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**14. ABSTRACT**

Investigations of the electron affinities of pyrazolyl, imidazolyl and triazoly radicals gave quantitative measurements of N–H bond strengths at the most acidic site, and provide the first detailed view of the low lying electronic excited states of the corresponding radicals. Importantly, very extensive vibronic coupling effects were observed, arising from lone pairs on adjacent nitrogen atoms. In collaboration with Professor John Stanton of the University ot Texas at Austin, state-of-the-art three-state vibronic coupling calculations were performed to understand the photoelectron spectrum of pyrazolide anion. The photoelectron spectrum of 1,2,3-triazolide anion was even more complex as a result of extensive vibronic coupling, and further development of computational capability will be required before quantitative calculations are possible. Qualitative three-state calculations were in much better agreement with experiment than those that ignore vibronic coupling, but more remains to be done.

In the process of these studies, it became clear that deprotonation of azoles also occurs at sites other than the most acidic sites and that ring-opened products may be formed. To test these ideas, studies of N-methylimidazole and N-methylpyrazole were carried out using methyl blocking groups.

**15. SUBJECT TERMS**

Azoles, thermochemistry, anion photoelectron spectroscopy, flowing afterglow ion reaction kinetics, gas-phase acidity, ab initio calculations, vibronic coupling, Jahn-Teller distortion

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# Final Progress Report

# Thermochemistry and Dynamics of Reactive Species: Nitrogen-rich Substituted Heterocycles and Anionic Components of Ionic Liquids

AFOSR Grant FA9550-06-1-0066

December 1, 2005 – November 30, 2008

W. Carl Lineberger and Veronica M. Bierbaum

## I. Introduction

A current program of critical Air Force interest concerns the synthesis and characterization of nitrogen-rich materials for high-energy content, environmentally neutral fuels. Our unique contribution to this ongoing program joins two complementary, sophisticated ion chemistry techniques (negative ion photoelectron spectroscopy and flow/drift selected ion flow kinetics) together with state-of-the-art quantum chemistry in a combined experimental and theoretical research program; our work addresses this area from the unique vantage point of gas phase anion chemistry.

The ion reactions and mechanisms research program at Colorado has focused on gas phase ion reactions, mechanisms, kinetics, and thermochemistry of a wide variety of organic and inorganic species, utilizing the flowing afterglow-selected ion flow tube-triple quadrupole (FA-SIFT-TQ) technique. This powerful and versatile approach has allowed the study of the chemistry of many nitrogenous ions and compounds. An arsenal of ionization and reaction methods generates a wide array of ionic precursors; these methods include ionization by electron impact, microwave discharge, and several dc discharge methods. Additional flexibility is provided by synthetic ion-molecule chemistry within the source region and collision-induced dissociation of ionic species.

An important feature of this reactor is its extreme sensitivity and ability to determine reaction rates and mechanisms with ion intensities several orders of magnitude too low to be easily utilized in the negative ion photoelectron spectroscopy (PES) apparatus. By initially carrying out reactions and identifying mechanisms, it often is possible to optimize ion production for photoelectron studies. It is the combination of these two sets of data that provides the deepest insight and the most detailed thermochemical information.

The complementary electron binding energies, structures, and excitation energies are generally obtained in our continuous flowing afterglow – negative ion photoelectron spectrometer.[1] This device has the ability to synthesize anions using rational gas phase ion chemistry, but the photon energy is limited to 3.5 eV, and electron binding energies > 3.3 eV are not accessible. A new photoelectron imaging spectrometer[2] extends the electron binding energy range to 6 eV, substantially enhances the sensitivity, and potentially improves the electron energy resolution to a few meV, compared to the cw photoelectron spectrometer. The prices paid to use the latter device are that the synthetic chemistry must be carried out in a pulsed jet expansion, and the near-threshold energy nature of the measurements distorts intensities, making the usual Franck-Condon structural analysis[1] less reliable. In the studies reported here, we have employed whichever instrument was most appropriate.

These investigations have provided basic thermochemical information (acidity at multiple sites, electron binding energies for the radicals, R–H dissociation energies) for a number of important nitrogen heterocycles, systems that are of considerable utility and yet virtually unstudied.

## II. Accomplishments During the Grant Period

This AFOSR Grant has provided partial support for three graduate students, one postdoctoral research associate, and one Senior Research Associate over the past 3 years. These workers have guided our recent research projects involving photoelectron spectroscopy, reactive ion thermochemistry, density functional theory, and *ab initio* computation, as briefly reviewed in the remainder of this section. The research described here builds and expands upon their results, with a strong focus on areas of relevance to several Air Force programs.

### IIa. Research Accomplishments

The past 3 years have seen significant progress in our studies of nitrogen-rich five member ring systems.[3-11]

Figure 1 shows the photoelectron spectrum for this anion, compared with simulations for the E- and Z- conformations of the anion.[8] The simulations clearly identify the conformer formed in this reaction. This ability to distinguish conformations in anion photoelectron spectroscopy has proven very valuable in a detailed study of the ion chemistry of triazole.

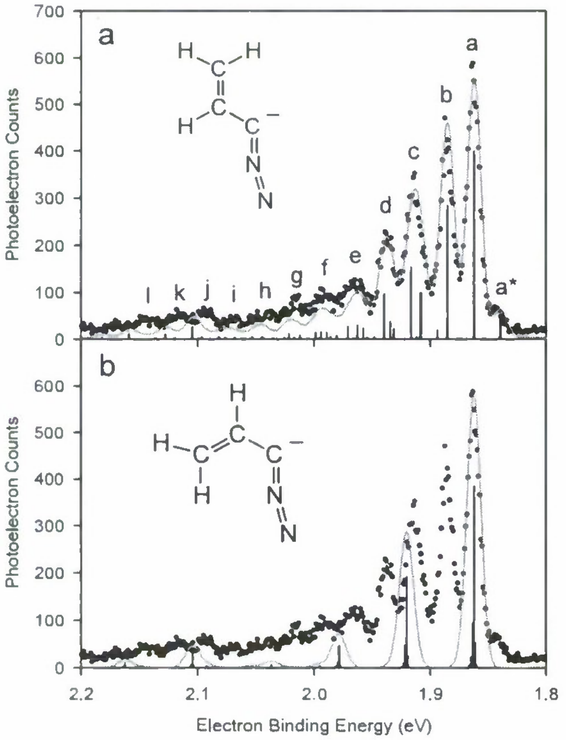

Figure 1. Simulations of the photoelectron spectrum of the vinyldiazomethyl (vdm) anion. The solid red lines are simulations of the photoelectron spectra of $\widetilde{X}\ ^{1}A'$ *E*-vdm anion **(a)** and *Z*-vdm anion **(b)**, compared with experiment (dots).

In an attempt to understand detailed chemistry and possible breakup of anions resulting from deprotonation of 1,2,3-triazole, we have carried out an extensive investigation of the products of this reaction. Interestingly, while the primary reaction product arises from deprotonation at the most acidic site, we see clear evidence for deprotonation at all hydrogen sites, rearrangements and ring-open products that arise with conformational selectivity. Details of this exceptionally thorough study of ionic reaction products are contained in a lengthy manuscript.[3]

Finally, we have carried out, in collaboration with Professor Mark Johnson at Yale and Drs. Al Viggiano and Thomas Miller at AFRL, a study of electron detachment from $SF_6^-$ and $C_4F_8^-$.[12] The photoelectron spectra of both species exhibit an exceptionally long vibrational progression in a single mode, and show essentially no intensity at the electron binding energy corresponding to the adiabatic electron affinity. This study helps to shed light on the exceptional ability of these fluorine-rich species to capture low energy electrons.

### IIb. Personnel

This grant has provided partial support for three chemistry graduate students, Ms. Stephanie Villano, Mr. Adam Gianola, and Mr. Scott Wren, post-doctoral research associate Dr. Takatoshi Ichino and Senior Research Associate Dr. Shuji Kato. Scott, Adam, Stephanie, and Takatoshi have carried out photoelectron spectroscopy experiments, and Shuji and Stephanie have performed acidity and collision-induced dissociation studies using the flowing afterglow-selected ion flow tube instrument. All have carried out *ab initio* and DFT calculations of the structures and energies of ionic and neutral species. Dr. Gianola completed his PhD in 2006 and is now a Patent Agent with Winter and Sullivan, LLC. Dr. Villano completed her PhD in November, 2008, and now holds a very competitive NREL Postdoctoral Fellowship working in the area of biomass combustion.

### IIc. Publications Supported in whole or in part by AFOSR Grant FA9550-06-1-0066

The following 10 publications were directly related to our AFOSR studies over the period of the current grant. Complete publication listings over the past four years can be found in the attached curriculum vitae.

1. Stephanie M. Villano, Nicole Eyet, W. Carl Lineberger, and Veronica M. Bierbaum "Gas-Phase Reactions of Halogenated Radical Carbene Anions with Sulfur and Oxygen Containing Species," Int. *J. Mass Spectrom.* **280,** 12-18 (2009).

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3. Takatoshi Ichino, Scott W. Wren, Kristen M. Vogelhuber, Adam J. Gianola, W. Carl Lineberger, and John F. Stanton, " The vibronic level structure of the cyclopentadienyl radical," *J. Chem. Phys.,* **129**, 084310 [19 pages] (2008),

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5. Matthew A. Thompson, Joshua P. Martin, Joshua P. Darr, W. Carl Lineberger and Robert Parson "A combined experimental/theoretical investigation of the near-infrared photodissociation of $IBR^-(CO_2)_n$," *J. Chem Phys.* **129**, 224304 [12 pages] (2008).

6. Takatoshi Ichino, Scott W. Wren, Veronica M. Bierbaum and W. Carl Lineberger, "Ion Chemistry of 1*H*-1,2,3-Triazole. 2. Photoelectron Spectrum of the Iminodiazomethyl Anion and Collision Induced Dissociation of the 1,2,3-Triazolide Ion," *J. Phys. Chem. A 112,* 9723–30 (2008).

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9. Shuji Kato, Veronica M. Bierbaum, and W. Carl Lineberger, "Collision-induced dissociation of fluoropyridinide anions," *Int. J. Mass Spectrom. Ion Processes* **266,** 166-79 (2007).

10. Takatoshi Ichino, Adam J. Gianola, Shuji Kato, Veronica M. Bierbaum, and W. Carl Lineberger, "Structure of the vinyldiazomethyl anion and energetic comparison to the cyclic isomers," *J. Phys. Chem. A* **111,** 8374-83 (2007).

11. Joseph C. Bopp, Joseph R. Roscioli, Mark A. Johnson, Thomas M. Miller, Albert A. Viggiano, Stephanie M. Villano, Scott W. Wren, and W. Carl Lineberger, "Spectroscopic characterization of the isolated $SF_6^-$ and $C_4F_8^-$ anions: Observation of very long harmonic progressions in symmetric deformation modes upon photodetachment," *J. Phys. Chem. A* **111,** 1214-21 (2007).

12. Takatoshi Ichino, Adam J. Gianola, W. Carl Lineberger, and John F. Stanton, "Nonadiabatic effects in the photoelectron spectrum of the pyrazolide-d(3) anion: Three-state interactions in the pyrazolyl-$d_3$ radical," *J. Chem. Phys.* **125,** 084312 [22 pages] (2006).

13. Adam J. Gianola, Takatoshi Ichino, Shuji Kato, Veronica M. Bierbaum, and W. Carl Lineberger, "Thermochemical studies of pyrazolide," *J. Phys. Chem. A* **110,** 8457-66 (2006).

14. Adam J. Gianola, Takatoshi Ichino, Rebecca L. Hoenigman, Shuji Kato, Veronica M. Bierbaum, and W. Carl Lineberger, "Photoelectron spectra and ion chemistry of imidazolide," *J. Phys. Chem. A* **109,** 11504-14 (2005).

## B. Anion Photoelectron Spectrometry

The photodetachment experiments were carried out using one of two negative ion photoelectron spectrometers. Our workhorse instrument for determination of electron affinities of chemically well characterized species has for many years been our cw flowing afterglow-negative ion photoelectron spectrometer. This instrument allows relatively complete control of the ion production chemistry and temperature, and offers an electron energy resolution of less than 10 meV.[1] It has been the instrument of choice for investigations of species with electron affinities less than 3.2 eV. However, this machine is not suitable to investigate species with higher binding energies, such as a number of the nitroazoles and it does not operate at sufficiently low temperatures to provide significant clustering.

In light of these limitations, we have developed a second pulsed, photoelectron imaging spectrometer, which has the ability to study anions with binding energies up to 6 eV.[2,13] The energy resolution of this spectrometer can be as good as a few meV, but anion formation is carried out in a pulsed supersonic expansion, with the result that sophisticated anion syntheses are not nearly as straightforward (or even possible) as with the flowing afterglow ion source. In addition, the useable electron intensity range is only a factor of 40, compared with the $10^4$

dynamic range available with the cw spectrometer. However, the ability to investigate strongly bound anions makes this the instrument of choice for a number of the strongly bound azoleides.

In both instruments, it is necessary to employ precursor compounds with very low vapor pressures. Both for the tetrazoles and the ionic liquids that we plan to study, a form of heated source will be essential. We have successfully demonstrated several methods of introducing low vapor pressure species into our flowing afterglow reactor. We have been very successful in introducing a heated crucible downstream from the ion source, producing significant quantities of highly involatile compounds and even clusters.[14,15]

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6. S. M. Villano, A. J. Gianola, N. Eyet, T. Ichino, S. Kato, V. M. Bierbaum, and W. C. Lineberger, "Thermochemical studies of N-methylpyrazole and N-methylimidazole," *J. Phys. Chem. A* **111,** 8579-87 (2007).

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# Thesis Abstracts

## Ultraviolet Photoelectron Spectroscopy of Organic Anions

by

**Adam J. Gianola**

B.S., University of Nevada-Reno, 2000

A thesis submitted to the

Faculty of the Graduate School of the

University of Colorado in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Department of Chemistry and Biochemistry

2006

Gianola, Adam J. (Ph.D. Physical Chemistry)
Ultraviolet Photoelectron Spectroscopy of Organic Anions
Thesis directed by Professor W. Carl Lineberger

## Abstract

Ultraviolet photoelectron spectroscopy has been used to study several negative organic ions and their corresponding neutrals: cyclopentadienide, pyrrolide, imidazolide, pyrazolide, vinyl diazomethyl anion, and 2-oxepinoxide. The photoelectron spectra obtained for these systems gives structural, vibrational, and electronic information about the corresponding neutral radicals.

Several of the ions listed above are related: cyclopentadienide, pyrrolide, imidazolide and pyrazolide. Each is a 5-membered ring system, with 0, 1, or 2 nitrogen atoms in the ring. The cyclopentadienyl radical system is a well know Jahn-Teller system, and these effects are evident in the photoelectron spectrum of cyclopentadienide. Substitution of one C—H group in cyclopentadienide by an N atom gives the pyrrolide ion. Jahn-Teller effects are no longer present in the radical counterpart, pyrrolyl; however, electronic interactions between the ground and first excited states are evident in the photoelectron spectrum. Imidazolide and pyrazolide are isomers of one another, and each has two N atoms in the ring. In imidazolide the N atoms are separated, while in pyrazolide they are adjacent. The corresponding radicals (imidazolyl and pyrazolyl) also show interesting electronic interactions between their ground and first excited states. In imidazolyl the interactions are weak, and the effects are not evident in the photoelectron spectrum. In pyrazolyl they are significantly stronger, and unexpected vibrational bands appear in the photoelectron spectrum as a result.

Also observed in the spectra of imidazolide and pyrazolide were photoelectron signals from other isomers. These isomers are nearly structurally identical to the imidazolide and pyrazolide ions, with the exception that a hydrogen atom is displaced from a carbon site to a nitrogen site. The photoelectron spectra of these isomers appear very different. Electronic interactions in the analogous radicals are not present, and the photoelectron spectra appear very Franck-Condon like. Gas-Phase Acidities for these ions were also obtained through bracketing experiments. Combination of the Electron Affinities obtained from the photoelectron spectra with these gas-phase acidities allows for determination of a C—H bond dissociation enthalpy of the parent molecules imidazole and pyrazole.

Although not a ring system, vinyldiazomethyl anion is an isomer of imidazolide and pyrazolide. It can be thought of as a ring opened pyrazolide ion (by breaking a C—N bond). Its photoelectron spectrum is rather simple, appearing very Franck-Condon like. Interestingly, it appears that the spectrum originates from the trans-vinyldiazomethyl anion only; there is no indication of the presence of the cis isomer. Franck-Condon simulations show each isomer would have a different spectral signature.

The 2-oxepinoxide anion is a seven-membered ring containing oxygen. The corresponding neutral, 2-oxepinoxy radical, is a suspected intermediate in the combustion of benzene. Phenyl radical is expected to be formed first in a benzene flame, and many pathways for reaction of phenyl radical with $O_2$ have been studied theoretically. The phenyl-peroxy radical is thought to isomerize into the 2-oxypinoxy radical as a first step to the formation of CO, $CO_2$, and other combustion products. Production of the 2-oxepinoxide ion and subsequent photodetachment to form 2-oxypinoxy radical is one of the first experimental steps to be taken to verify these combustion pathways.

# Gas-Phase Negative Ion Chemistry: Photoelectron Spectroscopy, Reactivity, and Thermochemical Studies

by

Stephanie M. Villano

B. S., University of Colorado at Denver, 2001

A thesis submitted to the Faculty of the Graduate School
of the University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Chemistry and Biochemistry
2008

Villano, Stephanie M. (Ph.D. Physical Chemistry)

Gas-Phase Negative Ion Chemistry: Photoelectron Spectroscopy, Reactivity, and Thermochemical Studies

Thesis directed by Professors Veronica M. Bierbaum and W. Carl Lineberger

Abstract:

This thesis describes the reactive and spectroscopic characterization of several anions. An overview of gas-phase ion-molecule reactivity and photoelectron spectroscopy is given in Chapters I-IV.

In Chapter V the competition between nucleophilic substitution and base-induced elimination for the reactions of $BrO^-$ and $ClO^-$ with a series of alkyl chlorides is investigated. These results are in stark contrast to prior theoretical work, and they indicate that the elimination channel becomes the dominant pathway as the neutral reagent becomes more sterically hindered. Additionally, the highly debated $\alpha$-nucleophilicity of these two anions and of $HO_2^-$ is examined; no enhanced reactivity is displayed suggesting that the $\alpha$-effect is not due to an intrinsic property of the anion.

The reactivity of simple halogen substituted carbene anions is investigated with a series of oxygen, sulfur, and halogen containing neutral reagents in Chapter VI. These carbanions display diverse reactivity that includes substitution, elimination, proton transfer, and electron transfer reactions. In addition to these classic transformations, isotopic labeling studies indicate that these carbanions can undergo an insertion-elimination mechanism. Such reactivity has been observed in neutral carbenes; however, this is the first report of such gas-phase anion reactivity.

Spectroscopic studies of $SF_6^-$ and *c*-$C_4F_8^-$ are reported in Chapter VII. The photoelectron spectra of both anions are consistent with a large geometry change between anionic and neutral species. The photoelectron spectrum of *c*-$C_4F_8^-$ is composed of combination bands of two symmetric ring-breathing modes. The photoelectron spectrum of $SF_6^-$ is dominated by an extended progression in the S−F stretching mode as well as a strong overtone/combination progression.

In Chapter VIII we report the photoelectron spectra of the *N*-methyl-5-pyrazolide and *N*-methyl-5-imidazolide anions, which provide electron affinities for the corresponding radicals. The gas-phase acidities of *N*-methylpyrazole and *N*-methyimidazole are also measured, and these measurements are used to determine the C-H bond strengths.

The thermochemistry of peroxyformic acid and peroxyacetic acid is investigated in Chapter IX. The electron affinities of the peroxyformyl and peroxyacetyl radicals are determined from the photoelectron spectra of the corresponding anion. The gas-phase acidities of both acids are determined, and these measurements are used to determine the O-H bond strengths.