Energy-Resolved Collision-Induced Dissociation Studies for Ion Thermochemistry: Bond Dissociation and Competitive Threshold Measurements

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Abstract

Energy-resolved competitive threshold collision-induced dissociation (TCID) measurements for radical species relevant to combustion were made using a guided ion beam tandem mass spectrometer. These ion thermochemistry methods can be used to obtain thermochemical properties of these neutral radicals through the use of thermochemical cycles. The high reactivity of radical species often makes them challenging to directly measure. Study of the peroxyformate anion (HC(O)OO⁻) revealed a singlet-triplet crossing in the oxygen-oxygen bond dissociation channel. Analysis of the thresholds gives the first experimentally determined enthalpies of formation for both peroxyformic acid and the peroxyformyl radical. We have also studied the TCID of linear and branched hexanol (C₆H₁₃OH) complexed with fluoride and acetylide to determine their gas-phase acidities. The role of conformation on the gas-phase acidities of 1-hexanol and 3, 3-dimethyl-1-butanol was explored using modified microcanonical statistical rate theory (RRKM) models with internal rotations treated as one-dimensional hindered rotors. These six-carbon primary alcohols have the same “intrinsic” gas-phase acidity, defined as deprotonation without conformational relaxation, but differ in observed acidity due to conformational stabilization of the anion.
Acknowledgements

First and foremost I would like to thank my advisor, Kent Ervin. To simply say that he is a great scientist, patient mentor, knowledgeable colleague and good friend would be a complete disservice to what I have come to learn during my time at University of Nevada, Reno so in true Ervin tradition I have collected multiple measurements and conservatively approximated the error after thorough analysis.

Previous acknowledgement sections of dissertations from former Ervin group members were analyzed gave initial indication that there might be some factual basis to the claim made above. Dr. Vince DeTuri included this comment in his dissertation, “His advice, unending questions, and critical reviews have helped to shape my attitude and approach to science. I am also indebted to Kent for making graduate school a rewarding and enjoyable experience.”

There was some concern that this data could be a geographically isolated phenomenon unique to the Reno area until some data came from Dr. Ervin’s former doctoral advisor, Dr. Peter Armentrout who had this to say about Kent, “Kent means a great deal to me as he was key to our development of guided ion beam mass spectrometry, doing some of the machining and thought behind the implementation. Our continued collaboration on developing CRUNCH, the software to analyze such kinetic energy dependent data, has also be very useful, with him making key contributions. Kent is an incredible colleague, an excellent and demanding scientist, as well as being a good guy. Wish there were more like him.”

Although the narrative seems fairly clear, more data were required in order to confirm this was not a gender specific effect. Dr. Veronica Bierbaum had this to say in
regards to Dr. Ervin, “Kent has been an incredible colleague and friend! His work is characterized by great creativity and exceptional rigor; his interactions are always supportive and thoughtful. Sharing a few years of science together in Boulder was a joy!”

This sentiment appears to be pressure (elevation) independent as Dr. Mary T. Rodgers further confirmed, “I would describe Kent as being amongst the most conscientious and rigorous scientists I know. I have always appreciated his attention to detail and his willingness, no insistence, on doing top quality science both carefully and comprehensively rather than taking short cuts and only providing superficial analyses that plague too many scientists today.”

Preliminary evidence suggests that Kent may in fact be a great scientist, mentor, colleague and friend although once the relatively few number of data points are each treated each as independent measurements and taking the sum of squares of the error gives a lower limit of a better than average scientist, mentor, colleague, and friend at the 95% confidence level. Clearly, more data needs to be taken and evaluated before any definitive conclusions can be made. (Thank you Kent!)

Thank you to all the past and current members of the Ervin Group. Specifically, my thanks to Dr. Nick Sassin for bringing me into the fold of the Ervin group and showing me the ropes. I thank Dr. Beni Dangi for all the scientific conversations and his relentless attempts to turn me into a soccer player. A special thank you to Jerry Lanorio for his help on all the projects in this dissertation. Finally thank you to the most recent Ervin group member, Surja Ghale.

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# Table of Contents

1 Introduction  
1.1 Ion-Molecule Chemistry 3  
1.2 Combustion Kinetics 4  
  1.2.1 Bond Dissociation Energies 5  

2 Methods 20  
  2.1 Experimental 20  
    2.1.1 Ion Source 20  
    2.1.2 Initial Ion Beam Shaping (Focusing Stage 1 and 2) 22  
    2.1.3 Mass Selection (Magnetic Sector Mass Spectrometer) 23  
    2.1.4 Reactant Ion Beam Shaping (Focusing Stage 3 and 4) 24  
    2.1.5 Reaction Region (Octopoles and Collision Cell) 25  
    2.1.6 Post-collision Ion Beam Shaping, Discrimination, and Counting 27  
  2.2 Data Acquisition 27  
  2.3 Data Analysis 31  
    2.3.1 Collision Cross Section Conversion 31  
    2.3.2 Collision Induced Dissociation Modeling 32  
      2.3.2.1 RRKM Modeling 33  
  2.4 Computational Chemistry Methods 38  
    2.4.1 Geometry Optimization 39  
    2.4.2 Frequency Calculation 39  
    2.4.3 Relaxed Potential Energy Scans 40  
    2.4.4 Hindered Rotor Calculations 41  
    2.4.5 Conformation, Symmetry, and Reaction Path Degeneracy 43  

3 Collision-Induced Dissociation of Peroxyformate Anion 49  
  3.1 Introduction 49  
  3.2 Methods 51
4.8 Conclusions

4.9 Acknowledgements

5 Conclusions

6 Appendicies

6.1 Sample GIB Program LabView Code

6.1.1 Front Panel

6.1.2 Mass Tuner VI

6.1.3 Mass Scan VI

6.1.4 Source Mass Scan VI

6.1.5 EO VI

6.1.6 GIB VI

6.1.7 Magnet Control

6.2 Dihedral Angle Scans

6.2.1 3, 3-dimethyl-1-butanol

6.2.2 bHexanol-F

6.2.3 Branched Hexanol-HCCH

6.2.4 Branched Hexanol

6.2.5 nHexanol

6.2.6 nHex-F

6.2.7 nHex-HCCH

6.2.8 nHexO

6.3 Frequencies
1 Introduction

Gas-phase chemistry plays a critical role in a wide variety of processes and phenomena from human respiration to interstellar cloud formation.\textsuperscript{1,2} Understanding of these events relies on knowledge of the underlying atomic and molecular gas-phase kinetics and reaction dynamics. Individual elementary gas-phase reactions are composed of one or more atoms and/or molecules in several possible combinations of charge state and electronic configuration, including neutrals, ions, neutral radicals, and ion radicals. An observed process such as combustion may actually be composed of multiple elementary reactions involving atoms and molecules from all four of these charge state and electronic configuration combinations.\textsuperscript{3}

Neutral molecules tend to be the most common of the four under ambient conditions because they are typically the least reactive. This low reactivity stems from the fact that the overall charge state is zero and many stable neutrals have no unpaired electrons (closed shell). This usually translates to high activation energies for unimolecular reactions and high barriers for neutral-neutral bimolecular reactions.\textsuperscript{4,5} The higher stability of neutral molecules is both an advantage and disadvantage compared to the other three types of species depending on the situation. Neutral molecules are almost exclusively used in gas-phase measurements that require high concentration in order to achieve statistically significant signal-to-noise ratio. Conversely, low reactivity means that neutral-neutral bimolecular reactions are often energetically unfavorable compared to reactions that involve at least one of the other types of species making them unlikely to significantly contribute to an overall reaction mechanism, especially at temperatures below 300 Kelvin.\textsuperscript{5}
Radicals, molecules with unpaired electrons, are typically much less stable and therefore much more reactive than closed-shell neutral molecules. While much less common in ambient conditions, radical atoms and molecules with one or more unpaired electron often play a significant role in processes such as combustion and atmospheric reactions precisely because they are more reactive. Radical-neutral bimolecular reactions typically have small or no barriers making them far more likely to occur at low temperatures. Higher reaction rates translate to higher product concentration which facilitates experimental studies. Radicals can be difficult to create experimentally in sufficient quantity for reaction measurements. Bimolecular reactions between two radicals are significantly more complicated than other bimolecular reactions because they involve multiple potential energy surfaces. There have been relatively fewer experimental measurements of this type of bimolecular reaction due to the significant challenge of creating two unstable radicals while being able to accurately measure or estimate at least one of the radical’s absolute concentration.

Ions also often play an important role in gas-phase chemical reactions. Similar to radicals, atoms and molecules in non-neutral charge states are often open shell and have high reactivity, and are consequently much less common than their neutral counterparts in ambient conditions. Experimentally, the charge on ions makes it possible to mass select, direct, and accelerate (or decelerate) to a significantly greater degree than neutrals or radicals. In ion-neutral bimolecular reactions, the electric charge has a significant effect on the reactivity and subsequently its corresponding potential energy surface. The charge on an ion induces an electric dipole on the neutral reactant. This force dominates the overall electrostatic interaction between the two species which is important because it is stronger,
longer range and less directionally dependent than the long-range forces between species in neutral charge states.\textsuperscript{5} Fundamentally, this means that reactions involving ions have a larger cross section, which translates to higher frequencies of collision and subsequently higher probability of reaction.\textsuperscript{6} The dominance of the ion-induced-dipole term makes radical ions best thought of as a special subset of ions.\textsuperscript{2,7,8} In addition to disadvantages associated with high reactivity, the charge on ions can be a limitation as ion concentration is limited by the space-charge effect where similarly charged, closely spaced ions repulse one another.\textsuperscript{9,10}

Ideally, each species and elementary reaction could be produced and isolated under controlled experimental conditions. In reality many of the intermediate species cannot be directly studied for a variety of reasons. Fortunately neutrals, ions and radicals are all related by thermochemical cycles. Figure 1 is an example of an energy level diagram that relates cationic, anionic, neutral and radical species. This relationship allows scientists to gain thermochemical insight into various intermediate species through study of its corresponding neutral, radical, or ion.

1.1 Ion-Molecule Chemistry

Ion-molecule chemistry is a subset of gas-phase chemistry that focuses on ions. Study of this subject is particularly useful for reaction dynamics and kinetics.\textsuperscript{11} Ion-molecule chemistry is particularly suited for gas-phase chemists interested in studying thermodynamic properties such as minimum reaction enthalpies, where the ability to finely control ion kinetic energy allows chemists to collide energy-selected ions with neutral molecules and measure these enthalpies. Mass spectrometry allows ions to be selected and isolated according to their mass-to-charge ratio. Experimental thermochemical measurements from
ion-molecule chemistry are often important in models of larger processes and systems such as combustion and the atmosphere.

1.2 Combustion Kinetics

Combustion chemistry is the study of exothermic reactions between a fuel and an oxidizing agent. A classic example of a combustion reaction is:

\[
C_n H_m + \left(n + \frac{m}{4}\right) O_2 \rightarrow nCO_2 + \frac{m}{2} H_2 O
\]  

(1.1)

where a hydrocarbon reacts with oxygen to form carbon dioxide and water. While this idealized overall reaction seems relatively straightforward, numerous elementary reactions required for this overall reaction that makes this process quite complicated. Methane combustion in pure oxygen involves at least 12 chemical species and 22 reactions. More accurate models use at least 40 species and 207 reactions. The standard model for combustion of methane in air involves 53 species and 400 reactions. The complexity of the model, number of species and reactions, increases at a near exponential rate with increasing number of carbons in the straight chain hydrocarbon fuel (Figure 2). The accuracy of these models is dependent on the accuracy of the thermodynamic data, specifically the enthalpy, entropy and heat capacity of the species involved.

Recent emphasis on alternatives to hydrocarbon fossil fuels has led to interest into biofuels, specifically alcohols. Currently most biofuels are ethanol-based, but for a variety of reasons ethanol may not be viable in the future. Research into the combustion of longer chain alcohols has been popular recently because of their higher energy content and lower water affinity. Similar to hydrocarbon combustion, alcohol combustion involves many intermediate species and elementary reactions. Proposed 1-hexanol combustion
mechanisms include as many as 600 species and 2977 reactions. Many of the species and reactions found in long chain alcohol combustion are the same as those found in hydrocarbon combustion. Although this reduces the number of new thermochemical values required for modeling, the accuracy of thermochemical data for shared species and reactions affect the accuracy of both combustion models.

Thermochemical data is used in combustion modeling to determine the bond dissociation energy, which is typically used in a modified Arrhenius equation (1.2) to determine the reaction rate, \( k \):

\[
k = A_0 T^n e^{-\frac{E_a}{RT}}
\]  

\( A_0 \) is the pre-exponential factor which is scaled by the temperature to the \( n \)-th power, \( T^n \), in order to account for the non-Arrhenius behavior of \( A_0 \). \( R \) is the gas constant and \( E_a \) is the activation energy. The bond dissociation energy is often assumed to be the activation energy in elementary steps in combustion reactions. In some cases, such as radical recombination, more complete statistical mechanical rate formulations are required. Independent measurements of the bond dissociation energies are necessary for full validation and implementation of combustion kinetic models.

1.2.1 Bond Dissociation Energies

Bond dissociation energies can be determined in four different ways: experimentally measured, derived from experimental thermochemical data, estimated by group additivity methods, or calculated computationally. Thermochemical data, specifically the enthalpy of formation, for many stable species are known to high accuracy through techniques such as bomb calorimetry and many tables of compiled experimental data exist.
where the species is not stable, such as for hydrocarbon radicals, indirect methods, computational or group additivity methods are used.\(^{14,15,33}\) Commonly used composite theoretical methods such as G4 and CBS-QB3 have a reported error of \(4 - 5 \text{ kJ mol}^{-1}\).\(^{34-37}\) Thermochemical data for larger molecules that are too computationally expensive for these type of calculations can be calculated at lower levels of theory or through group additivity methods, often resulting in errors of \(20 \text{ kJ mol}^{-1}\) or more.\(^{15}\) More direct experimental measurements of bond dissociation energies are critical for validating and improving combustion models.\(^{3,16,38,39}\)

Experimental measurements of hydrocarbon bond dissociation energies typically come from three methods: radical kinetics, photoionization mass spectrometry, and thermochemical cycles.\(^{40,41}\) Each method is experimentally an independent measurement of one another. Radical kinetics methods independently measure the forward and reverse rate of a reactions such as a hydrogen abstraction between a halide, \(X\), and a molecule of interest, \(RH\):

\[
x \cdot + RH \xrightarrow{k_1} HX + R \cdot
\]

The reaction rates are measured as a function of time by fluorescence\(^{42}\), photoionization mass spectrometry\(^{43}\), or other methods. The measured forward and reverse reaction rates are used to determine the Gibbs free energy of reaction and subsequently the reaction enthalpy (eq. 1.4).\(^{44}\)

\[
-RT \ln \left( \frac{k_1}{k_{-1}} \right) = \Delta_{\text{rxn}} G = \Delta_{\text{rxn}} H - T \Delta_{\text{rxn}} S
\]
The entropy is typically found theoretically and all these values must be extrapolated back to
standard temperature (298.15 K). The derived reaction enthalpy is then used in conjunction
with the bond dissociation energy of the hydrogen halide to determine the bond enthalpy:

$$\text{DH}_{298} (\text{RH}) = \Delta_{\text{rxn}} H_{298}^{\circ} + \text{DH}_{298} (\text{HX})$$  \hspace{1cm} (1.5)

This method is limited in cases where no side reactions occur.\(^{45}\)

Photoionization mass spectrometry methods use light to ionize and dissociate a
molecule of interest.\(^{46,47}\)

$$\text{RH} + h\nu \rightarrow \text{R}^+ + \text{H} + e^- \hspace{1cm} \text{AE}(\text{R}^+,\text{RH})$$  \hspace{1cm} (1.6)

$$\text{R}^- + h\nu \rightarrow \text{R}^+ + e^- \hspace{1cm} \text{IE}(\text{R}^-)$$  \hspace{1cm} (1.7)

$$D_{\text{b}} (\text{RH}) = \text{AE}(\text{R}^+, \text{RH}) - \text{IE}(\text{R}^-)$$  \hspace{1cm} (1.8)

The cation, R\(^+\), intensity is measured as a function of the photon energy. The minimum
photon energy necessary to dissociate the molecule of interest, called the appearance energy
threshold can be used with measurements of the ionization potential of the radical, R\(^-\) to find
the bond dissociation energy.\(^{48}\) These measurements are limited to relatively rigid molecules
in which photoionization does not drastically change the molecular geometry.\(^{40}\)

Bond dissociation energies can also be determined from thermodynamic
measurements of a molecule’s corresponding ion.\(^{11}\) The thermochemical information of
neutral, radical and an ion species are all interrelated as a result of Hess’s law by
thermochemical cycles.\(^{49}\) For example, the reaction:

$$\text{ROH} \rightarrow \text{RO}^- + \text{H} \hspace{1cm} D(\text{RO}^-\text{H})$$  \hspace{1cm} (1.9)

in which the oxygen bound hydrogen of an alcohol is removed can be determined by
measuring the three corresponding radical and ion reactions:
that form the negative ion thermochemical cycle in Figure 3. Reaction 1.12 is the ionization energy of hydrogen, $\text{IE}(\text{H})$ and is known very precisely. The minimum energy required for reaction 1.11 is called electron affinity of the RO neutral radical ($\text{EA}(\text{RO}^\cdot)$) and can be measured by photoelectron spectroscopy.\textsuperscript{50} This method collides photons with energy greater than the electron affinity of the anion and measures the kinetic energy of the electron ejected by photoexcitation.\textsuperscript{51} The accuracy of this measurement is limited to cases where the change in molecular geometry is small enough to give good Franck-Condon overlap.\textsuperscript{52}

Equation 1.10 is the gas-phase acidity, which is most commonly measured by one of five different types techniques; photoion-pair formation, bracketing, kinetic, equilibrium, and collision-induced dissociation. Photoion-pair measurements are a special subset of photoionization mass spectrometry where equations 1.6 and 1.7 are replaced by,

$$\text{RH} + h\nu_{\text{threshold}} \rightarrow \text{R}^- + \text{H}^+$$

In these experiments, the molecules of interest are either directly or indirectly photo-excited to a long-lived, weakly bound ion-pair state.\textsuperscript{53} This highly excited state is often called a “heavy Rydberg state”\textsuperscript{54} as the anion, $\text{R}^-$, behaves similar to a heavy electron in an excited hydrogen atom. These molecules are exposed to a gentle electric field which causes dissociation. The resulting ion fragment intensity is measured as a function of the initial laser pulse frequency.\textsuperscript{53} This technique is commonly called threshold ion-pair production spectroscopy (TIPPS) and typically has absolute enthalpy accuracies of $\pm$ 1 kJ·mol\textsuperscript{-1}. At
present, this method is limited to small, rigid molecules where the spectrum is not overly complicated and the origin can be accurately identified.\textsuperscript{55,56}

Bracketing measurements in the single collision limit offer a relatively quick and imprecise measurement relative to the other techniques presented. This method is useful in cases where the reverse of an equilibrium measurement cannot be directly measured. Bracketing methods compare the gas-phase acidity of a desired molecule with the acidities of a series of well-known reference acids.\textsuperscript{40} For example if the gas-phase acidity of ROH, $\Delta_{\text{acid}}^\text{H}(\text{ROH})$, could not be determined through other methods one could estimate the gas-phase acidity by examining its reactions with two reference acids, HA and HB,

$$\text{RO}^- + \text{HA} \rightarrow \text{ROH} + \text{A}^- \quad \Delta H_{\text{rxn}} > 0 \quad (1.15)$$

$$\text{RO}^- + \text{HB} \rightarrow \text{ROH} + \text{B}^- \quad \Delta H_{\text{rxn}} < 0 \quad (1.16)$$

where (1.15) is not observed and is assumed endothermic and (1.16) is observed and therefore exothermic. The reactions shown in equations 1.15 and 1.16 indicates that the acidity of ROH falls somewhere between HA and HB. These measurements typically have uncertainty on the order of 13 kJ·mol\textsuperscript{-1}.\textsuperscript{11}

Gas-phase acidities can also be measured with kinetic methods originally developed by Cooks and co-workers.\textsuperscript{57} A proton bound dimer between a molecule of interest, ROH, and a reference acid, HA, is formed and then monitored as it undergoes either metastable or collision-induced dissociation as show in equation 1.17.

$$[\text{RO}^- \text{H} - \text{A}] \rightarrow \text{RO}^- + \text{HA} \quad \text{A}^- + \text{ROH} \quad \frac{k_1}{k_2} \quad (1.17)$$

The intensities of the two ion channels (RO$^-$ and A$^-$), $I_1$ and $I_2$, are measured relative to one another and approximated to be the relative ratio of the two rate constants and subsequently
to the relative difference in free energy associated with the gas-phase acidities through equation 1.18,

\[
\ln \left( \frac{I_m}{I_1} \right) \approx \ln \left( \frac{k_m}{k_1} \right) = \frac{\Delta_m^G - \Delta_1^G}{RT} = \frac{\Delta_m^H - \Delta_1^H}{RT} - \frac{\Delta_m^S - \Delta_1^S}{R} \approx \frac{\Delta_m^H - \Delta_1^H}{RT}
\]  

(1.18)

where \( R \) is the gas constant, \( T \) is the “temperature”, and \( \Delta_m^G, \Delta_m^H, \) and \( \Delta_m^S \) are the free energy, enthalpy, and entropy of activation for channel \( m \). As the name implies, this method is the ratio of the kinetic intensities, not the thermodynamic or equilibrium intensities. The true relationship between kinetic method intensity ratios and equilibrium values is shown in equation 1.19:

\[
\ln \left( \frac{I_m}{I_1} \right) = -\frac{\Delta \Delta H}{RT_{\text{eff}}} + \frac{\Delta \Delta S_{\text{app}}}{R}
\]  

(1.19)

where \( \Delta \Delta H \) is the difference in enthalpies between the two channels, \( T \) is the effective temperature which can be approximately described for metastable dissociation as,

\[
T_{\text{eff}} \approx -\frac{1}{2} \left[ \frac{\Delta_m^H + \Delta_1^H}{R (s-1)} \right]^{1/2} \frac{1}{(2 \nu \tau)^{1/2}} - 1
\]  

(1.20)

where the term \( s \) is the number of vibrational degrees of freedom, \( \nu \) is the classical RRK reaction frequency, and \( \tau \) is the experimental time window.\(^{11,58}\)

The apparent entropy term, \( \Delta \Delta S_{\text{app}} \), in equation 1.19 can be approximated using microcanonical Rice-Ramsperger-Kassel-Marcus (RRKM) theory to be,

\[
\Delta \Delta S_{\text{app}} \approx \Delta \Delta S \left( \langle E_d \rangle \right) = R \ln \frac{W_m^i \left( \langle E_d \rangle - \Delta_m E_o \right)}{W_1^i \left( \langle E_d \rangle - \Delta_1 E_o \right)}
\]  

(1.21)

where \( W_m^i \left( \langle E_d \rangle - \Delta_m E_o \right) \) is the sum of rovibrational states between the internal energy of the proton bound complex, \( \langle E_d \rangle \) and the energy barrier threshold for the \( m \) dissociation
channel. If intensity ratios are from the kinetic method are treated as in equation 1.18 the error associated with the resulting derived relative gas-phase acidity value can have systematic deviations from true relative value by as much as fifty percent of the measurement. Reported experimental uncertainties for these methods are typically much smaller.

Equilibrium methods also measure the relative Gibbs free energy of a reaction. The relative free energy associated with the gas-phase acidity is derived from measurement of the ion intensities of the reactant and product ions in proton transfer reactions such as the one in equation 1.22,

\[ \text{ROH} + \text{A}^- \xrightleftharpoons[k_1]{k_{-1}} \text{RO}^- + \text{HA} \]  \hspace{1cm} (1.22)

where \( k_1 \) and \( k_{-1} \) are the forward and reverse reaction rates of the proton transfer reaction and HA is a reference acid whose free energy associated with acidity is well-known. The ion intensities of the products and reactants are related to the overall observed rate through equation 1.23,

\[ K_T^z = \frac{k_1}{k_{-1}} = \frac{(p_{\text{RO}^-})(p_{\text{HA}})}{(p_{\text{ROH}})(p_{\text{A}^-})} \approx \frac{I_{\text{RO}^-} \cdot p_{\text{HA}}}{I_{\text{A}^-} \cdot p_{\text{ROH}}} \]  \hspace{1cm} (1.23)

where \( K_T^z \) is the overall rate constant at temperature \( T \), \( k_1 \) and \( k_{-1} \) are the forward and reverse rate constants, \( p_m \) is the partial pressure of species \( m \), and \( I_m \) is the ion intensity of the \( m \) ion.

The total rate constant is related to the free energy associated with the proton transfer reaction by the equation and subsequently the free energies corresponding to the gas phase acidities,
These measurements typically give very accurate relative Gibbs free energies with a commonly reported relative error of \( \pm 1 \text{ kJ·mol}^{-1} \). The reported absolute errors for these measurements are significantly higher at roughly \( 8 \text{ kJ·mol}^{-1} \).

Energy-resolved threshold collision-induced dissociation (TCID) techniques are another method to measure the gas-phase acidities that will be the focus of the rest of this work. These measurements use tandem mass spectrometer to measure reaction energy barriers. Ions of interest are created and mass selected using the first mass spectrometer. The charge on the ion allows for fine control of the kinetic energy. The ion of interest passes through a collision cell where it is collided with an inert target gas, typically xenon. In cases where the collision between the target gas and reactant ion have sufficient energy the molecule will dissociate. Reactant and product ion intensities are measured and converted into collisional cross sections (see Methods). These measurements come in two flavors, single channel and competitive, both of which have been used in this work. In single channel measurements the absolute TCID threshold is measured to determine a reaction barrier.60–62 In cases where the reaction is barrierless, these measurements can be used in conjunction with modeling to determine the bond dissociation energy of a given reaction.63–65

Competitive TCID measurements compare the relative difference in barrier heights between competing dissociation channels.66–68 This method is particularly useful in measuring gas-phase acidities via dissociation of proton bound dimers.66,67,69 More detail regarding this method will be discussed in the following chapters.

\[
\Delta_{\text{pr}} G_T^* = -RT \ln K_T^* = -RT \ln \frac{k_1}{k_{-1}} = \Delta_{\text{acid}} G_T^* (\text{ROH}) - \Delta_{\text{acid}} G_T^* (\text{HA})
\]
Figure 1. Energy level diagram showing the relationship between neutral, ion, and radical species. Scaled for $XY = F_2^{30,69,70}$
Figure 2. Number of reactions in straight chain alkane combustion models as a function of the number of carbons.$^{33,42,71,72}$
Figure 3. Energy diagram for the deprotonation of an alcohol. Scaled to methanol.


(39) Sanderson, R. Chemical Bonds and Bonds Energy; Physical Chemistry, a Series of Monographs; Elsevier Science, 2012.


2 Methods

The methods used to arrive at the results in this dissertation can be divided into four categories: experimental, data acquisition, data analysis, and theoretical. All experiments were carried out using a guided ion beam tandem mass spectrometer. Briefly, ions are created, mass selected, collisionally activated at controlled collision energies, collected, analyzed, and counted. The raw, lab frame ion intensity data is converted to center-of-mass frame collisional cross sections. Collision induced dissociation models based on computational frequencies are fit to the analyzed cross sections to find bond dissociation barrier heights that ultimately leads to thermochemical information such as gas phase acidities and enthalpies of formation.

2.1 Experimental

An overview of the guided ion beam tandem mass spectrometer used for these experiments is described below. Extra attention is placed on modifications of the instrument since the last publication. Greater details of individual regions can be found elsewhere.

This instrument can be broken down into seven regions: source, initial ion beam shaping, reactant mass selection, reactant ion beam shaping, molecular collision, post-collision ion collection, and mass detection. A diagram of the overall instrument can be found in Figure 4. Each region will be described in further detail following the order that an ion would pass through the instrument.

2.1.1 Ion Source

The source, as its name implies, is the location where ions of interest are generated. This region begins at the buffer gas inlet and ends at focusing stage 1 nosecone. In typical operation mode, the pressure for the source region ranges from 0.4 Torr to 0.6 Torr,
maintained by a roots blower pump and mechanical pump (Leybold) capable of pumping 165 L/s.

Ions are created by passing atoms and molecules in a helium buffer gas (AirGas 99.99%) through a microwave discharge (Optos MPG-4M Microwave RF Power Generator and an Evenson Microwave Cavity). The cavity creates a microwave-induced plasma consisting of any atoms or molecules within the discharge cavity, their ions, excited states, and electrons. Changing cavity dimensions, gas composition, and microwave amplitude affect the degree of ionization in the plasma, which ultimately determines the number of reactant ions produced. In practice, the amplitude of the microwaves must be kept fairly low due to both electronic constraints (high amounts of reflected power can damage the microwave generator) and physical constraints (higher energy plasmas means higher energy ions which can lead to undesired chemical reactions such as intramolecular rearrangement and polymerization).

The newly formed ions pass by hydrodynamic flow of the buffer gas from the microwave discharge to the flow tube where ions are collisionally cooled and can be used for further reactions by introducing other gases in the flow tube downstream of the microwave discharge. The position of the gas inlet varies depending on the ion desired. To this end, two different flow tube lengths have been used (55 cm and 92 cm). The longer flow tube length allows for greater collisional cooling and more time for reactions but typically decreases the overall ion intensity.

Fluoride complexes were created by introducing hexafluorobenzene into the microwave discharge to create fluoride ions and then complexing those ions with the alcohol of interest in the flow tube. Introducing larger alcohols too close to the discharge tended to
cause the alcohol to fragment. Similarly, the acetylene complexes were created by first creating the acetylide ion using acetylene gas as the precursor and then complexing the ions with the alcohol of interest. Extra care had to be taken when producing the acetylide complexes due to the propensity for longer $C_{2n}H^-$ polymers to form.

### 2.1.2 Initial Ion Beam Shaping (Focusing Stage 1 and 2)

Focusing Stage 1 establishes the lab-frame zero potential energy of the ions and shapes them into a cylindrical ion beam. FS1 is composed of a nosecone with a 1 mm-diameter aperture, 5 cylindrical ion lenses (FS1-A through E), and a set of vertical and horizontal deflectors (FS1-V & FS1-H). Ions reach focusing stage 1 by traversing the flow tube and passing through the nosecone aperture. The nosecone is critical to the overall energy of the ion beam as the collisions in this last high-pressure region are primarily responsible for setting the lab-frame ion beam energy. The nosecone is set to within one volt of earth ground (-1 to 1 V). The other aperture lenses and deflectors focus and direct the ions into focusing stage 2 (FS-2). The baseline pressure of focusing stage 1 is $2 \times 10^{-6}$ Torr. Under normal operation, this region is typically at high $10^{-5}$ Torr. These pressures are achieved by using a diffusion pump (Varian VHS-10 4000 L/s) where the exhaust is then connected to a mechanical pump.

Focusing stage 2 (FS2) accelerates and reshapes the ion beam from cylindrical to a vertical ribbon to improve transmission through the magnetic sector. FS2 is again composed of a series of cylindrical ion lenses follow by two sets of quadrupole doublets. The lengths and spacing between the lenses is important to ion path and can be found documented elsewhere.\(^1\) FS-2 has a baseline pressure of $8 \times 10^{-7}$ Torr and operates at $3 \times 10^{-6}$ Torr. The vacuum is maintained by a 400 L/s diffusion pump (Varian VHS-4).
2.1.3 Mass Selection (Magnetic Sector Mass Spectrometer)

Ions of interest are mass selected by passing the vertical ribbon shaped ion beam through a magnetic sector mass spectrometer. Ions pass through entrance and exit slits before and after passing through the magnetic sector. Ions that hit the entrance slit plate rather than pass through can be measured in the form of current with a picoammeter (Keithley 485). The ion current is typically 0.1 to 1 nanoAmps for these experiments. The ion current can reach higher values, approximately 10 nAmps, when FS2 deflectors are adjusted to focus the ions on the entrance slit plate.

Ions that pass through the first slit are mass selected using a magnetic sector mass spectrometer. This region has a baseline pressure of low $10^{-7}$ Torr and operates at mid $10^{-7}$ Torr. The Ervin group magnetic sector was taken from a 1970s Varian MAT double sector instrument. The magnetic sector mass spectrometer separates ions based on their momentum to charge ratio; when the voltage being applied to the flight tube is constant for fixed acceleration of the ions, the magnetic sector effectively separates by mass-to-charge ratio. Originally, the magnetic sector was powered by the Varian MAT double sector power supply, which has been replaced with a new power supply (Kepco ATE 20-4). To correct for magnetic field drift as a function of time, a gaussmeter (Lakeshore 475) is connected in a feedback loop with the power supply. The gaussmeter has a Hall probe that measures the magnetic field and compares it to a value set by the user. The gaussmeter has a 0 to 10 V analog output that is used to adjust the magnet voltage power supply. The feedback response amplitude and speed must be closely controlled in order to avoid periodic oscillations in the magnetic field. Ions formed in the source with masses within approximately 0.5 mass to
charge (m/z) units cannot be separated by magnetic sector’s meaning both ions will be present downstream of the mass selection region.

Ions leave the mass selection region through the exit slit. Like the entrance slit, ions that hit the slit plate rather than passing through can be measured as a current. In standard operation, where most of the ions of interest are passing through the slit, the current ranges from 0.1 pAmp to 1 pAmp. The magnet voltage can be detuned so that the majority of the ions hit the second slit. In this case, the current ranges from 1 pAmp to 10 pAmp. The magnitude of the difference between the ion current when optimized for transmission and the current when the current is maximized at the second slit is a good indication of the number of ions available for reaction downstream.

2.1.4 Reactant Ion Beam Shaping (Focusing Stage 3 and 4)

Ions are focused, pulsed, bent ninety degrees, re-shaped to a cylindrical ion beam, and decelerated in the reactant ion beam shaping region. Focusing stage three (FS 3) focuses, pulses and bends the ions ninety degrees. This region is composed of a series of ion lenses, two sets of deflector lenses and a quadrupole bender lens. A 500 L/s Edwards E6 diffusion pump maintains a baseline pressure of $2 \times 10^{-7}$ Torr and operating pressure between $2 \times 10^{-7}$ Torr and $5 \times 10^{-6}$ Torr. The FS3 maintains the vertical ribbon ion beam shape for better transmission through the bender lens. A set of deflector lenses toward the front of FS3 serve as method to pulse the ion beam. A plate was added to the end of focusing stage 3 as an alternate method to measure ion transmission through the mass selection region by turning of the ninety degree bender lens.

Focusing stage 4 (FS4) re-shapes and decelerates the ion beam. It is composed of a series of cylindrical ion lenses set at the flight tube voltage, followed by two quadrupole
doublets which convert the beam back to cylindrical shape, and ending with cylindrical ion lenses that decelerate the ion beam from the flight tube voltage to the reaction cell voltage. This region baselines and operates at $2 \times 10^{-7}$ Torr. Decelerating the ion beam at the end of FS 4 is particularly important because it determines the velocity of the ions entering the reaction region. The last lens in FS4, FS 4 E, is exposed to radio-frequency fringe fields originating from the reaction region that causes electronic noise. The power cable to the FS 4 E lens was modified to include an RF choke to prevent this noise from reaching the power supply. This modification was also made to the first lens after the reaction region, FS 5 A.

### 2.1.5 Reaction Region (Octopoles and Collision Cell)

The reaction region accelerates the ion beam, passes the beam through a reaction cell where the reactant ion can undergo collisions with an inlet gas, traps the scattered ions, and accelerates them out of the region. The ions are initially injected into a radio-frequency octopole ion guide. The octopole consists of eight cylindrical rods 0.3175 centimeter (0.1250 inch) in diameter and 33.3 cm (13.1 in) in length. The inner diameter of the octopole is 0.864 cm (0.340 in) which was determined to be the optimal inner diameter for the rod diameter based on modeling by Ervin. The radiofrequency (RF) signal is generated by a custom built RF generator based on the design by Jones and Anderson. The generated signal has a frequency of roughly 5 MHz and a peak-to-peak amplitude that can be set from 0 to 450 V, 400 to 450 V typical. The generated RF signal floats on a DC voltage that fixes the ion beam to the desired laboratory energy.

The ion beam can be reacted or collided with another gas in the collision cell. The collision cell is 14.60 cm in length and is situated near the middle of the first octopole. The
cell has a side inlet for the collisional gas and an outlet attached to a capacitance manometer pressure gauge (MKS 127AA-000.1B). The collision cell is floated at the first octopole’s DC voltage, which fixes the ion beam energy relative to the FS1 nosecone potential. Two 600 L/s 6-inch diffusion pumps (Edwards) keep the baseline and the normal operating pressure without a collision gas for this region at $2 \times 10^{-7}$ Torr for the octopole chamber and below the detection limit, 0.01 mTorr, for the capacitance manometer measuring the gas cell. Introduction of a collision gas to the collision cell raises the chamber pressure to between 1 to $5 \times 10^{-6}$ Torr and 0.03 to 0.20 mTorr in the collision cell. Higher pressures are avoided because of increased multiple collision probability.\textsuperscript{10} The low collision gas pressure means that only 5-10\% of the total reactant ions are collisionally activated. The low percentage of collisionally activated ions makes high reactant ion density critical. The octopole ion guide effectively traps ions scattered by collision and accelerates them toward the second octopole.\textsuperscript{8,11}

The second octopole ion guide accelerates the ion beam out of the reaction region. This octopole increase the time available for activated reactant ions to dissociate and product ions to be trapped. Ions passing from the first octopole to the second are likely to encounter fringe RF fields in the narrow gap between the two octopoles. In order to limit the fringe field effect, the second octopole is floated 0.5 V higher DC than the first octopole which accelerates the ions toward the second octopole and reduces the number of ions lost in the gap. The second octopole is in the same chamber as the first and, as a result, has identical pressures to those found in the first octopole octopole. The second octopole is 67.0 cm long with the same inner and rod diameter as the first octopole.
2.1.6 Post-collision Ion Beam Shaping, Discrimination, and Counting

The post-collision region focuses, mass discriminates and counts ions. This region baselines and operates at high $10^{-8}$ to low $10^{-7}$ Torr, maintained by a 6-inch Edwards 600 L/s diffusion pump. The final focusing stage, focusing stage 5 (FS 5) focuses and accelerates ions for mass discrimination and is composed of 5 lenses. As mentioned previously, FS5 A was modified to decrease the effects of RF fringe fields from the reaction chamber. Ions are mass discriminated by a linear quardupole (Extrel C150) and then detected by an electron multiplier (Photonis or DETech). The resulting signal must then be further amplified and converted into positive pulses (Canberra 2126) for pulse counting (NI-6229 USB).

2.2 Data Acquisition

Successful competitive threshold collision induced dissociation experiments rely upon data from a number of different techniques including but not limited to reactant ion beam tuning, source mass spectra, mass selected ion beam mass spectra, retarding potential analysis scans, and guided ion beam scans. The data acquisition program that performs all of these tasks was re-written in LabVIEW. The LabVIEW visual programming language was chosen for its approachability and extensive instrument driver library. LabVIEW calls programs VI’s and its sub-programs sub VI’s. A more extensive introduction to LabVIEW can be found elsewhere. The data acquisition program is composed of seven VI’s: Ezero Scan, GIB Scan, Mass Tuner, Magnet Control, Lens Voltage Calibration, Mass Scan, and Magnet Mass Scan.

The Magnet Control VI allows the user to remotely control the magnetic sector mass spectrometer used for mass selection. More specifically, this program allows the user to set the parameters of the magnetic field feedback loop. Most of the code for this particular VI
was developed by Lakeshore (gaussmeter manufacturer). An modification made to the original coding was to require the user to enter a desired mass-to-charge ratio setpoint rather than a magnetic field setpoint. This requires more than a simple conversion because the magnetic field reading is highly dependent on the position of the probe and small changes in the position can cause large apparent changes in the magnetic field so additional calibration factors have been added.

Lens Voltage Calibration is another relatively simple VI used to calibrate three important quantities. First, this program calibrates the DC voltages applied to the octopoles. The ability to obtain highly resolved energy measurements depends on the precision and accuracy to which the collision energy is known. The DC voltage potential in the octopole dictates ion translational energy and subsequently ion collision energy. This program also calibrates the response time of the power supply. High voltage, low ripple (high precision) power supplies typically have low slew rate (long response times). The slew rate of the power supply depends on the load and the magnitude of the change in voltage. The program measures the voltage output as a function of time and then fits the curve to an exponential rise to a maximum. The parameters derived from this fit are saved as global variables so they can be used by the other data acquisition VI’s.

The Mass Tuner VI measures ion counts within a set bin time for a user-set mass as a function of time. This program is used in order to tune the instrument for maximum ion transmission. In this VI, the user initially sets the octopole voltages, quadrupole mass, and dwell time values. Once the parameters have been entered, Mass Tuner counts the number of ions reaching the detector within the set dwell time and measures the magnetic field simultaneous. The program then graphically displays ion counts bin as a function of time.
The actual ion counting is performed by a subVI called Count and is a core building block for the data acquisition program. Count uses both of the NI 6229 BNC 80 MHz 32-bit counter/timers, one to ensure that the collection time window (dwell time) is as accurate as possible (base time accuracy 50 ppm) and one to count the number of pulses coming from the constant fraction discriminator. This limits the highest theoretical counting rate to $8 \times 10^7$ counts/sec.

Source Mass Scan and Mass Scan are mass spectra VI’s that have similar program architecture. Mass Scan is a simple quadrupole mass spectrum VI where the number of ions within a given bin time are displayed as a function of the mass. The user sets the octopole energies, high and low mass, mass increment, and dwell time of the mass spectrum. These programs use the Count subVI to achieve accurate ion counting. Source Mass Scan counts ions being created in the source. Similar to Mass Scan, this VI measures ion counts as a function of the mass. In this program, however, the magnetic sector is scanned over a user-entered range of mass-to-charge ratios and the quadrupole mass spectrometer tracks the magnetic sector at low resolution to pass all ions. Ideally both the magnetic sector and the quadrupole would scan at the same speed. In practice, the magnetic sector is controlled by its magnetic field scan rate meaning that the mass-to-charge scan rate is non-linear. To correct for this, the program initially sets the magnet to the initial mass-to-charge ratio and then waits until the appropriate magnetic field is reached. The Count subVI is then called to count ions. This is repeated before every mass. The program allows for some tolerance in the acceptable field reading which can be set by the user. These scans can be saved in comma separated value format (.csv).
E0.vi is a program to set up and record an ion beam retarding potential energy scan. The program scans the octopole DC voltage near the laboratory ion energy zero. It initially takes a number of user-entered parameters to determine the energies it will count the reactant ion. The energy increment is instrumentally limited by the resolution of the NI box analog outputs (16-bit) and the DC voltage power supplies for the octopoles (0-500V range, 5mV jitter). The subVI accounts for these instrumental limits and creates a one dimensional array of energies at which reactant ions will be counted. If the energy increments falls below the minimum threshold, the program will create the array with the minimum possible energy increment. The E0 program creates two additional arrays for saving and viewing the collected data. The Save Array.VI is used to save the total number of counts for a specific ion and energy combination. This is fairly straightforward on the initial scan but with subsequent scans the VI must take the total previous count and add it to the current count. The second array is used to view the number of counts averaged over the number of scans. In order for this to be continuously visualized, each individual total must be averaged over the number of scans after each counting measurement. After each scan, the program calls Save.VI to save the data in .gib format so that it could be read by the data modeling program, CRUNCH.11,14

The GIB VI records energy-dependent ion intensity data that is subsequently converted into cross section measurement data. The program architecture of this VI is similar to that of the E0 VI with a few key differences. The primary differences between the two programs arise because of the added complexity of counting more than one mass and counting with and without a collision gas for background subtraction. The GIB program
also measures the temperature, magnetic field, and pressures immediately before and after a collision gas valve is switched as opposed to measuring only at the beginning of the scan.

2.3 Data Analysis

2.3.1 Collision Cross Section Conversion

Measurements of the reactant absolute ion intensity as a function of lab frame octopole energy are carried out at the beginning and end of each absolute ion cross section measurement. Retarding potential analysis is carried out on these scans in order to characterize the reactant ion beam by identifying the mean reactant ion energy and full-width at half-maximum (FWHM). The numerical derivative of the ion counts as a function of the lab frame energy is fit to a Gaussian function. The average reactant ion energy typically falls between -1 to 1 eV lab frame with a FWHM ranging from 0.15 to 0.35 eV.

Absolute lab frame energies are converted to relative center-of-mass frame energy. This relative energy is the reactant ion’s translational energy available for dissociation. Equation 2.1 converts the lab frame energies to the center-of-mass frame.

\[
E_{cm} = E_{lab} \left( \frac{M_{\text{gas}}}{M_{\text{gas}} + M_{\text{ion}}} \right)
\]  

Equation 2.1 does not account for the thermal motion of the collisional partner. Later analysis accounts for this motion.

Absolute ion counts are converted to experimental cross sections by using a Beer’s law like equation 2.2:

\[
I_{R} = I_{R_{0}} e^{-\sigma_{\text{tot}} n l}
\]
where \( I_R \) is reactant ion intensity, \( \sigma_{\text{tot}} \) is the total cross section, \( n \) is the gas density, \( l \) is the effective length of the collision cell, and \( I_{R_0} \) is the total ion intensity defined as,

\[
I_{R_0} = I_R + \sum I_m
\]  

(2.3)

Individual product cross sections can be determined by equation 2.4 where \( \sigma_m \) is the cross section of product \( m \), \( I_m \) is the intensity of product \( m \) and \( \sum I_m \) is the sum of all product channels.

\[
\sigma_m = \sigma_{\text{tot}} \left( \frac{I_m}{\sum I_m} \right)
\]  

(2.4)

Cross section analysis is repeated for at three to five different Xenon pressures ranging from 0.1 to 1.5 mTorr in the gas cell. The individual product channel cross sections at different pressures are then extrapolated back to zero xenon pressure (eq.2.5).

\[
\sigma_{m,p} = \sigma_{m,p=0} + \alpha_p
\]  

(2.5)

\( \sigma_{m,p} \) is the cross section of product \( m \) at pressure \( p \), \( \alpha \) is the experimentally determined slope and \( \sigma_{m,p=0} \) is the zero xenon pressure cross section. The extrapolation of cross sections to zero pressure ensures that the cross sections are in the single collision limit.

### 2.3.2 Collision Induced Dissociation Modeling

Cross section data are compared to a collision-induced dissociation threshold model based on equation 2.6.\(^{15}\)

\[
P(\varepsilon, E_t) = \sigma_0 N \frac{(E_t - \varepsilon)^{N-1}}{E_t}
\]  

(2.6)

where the energy transfer, \( P(\varepsilon, E_t) \), is a function of the relative collision energy, \( E_t \), and the collisionally transferred energy is \( \varepsilon \). \( \sigma_0 \) is an energy-independent scaling factor and \( N \) is an
adjustable parameter. In the simplest case, the dissociation probability integrated over the available collisionally transferred energy gives a collision induced dissociation cross section (eq. 2.7)

\[ \sigma(E_t) = \int_{E_t}^{E_i} P(\varepsilon, E_t) d\varepsilon \]  

(2.7)

in which the lower bound of this integration is the minimum threshold energy required for dissociation, which results in equation 2.8:

\[ \sigma(E_t) = \begin{cases} \sigma_0 \left( \frac{E_t - E_0}{E_i} \right)^N & E_t \geq E_0 \\ 0 & E_t < E_0 \end{cases} \]  

(2.8)

This function results in the simple hard-sphere line-of-center (LOC) collision model when \( N \) is set to one. In practice the adjustable parameter \( N \) is allowed to deviate from one in order to account for deviations from the hard-sphere LOC model. Equations 2.6, 2.7 and 2.8 have been shown to reproduce experimentally measured energy transfer distributions for CID of \( \text{Co(CO)}_n^- \) ions.\(^{16}\)

### 2.3.2.1 RRKM Modeling

The total internal energy of the collisionally-activated reactant molecule, \( E^* \), dictates the rate of dissociation. The total collisionally activated reactant ion energy can be defined as the sum of the pre-collision internal energy and the total energy transferred by collisional activation, \( E^* = E_i + \varepsilon \). Reactant molecules with total energy greater than the dissociation energy, \( D_0 \), can undergo dissociation.

The dissociation rate for the collisionally-activated molecule can be described using Rice-Ramsperger-Kassel-Marcus (RRKM) statistical rate theory.\(^{14,17–21}\) RRKM theory states
that the ratio between the number of states between the internal energy, \( E^* \), of the energized molecule and the energy barrier for dissociation, \( E_0 \), of the product and the density of states of the energized molecule at \( E^* \) determines the rate of reaction. The RRKM rate constants, \( k \), are calculated as a function of the total internal energy, \( E^* \), and the angular momentum using equation 2.9,\(^{21}\)

\[
k(E^*, J; E_0) = \frac{sN(r\rho)}{\hbar}(E^* - E^* r(J) - E_0)
\]

where \( s \) is the reaction path degeneracy, \( N(r\rho) \) is the number of available ro-vibrational states with energy \( E \), and \( \rho(E) \) is the density of ro-vibrational states in the reactant molecule, \( E^r(J) \) and \( E_r(J) \) are the overall rotational energies of the transition state (TS) and the reactant molecule, respectively, which are unavailable to promote reaction along the reaction coordinate. Transition states are described as either tight, in which the transition state has the same internal rotations as the reactant molecule, or loose, where the transition state has one or more additional internal rotation(s) not found in the reactant molecule.\(^{22}\) The specific methods for treating these different types of transition states are described in detail elsewhere.\(^{21}\)

The product ions will be detected if the activated ions dissociate during the time-of-flight from the gas cell to the detector. This time limit can result in a decrease in product ion intensity, shifting the apparent threshold for that channel to higher values. This is called a kinetic shift.\(^{23}\) Another complication arises from the fact that there are several competing product channels. This causes product channels with higher energy to shift toward higher energy because of competition from lower-energy products, commonly called a competitive
shift. The detection probability accounting for kinetic and competitive shifts for a given product channel is given by equation 2.10:

$$f_m(E^*, J) = \frac{k_m(E^*, J; E_{0,m})}{\sum_{m=1}^{m_{max}} k_m(E^*, J; E_{0,m})} \left[ 1 - \exp \left( -\tau(E_t) \cdot k_{tot}(E^*, J) \right) \right]$$ \hspace{1cm} (2.10)

where $f_m$ is the detection probability of product $m$, $\tau$ is the experimental time window. The total rate constant for all product channels is given by:

$$k_{tot}(E^*, J) = \sum_{m=1}^{m_{max}} k_m(E^*, J; E_{0,m})$$ \hspace{1cm} (2.11)

where $k_m$ is the rate coefficient for unimolecular dissociation of the reactant ion with internal energy $E^* = E_i + \varepsilon$, and rotational quantum number $J$. The experimentally observed cross section for a given relative translational energy, $E_t$, is determined by combining equations 2.6 and 2.10:

$$\sigma_m(E_t) = \left( \frac{N \sigma_{0,k}}{E_t} \right) \sum_i g_i \int_0^{E_i + E_r + E_{0,k}} (\Delta E)^{N-1} \times \left( \sum_{J=0}^{J_{max}} g_J \rho_{v,J}(E^* - E_r(J)) \left[ f_m(E^*, J) \right] \right) d(\Delta E_t)$$ \hspace{1cm} (2.12)

This resulting cross section, $\sigma_m(E_t)$, is an integration over the “statistically” populated angular momenta:

$$\sigma_m(E_t) = \left( \frac{N \sigma_{0,k}}{E_t} \right) \int_{E_r - E_i}^{E_r} (E_t - \varepsilon)^{N-1} \left( f_m(E^*, J) \right) d\varepsilon$$ \hspace{1cm} (2.13)

As the experimental time window increases or in the case of small molecules rapidly dissociating, the cross section reduces to equation 2.14,
\[ \sigma_m(E_i, E_i) = \begin{cases} \sigma_0 \left( E_i + E_i - E_0 \right)^N & E_i > E_0 \\ 0 & E_i \leq E_0 \end{cases} \]  

which is equation 2.8 with the translational reactant ion energy separated out from the internal energy. This is possible because the ability to separate translational, rotational, vibrational, and electronic motions is one of the basic assumptions of RRKM theory. This equation is commonly known as the modified line-of-centers threshold law and assumes that translational and internal energy are equally effective at promoting dissociation.\(^{15}\)

The electronic, \(E_e\), vibrational, \(E_v\), and rotational, \(E_r\), components of the reactant ion internal energy, \(E_i\), are all assumed to promote reaction equally as shown in equation 2.15:

\[ E_i = E_e + E_v + E_r \]  

(2.15)

The total internal energy is calculated by summation over the internal energy states of the reactant ion. In small systems, this is done explicitly, while in large systems, when summation cannot be done explicitly, the summation is replaced by integrating over the density of states, \(\rho(E_i)\). The density of states distribution is calculated using the Beyer-Swinehart Stein-Rabinovitch algorithm.\(^{25}\) Integrating the experimentally observed cross section (eq. 2.13) over the internal energies results in the cross section for thermal ions at fixed relative collision energies, equation 2.16.

\[ \sigma'_{m} (E_i) = \int_0^x \rho(E_i) \sigma_m(E_i) dE_i \]  

(2.16)

The density of states, \(\rho(E_i)\), for a given ion/molecule is found through a series of computational steps. First the global minimum is found and harmonic oscillator approximated frequencies are calculated. Next internal rotations are identified. Barrier
heights for internal rotation are found by approximating each to be independent, one-
dimensional rigid-rotors. In cases where the barrier height is high, the internal rotor is
considered to be “frozen” and the energy levels are approximated as harmonic oscillators
(HO). In cases where the barrier height is low, the internal rotation is treated as a free rotor.
This rotor has no distinct geometric conformations and its energy levels have become
doubly degenerate. If the barrier height falls somewhere between these two extremes the
internal rotation is treated as a hindered rotor. This case requires special attention because
different geometries can have different potential well depths and/or barrier heights resulting
in conformation dependent energy levels and densities of states. In the case of either free or
hindered rotors, the HO mode that most strongly couples with the internal rotation is
removed and replaced with more accurate energy levels. More computational detail for the
density of state calculations can be found in the theoretical section.

The Maxwell-Boltzmann thermal motion of the xenon target gas in the collision cell
creates a distribution of relative collision energies, which is described by eq. (2.17),

\[
P(E_t, E_{cm}) = \frac{1}{\sqrt{4\pi k_b T E_{cm}}} \left[ \exp \left( -\frac{\sqrt{E_t} - \sqrt{E_{cm}}}{\gamma k_b T} \right) - \exp \left( -\frac{\sqrt{E_t} + \sqrt{E_{cm}}}{\gamma k_b T} \right) \right] (2.17)
\]

\(E_t\) is the actual relative energy of a single collision, \(E_{cm}\) is the relative energy in the
stationary target approximation from equation 2.1, \(\gamma\) is a mass factor defined as

\[
\gamma = \frac{M_{\text{ion}}}{M_{\text{gas}} + M_{\text{ion}}} \quad (2.18)
\]

and \(k_b\) is the Boltzmann constant, and \(T\) is the gas temperature.

The reactant ion beam energy distribution is approximated as a Gaussian function

\[
P(E_{cm}, E_{\overline{cm}}),
\]
\[ P(\overline{E}_{cm}, E_{cm}) = \frac{1}{\sqrt{2\pi}s_{E_{cm}}} \exp \left[ -\frac{1}{2} \left( \frac{E_{cm} - \overline{E}_{cm}}{s_{E_{cm}}} \right)^2 \right] \]  

(2.19)

where \( \overline{E}_{cm} \) is the mean center-of-mass frame energy and \( s_{E_{cm}} \) is one standard deviation of the Gaussian distribution, as measured by the retarding potential analysis described above.

Accounting for these three distributions leads to the Tiernan double integral,

\[ \sigma_{m}(E_{cm}) = \int_0^\infty \sqrt{E_{cm}} \cdot \sigma_{i}(E_i) \cdot P(E_i, E_{cm}) \cdot P(E_{cm}, \overline{E}_{cm}) \, dE_i \, dE_{cm} \]  

(2.20)

where the cross section \( \sigma_{i} \) is the apparent product cross section convoluted over all translational and internal energy distributions and dependent on the average center-of-mass frame energy of the reactant ion \( \overline{E}_{cm} \).

Finally, the apparent cross section, \( \sigma_{m}(E_{cm}) \) in eq. (2.20) is calculated for comparison with the experimental cross section. The adjustable parameters are \( \sigma_0 \), \( N \), and the threshold energies for each product channel. A non-linear least squares fit is performed on these parameters to best replicate the experimental cross section data. These procedures have been incorporated in the CRUNCH data analysis program, which we use to analyze our data.¹⁴

### 2.4 Computational Chemistry Methods

The computational methods used comprise four techniques: geometry optimization, frequency calculations, relaxed potential energy scans, and hindered rotor energy level calculations. Gaussian 09 D.01²⁷ was used for the first three techniques and TORSION²,²⁸ was used to find the hindered rotor energy levels.
2.4.1 Geometry Optimization

All molecular geometries were initially created and optimized by molecular mechanics using Avogadro\textsuperscript{29} in z-matrix format. These initially optimized geometries were then used as the initial geometries for Gaussian\textsuperscript{27}. The molecules were optimized using two different density functional theory (DFT) functionals, B3LYP\textsuperscript{30} and M06-2X\textsuperscript{31}, in conjunction with the 6-311++G(2df,2p) basis set\textsuperscript{32}, as well as a composite method, Gaussian-4 (G4).\textsuperscript{33} B3LYP/6-311++G(2df,2p) was chosen because it is gives good accuracy for frequencies and geometries relative to its cost. The M06-2X functional was specifically chosen because it better estimates non-covalent interactions that can often be underestimated by traditional DFT methods.\textsuperscript{31,34} The Gaussian-4 composite method was chosen because it is an accurate, cost-effective alternate which can be used to compare the relative energies.\textsuperscript{33,35}

2.4.2 Frequency Calculation

Molecular frequencies were calculated at the same levels of theory used for geometry optimization. In all methods the frequencies are calculated under the harmonic oscillator approximation. The B3LYP/6-311++G(2df,2p) frequencies were used for modeling results. Before being included into the model, the B3LYP frequencies were scaled by 0.9679 for frequencies above 104 cm\textsuperscript{-1} and 1.01 for frequencies that fell below this threshold based on the findings of Andersson and Uvdal.\textsuperscript{36} Similar recommended scaling factors can be found with the M06-2X function.\textsuperscript{37} The G4 composite method uses B3LYP frequency calculations and uses the same scaling factors as B3LYP.\textsuperscript{27}
All final geometries were confirmed to be stable minima (no imaginary frequencies). Low-frequency high-amplitude vibrations such as internal torsional modes are not accurately modeled as harmonic oscillators. These models are treated separately as described below.

### 2.4.3 Relaxed Potential Energy Scans

Relaxed potential energy scans are a technique performed to give insight into the potential energy surface along the scanned parameter (bond length, angle, or dihedral angle). These scans begin by optimizing the initial geometry. This initially optimized geometry is then modified by incrementing the value of the scanned parameter by a fixed amount set by the user and then optimizing all other geometry parameters. This process is repeated for the number of steps specified by the user.

Ion complexes are scanned as a function of the bond length required to form the observed products. The anion complexes were scanned over both the O—H and H—X (X = F, CCH) bond length by 0.1 Å for 50 iterations to examine both observed decomposition pathways. These scans are particularly important in order to identify features along the pathway such as multiple wells and reaction barriers that elucidate the reaction path.3,38

The reactant anion complexes as well as all observed collision induced dissociation products were scanned over all dihedral angles to calculate the barrier heights for internal rotation.2 All scans were incremented by 5° degrees for 72 iterations which is more than sufficient for measuring the barrier height.39 In a few instances optimizing the geometry after incrementing the dihedral angle altered the overall molecular conformation and subsequently the relative energy. In cases where the conformational change was relatively small, the relaxed potential energy scan was repeated in the reverse direction (~5° degree increment for 72 iterations) and the two scans were merged into one with the points where the overall
geometry changed removed. In cases where the overall geometry changed drastically, relaxed potential energy scans were performed with additional parameters “frozen” in the initial geometry. The anion complexes also required the inclusion of “dummy” atoms when scanning about the C—O dihedral to prevent C—O—X from becoming collinear and causing the scan to fail because of the undefined dihedral angle.

2.4.4 Hindered Rotor Calculations

The first step for hindered rotor calculations is identification of the molecule’s global minimum energy conformation. The global minimum is typically found by starting geometry optimizations in multiple different conformations, optimizing, and then comparing the relative energies. The lowest energy conformation is then used as the starting geometry for dihedral angle relaxed potential energy scans. There were a few instances in which dihedral angle scans revealed a previously unidentified conformation with lower energy. In such cases, the relaxed potential energy scans were re-calculated using the newly identified, lower energy conformation as the initial geometry.

Dihedral angle relaxed potential energy scans at the global minimum are then used to least-squares fit the barrier height, $V(\phi)$, to a summation of sine and cosine potentials as a function of the dihedral angle, $\phi$:

$$V(\phi) = V_0 + \sum_n \frac{A_n}{2} (1 - \cos(n\phi)) + \sum_n B_n \sin(n\phi)$$  \hspace{1cm} (2.21)

In this expression, $n$ is the periodicity and $A_n$ and $B_n$ are the magnitudes of that periodicity’s sine and cosine contribution toward the overall barrier height. The number of terms in the summation is expanded (up to $n=6$) from previous work in order to better fit less symmetric potentials.\textsuperscript{1,2} The smallest number of terms that accurately fit the relaxed potential energy
scan is used. All relaxed potential energy torsional scans are fit by multiple linear regression in an Excel 2013 spreadsheet.

The reduced one dimensional moment of inertia are calculated by setting the bond between the second and third atom of the dihedral angle as the z-axis and then calculating the moment of inertia from that axis for each atom. The moments of inertia are summed together based on their position along the z-axis relative to the bond resulting in the moments of inertia for the two sides, $I_1$ and $I_2$, of the molecule relative to the dihedral rotation. The total moment of inertia is then found using the equation $^{40}$:

$$\frac{1}{I_{\text{total}}} = \frac{1}{I_1} + \frac{1}{I_2}$$

(2.22)

The total moment of inertia from equation 2.22, was used in conjunction with the terms in the cosine potential from equation 2.21 in a program called TORSION. This program calculates hindered rotor internal energy levels by solving the one-dimensional Schrödinger’s equation using a free rotor basis set.$^{1,2,41}$

The calculated hindered rotor internal energy levels are then incorporated into the density of states.$^{25,42,43}$ In order to maintain the proper degrees of freedom, one of the harmonic vibrational modes must be removed and replaced with the hindered rotor internal energy levels. The harmonic oscillator vibrational frequency is removed based on the degree of the rotation for that given mode. Most often this can be found relatively quickly by visualizing the HO approximated vibrational modes although in a few instances there were multiple vibrations with high degrees of apparent rotational contamination. In such cases, hindered rotor analysis during frequency calculations (freq=hinderedrotor in Gaussian09) was performed in addition to visual inspection to aid in finding the best vibrational mode to be replaced.$^{44-46}$
2.4.5 Conformation, Symmetry, and Reaction Path Degeneracy

Symmetric reactants, transition states, and/or products strongly affect reaction rates. Quantum mechanically, symmetry means that there are multiple indistinguishable spatial orientations separated only by rotation. These orientations have identical potential energy wells and consequently multiple possible reaction paths. It is important to note that this reaction path degeneracy ultimately affects the reaction rate, not symmetry. This subtle but critical point has two important ramifications. First, as the term “path” implies, the energetics must be the same over the entire reaction. Second, reactant and product species must be equivalent, but not necessarily quantum mechanically indistinguishable. A common method for assigning the reaction path degeneracy, \( n \), can be found in equation 2.23,

\[
 n = \frac{m^\dagger \sigma}{m \sigma^\dagger} \quad \text{(2.23)}
\]

where \( m \) and \( m^\dagger \) are the number of optical isomers for the reactant and transition state and the terms \( \sigma \) and \( \sigma^\dagger \) are the symmetry numbers of the reactant and transition state.

Reaction path degeneracy assignment is more complicated than might be initially predicted from equation 2.23. Part of the complication arises from the harmonic oscillator approximation of energy levels. Isomers separated by a small barriers do not have independent energy levels and treating them as separate species will give an incorrect reaction path degeneracy and density of states. Conformations separated by an internal rotation are a common example of isomers that do not have independent energy levels. In such cases it is best to treat the internal rotation as a hindered rotor. In cases where either side of the rotor is symmetric, the calculated density of states must be divided by the symmetry factor for that rotor. This means that a methyl rotor (–CH₃) would be divided by three, for example.
Another complication in reaction path degeneracy assignment occurs in reactions with transition states that are composed of two separated fragments that exhibit long range electrostatic effects upon one another. The interaction between the two fragments hampers the rotational freedom of both fragments. As a result, the symmetry and the density of states of these “nearly loose” transition states are dependent upon both the relative distance and orientation between the fragments. This complication is best accounted for with the use of variational transition state theory that optimizes both the relative distance and orientation.\textsuperscript{47} In order to account for “nearly loose” transition states with non-variational transition state theory, the symmetry of all transition states are varied by a factor of two and incorporated into our overall error.
Figure 4. Guided Ion Beam tandem mass spectrometer.


3 Collision-Induced Dissociation of Peroxyformate Anion\(^i\)

3.1 Introduction

The formyl radical, HCO·, is a reaction intermediate observed in the combustion of a variety of hydrocarbon species.\(^i\) Once formed, the formyl radical will undergo an oxidation reaction, eq. (3.1)\(^2–10\)

\[ \text{HCO} + \text{O}_2 \rightarrow [\text{HCO}_3\cdot] \rightarrow \text{HO}_2\cdot + \text{CO} \]  (3.1)

This reaction is a major source of hydroperoxy radicals, HO\(_2\)·, which play a role in the formation of photochemical smog from volatile organic compounds.\(^{5,11}\) The HCO· + O\(_2\) reaction can also produce HO· + CO\(_2\) products or, at high pressures, the stabilized peroxyformyl radical.\(^{3,4,9}\) Experimental evidence and theoretical calculations imply that the reaction intermediate for reaction 1 is a peroxyformyl radical.\(^{2,3,6–10}\) Matrix-isolation infrared spectroscopic measurements of photolyzed formaldehyde, H\(_2\)CO, in the presence of O\(_2\) show vibrational frequencies assigned to the peroxyformyl radical.\(^{7,13}\) There has been some debate as to whether the radical intermediate is sufficiently vibrationally excited to dissociate directly or whether the peroxyformyl radical (HCOO\(_2\)·) passes through the hydroperoxoxoxomethyl radical complex (HOOC·=O).\(^{8,9}\)

The thermochemistry of peroxyformic acid and the peroxyformyl radical is not yet experimentally established and is addressed in this work using ion chemistry techniques. The

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negative ion thermochemical cycles\textsuperscript{14} for formic acid (HCO$_2$H) and peroxyformic acid (HCO$_3$H) are shown in Figure 5. The negative ion thermochemical cycle, eq. (3.2), relates the gas phase acidity of the acid RH and the electron affinity of the radical $R\cdot$ to the bond dissociation energy of RH.

$$D(R - H) = \Delta_{\text{acid}} H(RH) + \text{EA}(R\cdot) - \text{IE}(H)$$  \hspace{1cm} (3.2)

For formic acid, shown on the left-hand side of Figure 5, these values as well as the enthalpies of formation of formic acid and formyl radical (HCO$_2$·) are fairly well established experimentally.\textsuperscript{15,16,17} Recent experiments by Villano et al.\textsuperscript{10} provide the energetics of the negative ion thermochemistry cycle for peroxyformic acid (HCO$_3$H), shown on the right-hand side of Figure 5. Villano et al.\textsuperscript{10} carried out negative ion photoelectron spectroscopy measurements to determine the electron affinity of the peroxyformyl radical (HCO$_3$·) and flowing-afterglow selected-ion flow tube measurements to determine the gas-phase acidity of peroxyformic acid. That provides the O–H bond dissociation energy of peroxyformic acid,\textsuperscript{10} $D$(HCO$_3$–H), via eq. (3.2). However, because the enthalpy of formation of the parent peroxyformic acid is not known experimentally, neither is the enthalpy of formation of the peroxyformyl radical. Villano et al.\textsuperscript{10} further observed that the peroxyformate anion undergoes collision-induced dissociation to form the formate anion (HCO$_2$–) and an oxygen atom in the ion injection region of their flow tube. In this work, we examine the threshold collision-induced dissociation (TCID) of the peroxyformate anion, eq (3.3),

$$\text{HCO}_3^- + \text{Xe} \rightarrow \text{HCO}_2^- + \text{O} + \text{Xe}$$  \hspace{1cm} (3.3)

where xenon is the target gas, in an energy-resolved fashion using guided ion beam tandem mass spectrometry. In the absence of a reverse activation energy, an assumption addressed herein, the measured reaction threshold energy for reaction 3.3 is equal to the oxygen–
oxygen bond dissociation energy of peroxyformate, $D(\text{HCO}_2^–\text{O})$. This dissociation process connects the thermochemical cycles for formic acid and peroxyformic acid, as shown in the center of Figure 5. Therefore, by measuring the energetics of reaction (3.3), we will be able to derive enthalpies of formation for peroxyformic acid and peroxyformyl radical experimentally for the first time, relative to the known enthalpy of formation of formic acid.

3.2 Methods

3.2.1 Threshold CID Experiments.

Energy-resolved threshold collision-induced dissociation experiments are performed with our guided ion beam tandem mass spectrometer, which can be divided into four regions: a flow tube ion reactor source, a magnetic sector mass spectrometer, a guided ion beam interaction region, and a quadrupole mass spectrometer.

Ions are initially created with a microwave discharge ion source in the flow tube reactor and are thermalized via collisions with the helium carrier gas. The pressure in this region is typically 0.3 to 0.5 Torr. Reactant gases may be introduced into the flow tube downstream of the discharge source to synthesize desired ions via ion-molecule reactions. At the end of the flow tube, ions are collected and gently focused into an ion beam using a series of ion lenses immediately following a nosecone aperture.

The peroxyformate anion is formed in the flow tube reactor source through a four-step process, eqs 4a-4d, using ion–molecule reactions first described by Bowie et al.

$$\text{N}_2\text{O} + e^- \rightarrow \text{O}^- + \text{N}_2 \quad (3.4)$$

$$\text{O}^- + \text{CH}_4 \rightarrow \text{OH}^- + \text{CH}_3 \quad (3.5)$$

$$\text{OH}^- + \text{HOOH} \rightarrow \text{O}_2\text{H}^- + \text{H}_2\text{O} \quad (3.6)$$
First, O⁻ ions are formed by passing N₂O (Airgas, 99.6%) in a helium carrier gas (Airgas, 99.98%) through the microwave discharge, eq. (3.4). Methane (Airgas, 99.0%) is then introduced downstream of the microwave discharge to form OH⁻ ions, eq. (3.5). Approximately 15 cm further downstream the OOH⁻ is created by leaking vapor from a solution of hydrogen peroxide (Sigma Aldrich, 50% by wt. in H₂O), eq. (3.6). The per oxyformate anion is formed by adding methyl formate (Sigma Aldrich, anhydrous >99%) within 1 cm downstream of the hydrogen peroxide, eq. (3.7). After each step in this reaction the product ion signal is optimized. We observe that reactions (3.5) and (3.7) go to completion quantitatively, as determined by ion intensities, while about 75% conversion is observed in reaction (3.6).

The photoelectron spectroscopy measurements by Villano et al.¹⁰ using a very similar ion source confirm that the final product from this series of reactions is exclusively the per oxyformate anion (HCO₃⁻) and not the more energetically favorable carbonate anion (HO₂CO⁻). The analysis of the photoelectron vibronic spectra using Franck-Condon simulations further indicates that the E conformer (“trans”) of per oxyformate is formed, rather than the Z conformer (“cis”), where the notation refers to the conformation around the C–O single bond.¹⁰ In contrast, the neutral acid HCO₃H adopts the Z conformation to take advantage of intramolecular hydrogen bonding with the carbonyl oxygen. Figure 6 shows the structures, relative energies, and isomerization energies of the E and Z conformations for HCO₃H, HCO₃⁻, and HCO₂⁻.

After exiting the flow tube into the first differential vacuum region, the ions are gently accelerated to 1.0 keV and then mass selected using a magnetic sector mass...
spectrometer. For this work, the previous 1970s era Varian/MAT electromagnet power supply and control system\textsuperscript{18} have been replaced. A new power supply (Kepco ATE 25-4DM) is used in conjunction with a precision decade resistor to control the output current. A Lakeview 475 DSP Gaussmeter is used to monitor the magnetic field. Ions are decelerated to a desired ion beam kinetic energy prior to entering the interaction region.

The interaction region consists of a split radio frequency octopole ion beam guide and a gas collision cell.\textsuperscript{20} The gas cell is located in the middle of the first octopole. The rf voltages on the octopole rods trap ions radially and the dc voltages are controlled to fix the translational energy of the ions. Reactant and product ions are extracted from the beam guide region, separated by mass using a linear quadrupole mass filter spectrometer, and detected with a channeltron-type electron multiplier using ion counting. Absolute ion intensities are measured as a function of ion beam energy and masses. Under optimized operating conditions, the peroxyformate ion abundance at the detector is about $10^{6}$ ions/sec.

Retarding potential analysis is carried out to determine the laboratory ion energy before and after the energy-resolved cross section measurements.\textsuperscript{18,23} The measured ion energy spread averages 0.23 eV (full-width at half-maximum). The total experimental cross section is found using a Beer's Law-like relation, as described elsewhere.\textsuperscript{18,23} This process is repeated at three to five different xenon pressures in the range of 0.1 to 0.5 mTorr in the gas cell. These pressure values are then linearly extrapolated to zero xenon pressure, which ensures that the cross sections are in the single-collision limit. To obtain a better measurement of the absolute cross section, detailed pressure dependence studies are carried out at $E_{cm} = 4.0$ eV, in the plateau region where there is little energy dependence of $\sigma(E)$ as shown in the Results section. The calibration using six pressures between 0.1 mTorr and 0.6
mTorr gives $\sigma = 0.29\pm0.02$ Å$^2$ in the zero-pressure limit for the HCO$_2^-$ product in reaction 3 at 4.0 eV. The absolute cross sections presented here have been scaled at 4.0 eV to the values obtained from this calibration.

The TCID cross sections are modeled to obtain threshold energies for competitive product channels as described in detail previously. The model accounts for kinetic and competitive shifts and for internal and translational energy distributions. First, the distribution of the energy transferred to the reactant ion upon a single collision with xenon is modeled using a modified line-of-centers collision theory, \[ P(\varepsilon, E_t) = \sigma_0 N \left( \frac{E_t - \varepsilon}{E_t} \right)^{N-1} \] where $\varepsilon$ is the energy transferred at relative collision energy $E_t$, $\sigma_0$ is a scaling factor for the cross section magnitude, and $N$ is an adjustable parameter. With $N = 1$, eq (3.8) is the distribution for a simple hard-sphere line-of-centers collision model; allowing $N$ to vary accounts for realistic variations from that model. The collisionally activated ion then dissociates at rates described by statistical rate theory. For this work, we use the Rice-Ramsperger-Kassel-Marcus (RRKM) unimolecular dissociation rate constant given by eq 3.9,

\[ k_m \left( E^*, J \right) = \frac{N_m \left( E^* - E_0 \left( m \right), J \right)}{h \rho \left( E^*, J \right)} \] where $k_m$ is the rate constant for product channel $m$, $E^* = \varepsilon + E_i$ is the total internal energy of the energized molecular ion including the collisionally transferred energy $\varepsilon$ and its initial thermal internal energy $E_i$, $J$ is the post-collision rotational quantum number, $E_0(m)$ is the 0 K reaction threshold energy and $N_m(E,J)$ is the sum of rovibrational states at the transition.
state for product channel \(m\), and \(g(E,J)\) is the density of rovibrational states of the energized molecular ion. See previous work for a complete description of the statistical rate treatment including rotational effects.\(^{24,26,27}\) The probability that the collisionally-energized ion will dissociate during its time-of-flight from the gas cell to the mass spectrometer detector is given by eq \(3.10,^{27}\)

\[
f(E^*,J) = \frac{k_m(E^*,J;E_{m_0})}{k_{\text{tot}}(E^*,J)} \left[ 1 - \exp \left( -\tau \cdot k_{\text{tot}}(E^*,J) \right) \right]
\]

(3.10)

where \(f_m\) is the detection probability of product \(m\), \(\tau\) denotes the experimental time window, and \(k_{\text{tot}}(E^*,J)\) is the sum of the rate constants for all product channels. For this work, \(\tau \approx 0.4\) ms near the observed threshold energy. Equations 5–7 are combined as described previously\(^{26,27}\) and convoluted over the experimental translational and internal energy distributions. These calculated model cross sections are fit to the experimental data by a non-linear least-squares regression. The adjustable parameters are \(\sigma_0\), \(N\), and the threshold energies \(E_0(m)\) for each product channel. The CRUNCH data analysis program is used to analyze the data.\(^{31}\)

We can model the transition states (TS) in RRKM theory as either a tight, fixed TS or a loose, orbiting TS.\(^{26,27,30}\) In a tight, fixed transition state the critical configuration has vibrational frequencies at the potential energy barrier (or other critical configuration), except one vibrational mode is removed and treated as the reaction coordinate. In a loose, orbiting transition state, the critical configuration is at the centrifugal barrier for dissociation on the ion–induced-dipole potential, the position of which is analytically determined variationally for each energy and angular momentum. The vibrational frequencies are those of the two fragments plus internal rotations treated as rotations of the free products. The energy of the
loose transition state corresponds to the collision-induced dissociation reaction energy at 0 K, i.e., the energy of product fragments relative to the reactant ion. A more complete description of these two transition state treatments may be found elsewhere.\textsuperscript{24,25,26,27} We also employ a transition state switching model,\textsuperscript{32} in which the dissociation passes through an intermediate. Typically, a tight inner transition state and a loose outer transition state are considered along the dissociation path, a simplification from full variational transition state theory. The transition state with the smallest sum of states at a given energy is considered to be the rate-determining step.\textsuperscript{32} For the transition state switching model, the sum of states $N_{m}(E, J)$ in eq (3.9) is replaced by $N_{m}(E, J) = \min[N_{\text{inner}}(E, J), N_{\text{outer}}(E, J)]$, where the minimum sum of states of the two configurations is evaluated for each energy and angular momentum.

3.2.2 Computational Methods.

Molecular geometry optimization and energy calculations are performed using Gaussian 03\textsuperscript{33} with Density Functional Theory (DFT) at the B3LYP/6-311++G(p,d) level\textsuperscript{34,35} and with coupled-cluster theory at the CCSD(T)/aug-cc-pVDZ level.\textsuperscript{36,37} The (Z)- and (E)-peroxyformate anion for both the singlet and triplet electronic states are included. Similar calculations are performed on the corresponding radical and neutral molecules as well as all observed fragments. Vibrational frequency calculations are carried out at the B3LYP/6-311++G(p,d) level and are scaled by empirical factors of 0.9679 for frequencies and 0.9877 for zero-point energies.\textsuperscript{38} Relaxed potential energy scans are calculated by DFT at the B3LYP/6-311++G(p,d) level to examine reaction pathways. The bond length or angle of interest is varied while all other geometry parameters are optimized. The energies of stationary points, reactants, and products are also calculated using Gaussian-3 at the G3//B3LYP level,\textsuperscript{39} a composite calculation method intended to provide accurate relative
energies that includes additive corrections for large basis sets, correlation energy, and other higher level effects.

3.3 Results

3.3.1 TCID Measurements.

The collisional activation of peroxyformate ions \((m/z = 61)\) with xenon leads to the appearance of three distinct product channels with mass-to-charge ratios of 17, 33, and 45. Experimental TCID cross sections are shown in Figure 7. The collision-induced dissociation products of peroxyformate anion are identified by reactions 3.11-3.13.

\[
\begin{align*}
\text{HCO}_3^- & \rightarrow \text{OH}^- + \text{CO}_2 & 17\frac{m}{z} \ (3.11) \\
\text{HCO}_3^- & \rightarrow \text{O}_2\text{H}^- + \text{CO} & 33\frac{m}{z} \ (3.12) \\
\text{HCO}_3^- & \rightarrow \text{HCO}_2^- + \text{O} & 45\frac{m}{z} \ (3.13)
\end{align*}
\]

The \(\text{HCO}_2^-\) ion has the largest cross section while the other two cross sections have similar, smaller magnitudes. The \(\text{OH}^-\) channel and the \(\text{HCO}_2^-\) channel have similar nominal threshold energies of about 1.2 eV while the \(\text{HO}_2^-\) channel has a higher threshold energy of about 1.6 eV.

An additional apparent product ion from collision-induced dissociation of \(m/z = 61\) ions was observed in preliminary work\(^{36}\) at \(m/z = 43\) (not shown here). This fragment ion must arise from a contaminant \(m/z = 61\) parent ion because it is impossible to lose 18 atomic mass units starting from the peroxyformate anion, \(\text{HCO}_3^-\). The observed CID threshold energy for the \(m/z = 43\) ion of about 0.5 eV is consistent with an electrostatically bound ion-water complex. The likely process is \(\text{H}_3\text{C}_2\text{O}(\text{H}_2\text{O})^- + \text{Xe} \rightarrow \text{H}_3\text{C}_2\text{O}^- + \text{H}_2\text{O} + \text{Xe}\). The intensity of this contaminant product ion was diminished in later work as the ion
source conditions were better optimized and became nearly negligible. The relative abundance of the contaminant ion may slightly affect absolute cross sections, but has no effect on reported energies.

3.3.2 Computational Results.

Relative energies of the peroxyformate anion, HCO$_3^-$, and its various dissociation products are presented in Table 1. Density functional theory energies at the B3LYP/6-311++G(d,p) level are compared with G3//B3LYP and CCSD(T) calculations for selected species.

DFT at the B3LYP/6-311++G(p,d) level is also used to calculate the potential energy surfaces along the various reaction paths. Figure 6 and Table 2 show the potential energies for conversion between the $Z$ and $E$ conformers. The $Z$ to $E$ barriers are found by rotating the dihedral angle in 2° increments and optimizing other geometric parameters. These calculations indicate that the singlet ($E$)-peroxyformate anion is lower in energy by approximately 19 kJ/mol than its ($Z$)-peroxyformate counterpart. The $E$ and $Z$ conformations of triplet peroxyformate anion are approximately the same energy. The barrier height for the $E$ to $Z$ isomerization for the singlet anion is approximately 79 kJ/mol, while there is no barrier in the triplet state. The relative energetics imply that our thermal ion source will produce predominantly the singlet ($E$)-peroxyformate ion, as confirmed experimentally in photoelectron spectroscopy measurements for a similar ion source.$^{10}$ Similarly, the singlet ($E$)-peroxyformyl radical is lower in energy than ($Z$)-peroxyformyl by approximately 8 kJ/mol and the $E$ to $Z$ barrier height for the peroxyformyl radical is 37 kJ/mol. The relative energies between these two conformations switch in the case of the neutral peroxyformic acid because intramolecular hydrogen bonding stabilizes the $Z$
conformation, which is lower in energy than the $E$ conformer by 8 kJ/mol (Figure 6 and Table 2). The barrier for $Z$ to $E$ isomerization for the neutral acid is 64 kJ/mol.

Figure 8 is a schematic potential energy surface of the reactants and products for the collision-induced dissociation process. The DFT energy values in Figure 8 are corrected for vibrational zero-point energies in the harmonic oscillator approximation. The connections between potential energy minima, barriers, and products shown in Figure 8 are all confirmed by relaxed potential energy scans along appropriate coordinates.

Figure 9 shows the DFT potential energy curves for dissociation along the oxygen-oxygen coordinate for singlet and triplet ($E$)-peroxyformate. The cleavage of the O-O bond is simulated by incrementally increasing the oxygen-oxygen bond length by 0.05 Å and optimizing the fragment geometry after each increase in bond length, at the B3LYP/6-311++G(d,p) level. Both $Z$- and $E$-peroxyformate have barrierless dissociations to HCO$_2^-$ + O($^1D$) on the singlet surface. For the triplet state, stretching the O-O bond of peroxyformate shows a small barrier initially, then the energy drops to a minimum before rising to its asymptotic value for HCO$_2^-$ + O($^3P$). The triplet electronic energy is the same as the singlet for the geometry at an O–O bond distance of 1.90 Å. The energy at this electronic crossing point is 72 kJ/mol relative to singlet HCO$_3^-$, which is well below the HCO$_2^-$ + O($^3P$) asymptote of 111 kJ/mol. The same crossing point at the G3//B3LYP level is at 1.98 Å and a slightly higher energy at 82 kJ/mol at 0 K, which is about the same energy relative to the HCO$_2^-$ + O($^3P$) asymptote of 122 kJ/mol at that level.
3.4 Discussion

3.4.1 Reaction Pathways.

The calculated singlet potential energy surface in Figure 8 for HCO$_3^-$ ($^1\text{A}^\prime$) → HCO$_2^-$ ($^1\text{A}_2$) + O($^1\text{D}$) has a dissociation energy of 319 kJ/mol (at 0 K using the G3//B3LYP calculations in Table 1) or 3.31 eV, while we observe a reaction threshold energy of approximately 1.2 eV. This large energy discrepancy clearly indicates that the experimental reaction pathway does not follow the singlet potential energy surface, but rather the ion dissociates to HCO$_2^-$ ($^1\text{A}_2$) + O($^3\text{P}$), which has a calculated dissociation energy of 122 kJ/mol or 1.26 eV. The experimental data thus imply that singlet HCO$_3^-$ undergoes a relatively efficient singlet to triplet transition to form HCO$_2^-$ ($^1\text{A}_2$) + O($^3\text{P}$) products. The observation that the calculated singlet–triplet crossing point is below the product energies on the triplet surface (Figure 9 and Table 1) indicates that the singlet–triplet crossing is accessible along the dissociation path. That is a necessary condition for relating the measured threshold energy to the thermochemical bond dissociation energy, although the necessity of a singlet-to-triplet conversion could affect the dissociation kinetics.

To form either of the other two products, HO$_2^-$ or HO$^-$, the peroxyformate anion must undergo a molecular rearrangement, shown in Figure 8 by a common potential energy barrier and the intermediate HOOCO$^-$ well corresponding to H-atom transfer from the carbon atom to the terminal oxygen atom. The presence of a barrier for this rearrangement agrees with our experimental data, as we observe an energy threshold for HO$^-$ despite the overall exothermicity of that channel. Figure 8 also shows there is a higher asymptotic energy after rearrangement for the HO$_2^-$ channel, which agrees with the observed higher threshold energy for this channel compared with HO$^-$. 
In addition to the H-atom transfer path shown in Fig. 4, the HO\(^{-}\) + CO\(_2\) channel could also proceed via a “roaming” type mechanism,\(^{40}\) in which a nearly-free oxygen atom in the nascent dissociation to HCO\(_2\)^\(^{-}\) + O returns to attack the hydrogen to form OH\(^{-}\) + CO\(_2\). That would be consistent with the observation that the OH\(^{-}\) product channel has nearly the same threshold energy as HCO\(_2\)^\(^{-}\). However, the only roaming-type pathway found in the DFT calculations for singlet HCO\(_3\)^\(^{-}\) → HCO\(_2\)^\(^{-}\) + O\(^{1}\)\(^D\) has a barrier of 2.7 eV, much too high to explain the observed threshold energy of about 1.2 eV. Therefore, if a roaming mechanism is operative for OH\(^{-}\) formation, then it must involve a transition to the HCO\(_2\)^\(^{-}\) + O\(^{3}\)\(^P\) triplet surface followed by another transition back to the singlet surface to form OH\(^{-}\) + CO\(_2\).

3.4.2 Cross Section Modeling.

The experimental reaction cross sections in Figure 7 are modeled using the RRKM theory treatment described in the Methods section (eqs 5-7) from below threshold to the beginning of the plateau region, 0.5 eV to 3.5 eV. Figure 7 shows the experimental data overlaid with the RRKM model fits.

Initial attempts to fit the data\(^{41}\) used empirically determined transition state parameters for each of the three channels. A “tight” transition state uses the frequencies of HCO\(_3\)^\(^{-}\) with one mode removed as the reaction coordinate; a “loose” transition state is at the centrifugal barrier for dissociation using the product molecule frequencies. As reported in preliminary work,\(^{41}\) none of the eight possible combinations of tight and loose transition states could reproduce the observed branching fractions for the three product channels. The cross sections could be fit using empirical scaling factors for individual product channels, but rather large correction factors (over an order of magnitude) were required.\(^{41}\) Therefore, we
are motivated to develop a more sophisticated dissociation model using the calculated potential energy surfaces in Figure 8 as a guide.

The fits to the data shown in Figure 7 employ transition state switching models for each of the three channels, with parameters presented in Table 3. For the \( \text{OH}^- \) and \( \text{O}_2\text{H}^- \) product channels, the inner tight transition state is at the H-atom transfer rearrangement barrier shown in Figure 7 and the outer loose transition state is the orbiting transition state for products. For the exothermic \( \text{OH}^- \) channel, only the tight transition state is limiting and needs to be included in the calculation. Although Figure 7 shows a common rearrangement barrier for \( \text{OH}^- \) and \( \text{O}_2\text{H}^- \), the best fits are obtained by treating the tight transition state energies as independently adjustable. That accounts for the possibility that the \( \text{OH}^- \) channel may also proceed via a “roaming” type transition state along the \( \text{HCO}_2^- + \text{O} \) dissociation coordinate as discussed above. For the \( \text{HCO}_2^- \) channel, the singlet-triplet crossing point is treated as a tight transition state with the O–O stretch as the reaction coordinate. That assumes that the frequency of access to the crossing region depends on the statistical vibrational sum of states at that point with a constant singlet-to-triplet transition probability for each passage through that region. The energy of this tight transition state is fixed to the energy of the singlet–triplet crossing calculated at the G3//B3LYP level. The outer loose transition state for \( \text{HCO}_2^- \) is the orbiting transition state for \( \text{HCO}_2^- + \text{O}(^3\text{P}) \).

Once these transition state parameters are employed, the product branching ratios can be fit with relatively minor optimization of energies from the calculated values and with no adjustable scaling factors for individual product channels. The quality of the fits is reasonably good; in particular, the model reproduces the relative cross section magnitudes of the three channels and the crossing of the cross sections for the \( \text{OH}^- \) and \( \text{O}_2\text{H}^- \) products
near 3 eV. This match of the model with the experimental data bolsters our confidence in the model, even though somewhat better fits for the HCO$_2^-$ channel can be obtained using adjustable scaling factors for the three product channels. The transition state switching model reproduces the competitive branching fractions for the OH$^-$ and O$_2$H$^-$ channels accurately; that implies that the kinetic and competitive shifts for the HCO$_2^-$ channel are estimated reasonably well, which is our primary concern for thermochemical determinations. Because there is a barrierless path via the singlet-triplet crossing for the dissociation reaction (eq 3), we treat the threshold energy for the outer, loose transition state as the thermochemical bond dissociation energy. We therefore report the HCO$_2^-$ + O (3P) threshold energy from the model as our best experimental value for the dissociation energy, giving $D_0$(HCO$_2^-$–O) = 1.30±0.13 eV or 126 ± 12 kJ/mol. This value refers to the lowest-energy E conformation of HCO$_3^-$. This experimental result is in good agreement with the theoretical value of 122 kJ/mol at the G3//B3LYP level (Table 1).

Various sources of uncertainty for the experimental threshold energy are combined as the root-sum-of-squares, treating them as independent sources of error. The uncertainty of the laboratory ion energy determination is estimated as ±0.01 eV. The uncertainty from the energy range of the fit is found by changing the upper energy limit from 3.0 to 4.0 eV. The uncertainty from the statistical rate model is estimated by changing the reaction degeneracies by factors of 2 and 0.5, equivalent to varying the calculated rate constants by those factors; this also accounts for uncertainties in the calculated vibrational frequencies. Because our primary focus is on the energy for the HCO$_2^-$ + O product channel, the transition state energies for the other channels (Table 3) as well as the adjustable $N$ parameter in eq 5 are each varied until the reduced sum of squared residuals ($\chi^2$) doubles to
determine the uncertainty in $D_0(HCO_2^-\text{–}O)$ contributed by correlation with those fit parameters. The calculated energy of the singlet-triplet crossing used in the fit as a non-optimized parameter is varied by $\pm 0.1$ eV. The statistical uncertainty of the threshold energy from the reproducibility of six independent data sets is incorporated into error estimates. The reported error limits represent our estimate of the combined standard uncertainty at the 95% confidence level.

An experimental upper limit for the threshold energy of reaction 3 may be obtained by fitting that channel using a single-channel fit with the modified line-of-centers model, eq 5, and neglecting any reduced probability of the singlet-triplet conversion and any competitive or kinetic shifts. That is, the RRKM model is not included. The single-channel result is $D_0(HCO_2^-\text{–}O) \leq 1.37$ eV, which is indeed higher than the value of 1.30 eV from the full model. This result serves as an additional check on our experimental estimate.

3.4.3 Thermochemical Results.

Our experimental value for the oxygen–oxygen bond dissociation energy of $D_0(HCO_2^-\text{–}O) = 126 \pm 12$ kJ/mol can be used to derive the enthalpies of formation of peroxyformic acid via eq (3.11) and peroxyformyl radical via eq (3.12).

$$
\Delta_f \text{H}(\text{HCO}_3\text{H}) = \Delta_f \text{H}(\text{HCO}_2\text{H}) + \Delta_f \text{H}(\text{O}) + \Delta_{\text{acid}} \text{H}(\text{HCO}_2\text{H}) - D(\text{HCO}_2^-\text{–}O) - \Delta_{\text{acid}} \text{H}(\text{HCO}_3\text{H})
$$

3.11

$$
\Delta_f \text{H}(\text{HCO}_3\cdot) = \Delta_f \text{H}(\text{HCO}_2\text{H}) + \Delta_f \text{H}(\text{O}) - \Delta_f \text{H}(\text{H}) + \Delta_{\text{acid}} \text{H}(\text{HCO}_2\text{H}) - D(\text{HCO}_2^-\text{–}O) + EA(\text{HCO}_3\cdot) - IE(\text{H})
$$

3.12

Equations 11 and 12 use our bond dissociation energy measurement in conjunction with known enthalpies of formation$^{15}$ for formic acid and the negative ion thermochemical cycles for formic acid$^{16}$ and peroxyformic acid,$^{10}$ as shown in Figure 7. The ancillary
thermochemical values\(^{10,15-17}\) are presented in Table 4 along with values derived in the present work. The kinetically determined gas-phase acidity of peroxyformic acid\(^{10}\) is based on proton transfer to the \(E\) conformer of \(\text{HCO}_3^-\) and therefore reflects the higher-energy \(E\) conformer of \(\text{HCO}_3\text{H}\). Villano et al.\(^{10}\) corrected that value to the ground-state \(Z\) conformation of \(\text{HCO}_3\text{H}\) using their calculated \(E\)-to-\(Z\) energy difference at the G3(MP2)//B3LYP level.\(^{39}\) The values in Table 4 for \(\Delta_{\text{acid}}H(\text{HCO}_3\text{H})\) and therefore the derived value for \(\Delta_fH(\text{HCO}_3\text{H})\) via eq 11 thus refer to the ground \(Z\) conformation. Because the experimental values for \(E\text{A}(\text{HCO}_3\text{H})\) and \(D(\text{HCO}_2^-\text{O})\) refer to the \(E\) conformations, the derived value for \(\Delta_fH(\text{HCO}_3\text{H})\) via eq 12 also refers to its ground \(E\) conformation (i.e., no theoretical correction is required). Thermal enthalpy and entropy corrections between 0 K and 298 K are calculated using the harmonic-oscillator rigid-rotor approximation with B3LYP vibrational frequencies. Minor corrections for the thermal populations of the \(E\) and \(Z\) conformations are included using the relative energies from Table 2.

A theoretical value for the enthalpy of formation \(\Delta_fH_{298}(\text{HCO}_3\text{H})\) can be obtained following the method previously established by Villano et al.,\(^{10}\) i.e., by using the isodesmic reaction \((Z)-\text{HCO}_3\text{H} + \text{H}_2\text{O} \rightarrow (Z)-\text{HCO}_2\text{H} + (E)-\text{H}_2\text{O}_2\). The enthalpies of formation of \(\text{H}_2\text{O}, \text{HCO}_2\text{H},\) and \(\text{H}_2\text{O}_2\) are experimentally known; literature values\(^{15}\) are given in Table 4. The calculated enthalpy of the isodesmic reaction is \(\Delta_fH_0 = 20.6\) kJ/mol at the G3//B3LYP level. The resulting isodesmic enthalpy of formation for peroxyformic acid is \(\Delta_fH_0[(Z)-\text{HCO}_3\text{H}] = -283.1\) kJ/mol, which agrees with our experimentally derived value of \(\Delta_fH_0[(Z)-\text{HCO}_3\text{H}] = -287 \pm 19\) kJ/mol (Table 4) well within the experimental uncertainty.
3.5 Conclusions

The measured bond dissociation energy for peroxyformate anion is $D_0(\text{HCO}_2^–\text{O}) = 126 \pm 12 \text{ kJ/mol}$ from our threshold collision-induced dissociation experiments. This is in good agreement with a theoretical value of 122 kJ/mol at the G3//B3LYP level (Table 1). The experimentally determined threshold energy of the formate anion clearly indicates that a singlet to triplet crossing occurs to give ground state products, $\text{HCO}_2^–(^1\text{A}_2) + \text{O}(^3\text{P})$. The ability of the RRKM model to fit the data well with the singlet-triplet crossing point treated as a fixed transition state implies that the singlet-triplet crossing is relatively efficient. Because the electron spin multiplicity is usually expected to be conserved in ion–molecule reactions without heavy atoms (i.e., with small spin-orbit coupling), it is of interest to consider why this process occurs facilely in this case. We note that the other two product channels to form $\text{HO}^–$ or $\text{HO}_2^–$ are effectively blocked near the threshold for $\text{HCO}_2^–$ by the H-atom transfer rearrangement barrier, as shown in Figure 8. Computational work also confirms the presence of a singlet–triplet crossing point on the $\text{HCO}_2^– + \text{O}$ dissociation path with shared geometry located below the asymptotic energy for the formate anion and the ground-state triplet atomic oxygen (Figure 9). Collisional activation of the parent $\text{HCO}_3^–$ ion at energies below the tight H-atom transfer transition state creates a vibrationally excited molecular anion with statistically populated vibrational states. This provides multiple opportunities for the energized peroxyformate anion to pass through the singlet–triplet crossing region. The probability of hopping between these two electronic states on a single pass through the crossing point may well be less than unity, but the probability becomes relatively high when multiplied by many opportunities. Once the crossing occurs, those species are quickly removed by dissociation on the triplet surface.
The oxygen–oxygen bond dissociation energy of peroxyformate connects the formic acid thermochemical cycle, where enthalpies of formation are known, with the peroxyformic acid cycle (Figure 5). This allows us to derive the enthalpies of formation of peroxyformic acid and peroxyformyl radical, as presented in Table 4. We obtain the first experimental determinations of the enthalpies of formation of HCO$_3$H and HCO$_3^\cdot$, $\Delta H_{298}(\text{HCO}_3\text{H}) = -287 \pm 19$ kJ/mol and $\Delta H_{298}(\text{HCO}_3^\cdot) = -98 \pm 12$ kJ/mol, respectively. This work demonstrates the capability of experimental ion chemistry techniques for measurement of thermochemical properties of neutral molecules and radicals that may be difficult to obtain by other methods.

Finally, the enthalpy of the peroxyformyl radical gives some insight into the landscape of the oxidation reaction in eq 1. Relative to HCO$^\cdot$ + O$_2$ reactants, formation of the peroxyformyl radical intermediate is exothermic by $-139 \pm 12$ kJ/mol at 0 K, using auxiliary enthalpies of formation from Gurvich et al.$^{15}$ The formation of HO$_2$ + CO products from the HCO$_3^\cdot$ intermediate is nearly thermoneutral, $-4 \pm 12$ kJ/mol. Although there is a significant rearrangement energy barrier from HCO$_3^\cdot$ to HO + CO$_2$ products, calculated as 98 kJ/mol by a concerted mechanism,$^{6}$ the energy provided by the exothermic formation of the intermediate most likely can drive the reaction at low pressures.

3.6 Acknowledgements

This research is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. We thank Peter B. Armentrout, Veronica M. Bierbaum, William H. Green, Stephen J. Klippenstein, Mary T. Rodgers, Sergey A. Varganov, and Stephanie M. Villano for helpful discussions.


Table 1. Energies relative to the peroxyformate anion.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Species</th>
<th>Configuration</th>
<th>B3LYP/6-311++G(d,p)</th>
<th>G3//B3LYP</th>
<th>CCSD(T)/aug-cc-pVDZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_3^-$ ($^1A'$)</td>
<td>$E$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$Z$</td>
<td>19</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>HCO$_3^-$ ($^3A''$)</td>
<td>$E$</td>
<td>216</td>
<td>256</td>
<td>237</td>
</tr>
<tr>
<td></td>
<td>$Z$</td>
<td>227</td>
<td>267</td>
<td>249</td>
</tr>
<tr>
<td>HCO$_2$–O$^-$</td>
<td>S–T crossing</td>
<td>72</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>HOOCO$^-$</td>
<td>H-transfer well</td>
<td>73</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-transfer t.s.</td>
<td>109</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>OH$^-$ + CO$_2$</td>
<td></td>
<td>$-181$</td>
<td>$-192$</td>
<td>$-188$</td>
</tr>
<tr>
<td>O$_2$H$^-$ + CO</td>
<td></td>
<td>154</td>
<td>142</td>
<td>142</td>
</tr>
<tr>
<td>HCO$_2^-$ + O($^3P$)</td>
<td></td>
<td>111</td>
<td>122</td>
<td>119</td>
</tr>
<tr>
<td>HCO$_2^-$ + O($^1D$)</td>
<td></td>
<td>301\textsuperscript{b}</td>
<td>319</td>
<td>320</td>
</tr>
<tr>
<td>HOCO$_2^-$</td>
<td></td>
<td>$-367$</td>
<td>$-364$</td>
<td>$-371$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Energies in kJ/mol at 0 K. Zero point corrections for CCSD(T) are from the B3LYP calculations. Species refer to singlet states except as noted. \textsuperscript{b}Because of the inability of a single-determinant DFT wave function to describe the O($^1D$) state, the experimental singlet-triplet splitting for oxygen atom is used.
Table 2. Relative conformer energies (kJ/mol). $^a$

<table>
<thead>
<tr>
<th>Species</th>
<th>$Z$</th>
<th>$Z-E$ barrier</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_3$H</td>
<td>0</td>
<td>64</td>
<td>8.3</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>8.4</td>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>HCO$_3^-$ ($^t\ A$)</td>
<td>19</td>
<td>79</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a\Delta E$ at the B3LYP/6-311++G(d,p) level at 0 K, relative to the lower-energy conformer of each species.
Table 3. Fit parameters for cross section model

<table>
<thead>
<tr>
<th>Product channel</th>
<th>Transition state</th>
<th>$\sigma_0$</th>
<th>$N$</th>
<th>$E_0$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>all</td>
<td></td>
<td>0.50</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>HO$^-$</td>
<td>tight</td>
<td></td>
<td></td>
<td>1.17</td>
</tr>
<tr>
<td>HO$_2^-$</td>
<td>tight inner</td>
<td></td>
<td></td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>loose outer</td>
<td></td>
<td></td>
<td>1.48</td>
</tr>
<tr>
<td>HCO$_2^-$</td>
<td>S-T crossing, tight</td>
<td>[0.853]$^a$</td>
<td></td>
<td>1.30±0.13</td>
</tr>
<tr>
<td></td>
<td>loose outer</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Value in square brackets fixed at G3//B3LYP singlet-triplet crossing energy.
Table 4. Thermochemical values\(^a, b\)

<table>
<thead>
<tr>
<th>quantity</th>
<th>value (0 K)</th>
<th>value (298 K)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta_f H(H))</td>
<td>216.035±0.006</td>
<td>217.998±0.006</td>
<td>c</td>
</tr>
<tr>
<td>(\Delta_f H(O))</td>
<td>246.80±0.10</td>
<td>249.18±0.10</td>
<td>c</td>
</tr>
<tr>
<td>(\Delta_f H(H_2O))</td>
<td>−238.92±0.04</td>
<td>−241.83±0.04</td>
<td>c</td>
</tr>
<tr>
<td>(\Delta_f H(HOOH))</td>
<td>−129.89±0.22</td>
<td>−135.88±0.22</td>
<td>c</td>
</tr>
<tr>
<td>(\Delta_f H(HCO_2H))</td>
<td>−371.5±0.5</td>
<td>−378.8±0.5</td>
<td>c</td>
</tr>
<tr>
<td>IE(H)</td>
<td>1312.049±0.001</td>
<td>1318.246±0.001</td>
<td>c</td>
</tr>
<tr>
<td>(\Delta_{acid} H(HCO_2H))</td>
<td>1440.5±2.1</td>
<td>1446.2±2.1</td>
<td>b,d</td>
</tr>
<tr>
<td>(\Delta_{acid} H(HCO_3H))</td>
<td>1477±14</td>
<td>1483±14</td>
<td>b,e</td>
</tr>
<tr>
<td>EA(HCO(_3))(^c)</td>
<td>240.5±0.6</td>
<td>247.1±0.6</td>
<td>f</td>
</tr>
<tr>
<td>EA(HCO(_2))(^c)</td>
<td>337.5±1.4</td>
<td>345.0±1.4</td>
<td>g</td>
</tr>
</tbody>
</table>

**this work and derived results**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(D(HCO_3^-−O))</td>
<td>126±12</td>
<td>130±12</td>
<td>b</td>
</tr>
<tr>
<td>(D(HCO_2^-−O))</td>
<td>223±12</td>
<td>228±12</td>
<td>i</td>
</tr>
<tr>
<td>(D(HCO_2^-−H))</td>
<td>466.0±2.5</td>
<td>473.0±2.5</td>
<td>eq</td>
</tr>
<tr>
<td>(D(HCO_3^-−H))</td>
<td>405±14</td>
<td>412±14</td>
<td>eq</td>
</tr>
<tr>
<td>(\Delta_f H(HCO_3H))</td>
<td>−287 ± 19</td>
<td>−296 ± 19</td>
<td>eq</td>
</tr>
<tr>
<td>(\Delta_f H(HCO_3(^c)))</td>
<td>−98 ± 12</td>
<td>−103 ± 12</td>
<td>eq</td>
</tr>
</tbody>
</table>

\(^a\)For gas-phase species in kJ/mol using the electron convention, \(H_{298}(e)−H_0(e)\) =6.197 kJ/mol.

\(^b\)Thermal entropy and entropy corrections from vibrational frequencies at the B3LYP/6-311++D(d,p) level, with (minor) corrections for populations of Z and E conformers.

\(^c\)Gurvich et al.\(^{15}\)

\(^d\)From Eyet et al.,\(^{17}\) \(\Delta_{acid} G_{298}(HCO_2H)\) =338.6±0.5 kcal/mol.

\(^e\)From Villano et al.,\(^{10}\) \(\Delta_{acid} G_{298}(HCO_3H)\) = 346.8±3.3 kcal/mol. Value at 0 K refers to \((Z)\)-HCO\(_3\)H \(\rightarrow\) \((E)\)-HCO\(_3\)\(^−\) + H\(^+\).
"From $E_{A0}(\text{HCO}_3^-) = 2.493 \pm 0.006$ eV.\textsuperscript{10} Value at 0 K refers to $(E)\text{-HCO}_3^- \rightarrow (E)\text{-HCO}_3^+ + e^-$."

"From $E_{A0}(\text{HCO}_2^-) = 3.498 \pm 0.015$ eV.\textsuperscript{17}"

"This work, $D_0(\text{HCO}_2^-\text{-O}) = 1.30 \pm 0.13$ eV."

"$D(\text{HCO}_2^-\text{-O}) = D(\text{HCO}_2^-\text{-O}) - E_{A}(\text{HCO}_3^-) - E_{A}(\text{HCO}_2^-)$\textsuperscript{17}"
Figure 5. Negative ion thermochemical cycles for formic acid (left) and peroxymethyl acid (right). Energies in kJ/mol relative to singlet (Z)-HCO$_3$H.
Figure 6. Relative energies calculated at the B3LYP/6-311++G(d,p) level as a function of the OCOO dihedral angle for peroxyformic acid (HCO$_3$H, lower trace), peroxyformyl radical (HCO$_3^+$ + H, middle trace), and peroxyformyl anion (HCO$_3^-$ + H$^+$, upper trace). The structures are shown for the $E$ conformers (left-hand side) and $Z$ conformers (right-hand side). The vertical dashed lines indicate the thermochemical energy differences corresponding to the gas-phase acidity ($Z$ to $E$ ground states) and bond dissociation energy ($Z$ to $E$).
Figure 7. Experimental reaction cross sections for threshold collision-induced dissociation of \( \text{HCO}_3^- \) for the three product channels, reactions 8-10, as a function of relative collision energy in the center-of-mass frame. Symbols are the measured cross sections extrapolated to zero-pressure. Lines are the model cross sections described in the text.
Figure 8. Potential energy surface for the dissociation of peroxyformate into the three observed fragment ions. Energies relative to singlet $^1\text{A}''$-HCO$_3^-$ are given in kJ/mol and have been calculated at the B3LYP/6-311++G(d,p) level (Table 1).
Figure 9. Singlet-triplet crossing potential energy surfaces for the oxygen–oxygen bond dissociation of the \((E)\)-peroxyformate anion. Total electronic energies are plotted for fixed O-O bond distances at the B3LYP/6-311++G(d,p) level, with other bond lengths and angles optimized and with no zero point energy corrections.
4 Gas-Phase Acidities of Linear and Branched Hexanols

4.1 Introduction

The gas-phase acidity of a molecule is dependent on its structure.¹ A classic example of the relationship between intrinsic acidity and structure is the examination of gas-phase acidities of primary, secondary and tertiary alcohols by Brauman and Blair.² This seminal work found that the gas-phase acid strength increased with increasing hydrocarbon tail length up through 1-butanol,

\[
\text{CH}_3\text{OH} < \text{CH}_3\text{CH}_2\text{OH} < \text{CH}_3\left(\text{CH}_2\right)_2\text{OH} < \text{CH}_3\left(\text{CH}_2\right)_3\text{OH}
\]  

(Note that stronger acids correspond with smaller magnitudes of the gas phase acidity, \(\Delta_{\text{acid}} G(\text{ROH})\) for the process \(\text{ROH} \rightarrow \text{RO}^- + \text{H}^+\).) This is opposite the acidity trend in aqueous solution which results from the higher solvation energy for smaller alkoxide ions. Brauman and Blair² proposed that the observed trend in gas-phase acidity was due to the polarizability of the alkyl tail group and the gas-phase acidity for linear alcohols would decrease as a function of \(r^{-4}\), where \(r\) is the distance between the alkyl tail and the hydroxyl group. Later experiments using the Kinetic Method³,⁴ found that this trend in acidity significantly different from that predicted by Brauman and Blair for straight chain alcohols with hydrocarbon tails consisting of six or more carbons.³,⁴ The observed difference in straight chain alcohol acidity was complicated by the fact that relative acidity measured depended on the specific kinetic method used. These experiments also examined the relative gas-phase acidities of branched alcohols. These studies found that branching increased the overall acidity and that the different specific kinetic methods agreed more closely on the relative gas-phase acidities. The gas-phase acidities of these longer chain alcohols and
branched alcohols were re-examined by ion cyclotron resonance mass spectrometry by Higgins and Bartmess in 1997 using the equilibrium method. These measurements disagreed with the Kinetic Method acidities for the 1-alkanols. Specifically, Higgins and Bartmess observed that 1-pentanol and 1-hexanol are more acidic than either the prediction of the trend proposed by Brauman and Blair or the previous kinetic measurements. Higgins and Bartmess hypothesized that the reason that gas-phase acidities of 1-pentanol and 1-hexanol were higher than expected was due to the fact that the deprotonated alcohol anion was stabilized by a low-energy cyclic conformation that could not be formed by 1-butanol and was energetically unfavorable for longer chain alcohols. They further concluded that the Kinetic Method only measured the dissociative transfer of a higher-energy non-cyclic conformation which led to the kinetic methods underestimating the gas-phase acidities for these two 1-alkanols. We chose to study 1-hexanol to compare our threshold collision-induced dissociation method to these experiments to see if our method actually measured deprotonation process yielding the lowest energy conformations. We also chose to study a branched hexanol, 3,3-dimethyl-1-butanol, to try to elucidate why two primary alcohols of the same size and with identical structure up to the gamma carbon have significantly different gas-phase acidities. These two hexanols were complexed with either hydrogen fluoride or acetylene and then competitive threshold collision-induced dissociation experiments were carried out based on the methods described in Chapter 2. The observed primary product ion masses from dissociation of the hexanol-fluoride complexes are 19 and 101., corresponding to the dissociation pathways in reactions (4.2) and (4.3).

\[
\left[\text{C}_6\text{H}_{13}\text{O} - \text{H} - \text{F}\right]^- + \text{Xe} \rightarrow \text{F}^- + \text{C}_6\text{H}_{13}\text{OH} + \text{Xe} \quad 19 \frac{m}{z} \quad (4.2)
\]

\[
\left[\text{C}_6\text{H}_{13}\text{O} - \text{H} - \text{F}\right]^- + \text{Xe} \rightarrow \text{C}_6\text{H}_{13}\text{O}^- + \text{HF} + \text{Xe} \quad 101 \frac{m}{z} \quad (4.3)
\]
Similarly, the observed product channel ions for dissociation of the alcohol-acetylide complexes were the acetylide and the alkoxide ions, reactions (4.4) and (4.5).

\[
\left[ \text{C}_6\text{H}_{13}\text{O} - \text{H} - \text{CCH} \right]^- + \text{Xe} \rightarrow \text{HCC}^- + \text{C}_6\text{H}_{13}\text{OH} + \text{Xe} \quad 25 \, \text{m/z} \quad (4.4)
\]

\[
\left[ \text{C}_6\text{H}_{13}\text{O} - \text{H} - \text{CCH} \right]^- + \text{Xe} \rightarrow \text{C}_6\text{H}_{13}\text{O}^- + \text{HCCH} + \text{Xe} \quad 101 \, \text{m/z} \quad (4.5)
\]

4.2 Experimental Results

Mass spectra of the alcohol complexes in the presence and absence of xenon are shown in Figures 10 and 11. Without xenon both spectra have only the reactant ion peak of for the fluoride bound complexes and for the acetylide complexes. The acetylide-hexanol complexes show two product ion peaks (three total peaks) corresponding to the expected products, acetylide and hexoxide, from equation 4.4 and 4.5. The fluoride-hexanol mass spectrum with xenon shows four total peaks due to the reactant ion and three collision-induced fragment ions. The primary products are those in equations 4.2 and 4.3. The extra peak at 99 m/z results from the dehydrogenation of the hexoxide anion. The double bond most likely forms between the alpha and beta carbon of the alkoxide. \(^6\) The 99 m/z ions are observed only at high collision energies above 3 eV center-of-mass frame. This sequential dissociation product was monitored for all experiments but was not incorporated into subsequent analysis because the reaction cross section for this product was below the detection limit over the near-threshold range used for fitting in all cases.

4.2.1 Cross Section Measurements

Representative competitive threshold collision-induced dissociation cross section measurements for all four complexes are plotted in Figures 12 through 16 as functions of the center-of-mass frame energy. Each complex produced the two primary ion product
channels over the range shown, with Figure 14 also showing the sequential dehydrogenation product channel at high collision energy.

4.2.1.1 Fluoride complexes

The TCID cross sections for the fluoride-hexanol complex are shown in Figures 12 and 13. The fluoride ion product channel has a lower barrier and higher cross section than the alcohol channel indicating hydrogen fluoride has a higher gas-phase acidity than the hexanols, i.e.,

$$\Delta_{\text{acid}} H(C_6H_{13}OH) > \Delta_{\text{acid}} H(HF) \quad (4.6)$$

By definition stronger acids have a smaller deprotonation enthalpies, $\Delta_{\text{acid}} H$. The alkoxide channel cross section is roughly an order of magnitude smaller than the fluoride channel for both alcohols. The relative difference in energy at which the product anion channels rise from the signal-to-noise baseline is slightly lower for the 3,3-dimethyl-1-butoxide anion, which qualitatively indicates that the branched hexanol is more acidic than 1-hexanol.

4.2.1.2 Acetylide Complexes

The TCID cross sections for the acetylide-hexanol complexes are shown in Figures 15 and 16. The alkoxide anion product channels have a lower relative threshold energy and higher cross section than the acetylide ion channel indicating that both alcohols have smaller gas-phase acidities than acetylene,

$$\Delta_{\text{acid}} H(C_6H_{13}OH) < \Delta_{\text{acid}} H(HCCH) \quad (4.7)$$

The alkoxide product channel cross sections are approximately one order of magnitude larger than the acetylide complexes. The relative difference in energy at which the product anion channel have a cross section of 0.001 Å² is less for 1-hexoxide anion, which
qualitatively indicates that the linear hexanol is less acidic than branched hexanol. That is, the experimental cross sections for both the fluoride and acetylide complexes indicate qualitatively that:

\[
\Delta_{\text{acid}} H(\text{HCCH}) > \Delta_{\text{acid}} H(\text{nHexanol}) > \Delta_{\text{acid}} H(\text{bHexanol}) > \Delta_{\text{acid}} H(\text{HF})
\]  

The observed absolute cross sections for the acetylide anion complexes were approximately an order of magnitude larger than the observed cross sections for the fluoride anion complexes. The acetylide complex product ion thresholds are lower than those of the fluoride ion complexes which indicates that the acetylide ion complex potential energy wells are shallower than those of the fluoride complex.

### 4.3 Computational Results

#### 4.3.1 Optimized Geometries

Optimized geometries as well as relative electronic energies for 6 conformations of 1-hexanol are shown in figure 17. The lowest energy geometry at the B3LYP/6-311++G(2df,2p) level is referred to as the extended or trans conformation because all backbone dihedral angles are trans (180 degrees). The 0.2 kJ·mol\(^{-1}\) relative difference in electronic energy from this minimum and the second lowest energy conformation, which differs by a 120 degree rotation about the bond between the alpha and beta carbon, is within the expected accuracy of this computational method, however. Increasing the basis set to 6-311++G(3df,3pd) minimally increases the relative difference to 0.21 kJ·mol\(^{-1}\). Switching to the aug-cc-pVTZ basis set decreases the relative difference to 0.05 kJ·mol\(^{-1}\). Changing the method to second-order Møller-Plesset perturbation theory (MP2/6-311++G(2df,2p)) flips the relative order of the two conformers but again falls within the absolute accuracy for this
method at 0.3 kJ·mol\(^{-1}\). The relative energy difference basis set dependence for MP2 is similar in magnitude to that of B3LYP with differences of 0.27 kJ·mol\(^{-1}\) and 0.34 kJ·mol\(^{-1}\) for 6-311++G(3df,3pd) and aug-cc-pVTZ respectively. The M06-2X DFT method with these basis set agrees with the relative order of the MP2 calculations and has a magnitude of 1.09 kJ·mol\(^{-1}\). The fluctuation due to basis set was higher than other methods, with relative differences of 1.31 kJ·mol\(^{-1}\) for 6-311++G(3df,3pd) and 0.85 kJ/mol for aug-cc-pVTZ. The G4 composite method agreed with the order from MP2 calculations with a relative difference of 1.03 kJ·mol\(^{-1}\). Since there is no consensus among the methods or basis sets, we will ultimately fit the experimental data using frequencies and hindered rotor calculations from both conformations for model testing.

3,3-dimethyl-1-butanol conformations and energies are shown in figure 21. Similar to 1-hexanol, the lowest energy conformation of 3,3-dimethyl-1-butanol is the extended or trans conformation for the O-C\(_\alpha\)-C\(_\beta\)-C\(_\gamma\) backbone. The difference in electronic energy between the two lowest conformations at the B3LYP/6-311++G(2df,2p) level is 3 kJ/mol. Unlike 1-hexanol, all methods and basis sets agree that the extended form is lowest in energy by 2 - 3 kJ·mol\(^{-1}\). Interconversion to the second lowest energy structure requires the rotation of two dihedral angles by 120 degrees, around both the bond between the alpha and beta carbon and the bond between the oxygen and alpha carbon. This means that 1-dimensional internal rotations from the extended form, i.e., rotating around one bond at a time from the lowest configuration, cannot reach this conformation.

In order to thoroughly test the hypothesis put forward by Higgins and Bartmess\(^5\) of stabilization of the anion by interaction between the O\(^-\) and the terminal methyl group, the 1-hexoxide anion was optimized from many different starting geometries including those
that had these “cyclic” conformations. Figure 18 shows the lower energy conformations. The lowest energy conformation has one gauche dihedral angle between the alpha and beta carbon. All methods and basis sets agree on this being the lowest energy conformation. The next lowest energy conformation is cyclic and requires rotating two dihedral angles for interconversion. This conformation is higher in energy by 5.9 kJ·mol\(^{-1}\) at the B3LYP/6-311++G(2df,2p) level.

The lowest energy conformation of the 3,3-dimethyl-1-butoxide anion (Figure 20) has two gauche dihedral angles along the 1-butoxy backbone. This conformation is the same structure one would arrive at by deprotonating the higher energy neutral conformer. It is stabilized by the interaction between the O\(^-\) and one of the methyl groups on the tert butyl terminus. The relative electronic energy difference between the two lowest energy conformers is 12.7 kJ·mol\(^{-1}\) at the B3LYP/6-311++G(2df,2p) level. All other methods and basis set combinations agreed with the relative order with higher relative electronic energy differences.

The 1-hexanol fluoride and 1-hexanol acetylide complexes (Figure 19) have minimum energy conformations at the B3LYP/6-311++G(2df,2p) that are more twisted than either the extended neutral or the anion. These more twisted forms differ from the anion by one gauche dihedral angle between the beta and gamma carbon. The relative difference in electronic energy between the two lowest energy conformers is 3.6 kJ·mol\(^{-1}\) for the fluoride complex and 1.4 kJ·mol\(^{-1}\) for the acetylide In both cases the second lowest energy conformation differs by one dihedral angle rotation.

The lowest energy conformations for the 3,3-dimethyl-1-butanol fluoride and 3,3-dimethyl-1-butanol acetylide (Figure 22) complexes have conformations similar to the anion
with two gauche dihedral angles on the 1-butanol backbone. The relative electronic energy
difference between the two lowest conformers of 3,3-dimethyl-1-butanol fluoride complex
differed in energy by 11.7 kJ·mol$^{-1}$ while the acetylide complex differs in energy by 3.0
kJ·mol$^{-1}$. Interconversion between the two lowest energy geometries requires two dihedral
angle rotations.

4.3.2 Frequencies

For all lowest-energy conformations, harmonic vibrational frequencies were
calculated at the B3LYP/6-311++G(2df,2p) level. The frequencies for 1-hexanol and the 1-
hexoxide anion were also performed with two other methods, M06-2X and MP2, and two
other basis sets, 3-11++G(3df,3pd) and aug-cc-pVTZ. This was repeated for the next lowest
energy conformation of both the neutral alcohol and the deprotonated anion. The hindered
rotor analysis$^7$–$^9$ in Gaussian 09$^{10}$ identified six harmonic frequencies associated with internal
rotation for the neutral and five frequencies for the anion.$^7$–$^{10}$ All method and basis set
combinations identified the same frequencies associated with hindered internal rotation.
Visual inspection of the animated normal modes confirmed that these vibrational
frequencies are internal rotations. All calculated frequencies for the same conformational
geometry for modes not associated with internal rotation agree to within five percent of one
another.

The difference in the frequencies for different conformations primarily involves the
four lowest frequencies not associated with internal rotation. This subset of frequencies can
vary by as much as 15 percent. Conformational change affects other frequencies by less than
3 percent.
The Gaussian 09\textsuperscript{10} hindered rotor analysis\textsuperscript{7–9} for the alcohol fluoride complex only identified three frequencies for the 3,3-dimethyl-1-butanol fluoride complex and four frequencies for the 1-hexanol fluoride complex.\textsuperscript{7–10} In these cases visual inspection was used to identify the other two or three frequencies that are internal rotations.

### 4.3.3 Dissociation Potential Energy Scans

Bond dissociation relaxed potential energy scans were performed for all four complexes. Figure 23 shows the relaxed potential energy scan for the linear hexanol fluoride complex. The complex has a smooth, featureless potential energy curve for both dissociation channels. The fluoride anion channel has the lower asymptotic energy at approximately 140 kJ\cdot mol\textsuperscript{−1} and the hexoxide channel has an energy of approximately 165 kJ\cdot mol\textsuperscript{−1}. There is a single minimum indicating strong hydrogen bonding between the oxygen and hydrogen as well as the fluoride and hydrogen.

The 1-hexanol acetylide complex bond dissociation relaxed potential energy scan (Figure 24) shows that the dissociation of the lower energy linear hexoxide channel to be and smooth with a barrier of approximately 78 kJ\cdot mol\textsuperscript{−1}. The 1-hexanol acetylide complex well is shallower than the 1-hexanol fluoride complex as would be expected by the threshold shift toward lower energy observed in the cross sections. The acetylide ion channel has a clear inflection point at 11.5 kJ\cdot mol\textsuperscript{−1}. No second minimum was found indicating that the inflection point may only be incipient formation of a structure versus the overall minimum with a structure. The harmonic vibrational frequency for the hydrogen to oscillate between the two fragments is 2578 cm\textsuperscript{−1} (2495 cm\textsuperscript{−1} with correction factor) which means the zero point energy for the well is approximately 13 kJ mol\textsuperscript{−1} so there will likely be only one quantum mechanical zero-point average structure.
4.3.4 Dihedral Angle Relaxed Potential Energy Scans

Dihedral angle relaxed potential energy scans were performed for all dihedral angles for the neutral, anion, and complex. In general, there is good agreement both among methods and basis sets for well depths, barrier heights, and overall shapes of the dihedral angle relaxed potential energy scans although a few discrepancies between the methods were observed. The largest observed differences occurred when scanning the dihedral angle between the beta and gamma carbons of the linear hexoxide anion. Figure 25 compares scans about this dihedral angle with different methods. Figure 26 compares scans of same rotation with different basis sets. The B3LYP scan has the lowest energy conformation at zero degrees with the two other conformations higher in energy by approximately 160 cm$^{-1}$ and 140 cm$^{-1}$ at 120 and 265 degrees respectively. The M06-2X and MP2 scans find the minimum energy conformation to be near the 120 degree well (130 and 125 degrees respectively). These two methods predict the zero degree conformational well to be higher in energy by over 200 cm$^{-1}$ (220 cm$^{-1}$ and 240 cm$^{-1}$) and the 265 degree conformational well to be higher in energy by 70 cm$^{-1}$ for the MP2 and 140 cm$^{-1}$ for M06-2X. All three basis sets show very close agreement in the potential energy scan.

The resulting curves from the different basis sets and methods were then fit to the sine and cosine function and subsequently used to solve the one dimensional hindered rotor Schrödinger equation as discussed in Chapter 2. Table 5 shows a comparison of the resulting thermodynamic functions for each fit. Different basis sets had very little effect on the thermodynamic functions for the hindered rotor. This is expected based on the very similar shapes of the relaxed potential energy scans from Figures 25 and 26. Comparison of the thermodynamic functions from the relaxed potential energy scans using different methods
did not have the same apparent discrepancy between B3LYP and the other two methods that is observed in the relaxed potential energy scans. In fact, B3LYP and MP2 method agree more closely with one another than the MP2 and M06-2X methods agree with one another for four of the five calculated thermodynamic functions. The very similar partition functions, for all methods and basis sets (within 15%) implies the density of states for RRKM will also be similar. Because this particular dihedral potential had the worst agreement among methods, we can conclude that using B3LYP/6-311++G(2df,2p) values for all dihedral angles is acceptable. The other dihedral relaxed potential energy scans are included in the Appendix.

4.4 Cross Section Modeling

Chapter 2 describes the general methods for using RRKM theory to fit the data and account for kinetic and competitive shifts. Three different RRKM models were used for fitting the experimental cross sections. The first method, I, is the traditional method in which all vibrations are treated as harmonic oscillators. Method two, II, treats the bond between the hydroxyl group (–OH) and the alpha carbon as a hindered rotor in both the neutral and reactant complex while all other modes are treated as harmonic oscillators. This method was used previously by DeTuri and Ervin to examine the gas-phase acidities of smaller alkanols. The third method, III, treats all bonds between heavy atoms as hindered rotors. This method more fully accounts for multiple conformations. Table 9 gives the average fit parameters. Tables 7 and 8 summarize the results. Example fits for all three methods are shown in Figures 27 through 30.
4.4.1 Fluoride Complex Modeling

The 1-hexanol-fluoride complex showed good agreement between experimental data and all three models. Figure 27 shows an overlay of the three different fitting methods. The convoluted fits (solid lines in figures) for all three methods agree well with the experimental data although the unconvoluted fits (dashed line in figures) indicates that the methods do not exactly agree on the relative acidity difference. The 1-hexoxide channel convoluted fit more clearly shows the difference in the three methods. The harmonic oscillator fit (method I) for this channel underestimates the cross section at low energies and overestimates the cross section at higher energies. The fit based on model II (bond between alpha carbon and hydroxyl group treated as hindered rotor) shows nearly the opposite behavior of the fit based on method I as it overestimates the cross section at low energies and underestimates the cross section at higher energies. Incorporating all of the hindered rotors into the model (method III) gives the overall best fit which closely predicts the experimental cross section over the entire range modeled.

Fitting complex experimental collisional cross sections for the 3,3-dimethyl-1-butanol fluoride also gives relatively good fits. A comparison of the different fitting methods can be found in Figure 28. Similar to the 1-hexanol fluoride complex fits, the branched hexanol all three fitting methods show good agreement to between the fluoride experimental cross section and the respective convoluted fit. The convoluted harmonic oscillator fit for the 3,3-dimethyl-1-butoxide channel underestimates the experimental cross section at low energies and overestimates the cross section at higher energies. Fitting the cross section while treating the hydroxyl group as a hindered rotor gives good agreement with the experimental data and the more complete hindered rotor treatment.
4.4.2 Acetylide Complex Modeling

Figure 29 shows the three different models for the 1-hexanol acetylide TCID cross sections. All three models have less success in accurately predicting the experimental cross sections and were only fit to the near threshold region as it is the most critical for thermochemistry measurements. The three models fit from 0 to 1 eV center-of-mass frame energy have good agreement between the experimental 1-hexanol cross sections and the predicted convoluted cross sections over the fit range but overestimates the cross sections at energies higher than the fit range. As seen in Figure 29, all three models underestimate the experimental cross sections at low energy and overestimate the cross sections at high energy when fit over the same range. A possible reason for the poor fits at high energy for the acetylide complexes is that the shallower well for the proton-bound complex causes a smaller range for statistical behavior that can be treated by RRKM theory.

Similar to the 1-hexanol acetylide complex, the 3,3-dimethyl-1-butanol acetylide complex cross section models were only fit to the experimental data in the near threshold region (0 to 1 eV) (figure 30). The convoluted models accurately recreate the experimentally measured 3,3-dimethyl-1-butoxide TCID cross section over the fitting range but overestimate the cross section at higher energies. All three fitted models underestimate the experimental acetylide cross sections at low energies and overestimate them at high energies.

A rigorous criterion to evaluate the overall fits of the data is to compare the sum of the relative gas-phase acidity differences between hexanol and hydrogen fluoride plus hexanol and acetylene to the well-established relative gas-phase acidity difference between acetylene and hydrogen fluoride. The literature value for the zero kelvin relative gas-phase acidity difference between acetylene and hydrogen fluoride is $26.9 \pm 0.6 \text{kJ}\cdot\text{mol}^{-1}$. According to 17-20 A
comparison of the different fitting methods agreement to this literature value for 1-hexanol is shown in Figure 34 and for the branched hexanol in Figure 35. The best agreement between model and literature value comes from the model in which all bonds between heavy atoms are treated as hindered rotors (model III). Although this comparison does not completely rule out the model I (harmonic oscillator model), we do not further consider this method in subsequent analysis.

In order to better understand the reason for our limited success in fitting the experimental TCID cross sections for the acetylide complexes, an additional adjustable scaling factor was used in the reaction degeneracy for the acetylide anion product channel. The resulting fit can be found in Figures 34 and 35. Although incorporating an additional scaling factor to the reaction degeneracy has been previously used as an ad hoc method to account for incorrect reaction degeneracies, symmetry numbers, anharmonic vibrational modes, and dipoles in neutral molecules\textsuperscript{12-16} we simply use it as a starting point to identify the source of our models deficiencies. We avoid using any of these subsequent fits for thermochemistry determinations to avoid any chance of over parameterization as any extra parameters improve the overall fit. The additional scaling factor for the acetylide ion channel optimizes to values less than one and the relative energy difference between the two product channels decreases for all channels.

Although the poor agreement between the three models and the experimental cross sections over the larger ranges (0 - 2 eV) can be dramatically improved with an adjustable scaling factor, its inclusion fails to accurately reproduce the relative gas-phase acidity difference between the two reference acids. The additional reaction degeneracy scaling factor
gives a relative energy difference between hydrogen fluoride and acetylene of 23 kJ·mol$^{-1}$ and for 1-hexanol (figure 34) and 16 kJ·mol$^{-1}$ for 3,3-dimethyl-1-butanol (figure 35).

Models I, II and III do not account for permanent dipoles on the neutral molecules. A net dipole on a neutral molecules can affect the overall unimolecular rate constant by as much as an order of magnitude. Inclusion of a neutral molecule dipole term would change the relative density of states between the two channels by changing the density of states for the acetylide ion channel. The deprotonated alcohol anion channel would not be affected since acetylene is a nonpolar molecule. Inclusion of a molecular dipole term can be done approximately based on the work by Chesnavich, Su, and Bowers, which however makes an arbitrary assumption about the rotational temperature of the neutral product molecule.

Figure 31 and 32 show model III (full hindered rotor) fit to the data with the inclusion of a dipole term. Inclusion of the dipole term tends to have better agreement with the experimental cross section over the fit range, but the fits overestimate the relative energy difference between hydrogen fluoride and acetylene at approximately 30 and 36 kJ·mol$^{-1}$ from 1-hexanol and 3,3-dimethyl-1-butanol measurements respectively. A possible conclusion from the previous two fitting methods would be to think that there is some combination of anharmonic and dipole effects affecting the overall fit. Including both a dipole and an adjustable reaction degeneracy scaling term still fails to accurately reproduce the relative difference in gas-phase acidity between hydrogen fluoride and acetylene with values of 25 kJ·mol$^{-1}$ for 3,3-dimethyl-1-butanol and 32 kJ·mol$^{-1}$ for 1-hexanol.

4.5 Acidity Ladder Least-Squared Optimization

The relative differences in acidity for model III were evaluated in a least-squares acidity ladder optimization based on previous work to find the absolute acidity of 1-hexanol.
and 3,3-dimethyl-1-butanol. The gas-phase acidities of these alcohols were made relative to hydrogen fluoride and acetylene because these molecules have well known absolute gas-phase acidities. The accuracy of these absolute gas-phase acidity measurements are used to anchor and fit the relative acidities into a thermochemical ladder network which results in more accurate absolute gas-phase acidities for the two alcohol species. Figure 33 is the fitted gas-phase acidity ladders for the model in which all bonds between heavy atoms were treated as hindered rotors (model III). After the least-squared fitting, the zero kelvin relative differences in gas-phase acidity between 1-hexanol and 3,3-dimethyl-1-butanol is 6.9 ± 0.9 kJ·mol⁻¹. The absolute zero kelvin gas-phase acidity values for n-hexanol is 1559.8 ± 1.5 kJ·mol⁻¹ and 1552.9 ± 1.5 kJ·mol⁻¹ for 3,3-dimethyl-1-butanol.

4.6 Thermochemical Results

Table 6 shows the measured zero kelvin gas-phase acidities converted to standard thermodynamic values at 298.15 K for 1-hexanol and 3,3-dimethyl-1-butanol. The thermal and entropy corrections are based on the lowest energy conformations of the neutral and anion species. Other higher energy conformations were examined but did not substantially affect the correction values except for the branched hexanol anion. There was a significant difference in the entropy correction between the extended and lowest-energy forms. The significantly lower entropy associated with the gas-phase acidity for the cyclic branched hexoxide is primarily due to the internal rotation about the beta and gamma carbon. The tert-butyl internal rotation in the extended conformation behaves as a near free rotor, but has a significant barrier for internal rotation in the lowest-energy conformer. Since difference in energy between these two conformations is significant, 12 kJ·mol⁻¹, the entropy term for the extended form was not further considered.
4.7 Discussion

The literature values for absolute free energy associated with the gas-phase acidity for both the Kinetic Methods\textsuperscript{3,4} and the Equilibrium methods\textsuperscript{5} are referenced to the acidities of tert-butanol and isopropanol, which have since been improved.\textsuperscript{19} Table 7 shows the originally reported values while the Table 8 has corrected values. The reported free energy values\textsuperscript{5} are corrected by 4.6 kJ·mol\textsuperscript{−1} based on an anchored gas-phase acidity evaluation of multiple methods and measurements.\textsuperscript{19} The updated values for tert-butanol and isopropanol improve the error bars for the absolute equilibrium measurements from 9 kJ·mol\textsuperscript{−1} to approximately 4 kJ·mol\textsuperscript{−1}. The error associated with the absolute Kinetic Method measurements was not improved for reasons explained in the introduction section.

Current measurements compared with corrected previous measurements (Table 8) show agreement in the gas-phase acidity and free energy among all three experimental methods for 1-hexanol. After these corrections, there is no clear indication that the Kinetic Methods has systematically higher acidities than current or equilibrium values for this alcohol. We therefore find no conclusive evidence to support the hypothesis by Higgins and Bartmess\textsuperscript{5} that the Kinetic Method experiments systematically underestimate the free energy associated with the gas-phase acidity because the 1-hexoxide anions cannot reach a lowest energy cyclic conformation. Theoretical work further corroborates this as no low energy cyclic hexoxide conformation was observed. The lowest energy conformation is similar to the extended form with a single twist about the alpha and beta carbon. The cyclic conformations are systematically higher in energy based on current calculations.

Our current measurement of branched hexanol, 3, 3-dimethyl-1-butanol, agrees with the equilibrium value more closely than the Kinetic Methods although all are within the
experimental uncertainties. The Kinetic Methods have higher gas phase acidities than the
TCID and equilibrium methods by 7 and 11 kJ·mol$^{-1}$. The discrepancy between Kinetic
Method measurements versus TCID and equilibrium methods may be due to an inability to
observe the lowest energy, more twisted conformation of the branched hexoxide anion.
Theory suggests that the cyclic conformation is lower in energy by roughly 12 kJ·mol$^{-1}$
which would be consistent with the observed difference in gas-phase acidity seen for the
kinetic method measurements relative to equilibrium and TCID methods. Ultimately, the
overall error for these measurements makes it impossible to come to any firm conclusions
for the differences in acidities observed with the kinetic method measurements.

Figure 36 shows the relationship between conformation and acidity. For this figure we
have defined an “intrinsic acidity” (shown by the central vertical arrow) as the energy
required to remove the proton from the extended form of the neutral species without
allowing the anion to conformationally relax to the lowest energy form. This “intrinsic”
acidity is equal to 1565 ± 2 kJ·mol$^{-1}$ for both hexanol species. The experimentally observed
zero kelvin gas-phase acidity is the subsequently the intrinsic acidity less the energy
difference between the extended and lowest energy conformation which is 5 kJ·mol$^{-1}$ for
linear hexanol and 12 kJ·mol$^{-1}$ for the branched species. The observed hexanol species are
more acidic than the intrinsic acidity predicts because of anion conformational stabilization.
Furthermore, the difference in gas-phase acidity between these two skeletal isomers is due to
the difference in conformational relaxation of the more stable twisted anion conformations.

4.8 Conclusions

The experimentally observed zero kelvin gas-phase acidity for 1-hexanol is 1559.7 ±
1.5 kJ·mol$^{-1}$ and 1552.8 ± 1.5 kJ·mol$^{-1}$ for 3, 3-dimethyl-1-butanol. The observed
difference in gas-phase acidity between these two species is 6.9 ± 0.9 kJ mol. Figure 36 shows that both of these six carbon primary alcohols have the same “intrinsic” zero kelvin gas-phase acidity of roughly 1565 kJ·mol⁻¹ and the observed difference in acidity is due to conformational stabilization of the anion. For both hexanols, the lowest-energy conformation of the neutral is different than the lowest-energy conformation of the deprotonated anion.

From this work, one would predict that long chain alcohols with a branching methyl group at the gamma carbon would have greater anion conformational relaxation due to favorable electrostatic interactions between the O⁻ and CH₂ group at the delta carbon. This is in part due to the fact that increased branching at the gamma carbon substantially decreases the number of sterically favorable conformations available to the alcohol. Longer straight chain alcohols would not see this same type of stabilization without introducing unfavorable gauche interaction.

This work highlights the importance of accounting for multiple conformations in gas-phase thermochemical measurements and that deprotonation can significantly alter a molecule’s conformational distribution. Figure 17 shows that the two lowest energy conformations of 1-hexanol are very similar in energy. However the deprotonated 1-hexoxide species shown in figure 18 has one clear lowest energy conformation.

4.9 Acknowledgements

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Figure 10. Mass spectra of $[\text{C}_6\text{H}_{13}\text{O}^{-}\text{H}^{-}\text{F}^-]$ with (black) and without (dashed red) xenon at 5.5 eV center of mass frame. The reactant ion, $[\text{C}_6\text{H}_{13}\text{O}^{-}\text{H}^{-}\text{F}^-]^- = 121 \text{ m/z}$, is the only peak observed without xenon. Three fragment ions are observed with xenon. The two expected fragment ions, $\text{F}^- = 19 \text{ m/z}$ and $\text{C}_6\text{H}_{13}\text{O}^- = 101 \text{ m/z}$, as well as $\text{C}_6\text{H}_{11}\text{O}^- = 99 \text{ m/z}$ ion.
Figure 11. Mass spectra of $[C_6H_{13}O-H-CCH]^- \text{ with (black) and (dashed red) without xenon}$ at 5.5 eV center of mass frame. The reactant ion, $[C_6H_{13}O-H-CCH]^- = 127$ m/z, is the only peak observed without xenon. The two fragment ions are observed with xenon at HCC$^- = 25$ m/z and C$_6$H$_{13}$O$^- = 101$ m/z corresponding to the two expected product ion channels based on equations 4.4 and 4.5.
Figure 12. Collision-induced dissociation cross section as a function of the center-of-mass energy for the 1-hexanol-fluoride complex.
Figure 13. Collision-induced dissociation cross section of branched hexanol complexed with fluoride as a function of relative collision energy.
Figure 14. Collision-induced dissociation cross section including the dehydrogenation channel.
Figure 15. Collision-induced dissociation cross section of 1-hexanol with acetylide as a function of relative collision energy with xenon.
Figure 16. Collision-induced dissociation cross section of the branched hexanol acetylide complex as a function of relative collision energy with xenon.
Figure 17. Conformations of 1-hexanol with calculated energies at the level relative to the minimum energy conformation.
Figure 18. Conformations of 1-hexoxide anion with calculated energies at the level relative to the minimum energy conformation.
Figure 19. Conformations of 1-hexanol fluoride and 1-hexanol acetylide complexes with calculated energies at the B3LYP/6-311++G(2df,2p) level relative to the minimum energy conformation.
Figure 20. Conformations of branched hexanol with calculated energies at the B3LYP/6−311++G(2df,2p) level relative to the minimum energy conformation.
Figure 21. Conformations of branched hexanol with calculated energies at the
B3LYP/6-311++G(2df,2p) level relative to the minimum energy conformation.
Figure 22. Conformations of branched hexanol fluoride and branched hexanol acetylide complexes with calculated energies at the B3LYP/6-311++G(2df,2p) level relative to the minimum energy conformation.
Figure 23. Relaxed potential energy scan of the 1-hexanol fluoride complex.
Figure 24. Relaxed potential energy scan of the 1-hexanol acetylide complex. The dashed line shows the approximate zero-point energy for the vibrational mode corresponding to proton motion.
Figure 25. Comparison of dihedral angle scans performed with different methods (B3LYP, MP2, and M06-2X).
Figure 26. Comparison of B3LYP calculations performed with different basis sets: 6-311++G(2df,2p), 6-311++G(3df,3pd), and aug-cc-pVTZ.
Table 5. Thermodynamic values at 298 k using one dimensional hindered rotor treatment of relaxed potential energy scans from figure 25 and figure 26.

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<td>B3LYP</td>
<td>6-311++(2df,2p)</td>
<td>298.15</td>
<td>11.64</td>
<td>3.22</td>
<td>3.22</td>
<td>31.21</td>
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<td>11.53</td>
<td>3.24</td>
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<td>31.21</td>
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Figure 27. Comparison of different models for fitting the collisional cross sections of 1-hexanol fluoride complex. Model I refers to treating all modes as harmonic oscillators. Model II treats the bond between the alpha carbon and the hydroxyl group (-OH) as a hindered rotor only. Model III refers to treating all bonds between heavy atoms as internal rotors. The solid line represents the convoluted fit and the dashed line is the unconvoluted zero Kelvin cross section.
Figure 28. Comparison of different models for fitting the collisional cross sections of the branched hexanol (3,3-dimethyl-1-butanol) fluoride complex. Model I refers to treating all modes as harmonic oscillators. Model II treats the bond between the alpha carbon and the hydroxyl group (-OH) as a hindered rotor only. Model III refers to treating all bonds between heavy atoms as internal rotors. The solid line represents the convoluted fit and the dashed line is the unconvoluted zero Kelvin cross section.
Figure 29. Comparison of different models for fitting the collisional cross sections of 1-hexanol acetylide complex. All models were fit to the near threshold region (0 – 1 eV).
Figure 30. Comparison of different models for fitting the collisional cross sections of the branched hexanol acetylide complex. All models were fit to the near threshold region (0 – 1 eV).
Figure 31. Comparison of fits for the 1-hexanol acetylide complex when additional adjustable parameters are considered.
Figure 32. Comparison of fits for the branched hexanol acetylide complex when additional adjustable parameters are considered.
Figure 33. Optimized gas-phase acidity ladder with $\Delta_{\text{acid}H_0}$ values in kJ·mol$^{-1}$. 
Figure 34. Comparison of sum of the relative acidity differences achieved through various models fit used to find the relative acidity differences between reference acids and linear hexanol compared to the literature acidity difference between acetylene and hydrogen fluoride.
Figure 35 Comparison of sum of the relative acidity differences achieved through various models fit used to find the relative acidity differences between reference acids and branched hexanol compared to the literature acidity difference between acetylene and hydrogen fluoride
Table 6. Conversion of the absolute zero kelvin gas-phase acidities to standard thermodynamic values.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta_{\text{acid}}H_0$ kJ mol$^{-1}$</th>
<th>$\Delta_{\text{acid}}H_{298}$ kJ mol$^{-1}$</th>
<th>$\Delta_{\text{acid}}S_{298}$ J mol$^{-1}$ k$^{-1}$</th>
<th>$\Delta_{\text{acid}}G_{298}$ kJ mol$^{-1}$</th>
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<tbody>
<tr>
<td>1-Hexanol</td>
<td>1559.8 ± 0.9</td>
<td>1564 ± 4</td>
<td>87 ± 6</td>
<td>1538.0 ± 0.7</td>
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<td>3,3-dimethyl-1-Butanol</td>
<td>1552.9 ± 0.9</td>
<td>1557 ± 4</td>
<td>79 ± 6</td>
<td>1533.0 ± 0.8</td>
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Table 7. Originally Reported Values

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<th>$\Delta_{\text{acid}}H_{298}^{\ddagger}$ kJ mol$^{-1}$</th>
<th>$\Delta_{\text{acid}}G_{298}^{\ddagger}$ kJ mol$^{-1}$</th>
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<tr>
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<td>1530 ± 11</td>
<td>Boand, Houriet, &amp; Gaümann 1983</td>
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<td>Haas &amp; Harrison 1993</td>
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<td>1537 ± 8</td>
<td>Higgins &amp; Bartmess 1998</td>
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<td></td>
<td>1564 ± 4</td>
<td>1538 ± 3</td>
<td>This Work</td>
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<tr>
<td>3,3-dimethyl-1-Butanol</td>
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<td>1527 ± 11</td>
<td>Boand, Houriet, &amp; Gaümann 1983</td>
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Table 8. Corrected values for gas-phase acidities. Entropy conversion factors from Table 5.

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<th>$\Delta_{\text{acid}}G_{298}^{\circ}$ kJ mol$^{-1}$</th>
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<td>1564 ± 4</td>
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<td>Current</td>
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<td>1556 ± 4</td>
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Table 9. Fit Parameters

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<td>0.3</td>
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<td>1.53</td>
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<tr>
<td>[bHexO-H-F]$^-$</td>
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<td>-0.12</td>
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<td>-0.17</td>
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<tr>
<td>[nHexO-H-CCH]$^-$</td>
<td>Model I</td>
<td>0.0 - 1.0</td>
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<td>2.7</td>
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<td>-1.05</td>
<td>-0.25</td>
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Figure 36. Intrinsic Acidity Scale. The “intrinsic” zero kelvin gas-phase acidity for both hexanols is roughly 1565 kJ·mol⁻¹. Calculations show the difference in energy between the extended and twisted conformations of n-hexanol to be roughly 5 - 6 kJ·mol⁻¹ and 12 – 15 kJ·mol⁻¹ for the extended and twisted branched hexanol conformation.


5 Conclusions

Guided ion beam tandem mass spectrometry techniques have been used to measure the oxygen-oxygen bond dissociation energy in the peroxyformate anion and the gas-phase acidity of two hexanol species. These measurements required modification of classical RRKM theory in order to account for singlet-triplet crossing as well as multiple conformations.

The presented energy resolved collision-induced dissociation experiments on the peroxyformate anion have shown that the dissociation process requires a singlet to triplet crossing for the oxygen-oxygen bond dissociation and a hydrogen rearrangement is required in order to lose either hydroxide or hydroperoxide ions. A logical next step would be to examine the dissociation of the peroxyacetate anion. Initial experiments have shown that there are at least six product ion channels that would need to be monitored. The time required for one dataset (three pressures) is estimated to be over 60 continuous hours. At this long of a timescale, electronic drift and the ability to maintain a stable reactant ion beam become significant challenges. In light of these barriers, the peroxyacetate system was not further considered for study. A radical solution to improve the data acquisition time would be to replace the linear quadrupole mass spectrometer at the end of the guided ion beam tandem mass spectrometer with an orthogonal time-of-flight mass spectrometer. This alternative detection method would significantly cut down on the time required for data acquisition but would require significant capital, labor, and time and is therefore not feasible at this time. An alternative opportunity to examine the oxygen-oxygen bond dissociation energy of small peroxy anions relevant to combustion is to examine the peroxymethoxide anion.
We have also measured the gas-phase acidities of two hexanol species. The ability to accurately determine the gas-phase acidity of these alcohols is dependent on the accuracy of the reference acids used. An important next step for these type of gas-phase acidity measurements is to find suitable reference acids. These experiments have shown that hydrogen fluoride is an ideal reference acid. Acetylene, on the other hand, is not ideal due to the relatively shallow well formed by the complex. One potential reference acid would be ethanol.

Measuring the gas-phase acidities of linear and branched hexanol revealed that the gas-phase acidity of the branched species is more acidic than the linear species because of favorable electrostatic interaction between the negative charge and the branched methyl group at the gamma carbon. Theory indicated that there is no similar interaction between the linear hexoxide charge and the methyl tail. The linear and branched hexanol species have similar “intrinsic” acidities which we have defined as the energy required to deprotonated the extended form of the neutral species without allowing for conformational relaxation. The observed difference in acidity is primarily due to conformational stabilization of the anion. A potential future direction for these experiments would be to examine other linear alcohols to see if longer chain hydrocarbon follow the trends predicted by other groups. Also future experiments that look at replacing methyl branching with larger, bulkier hydrocarbon groups could be of potential interest as bulkier side chains might be less stable due to steric interactions.
6 Appendicies

6.1 Sample GIB Program LabView Code

The following are samples of the new LabView code used for data acquisition and control of the Guided Ion Beam Tandem Mass Spectrometer.
6.1.1 Front Panel
Wire Diagram
6.1.2 Mass Tuner VI
6.1.3 Mass Scan VI
6.1.4 Source Mass Scan VI
6.1.5 EO VI
6.1.6 GIB VI
6.1.7 Magnet Control

Figure 37. Wire diagram for Magnet Control. Built around a subVi created by Lakeshore (Gaussmeter manufacturers).

Figure 38. SubVi to set the voltage sent to the linear quardupole (first frame) and start the counter program.
Figure 39. Continuous counter wire diagram

Figure 40. Pulsed counter wire diagram

Figure 41. Wire diagram of the voltage calibration program used to calibrate the octopole voltages.
6.2 Dihedral Angle Scans

Relaxed dihedral potential energy scans at the B3LYP/6-311++G(2df,2p) level (circles) and fits (lines).

6.2.1 3, 3,-dimethyl-1-butanol

![Dihedral Angle 1 Scan bHexanol - Linear](image)
Dihedral Angle 2 Scan bHexanol - Linear
Dihedral Angle 3 Scan bHexanol - Linear

Energy Relative to Minimum / cm⁻¹ vs. Dihedral Angle / Degrees
Dihedral Angle 4 Scan bHexanol - Linear
Dihedral Angle 5 Scan bHexanol - Linear

Energy Relative to Minimum / cm⁻¹

Dihedral Angle / Degrees
Dihedral Angle 6 Scan bHexanol - Linear
6.2.2 bHexanol-F

Dihedral Angle Scan D1 [bHexOH-F]−
Dihedral Angle 2 Scan bHex-F Complex

Energy Relative to Minimum / cm$^{-1}$ vs Dihedral Angle / Degrees
Dihedral Angle 3 Scan bHex-F Complex

Energy Relative to Minimum / cm⁻¹ vs. Dihedral Angle / Degrees
6.2.3 Branched Hexanol-HCCH
Dihedral Angle 5 Scan nHexOHCCH

Dihedral Angle / Degrees

Energy Relative to Minimum / cm$^{-1}$
6.2.4 Branched Hexanol
Dihedral Angle 2 Scan bHexO Anion - Cyclic

Energy Relative to Minimum / cm$^{-1}$ vs. Dihedral Angle / Degrees
6.2.5 nHexanol
Dihedral Angle 2 Scan nHexanol - Linear
Dihedral Angle 6 Scan nHexanol - Linear

Energy Relative to Minimum / cm$^{-1}$ vs. Dihedral Angle / Degrees
6.2.6 nHex-F
Dihedral Angle 3 Scan nHexanol-F

Dihedral Angle / Degrees

Energy Relative to Minimum / cm⁻¹
Dihedral Angle 4 Scan nHexanol-F
Dihedral Angle 6 Scan nHexanol-F

Energy Relative to Minimum / cm⁻¹

Dihedral Angle / Degrees
6.2.7 nHex-HCCH

Dihedral Angle 1 Scan nHex-HCCH Complex

Energy Relative to Minimum / cm\(^{-1}\)

Dihedral Angle / Degrees
Dihedral Angle 2 Scan nHex-HCCH Complex

Energy Relative to Minimum / cm⁻¹

Dihedral Angle / Degrees
Dihedral Angle 3 Scan nHex-HCCH Complex
Dihedral Angle 4 Scan nHex-HCCH Complex

Energy Relative to Minimum / cm⁻¹

Dihedral Angle / Degrees
Dihedral Angle 5 Scan nHex-HCCH Complex

Energy Relative to Minimum / cm⁻¹

Dihedral Angle / Degrees
6.2.8 nHexO
Dihedral Angle 2 Scan nHexO

Energy Relative to Minimum / cm\(^{-1}\)

Dihedral Angle / Degrees
Dihedral Angle 3 Scan nHexO

Energy Relative to Minimum / cm⁻¹

Dihedral Angle / Degrees
6.3 Frequencies

All the frequencies were performed at the B3LYP/6–311++G(2df,2p) level. The frequencies in red are those that were replaced with one dimensional hindered rotor energy levels in CRUNCH calculations.
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<th>ν_{bHexO}</th>
<th>ν_{bHexOH}</th>
<th>ν_{[bHexO-H-F]}</th>
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**Memory Reference:**
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