

## **Final Scientific/Technical Report**

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**Recipient:** Board of Regents, Nevada System of Higher Education, on behalf of the University of Nevada, Reno

**Project Title:** Hydrocarbon Radical Thermochemistry: Gas-Phase Ion Chemistry Techniques

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### **Executive Summary**

The objective of this project is to exploit gas-phase ion chemistry techniques for determination of thermochemical values for neutral hydrocarbon radicals of importance in combustion kinetics.

Mass spectrometry techniques are used to investigate the activation of ion-molecule reactions as a function of kinetic energy and to monitor the disposal of energy into the products. Modeling the measured reaction cross sections using statistical rate theories allows extraction of reaction threshold energies. These reaction energies yield relative gas-phase acidities, proton affinities, or hydrogen-atom affinities, which may then be used to derive neutral R–H bond dissociation enthalpies using thermochemical cycles involving established electron affinities or ionization energies. The reactive systems employed in these studies include bimolecular proton transfer reactions, hydrogen-atom transfer reactions, and collision-induced dissociation of hydrogen-bonded heterodimer complexes. The targeted hydrocarbon radical species include the dehydrogenation products of oxygen-containing molecules that are increasingly important in synthetically oxygenated fuels and biofuels such as biodiesel and their intermediate combustion products. Such molecules include fatty acids, for example, for which model compounds are carboxylic acids.

This project uses guided ion beam tandem mass spectrometry experiments on proton bound ion clusters. Energy-resolved collision-induced dissociation experiments provide relative gas-phase acidities (negative ion systems) or proton affinities (positive ion systems), which can then be employed to derive energies of neutral hydrocarbon radicals of interest in combustion kinetics using standard thermochemical cycles. High-level computational chemistry calculations are used for kinetics modeling and for thermochemical comparisons. Thermochemical quantities are measured for molecular radicals that are either too large for accurate ab initio energy calculations, or else have complex electronic structures that are challenging for theory.

### **Goals and Accomplishments**

The project succeeded in its primary goal producing new or refined thermochemical values for hydrocarbon radical species of importance in combustion kinetics. The results of this work provide accurate thermochemical information for use in combustion kinetics databases,

computer simulations of combustion, and as benchmarks for theoretical calculations on similar classes of molecules. The research has been published in peer-reviewed scientific journals.[1-9] The project also has provided valuable training for graduate student and postdoctoral research participants.

## Summary of Project Activities

### *Threshold Collision-Induced Dissociation of Hydrogen-Bonded Dimers of Carboxylic Acids [1]*

This work provides gas-phase acidities and of carboxylic acids and enthalpies of formation of the corresponding carboxyl radicals. These radical species are models for intermediates in the combustion of fatty acids contained in biodiesel.

Published abstract [1]: Energy-resolved competitive collision-induced dissociation is used to investigate the proton-bound heterodimer anions of a series of carboxylic acids (formic, acetic, and benzoic acid) and nitrous acid with their conjugate bases. The dissociation reactions of the complexes  $[\text{CH}_3\text{COO-HOOCH}]^-$ ,  $[\text{CH}_3\text{COO-H-ONO}]^-$ ,  $[\text{HCOO-H-ONO}]^-$ ,  $[\text{C}_6\text{H}_5\text{COO-H-OOCH}]^-$ , and  $[\text{C}_6\text{H}_5\text{COO-H-ONO}]^-$  are investigated using a guided ion beam tandem mass spectrometer. Cross sections of the two dissociation channels are measured as a function of the collision energy between the complex ions and xenon target gas. Apparent relative gas-phase acidities are found by modeling the cross sections near the dissociation thresholds using statistical rate theory. Internal inconsistencies are found in the resulting relative acidities. These deviations apparently result from the formation of higher-energy conformers of the acids within the complex ions induced by double hydrogen bonding, which impedes the kinetics of dissociation to ground-state product acid conformations.

### *Hydrogen Atom Transfer Reactions of $\text{C}_2^-$ , $\text{C}_4^-$ , and $\text{C}_6^-$ : Bond Dissociation Energies of Linear $\text{H-C}_{2n}^-$ and $\text{H-C}_{2n}$ ( $n = 1, 2, 3$ ) [2]*

Experimental determinations of the C-H bond dissociation energies of ethynyl radical,  $\text{HC}_2^\cdot$ , and the polyynyl radicals  $\text{HC}_4^\cdot$  and  $\text{HC}_8^\cdot$ , which are of interest in the pyrolysis of acetylene.

Published abstract [2]: The reactions of  $\text{C}_2^-$ ,  $\text{C}_4^-$ , and  $\text{C}_6^-$  with  $\text{D}_2\text{O}$  and  $\text{ND}_3$  and of  $\text{C}_4^-$  with  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_6$  have been investigated using guided ion beam tandem mass spectrometry. Hydrogen (or deuterium) atom transfer is the major product channel for each of the reactions. The reaction threshold energies for collisional activation are reported. Several of the reactions exhibit threshold energies in excess of the reaction endothermicity. Potential energy calculations using density functional theory show energy barriers for some of the reactions. Dynamic restrictions related to multiple wells along the reaction path may also contribute to elevated threshold energies. The results indicate that the reactions with  $\text{D}_2\text{O}$  have the smallest excess threshold energies, which may therefore be used to derive lower limits on the C-H bond dissociation energies of the  $\text{C}_{2n}\text{H}^-$  and  $\text{C}_{2n}\text{H}$  ( $n = 1-3$ ) linear species. The experimental lower limits for the bond dissociation energies of the neutral radicals to linear products are  $D_0(\text{C}_2\text{-H}) \leq 460 \pm 15$  kJ/mol,  $D_0(\text{C}_4\text{-H}) \leq 427 \pm 12$  kJ/mol, and  $D_0(\text{C}_6\text{-H}) \leq 405 \pm 11$  kJ/mol.

*Statistical Rate Theory and Kinetic Energy-Resolved Ion Chemistry: Theory and Applications* [3]

Exposition of the theory and modeling of energy-resolved reaction cross sections and threshold collision-induced dissociation experiments, as developed by the PI in collaboration with the coauthors at the University of Utah and Wayne State University and used for analysis of experimental work in this project. Feature article in the *Journal of Physical Chemistry A*.

Published abstract [3]: Ion chemistry, first discovered 100 years ago, has profitably been coupled with statistical rate theories, developed about 80 years ago and refined since. In this overview, the application of statistical rate theory to the analysis of kinetic-energy-dependent collision-induced dissociation (CID) reactions is reviewed. This procedure accounts for and quantifies the kinetic shifts that are observed as systems increase in size. The statistical approach developed allows straightforward extension to systems undergoing competitive or sequential dissociations. Such methods can also be applied to the reverse of the CID process, association reactions, as well as to quantitative analysis of ligand exchange processes. Examples of each of these types of reactions are provided and the literature surveyed for successful applications of this statistical approach to provide quantitative thermochemical information. Such applications include metal-ligand complexes, metal clusters, proton-bound complexes, organic intermediates, biological systems, saturated organometallic complexes, and hydrated and solvated species.

*Low-Energy Photoelectron Imaging Spectroscopy of Nitromethane Anions: Electron Affinity, Vibrational features, Anisotropies, and the Dipole-bound State* [4]

Collaboration by the PI of the present project on analysis of photoelectron spectra of anions, which are used to obtain the electron affinities of radical species used along with the gas phase acidities measured in the PI's laboratory to determine neutral bond dissociation energies. This collaboration focused on photoelectron spectra of weakly bound anionic species. The PI of the present project contributed the model and analysis of Franck-Condon factors for the torsional mode of nitromethane anion.

Published abstract: We present low-energy velocity map photoelectron imaging results for nitromethane anions. The photoelectron spectrum is interpreted with the aid of ab initio theory and Franck-Condon factor calculations. We obtain a new value for the adiabatic electron affinity of nitromethane of  $(172 \pm 6)$  meV and observe the dipole-bound state of nitromethane. The photoelectron angular distributions of the observed features are discussed in the context of threshold laws for photodetachment.

*The Photoelectron Spectrum of  $\text{CCl}_2^-$ : The Convergence of Theory and Experiment After a Decade of Debate*; [5] *Photoelectron Spectra of Dihalomethyl Anions: Testing the Limits of Normal Mode Analysis* [7]

These collaborative works focus on the Franck-Condon analysis of photoelectron spectra of species that are not amenable to the standard harmonic oscillator normal mode approach in Cartesian displacement coordinates. The PI adapted methods using for the Franck-Condon analyses of these systems in internal coordinates, accommodating the large energy changes.

Published abstract [5]: We report the 364-nm negative ion photoelectron spectra of  $\text{CHX}_2^-$  and  $\text{CDX}_2^-$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ . The pyramidal dihalomethyl anions undergo a large geometry change upon electron photodetachment to become nearly planar, resulting in multiple extended vibrational progressions in the photoelectron spectra. The normal mode analysis that successfully models photoelectron spectra when geometry changes are modest is unable to reproduce qualitatively the experimental data using physically reasonable parameters. Specifically, the harmonic normal mode analysis using Cartesian displacement coordinates results in much more C-H stretch excitation than is observed, leading to a simulated photoelectron spectrum that is much broader than that which is seen experimentally. A  $(2 + 1)$ -dimensional anharmonic coupled-mode analysis much better reproduces the observed vibrational structure. We obtain an estimate of the adiabatic electron affinity of each dihalomethyl radical studied. The electron affinity of  $\text{CHCl}_2$  and  $\text{CDCl}_2$  is 1.3(2) eV, of  $\text{CHBr}_2$  and  $\text{CDBr}_2$  is 1.9(2) eV, and of  $\text{CHI}_2$  and  $\text{CDI}_2$  is 1.9(2) eV. Analysis of the experimental spectra illustrates the limits of the conventional normal mode approach and shows the type of analysis required for substantial geometry changes when multiple modes are active upon photodetachment.

Published abstract [7]: We report new 351 nm negative ion photoelectron spectra of  $\text{CCl}_2^-$ ,  $\text{CBr}_2^-$ , and  $\text{CI}_2^-$ . This study was undertaken in an attempt to understand the major discrepancy between dihalocarbene ( $\text{CX}_2$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) singlet–triplet splittings reported by our laboratory and new theoretical values. Our recent experiments show that a dihalomethyl anion ( $\text{CHX}_2^-$ ) contaminant in the dihalocarbene anion beam, previously considered insignificant, made a major contribution to the reported  $\text{CX}_2^-$  photoelectron spectra. Thus, the interpretations of the earlier  $\text{CX}_2^-$  spectra and the reported singlet–triplet splittings were incorrect. Replacing  $\text{O}^-$  with  $\text{OH}^-$  in the anion formation process yields a pure dihalomethyl anion, whose highly structured photoelectron spectrum can be subtracted from the contaminated spectrum, yielding a clean  $\text{CX}_2^-$  photoelectron spectrum. The new  $\text{CCl}_2$  photoelectron spectrum displays resolved vibronic transitions to the two lowest electronic states of  $\text{CCl}_2$ :  $\text{X } ^1\text{A}_1$  and a  $^3\text{B}_1$ . The electron affinity of  $\text{X } ^1\text{A}_1 \text{ CCl}_2$  is 1.593(6) eV. A large change in geometry between the anion and the neutral triplet state precludes the direct observation of the triplet origin. The energy difference between the  $\text{X } ^1\text{A}_1$  and a  $^3\text{B}_1$  states of  $\text{CCl}_2$  is estimated to be  $\sim 0.9(2)$  eV, consistent with high-level theoretical studies. While we confirm similar dihalomethyl anion contaminants in the earlier photoelectron spectra of  $\text{CBr}_2^-$  and  $\text{CI}_2^-$  and report new photoelectron spectra for these ions, the paucity of resolved features in the spectra provides limited additional thermochemical information.

*Pulsed ion extraction diagnostics in a quadrupole ion trap linear time-of-flight mass spectrometer*; [6] *Optimization of a quadrupole ion storage trap as a source for time-of-flight mass spectrometry* [8]

Instrumentation projects toward the project goal of analyzing the product velocity distributions of ion-molecule reactions for refined thermochemical determinations. These results optimized and provided diagnostics the quadrupole ion trap to be as an ion source for energy-resolved reaction measurements.

Published abstract [6]: Pulsed extraction techniques are investigated for a quadrupole ion trap (QIT) interfaced to a linear time-of-flight (TOF) mass analyzer. A nonfocusing short-pulse mode

of operation is developed and characterized. The short-pulse mode creates a near-monoenergetic ion packet, which is useful for reaction kinetics experiments and for making diagnostic measurements of the ion cloud size in the trap. Monopolar and bipolar pulsing modes, with the voltage pulses applied to one or both QIT endcaps to extract the ions into the TOF region, are compared. Ion TOF peak distributions are characterized experimentally and by ion trajectory simulations. Also, first-order spatial (Wiley–McLaren) focusing of ions is characterized for the conventional long-pulse extraction mode. The nonparallel fields in the QIT, which serves as the first acceleration region in the linear-TOF mass spectrometer, are shown to degrade spatial focusing and mass resolution.

Published abstract [8]: Designs of a quadrupole ion trap (QIT) as a source for time-of-flight (TOF) mass spectrometry are evaluated for mass resolution, ion trapping, and laser activation of trapped ions. Comparisons are made with the standard hyperbolic electrode ion trap geometry for TOF mass analysis in both linear and reflectron modes. A parallel-plate design for the QIT is found to give significantly improved TOF mass spectrometer performance. Effects of ion temperature, trapped ion cloud size, mass, and extraction field on mass resolution are investigated in detail by simulation of the TOF peak profiles. Mass resolution ( $m/\Delta m$ ) values of several thousand are predicted even at room temperature with moderate extraction fields for the optimized design. The optimized design also allows larger radial ion collection size compared with the hyperbolic ion trap, without compromising the mass resolution. The proposed design of the QIT also improves the ion–laser interaction volume and photon collection efficiency for fluorescence measurements on trapped ions.

*Energy-Resolved Collision-Induced Dissociation of Peroxyformate Anion: Enthalpies of formation of Peroxyformic Acid and Peroxyformyl Radical [9]*

The peroxyformyl radical  $\text{HCOO}\cdot$  is an important intermediate in the oxidation of  $\text{HCO}\cdot$  in combustion and the atmosphere from hydrocarbon emissions. This work from the project provides the first experimental enthalpies of formation of peroxyformic acid,  $\text{HCOOH}$ , and the peroxyformyl radical.

Published abstract [9]: We measure the oxygen–oxygen bond dissociation energy of the peroxyformate anion ( $\text{HCO}_3^-$ ) using energy-resolved collision-induced dissociation with a guided ion beam tandem mass spectrometer. The analysis of the dissociation process from  $\text{HCO}_3^-$  ( $^1\text{A}'$ ) to  $\text{HCO}_2^-$  ( $^1\text{A}_2$ ) +  $\text{O}(^3\text{P})$  requires consideration of the singlet–triplet crossing along the reaction path and of the competing  $\text{OH}^-$  and  $\text{O}_2\text{H}^-$  product channels. The measured oxygen–oxygen bond dissociation energy is  $D_0(\text{HCO}_2^-\text{--O}) = 1.30 \pm 0.13$  eV ( $126 \pm 12$  kJ/mol). This threshold energy measurement is used in thermochemical cycles to derive the enthalpies of formation for peroxyformic acid,  $\Delta_f H_0(\text{HCO}_3\text{H}) = -287 \pm 19$  kJ/mol, and peroxyformyl radical,  $\Delta_f H_0(\text{HCO}_3\cdot) = -98 \pm 12$  kJ/mol. These values are in good agreement with computational energies.

### *Threshold Collision-Induced Dissociation Experiments for the Determination of Gas-Phase Acidities of Isomeric Butanols and Hexanols*

Experimental work in progress for future publication. The four isomeric structures of butanol have garnered attention as a components of biofuels. This work in progress as of the end of the grant period is aimed at determining the relative gas-phase acidities of isomeric alcohols using threshold collision-induced dissociation experiments on proton-bound alkoxide anion complexes. Combined with photoelectron spectra of the corresponding anions (the deprotonated alcohols), this work will provide gas-phase O-H bond dissociation energies of the isomeric alcohols and enthalpies of formation of the alkoxyl radicals.

### *Experimental Examination of the Proton Affinity of Phenoxyl Radical*

Preliminary experimental work in progress for future publication. The OH bond dissociation energy of phenol has been controversial in the past and there remains a discrepancy between the value obtained by the negative ion thermochemical cycle using the gas-phase acidity of phenol and the electron affinity of phenoxyl radical vs. the positive ion thermochemical cycle using the proton affinity of the radical and ionization energies of phenol. This work uses energy-resolved collision-induced dissociation of proton-bound complexes, for example  $[\text{C}_6\text{H}_5\text{O-H-NH}_3]^+$  to determine the proton affinity of phenoxyl radical relative to ammonia.

### **Publications from this grant period (July 1, 2008 to December 31, 2013)**

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5. S. W. Wren, K. M. Vogelhuber, K. M. Ervin, and W. C. Lineberger, "The photoelectron spectrum of  $\text{CCl}_2^-$ : The convergence of theory and experiment after a decade of debate", *Phys. Chem. Chem. Phys.* **11**, 4745-4753 (2009).
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9. Nickel, A. A.; Lanorio, J. G.; Ervin, K. M. "Energy-resolved collision-induced dissociation of peroxyformate anion: Enthalpies of formation of peroxyformic acid and peroxyformyl radical", *J. Phys. Chem. A.* **2013**, *117*, 1021-1029.