute scale using the experimentally known value of 49.9 kcal/mol [3,14,15] for the fluoride ion affinity of COF_2 . In this manner, absolute F^- affinities were obtained for 106 different Lewis acids. To obtain a

more convenient scale range, we propose to divide these F^- affinities, expressed in kcal/mol, by 10 and use the resulting set of numbers as a quantitative pF^- scale for Lewis acidity.

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

An abbreviated version of this scale is given in Table 1 and shows the expected trend of acid strengths, i.e., $SbF_5 > AsF_5 > PF_5 > BF_3 > SiF_4 > COF_2 > HF$. It is important to note that the range of values given in Table 2 does not encompass the entire range of possible pF^- values; the very strong Lewis acid F^+ exhibits a pF^- value of 36.1, whereas CF_4 , whose F^- adduct is unstable and spontaneously loses F^- , possesses a pF^- value of -1.5.

Some other noteworthy aspects of our pF^- scale are: (i) The given values were calculated for the free gaseous molecules; (ii) for polymeric solids, such as AlF_3 , the actual pF^- values are smaller than those given in Table 1 and must be corrected for their association energies; and (iii) the stability of novel complex fluoro anions can be predicted from the pF^- values. For a compound to form a stable complex fluoro anion, its pF^- value should be about 3.5 or larger.

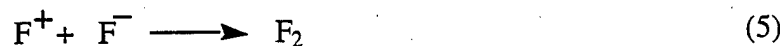
Complementary Lewis basicity scales can be envisioned which are based on H^+ (2),



or the ultimate Lewis acid F^+ (3),



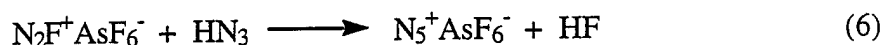
and are connected to our pF^- scale through equations (4) and (5), respectively.



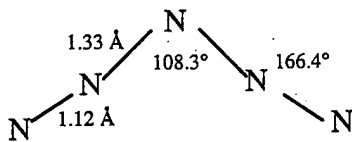
Integration of these scales with the pF^- scale into a unified Lewis acid-Lewis base system is in progress.

3. Polynitrogen chemistry

The reaction of $\text{N}_2\text{F}^+\text{AsF}_6^-$ [16] with HN_3 in anhydrous HF solution at -78°C has led to the synthesis of the novel $\text{N}_5^+\text{AsF}_6^-$ salt in almost quantitative yield (6), with the only detectable by-product being $\text{H}_2\text{N}_3^+\text{AsF}_6^-$ [17].



The N_5^+ cation, the first novel homoleptic polynitrogen species discovered in more than 100 years and preparable in bulk, was characterized by low-temperature vibrational NMR spectroscopy and theoretical calculations. $\text{N}_5^+\text{AsF}_6^-$ is a white solid that is sparingly soluble in HF, marginally stable at 22°C , and highly energetic; its calculated enthalpy of formation (ΔH_f°) is 353 kcal/mol. The geometry of N_5^+ was calculated at the CCSD(T)/6-311+G(2d) level of theory as



and is supported by the very good agreement between observed and calculated nitrogen NMR shifts and vibrational frequencies, including their ^{14}N - ^{15}N isotopic shifts. A detailed discussion of these data is given elsewhere [18].

Acknowledgements

This work was funded by the Defense Advanced Research Projects Agency, the Air Force Office of Scientific Research, the National Science Foundation, and the Department of Energy. We thank A. Kershaw for recording the NMR spectra and Prof. J. Stanton for calculating the nitrogen NMR shifts at the CCSD(T) level, and Drs. G. Olah, P. Carrick, S. Rodgers, M. Berman, and A. Morrish for continuing encouragement and support.

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Table 1. ABBREVIATED pF⁻ SCALE

<u>COMPOUND</u>	<u>pF⁻</u>	<u>COMPOUND</u>	<u>pF⁻</u>	<u>COMPOUND</u>	<u>pF⁻</u>
SbF ₅	12.03	cis-IO ₂ F ₃	9.66	SOF ₄	6.60
AlF ₃	11.50	PF ₅	9.49	XeOF ₄	6.37
AlFCl ₂	11.50	SeOF ₄	8.69	TeF ₆	6.15
AlF ₂ Cl	11.47	TeF ₄	8.34	POF ₃	5.86
AlCl ₃	11.46	BF ₃	8.31	XeF ₄	5.71
TeOF ₄	10.79	GeF ₄	8.30	SF ₄	5.67
InF ₃	10.75	ClF ₅	7.47	COF ₂	4.99
GaF ₃	10.70	BrF ₃	7.35	PF ₃	4.49
AsF ₅	10.59	SiF ₄	7.35	HF	3.68
SnF ₄	9.82	SeF ₄	7.12	NO ₂ F	1.92
				NOF	1.74