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14. ABSTRACT This project combined a variety of experimental and computational approaches to determine thermochemical properties of a number of nitrogen-rich energetic materials. A rapid flow, negative ion – molecule flow reactor was employed to obtain gas phase acidities, and negative ion photoelectron spectroscopy provided electron affinities and structural information. The combination of these data with electronic structure calculations provided quantitative C-H bond strengths and site-specific acidities. The focus of these studies was nitrogen-rich five- and six-member heterocycles, azoles and azines. One special focus in this project was the symmetric six-member ring, 1,3,5-triazine. Other types of reactive molecules investigated included peroxy radicals that are important atmospheric oxidizers and potentially signatures of partial combustion. Information similar to that obtained for the heterocycles was obtained for hydroperoxyl, peroxyformyl and peroxyacetyl radicals. All results are documented in open research literature.						
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Final Performance Report

1 December 2008 to 30 November 2011

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

Agreement FA9550-09-1-0046

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Research Accomplishments

The past three years have seen significant progress in our studies of nitrogen-rich heterocyclic compounds. We have carried out a systematic and comprehensive study of the gas phase acidity and characterized the complex reactivity patterns of 1,3,5 triazinide, $C_3H_2N_3^-$. A complex pattern of reactivity and clustering reactions had to be unraveled before an accurate gas phase acidity could be determined.⁵ The acidity of 1,3,5-triazine is particularly intriguing. The deprotonated 1,3,5-triazine presents a rare example of an anion with three contiguous lone pairs in a single molecule. The photoelectron spectra of 1,3,5 triazinide provide the electron affinity of the radical, detailed structural information and an

accurate C-H bond strength in 1,3,5 triazinide.⁶ As an example, Fig. 1 shows the 364 nm photoelectron spectrum of 1,3,5 triazinide anion.⁶ The proton affinity, reactivity, and spectroscopy have provided important clues to understanding the stability of highly N-substituted azines and aromatics.⁵

In addition to the very detailed study of the previously unobserved 1,3,5 triazinide anion, we have carried out computational and experimental investigations of four other mono- and di-azines, determining unambiguously the most acidic proton for each azine, the corresponding azinyl radical electron affinity, and the C-H bond strength of the most acidic H atom. The full set of data allows one to imply behavior of other azines not yet investigated. A detailed manuscript describing these results will be completed in the coming weeks.⁶ Finally, we note that, in analogy with the phenyl radical, azinyl radicals are implicated as key intermediates in combustion processes. The full set of azines studied is shown below.

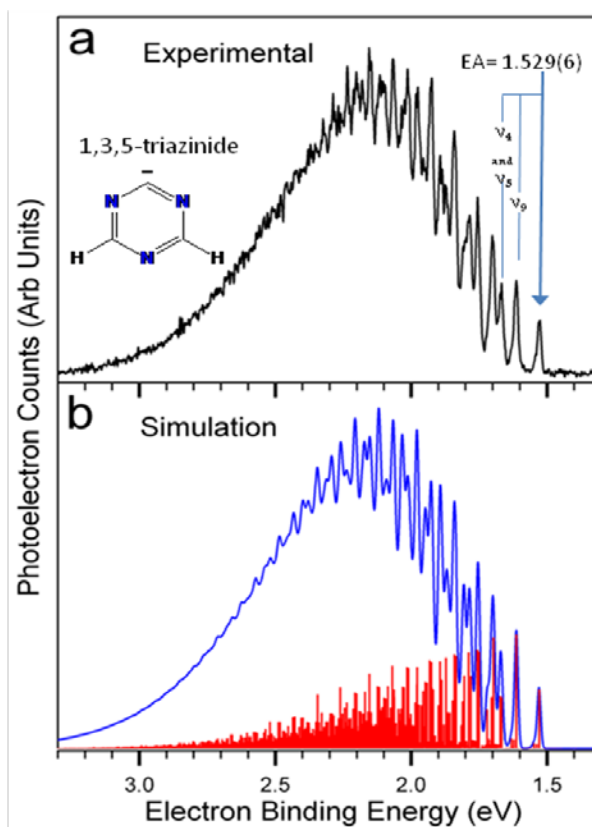
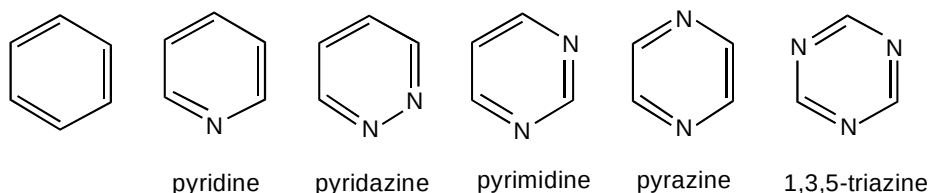


Fig. 1 Experimental and simulated photoelectron spectra of 1,3,5 triazinide anion.

The photoelectron spectra of all of the azinides and earlier photoelectron spectra of SF_6^- and C_4F_8^- anions⁷ exhibited extended vibrational progressions and low intensities at the origin, the consequence of significant geometry changes between the anion and the neutral. While this was not a critical problem in the study of the azinides, it was apparent that a more comprehensive study of photoelectron spectra in the case of substantial structural distortions upon electron detachment was needed. To this end, we (collaborating with Professors Kent Ervin and Anne McCoy) have carried out an extensive investigation of photoelectron spectra of halomethyl anions,⁸ where there are exceedingly large geometry changes between the near pyramidal anion and the quasi-planar neutral radical. In addition, the single hydrogen atom provides an exceptionally floppy vibrational coordinate. We have carried out analyses at levels extending from our normal Franck-Condon analysis in rectangular coordinates through analyses in internal molecular coordinates to coupled multidimensional vibrational level calculations. The normal, first approximation method that works so well for most species⁹ fails terribly in this case, and modifications improve matters but only when one looks at the multidimensional neutral potential energy surface as a whole does one regain the ability to produce predictive photoelectron spectra. An extensive publication describes the methodologies, the indications when such failures are likely, and a systematic method by which one can improve the level of approximation.⁸ It is our expectation that this general information will be very valuable in future studies as well.

While not directly related to Air Force energetic materials interest, we have carried out studies of organic radical transition states, employing an approach that is very likely to be of great value in investigations of transient species of more direct AF energetic materials interest. For example, the oxyallyl diradical has been investigated by photoelectron spectroscopy of the corresponding anion ($\text{H}_2\text{COCH}_2^-$), and we have shown unequivocally that the ground state is a singlet state unstable to rearrangement to cyclopropanone.¹⁰ In this case, the ground singlet and first excited (stable) triplet state are separated by only 55 meV. Quite detailed electronic structure calculations and photoelectron spectral simulations were required to obtain full understanding, as described in the short communication¹⁰ and in a full manuscript.¹¹

In another related area, we continue to be engaged in studies of unstable peroxy radicals that are both weakly held together and are likely important components of the earth's atmosphere. Many of the details of production and analysis are of relevance to Air Force needs, and the peroxy products are also possible signatures of partial combustion. We have carried out studies of thermochemistry and structure of peroxyacetate¹² and peroxyformate¹³ anions and the properties of the corresponding radicals. Again, this work has been a joint effort involving gas-phase acidity measurements, photoelectron spectroscopy studies and state-of-the-art computations. The results show that some of

these species may well be of importance in the overall chemistry of the lower atmosphere.

A photodetachment process that results in a neutral molecule whose structure is close to a reaction transition state produces a time-evolving neutral radical on a reaction coordinate. We take advantage of this process, for example, by utilizing an ultrafast laser to photodetach an electron from oxyallyl anion to produce the oxyallyl diradical in a non-stationary state. Its evolution can then be followed by time-resolved photoelectron spectroscopy. The initial excitation step can in principle be either photodetachment to produce a time evolving neutral or photodissociation of an anion to produce a time-evolving anion state. The latter is experimentally much easier to accomplish, as the probe photon energy required is generally less than 4 eV. We have recently carried out studies of such processes involving the IBr^- anion both with and without solvent molecules.^{4,14} The data show definitively the ability of a single solvent molecule to facilitate intramolecular electron transfer in a dissociating molecule when the distance between the donating and accepting centers is as much as 7 Å.⁴ Again, elaborate experiments and state-of-the-art electronic structure and molecular dynamics simulations are required in order to obtain convincing understanding of the experimental result. The outcome, however, is a simple physical picture that makes great intuitive sense and will have predictive value, although the picture would not have been compelling without the high-level experiments and calculations that preceded the result.

We have extended our studies of the gas phase ion chemistry of nitrogen-rich systems to include the reactivity of carbanions and cyano anions with atomic nitrogen and atomic oxygen. This experimental and computational work has revealed the critical role of spin effects in determining reactivity. Pure carbon chain anions C_n^- ($n=2,4-7$), hydrogenated carbon chain anions HC_n^- ($n=2,4,6$), and cyano anions (CH_2CN^- , CH_3CHCN^- , $(\text{CH}_3)_2\text{CCN}^-$) exhibit larger reaction rate constants with O atoms relative to the corresponding reactions with N atoms. Our computational studies indicate that spin-forbidden reactions are the probable pathways in the reactions with N atoms, and spin conversion limits the reaction efficiency. In contrast, spin-allowed reactions are the dominant processes for O atoms. Thus, a major factor influencing the reactivity of these anion-atom processes is whether a spin-allowed barrierless pathway exists.^{15,16}

We have also examined the reactivity of novel radical carbene anions. Our studies demonstrate that these anions initiate classic transformations of proton transfer and substitution reactions, but also participate in insertion-elimination mechanisms, analogous to neutral carbene processes; this is the first report of such reactivity for carbene anions.^{17,18}

Finally, in collaboration with Dr. Al Viggiano of the Air Force Research Laboratory, we have examined the negative ion chemistry of electronically excited molecular oxygen, O_2 ($a^1\Delta_g$). Although appreciable concentrations of O_2 (a) exist in the earth's ionosphere, little is known about the reactivity

of this species in the gas phase. We have measured reaction rate constants and product ion branching ratios for the reactions of fourteen anions with O₂ (a), and three mechanistic pathways were observed and supported by computations: addition-fragmentation, proton transfer, and hydride transfer. We have also explored dissociative excitation transfer in the reaction of O₂(a) with OH⁻(H₂O)_{1,2} clusters as a function of temperature. The reaction of the monohydrate is slightly endothermic and exhibits a positive temperature dependence. In contrast the reaction of the dihydrate is exothermic and exhibits a negative temperature dependence.^{19,20}

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Personnel Supported by or Associated with this Research Project

W. Carl Lineberger and Veronica M. Bierbaum, Co-Principal Investigators

Dr. Stephanie Villano completed her PhD, and is now a postdoctoral scholar at the National Renewable Energy Laboratory and the Colorado School of Mines.

Dr. Nicole Eyet completed her PhD, and is now an Assistant Professor at St. Anselm College. She was selected as an AFOSR Summer Scholar, and has been able to continue her long term collaboration with Al Viggiano at AFRL.

Dr. Scott Wren completed his PhD in July, 2011, and is now a Principal Scientist/Engineer at Intel Corporation in Portland, OR.

Dr. Zhibo Yang will assume an Assistant Professorship in the Department of Chemistry at the University of Oklahoma, Norman in August, 2012.

Lt Col John Garver, AF Academy Faculty, completed his PhD research in July, 2011, working on ionic liquids and energetic materials thermochemistry efforts associated with this program. He has returned to the US Air Force Academy as a senior faculty member.

Kristen Lemke will complete her PhD in February, 2012, and will spend a short time as a Postdoctoral Associate at JILA.

Individuals newly associated with this program are Captain-Select Benjamin Worker (AFIT CI) who is carrying out research for his Masters degree in Chemistry, Postdoctoral Associate Dr. Wilson Gichuhi, and Mr. Charles Nichols, a second year graduate student.

Abstracts of the PhD Theses resulting from this research are provided at the end of this report.

Publications Submitted or Accepted during reporting period:

1. S. M. Villano, N. Eyet, W. C. Lineberger, and V. M. Bierbaum, "Gas-phase carbene radical anions: New mechanistic insights," *J. Am. Chem. Soc.* **130**, 7214-15 (2008).
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Thesis Abstracts

Garver, John M. (Ph.D. Physical Chemistry, 2011)

Gas Phase Negative Ion Chemistry: Reactivity and Mechanism in Organic Reactions

Thesis directed by Professor Veronica M. Bierbaum

Abstract

Numerous experimental and theoretical studies have probed reactions using gas phase ion chemistry to develop an intrinsic understanding of kinetics, mechanisms and structure-energy relationships. The fundamental knowledge gained from these studies allows predictive tools to be developed for understanding chemical systems (earth's atmosphere, biological, etc.). This thesis describes the reactive characteristics and competitive processes within several organic ion-molecule reactions. An overview of the basic principles of gas phase ion-molecule reactions and the experimental methods employed in our studies are given in Chapters 1-2.

In Chapter 3, comparisons of the reactivity and mechanistic pathways between the reactions of alkyl iodides with CN^- in the gas phase and several solvents are reported. The mechanistic results are strikingly similar; however, a tighter gas phase transition state is suggested.

In Chapter 4, competition between the substitution ($\text{S}_{\text{N}}2$) and elimination ($\text{E}2$) reactions of alkyl iodides with CN^- , CN^- , and HS^- is evaluated. Contrary to previous studies, our results reveal competition between the $\text{S}_{\text{N}}2$ and $\text{E}2$ pathways. Discussions cover reaction efficiencies, kinetic isotope effects, linear basicity-reactivity relationships, electrostatic models, and transition state looseness parameters.

In Chapter 5, our investigation of the α -effect in the gas phase shows enhanced nucleophilicity for HOO^- relative to "normal" alkoxides in three separate reaction series validating an intrinsic origin of the effect. Variations in electron affinities and bond strengths between the normal and α -anions indicate that HOO^- has distinctive thermochemical properties.

In Chapter 6, we apply Marcus theory in an attempt to resolve discrepancies between experimental and computational studies on the existence of the α -effect in $\text{S}_{\text{N}}2$ reactions with $\text{CH}_3\text{C1}$. Marcus theory indicates that the intrinsic differences between normal and α -nucleophiles are small and can be easily masked by thermodynamic driving forces.

In Chapter 7, we explore the intrinsic behavior of α -nucleophiles in competitive reaction mechanisms. The α -effect is not seen in the $\text{E}2$ mechanism, but is reported for nucleophilic attack at both sp^2 and sp^3 carbon sites. This is rationalized by "soft" base behavior.

In Chapter 8, the reactivity of 1,3,5-triazine is investigated. Significant hydride acceptor properties are observed. Anion-arene binding modes and their influence on reaction pathways are discussed.

Lemke, Kristen M. (Ph.D., Physical Chemistry, 2011)

Negative Ion Photoelectron Spectroscopy: Testing the Limits of Normal Mode Analysis

Thesis directed by Professor W. Carl Lineberger

Abstract

Negative ion photoelectron spectroscopy has been used to study the furanide anion ($\text{C}_4\text{H}_3\text{O}^-$), dihalomethyl anions (CHX_2^- , where $\text{X} = \text{Cl}, \text{Br}, \text{and I}$), the cyanopolyyne anions HC_4N^- and HCCN^- , propadienylidenide (H_2CCC^-), and propargylenide (HCCCH^-). Using this experimental technique in combination with calculations and Franck-Condon simulations, we learn about the electronic and vibrational structure of these molecules.

Furanide is an ideal anion to interrogate using photoelectron spectroscopy. The five-membered ring structure of furanide constrains it to a relatively small geometry change upon photodetachment. Thus, there is substantial Franck-Condon overlap between the wavefunctions of the ground vibrational state of the anion and of the ground vibrational state of the neutral. A prominent origin peak is observed in the photoelectron spectrum, from which we measure its electron affinity (EA). Our standard Franck-Condon analysis, which assumes uncoupled and harmonic normal modes, reproduces the observed photoelectron spectrum. The excellent agreement between simulation and experiment enables the identification of individual vibronic transitions that give rise to the peaks in the spectrum. With peak assignments, we measure the frequencies of several active vibrational modes.

In sharp contrast to the rigid furanide anion, the dihalomethyl anions undergo a large geometry change upon photodetachment. When an electron is removed, the pyramidal anion becomes nearly planar, exciting multiple large-amplitude vibrations. As a result of the large geometry change between the anion and the neutral, the best Franck-Condon overlap occurs with high vibrational levels of the neutral—where mode-coupling and anharmonicity become important. Our standard Franck-Condon analysis breaks down under these circumstances, and the origin peak is unobservable. Only by applying very sophisticated theoretical methods can we interpret the structure of the photoelectron spectra of the dihalomethyl anions.

The cyanopolyyne anions HC_4N^- and HCCN^- are also challenging to investigate via photoelectron spectroscopy. The bent anion becomes quasilinear upon photodetachment to the $^3\text{A}''$ neutral ground state. However, unlike the spectra of the dihalomethyl anions, the origin peaks of HC_4N^- and HCCN^- have observable intensity in their photoelectron spectra. The geometries of the $^1\text{A}'$ excited states are very similar to that of their respective anions, leading to short vibrational progressions and intense origin peaks of the excited states.

Propadienylidenide and propargylenide, both with m/z 38, display very different photoelectron spectra. The rational synthesis made possible by the flowing-afterglow anion source allows selective preparation of the different isomers by choosing the appropriate precursor. Reacting O^- with allene produces primarily H_2CCC^- , which is a relatively rigid molecule that exhibits modest, resolved vibrational progressions with an intense origin peak. The reaction of O^- with propyne yields a mixture of both H_2CCC^- and HCCCH^- we subtract the spectrum of H_2CCC^- to obtain the spectrum of HCCCH^- . Unlike its isomer, HCCCH^- undergoes a significant geometry change when an electron is detached, and the photoelectron spectrum of the ground state of propargylene is characterized by an extended vibrational progression. Again, because the best Franck-Condon overlap occurs with higher vibrational levels of the neutral, assignment of the origin peak is not straightforward, and our standard Franck-Condon simulations are of no help.

. These species illustrate the difficulties involved in probing the electronic and vibrational structure of floppy molecules, as well as the theoretical methods that are required to understand their complex spectra.

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Photoelectron Spectroscopy of Organic Anions

Thesis directed by Professor W. Carl Lineberger

Abstract

Negative ion photoelectron spectroscopy is a very useful tool to investigate the properties of anions and their related neutral molecules. The neutral molecules that are formed when an electron is photodetached are often short-lived reactive radicals, which are difficult to study using other optical spectroscopy techniques. This Thesis comprises several investigations performed on a series of related gas-phase anionic systems; these systems highlight the advantages and challenges associated with negative ion photoelectron spectroscopy. Additionally, a new innovative velocity mass filter was integrated into the existing instrument and its design and performance is described in detail.

The systems studied in this thesis can be coarsely divided into two classes of molecules. First, a series of six-membered aromatic rings are studied, where a nitrogen atom(s) is either inserted into the phenyl ring or is added as a substituent. Anilide ($\text{C}_6\text{H}_5\text{NH}^-$) offers a straightforward example of a rigid molecular system having a simple photoelectron spectrum where all the spectral features are easily assigned. A series of five azinide anions (with 1,2, or 3 nitrogen atoms replacing CH groups) were investigated to understand how the number of nitrogen atom(s) inserted into the phenyl ring and their position within the ring affect the thermochemical properties of the anion and neutral molecules. The photoelectron spectra of all five azinide anions have similar structure, though the measured electron affinities strongly depend on the proximity of the deprotonation site relative to the nitrogen atom(s).

The second class of molecules concerns anions that undergo drastic geometry changes when an electron is photodetached to form the neutral molecule. A series of halocarbene anions (CX_2^- with $\text{X} = \text{Cl}, \text{Br}, \text{I}$) was investigated to definitively determine the energy difference between the ground state singlet and excited triplet state in the neutral carbene. The related dihalomethyl anions (CHX_2^-) are a much more challenging system to understand. The photoelectron spectra display an extended, structured vibrational progression due to the large geometry change between the anion and the neutral. A similar phenomenon is also found in the final two anions studied, $\text{c-C}_4\text{F}_8^-$ and SF_6^- , where high-level theoretical modeling is required to analyze the photoelectron spectra.