Modeling of Complex Ionic Dissociation Reactions

Observed by TPEPICO Spectroscopy

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ABSTRACT

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(Under the direction of Prof. Tomas Baer)

TPEPICO spectra of dissociatively ionized chlorobenzene, bromobenzene, and iodobenzene have been measured to test the ability of different statistical rate theories to accurately calculate rate constants of homolytic bond cleavages of ions. For this purpose we have developed a method for extracting experimental rate constants at a single internal energy from TPEPICO spectra of thermal ions. It was determined that, of the theories tested, simplified versions of variational transition state theory (VTST) and statistical adiabatic channel model (SACM) were both capable of fitting the rate constants and predicting the known bond energies of all three halobenzenes. RRKM theory was capable of fitting the rate constants but predicted a bond energy that was too low. PST could neither fit the data nor predict the correct $E_0$. The much simpler to employ
simplified SACM (SSACM) was applied in the dissociations of nitrosobenzene and neopentane.

Chapter 1 is an introduction to the following chapters, dealing with the motivation to determine high precision bond energies of complex dissociations. Chapter 2 is a discussion of the experimental methods employed to observe photoionization and photodissociation processes. Chapter 3 describes the study of the simple isopropyl halide dissociation to determine the isopropyl ion heat of formation. In Chapter 4 we discuss the measurement of rate constants at specific ion internal energies for the dissociation of the halobenzenes in order to compare the ability of different rate theories to model homolytic bond cleavages. Chapters 5 and 6 are applications of the SSACM described in Chapter 4 to the dissociations of the nitrosobenzene and neopentane ions. Like the halobenzenes in chapter 4, the nitrosobenzene ion dissociation is slow and requires rate theories to determine the bond energy. The thermochemistry of the dissociation of both ionic and neutral dissociations of nitrosobenzene are improved using active thermochemical tables. In chapter 6 the bond energy for the methyl loss of neopentane is determined. Although this reaction occurs rapidly, there is a lower energy dissociation pathway that masks the methyl loss channel at threshold thus requiring extrapolation to determine the bond energy.
DEDICATION

This work is dedicated to my parents, Bruce and Janie Stevens, and to my wife, Vanessa Stevens; they have acted selflessly, as if by instinct, to provide me every opportunity possible. My achievements are a direct result of your support.
ACKNOWLEDGEMENT

I wish to thank my advisor Dr. Tomas Baer, who has taught me about what it takes to be a good scientist and how important it is to love your craft. I would also like to thank my friends and former members of the Baer group, Dr. Nick Shuman, Dr. Balint Sztaray, Dr. Andras Bodi, Csaba Pongor Dr. Jim Kercher, Dr. Eli Rosen, and Dr. Eva Garland.
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<tr>
<td>AE</td>
<td>Appearance Energy</td>
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<td>BDE</td>
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<td>IE</td>
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<td>iPEPICO</td>
<td>Imaging Photoelectron-Photoion Coincidence</td>
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<td>KE</td>
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<td>MCP</td>
<td>Multichannel Plate</td>
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<td>PA</td>
<td>Proton Affinity</td>
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<tr>
<td>PES</td>
<td>Photoelectron Spectroscopy</td>
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<td>PIMS</td>
<td>Photoionization Mass Spectrometry</td>
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<tr>
<td>TOF</td>
<td>Time of Flight</td>
</tr>
<tr>
<td>TPEPICO</td>
<td>Threshold Photoelectron-Photoion Coincidence</td>
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<td>VUV</td>
<td>Vacuum Ultraviolet</td>
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LIST OF SYMBOLS

$\Delta H$: Heat of formation

$E_0$: 0 K Dissociation Onset measured relative to neutral ground state

$E_{int}$: Ion Internal Energy measured relative to ion ground state
CHAPTER 1: Introduction

1.1 Motivation for studying complex dissociations

The current state of the art theoretical thermochemical methods such as HEAT\(^1\) or W4\(^2\) theory are able to reliably determine the energetics of smaller molecules to within 1 kJ\(\cdot\)mol\(^{-1}\). In order to produce relevant results and to help theoreticians improve their models, we must look to larger systems with heavier atoms. However, dissociations of interest from larger molecules tend to be more complex, \(i.e.\) they are more prone to dissociate at rates that are too slow to be measured and/or dissociate via multiple pathways at lower energies, both of which can shift the observed dissociation threshold to significantly higher energies. Additionally, large molecules with heavier atoms often have poorly defined heats of formation, which makes it difficult to derive reaction thermochemistry unless the thermochemistry of the fragments is well known.

Traditional calorimetric methods have providee high precision values for many hydrocarbons but are limited as molecular size increases and especially as functional groups with heavier atoms are substituted. Reported uncertainties in the alkanes range from \(\pm 0.4\) kJ\(\cdot\)mol\(^{-1}\) for methane to \(\pm 1.3\) kJ\(\cdot\)mol\(^{-1}\) for octane.\(^3\) The chloro-, bromo-, and iodobenzene are known to 1.3, 4.1 and 5.9 kJ\(\cdot\)mol\(^{-1}\) respectively. As the size of the molecule increases, the heats of combustion typically become higher, requiring higher precision in temperature measurement to obtain the same precision thermochemistry. Additionally these measurements rely upon complete reaction of the
species which becomes less likely with larger molecules and heavier atoms. For heavier atoms, especially metal atoms, multiple oxidation states can be formed, which greatly complicates the extraction of reliable thermochemistry.

Previously overlooked factors also become significant when determining high precision thermochemical values. Theoretical methods, as well as photoionization techniques (e.g., photoionization mass spectrometry (PIMS) and photoelectron-photoion coincidence (PEPICO)) rely upon heat capacity functions to convert the 0K to 298 K thermochemistry. Uncertainty in the heat capacity, becomes significant when dealing with sub kJ/mol precision because of uncertainties in the calculated vibrational frequencies, their anharmonic corrections, and the treatment of multiple internal rotations to determine the heat capacity function. There are several models for treating internal rotations however most deal with only a single rotor and, depending on which one is used, results for the $H_{298} - H_0$ can differ by 1 kJ•mol$^{-1}$.

1.1.1 Active Thermochemical Tables (ATcT)

The ATcT currently in development by Ruscic et al$^{8,9}$ are a network of experimentally measured bond energies, heats of combustion, heats of hydrogenation, electron affinities, etc. for neutral and ionic species. By minimizing the error in the network, uncertainties in thermochemical values are significantly reduced. Measuring accurate bond dissociation energies of larger molecules to common fragments links these molecules into the thermochemical network. It is especially important to determine accurate energetics for stable ions for which the heats of formation have been elusive such as the ones studied here: $C_6H_5^+$, $i$-$C_3H_7^+$, and $t$-$C_4H_9^+$.

1.1.2 Useful values derived from the $E_0$

1.1.2.1 Heats of formation of Ions

Mass spectrometry provides a direct route to the heats of formation of gas phase ions. The $E_0$ is related to the thermochemistry of the reaction constituents by the equation below.
Therefore, if the thermochemistry of any two of the reaction participants, HAB, B and HA⁺, are known, the heat of formation of the third species can be determined from the measured $E_0$. Related thermochemistry can then be derived from $\Delta H(HA⁺)$. If the $\Delta H(A)$ is known, then the proton affinity of A can be determined by the following reaction.

$$A + H^+ \rightarrow HA⁺ \quad PA(A) = -\Delta_{\text{rxn}}H$$  \hspace{1cm} 1.2

In Ch. 4 a new value for $PA(i\text{-C}_4\text{H}_{10})$, which is an important value for the anchoring the proton affinity scale, is determined from $\Delta H(i\text{-C}_4\text{H}_9⁺)$

### 1.1.2.2 Neutral bond dissociation energies and radical ionization energies

Neutral thermochemistry can be linked to more easily measured ionic onset energies by the ionization energy of the radical product of the neutral dissociation. The neutral bond dissociation energy can be derived from the $E_0$ using Eqn. 1.3.

$$BDE = E_0 - IE_{rad}$$  \hspace{1cm} 1.3

However, radical ionization energies are often difficult to determine by conventional methods such as PIMS or photoelectron spectroscopy (PES). First, it is often difficult to cool radicals sufficiently in a molecular beam, which for large molecules often results in significant population of vibrationally excited radicals that ionize at photon energies lower than the ionization energy (i.e. hot bands). Second, it is common for removal of the lone electron of the radical to result in a geometry change which will result in poor Franck-Condon factors for the $v₀→v'₀$ transition. These factors respectively cause underestimation and overestimation of the ionization energy, obscuring direct measurement of the adiabatic $IE$. Measuring the $E_0$ for systems where the neutral BDE is known will yield the $IE_{rad}$. The $IE_{rad}$ can then be used in similar systems where the BDE is unknown.
1.2 Measurement of Ionic Dissociations

1.2.1 Photoionization Mass Spectrometry (PIMS)

In PIMS, the mass analyzed ion signal is measured as the photon energy is scanned. The resulting spectrum is called the photoionization efficiency (PIE) curve. Figure 1-1 shows that, as the photon energy is increased, fragment ions of a particular mass are formed and the mass selected signal for that ion will increases. The energy at which this begins to occur is called the appearance energy ($AE$). Figure 1-1 also shows that the appearance energy is related to the dissociation onset $E_0$ by the internal energy ($<E_{vib}> + <E_{rot}>$) of the neutral precursor. The $AE$ is determined by drawing a line through a linear portion of the PIE curve to the baseline. The point where this line and the baseline intersect is then defined as the $AE$. The PIE curve is dependent upon experimental conditions such as photon intensity, sample pressure, or a broad internal energy distribution as well as Franck-Condon factors and competition from lower energy channels. Often these factors make determining the “linear portion” of the PIE curve somewhat subjective and results in impractically large uncertainties that are underestimated.

1.2.2 Photoelectron-Photoion Coincidence (PEPICO)

PEPICO experiments measure ions in coincidence with their emitted electron. This allows energy selection of ions by use of energy conservation. The excess photon energy, $h \nu - IE_{aa}$, is partitioned between the internal energy of the ion and the kinetic energies of the electron and ion.

$$h \nu = IE_{aa} + E_{int} + KE_e$$  \hspace{1cm} 1.4
Figure 1 - 1 Experimental and Theoretical Definitions of $E_0$ and $AE_T$. 
Due to conservation of momentum, the $KE_{ion}$ term is negligible and can be excluded. For a given photon energy, there will be a distribution of electron kinetic energies (i.e. the photoelectron spectrum) and therefore a distribution of ion internal energies. This means that even at photon energies well above the $E_0$, some parent ions will be generated because most of the excess energy is partitioned into the kinetic energy of the electron. We can simplify the equation above by only collecting ions that are in coincidence with zero kinetic energy electrons (ZEKE). This eliminates the last term in eq. 1.7 making the total ion internal energy:

$$E_{\text{int}} = h\nu - IE_{ad} + E_{Th}$$

where $E_{Th}$ is the thermal energy of the neutral molecule which is determined from the experimental sample temperature and calculated vibrational frequencies and rotational constants. The degree to which we know the ion internal energy corresponds directly to the photon energy resolution and how effectively we can discriminate against energetic (hot) electrons.

PEPICO spectra are TOF spectra consisting of energy selected ions. These spectra are acquired at different photon energies and therefore different ion internal energies. Relative abundances of the observed ion from each spectrum are plotted as a function of the photon energy to generate a breakdown diagram (see Figure 1-1). Unlike a PIE curve, the breakdown diagram has the advantage of being independent of Franck-Condon factors and experimental conditions such as light intensity and sample pressure. For simple rapid dissociations, Figure 1-1 also shows that the relative abundances in the breakdown diagram are determined by the fraction of the ion internal energy distribution that lies above the dissociation threshold (red portion of the thermal energy distribution in Figure 1-1) and that the photon energy at which the parent ion abundance disappears is equal to the observed $E_0$. There is, thus, no arbitrariness in establishing the dissociation limit.

1.3 Kinetic and Competitive Shifts
According to unimolecular statistical theory, the dissociation rate is directly proportional to the probability that the ion will “find” a dissociative state. The Rice, Ramsperger, Kassel, Marcus (RRKM) equation is an improved version of the RRK equation, which assumes incorrectly that the molecule is composed of identical oscillators and that internal energy is large enough to treat these oscillators classically. R. A. Marcus (then a post doctoral fellow with O.K. Rice at the University of North Carolina) modified the theory to consider individual oscillators using quantum mechanics. The RRKM equation defines the dissociation rate as

\[ k(E) = \frac{g^{N^4(E-E_0+IE_{ad})}}{h\rho(E)} \]  

where \( g \) is the reaction degeneracy, \( E \) is the ion internal energy measured relative to the ion ground state, \( E_0 \) and \( IE \) are measured from the neutral ground state, \( N^4(E-E_0+IE_{ad}) \) is the transition state sum of states (the number of states that will lead to dissociation), \( h \) is Planck’s constant, and \( \rho(E) \) is the ion density of states (the total number of states for an ion of a given internal energy). The minimum rate constant is located at the ion internal energy, \( E = E_0 - IE_{ad} \). Thus the minimum rate constant, \( k_{min} \), is

\[ k_{min} = \frac{1}{h\rho(E_0-IE)} \]

The minimum rate constant is dependent upon the height of the barrier and the energy dependence of \( \rho(E) \). The latter depends upon the number of vibrational degrees of freedom of the molecule. If \( k_{min} \) is too slow to be measured by a particular experiment, as is shown by the experimental window in Figure 1-2, then ions with enough energy to dissociate will not have enough time to do so before detection and a false threshold that is dependent upon experimental conditions will be observed. It should be noted the experimental window is determined by the ion residence time and that trapping experiments could extend this indefinitely. However if \( k_{min} \) is low enough (~\( 10^3 \) s\(^{-1} \)), then radiative cooling by emission of infrared photons eventually becomes competitive with the dissociation rate and fragmentation at threshold will be impossible.
Figure 1-2 Definition of Kinetic Shift.
to observe experimentally. The use of eq. 1.6 to extrapolate to the true $E_0$ is thus required for slow dissociations. Figure 1-2 shows the kinetic shift as the difference in energy between the observed and the true threshold.

When a dissociation of interest competes with a lower energy dissociation pathway, the branching ratios are determined by the ratio of the rate constants of the dissociating channels.

$$\frac{[A]}{[B]} = \frac{k_A(E)}{k_B(E)} = \frac{\sigma_A N^\dagger(E - E_A + IE)}{\sigma_B N^\dagger(E - E_B + IE)} \quad 1.8$$

Higher energy channels only become visible when they are within about 2 orders of magnitude of the fastest dissociation pathway. This results in fragments not being observable at their dissociation threshold due to a competitive shift. For dissociations of interest with a competitive shift, the only way to extract energetic information is by modeling the data using eq. 1.3 and statistical rate theories to model the experimental data.

1.3.1 The Various Unimolecular Reaction Rate theories

In the presence of a shift, either competitive or kinetic, unimolecular rate theories are required to extrapolate to the dissociation threshold. These theories differ in their models of the transition state (TS), which determine the energy dependence of $N^\dagger(E)$ and $k(E)$. Using different rate theories will result in different values determined for $E_0$.

Phase space theory (PST)\textsuperscript{12-16} assumes that (in absence of a centrifugal barrier) the transition state is fixed at infinity along the reaction coordinate. As the molecule dissociates, energy in the vibrational modes corresponding to the bending and (if applicable) torsional motion of the broken bonds is converted into rotational motion of the fragments. Thus by placing the transition state at infinity, PST assumes that the transitional modes have completely converted into rotations. For a polyatomic ion dissociating to non-linear polyatomic fragments, one vibrational mode is converted into the reaction coordinate, and five vibrational modes are converted into...
product rotations. Because of these free rotors, the energy dependence of $N^\dagger(E)$ is very strong. As a result, PST represents the upper limit to $k(E)$ and therefore the extrapolated $E_0$.

RRKM theory$^{17}$ assumes that the TS is composed entirely of $n$-1 vibrational oscillators (compared to $n$-6 for PST), where $n$ is the number of vibrational modes in the ion. The RRKM TS is therefore located further inward on the reaction coordinate (where the ion is still intact) than the PST TS. RRKM theory works best for dissociations with an energetic barrier along the reaction coordinate, usually associated with a rearrangement process. Often, this energetic barrier corresponds to a transition state geometry that is tighter (i.e. the vibrational frequencies of the TS are higher) than for the ion equilibrium geometry. Because of these higher vibrational frequencies, the energy dependence of $N^\dagger(E)$ is weaker, and $k(E)$ rises more slowly with $E$.

The two rate theories, which assume that the transition state is located close in (RRKM) and at infinite product separation (PST), assume that the TS is independent of the ion internal energy. This is often not true for dissociations that occur homolytically. For such dissociations, the potential energy increases monotonically along the reaction coordinate without an energetic barrier. As a result, the TS is determined by an entropic bottleneck which, at low energies, is located at infinite bond distances and moves inward as the ion internal energy is increased.$^{17}$

Variational transition state theory (VTST)$^{18-20}$ locates the transition state by determining the minimum in $N^\dagger(E-V(R))$ as the molecule moves on the potential energy curve $V(R)$ along the reaction coordinate ($R$). This minimum results from competing trends in $N^\dagger(E-V(R))$. Increasing the bond distance causes $E-V(R)$ and $N^\dagger(E-V(R))$ to decrease. At the same time, the disappearing vibrational modes, which turn into rotations, cause the $N^\dagger(E-V(R))$ to increase. Determining this minimum requires $V(R)$ to be determined, as well as the vibrational frequencies as a function of the reaction coordinate. However, there is considerable uncertainty in the calculated potential and vibrational frequencies at large $R$. Several models have been proposed that use analytical functions to describe $V(R)$ and the changing vibrational modes.$^{18-20}$ Depending on which model is used, one
or two minima may be observed in $N^2(E-V(R))$, a tight transition state (TTS) at shorter R and an outer orbiting transition state (OTS).\textsuperscript{21} At low energies, the OTS is the global minimum but as the internal energy is increased, the tight transition state becomes the global minimum. It is not clear whether this transition state switching is an artifact of particular approximations used in the model.\textsuperscript{22}

Another model is the statistical adiabatic channel model (SACM) in which the quantum states of the reactant are assumed not to change (although their energies change as the vibrational frequency changes during the reaction) throughout the dissociation. For a given quantum state dissociation is assumed to proceed by an adiabatic potential energy curve that links reactant and product. Each potential curve has a barrier, the maximum of which moves inward along the reaction coordinate as the energy and angular momentum of the channel increase. If the molecule has enough energy to dissociate along a particular curve then the rate constant for that quantum state is determined using eqn. 1.2. A total rate constant is obtained by summing these rates over a statistical distribution of quantum states.\textsuperscript{17}

A full implementation of either VTST or SACM requires significant computational effort. It is shown in Ch. 4 that both a parameterized version of VTST as well as a simplified SACM (SSACM), which calculates $k(E)$ using the much simpler PST with suitable scaling factors, are capable of extrapolating the $k(E)$ function to within the uncertainty of the correct $E_0$ over nearly 500 meV.\textsuperscript{23} Additionally, SSACM, has been shown to reproduce rate constants derived from a full SACM-classical trajectory (SACM-CT) treatment.\textsuperscript{24} It is also shown in Chapter 4 that using PST and RRKM theory to extrapolate to the $E_0$ for the halogen loss of the halobenzenes disagree by as much as 200 meV, with PST over estimating, and RRKM underestimating the $E_0$.\textsuperscript{23,24}

1.3.2 Synchrotron based studies (iPEPICO)

Synchrotron radiation is tunable over, for our purposes, an essentially unlimited range ($<8\rightarrow 4000$ eV). Additionally the photon flux of synchrotron radiation ($10^{11}-10^{12}$ photons/s at 10
eV$^{25}$) is significantly higher than those achieved by tunable monochromatized laboratory emission sources. Because of this high flux, higher photon energy resolution is possible for coincidence experiments which are often limited by low signal intensity. Several new PEPICO apparatuses have been built at synchrotrons around the world. Two have been built in Europe, DELICIOUS II$^{26}$ at the French Synchrotron Soleil and the iPEPICO apparatus$^{27}$ at the Swiss Light Source (SLS) synchrotron and a third in China at the Beijing Synchrotron Radiation Facility.


CHAPTER 2: Experimental Description

2.1 TPEPICO Description

The TPEPICO apparatus, which has been described in several publications,\textsuperscript{1-3} consists of a VUV light source, a temperature controlled inlet, an electron energy analyzer, either a linear or reflectron time of flight (TOF) analyzer, and electronics to correlate the ion and electron signals. The sample gas enters the chamber effusively through a stainless steel needle. A needle valve regulates the flow of gas into the chamber so that the chamber pressure is about $10^{-5}$ mbar (base pressure = $10^{-7}$ mbar). Vacuum ultraviolet (VUV) light emitted from a H\textsubscript{2} discharge lamp dispersed by a 1 m normal incidence monochromator ionizes the sample gas in a temperature controlled ionization region. The width of the entrance and exit slits of the monochromator were set to 100 \(\mu\)m, providing a resolution of 1 Å. The wavelength was calibrated using the Lyman-\(\alpha\) emission line.

Upon ionization, an extraction field of 20 V\(\times\)cm\(^{-1}\) accelerates the electrons and ions in opposite directions. Ions travel through either a linear or reflectron TOF analyzer before impacting a tandem MCP detector. Velocity focusing optics direct both threshold electrons and hot electrons that have zero velocity perpendicular to the extraction axis onto a 1.3 mm circular aperture at the end of a 12 cm electron drift region where they are detected by a Burle channeltron detector (see Figure 2-1). A second off-axis channeltron detector behind a 3x5 mm rectangular aperture collects the background signal of
energetic or hot electrons. We assume that this hot electron signal is representative of the hot electron signal at the center detector. The hot electron signal is used to correct the contaminated center threshold signal for hot electrons whose initial velocity vector is perpendicular to the extraction axis. (See Section 2.1.3.3)

A time-to-pulse height converter (TPHC) converts the time difference between the center or cold electron detector signal and ion MCP signal \(i.e.\) the ion TOF \(i.e.\) to pulse height. A multichannel pulse height analyzer (MCPHA) generates the center TOF spectrum from the TPHC pulses. A second TPHC and MCPHA generate the hot electron TOF spectrum using the off-axis electron detector signal as a start and the ion signal as a stop.

2.1.1 Linear Time of Flight Mass Configuration

In the linear time of flight configuration, a field voltage of 20 \(\text{V} \cdot \text{cm}^{-1}\) is used to accelerate the ions over 5 cm to 100 eV. The ions are accelerated again from 100 eV to 250 eV over 2 mm before entering a 25 cm drift region. The ions then enter a second shorter drift region of 8 cm, the voltage of which can be varied to separate fragment ions formed in the first drift region before impacting a tandem MCP detector. When the voltage applied to the second drift region is 250 V, the same as the first drift region, the voltages meet the Wiley-McLaren space focusing condition.\(^4\) The peak width is This means that all ions of the same mass will have the same time of flight regardless of starting position and therefore determined by the sample’s thermal translational energy.

Figure 2-1 shows the dependence of the total time of flight of a fragment ion upon the position in the spectrometer where it was formed as well as the kinetic information available from its TOF spectrum. Dissociations with \(k(E)\) greater than \(10^7 \text{ s}^{-1}\)
occur essentially instantaneously. For instance, an ion with an m/z of 50 travels only 0.02 mm in the first $10^{-7}$ s in a 20 V/cm field. As a result these rapidly formed fragment ions appear at the time of flight corresponding to the mass of the fragment ion. Fragment ions that are formed in the first acceleration region have a time of flight that corresponds to the position in the acceleration region at which they were formed. Ions that dissociate sooner have shorter times of flight than those that dissociate later in the acceleration region. This dependence results in an asymmetric fragment peak (peak a, Figure 2-1). The shape of the fragment peak corresponds to the decay of the parent ion abundance. If fragments are formed in the first drift region of the spectrometer then the lighter ions will have the same velocity as the parent ion and therefore less kinetic energy. These slow moving fragment ions can be separated from the parent ions by setting the second drift region to a higher potential than the first drift region. The potential difference between the two drift regions provides a barrier over which the slow moving fragment ions must cross. Because the fragment ions are lighter, they are decelerated more and thus have a longer time of flight than the parent ion (peak b, Figure 2-1). The drift peak area provides a point significantly further along parent ion decay curve than the asymmetric fragment peak. This extends the window over which we can determine kinetic information to rates below $10^3$ s$^{-1}$ for m/z=100. Decelerating the ions between the first and second drift region moves the Wiley-McLaren focal point away from the detector and therefore causes an increase in the TOF peak widths. However, this was not a problem for the metastable systems studied because the mass difference between the
Figure 2-1 TPEPICO experimental apparatus with linear TOF analyzer. The fragment ion time of flight is dependent upon the location at which it dissociates. (a) If the fragment is formed in the first acceleration region (blue) then the fragment ion will appear as part of the asymmetric fragment peak. (b) If the fragment ion is formed in the first drift region (green) then the fragment will appear as a drift peak at longer times of flight than the parent ion. (c) Lastly, if the fragment ion does not dissociate before the end of the first drift region, then the fragment ions will appear as parent. (red)
the fragment peak corresponds to the decay of the parent ion abundance. If fragments are formed in the first drift region of the spectrometer then the lighter ions will have the same parent and fragment ions was large. Lastly the peak area of the parent ion (peak c, Figure 2-1) corresponds to ions that either dissociated in the second drift region or did not dissociate at all. The peak area of the parent allows normalization of the parent ion decay curve.

2.1.2 Reflectron TOF Configuration

Figure 2-2 shows the PEPICO apparatus with the reflectron TOF configuration. As in the linear TOF configuration, ions are accelerated to 100 eV over 5 cm before entering the 40 cm long drift region without a second acceleration. Ions starting from different points in the ionization region come into focus near the front of the reflectron. The ions then travel through a 35 cm drift region before coming back into focus as they are detected on a tandem MCP detector. Voltages are once again determined using the Wiley-McLaren space focusing conditions. Similar to the linear TOF configuration, kinetic information is present in the TOF spectra of metastable ions in the form of an asymmetric fragment peak. However lower velocities and longer flight paths in the drift region mean that the metastable ions have more time to dissociate and that slower rate constants can therefore be determined from the reflectron drift peak.

The primary advantage the reflectron TOF configuration is its mass resolution of 350 which is better than the linear TOF by a factor of about 3.5. This is due to the longer flight times of the ions in the reflectron. These longer flight times result in a disadvantage due to the fact that fragment ions formed in the drift region that are significantly lighter than the parent ion have much less kinetic energy. These ions are not efficiently reflected toward the detector and can be lost.
Figure 2-2 TPEPICO experimental apparatus with reflectron TOF analyzer. The fragment ion time of flight is dependent upon the location at which it dissociates. (a) If the fragment is formed in the first acceleration region (blue) then the fragment ion will appear as part of the asymmetric fragment peak. (b) If the fragment ion is formed in the first drift region (green) then the fragment will appear as a drift peak at the end of the fragment peak. (c) Lastly if the fragment ion does not dissociate before the end of the first drift region, then the fragment ions will appear as parent. (red)
2.1.3 Detailed Experimental information

2.1.3.1 Temperature Controlled Inlet

A temperature controlled inlet is used to control the temperature of the neutral sample gas flowing into the chamber. The inlet consists of a 1.5” x 1.5” x 5” copper block housing which contains a sample line, cooling line, and cartridge heater. The sample line runs through the center of the block and terminates in a stainless steel capillary just above the ionization region. The first extraction plates of both the electrons and the ions are located 6 mm away from the ionization spot. They are each copper plates with a central hole 0.5” in diameter. These plates are in thermal contact with the copper block so that the entire ionization region is isothermal, however Teflon spacers serve as electrical insulators so that voltages can be applied. A thermocouple placed between the Teflon sheet and copper block allows direct monitoring of the sample temperature. Temperatures below room temperature are maintained by a Neslab ULT-80 ultralow temperature circulating bath containing denatured ethanol which is capable of maintaining constant temperatures at the copper block over a range from 240 K to 300 K. Using this method, the temperature drift was less than 1° over the course of an experiment.

2.1.3.2 Velocity Focusing

Threshold PEPICO experiments must compromise between electron energy resolution, which increases with decreasing electric field, and mass resolution, which increases with increasing electric field. Traditionally, fields of about 1 V/cm were used for adequate electron energy resolution while typical fields for mass spectrometry were at least an order of magnitude greater. A major breakthrough for PEPICO techniques has been the use of velocity focusing
Figure 2-3 Schematic of temperature controlled inlet.
optics for the energy analysis of electrons. Velocity focusing of the electrons is accomplished by extracting them from the ionization region through an electrostatic lens, consisting of extraction plates with no grids. Figure 2-4 shows that by properly adjusting the voltages, threshold electrons are focused to a central spot at the end of the flight tube while energetic or hot electrons are focused to concentric rings around the central spot. The radius of the rings is determined by their velocity perpendicular to the extraction axis. Velocity focusing allows for the use of larger extraction fields without sacrificing electron energy resolution. Velocity focusing optics permits threshold electrons to be focused from a much larger ionization region than was previously possible with an electrostatic analyzer and gridded extraction plates which do not focus the electrons. Additionally it allows for extraction fields as high as 40 V/cm. Electron and ion collection efficiencies are often 35% and 25% respectively.

2.1.3.3 Correction for energetic electron contamination in TOF spectra.

PEPICO spectra consist of TOF spectra from energy selected ions. These spectra must be corrected for contamination from ions with lower internal energy due to emitting an energetic electron directly toward the detector. This is done by subtracting a fraction of the off-axis TOF spectrum from the center TOF spectrum. The peak areas in the spectra are corrected using eq. 2.1

\[ T_i = C_i - f H_i \]

2.1

Where \( T_i \) is the true threshold peak area of ion \( i \), \( C_i \) is the peak area of ion \( i \) in the center spectrum, \( f \) is an experimentally determined factor, and \( H_i \) is the peak area of ion \( i \) in the off-axis (hot electron) spectrum. The magnitude of \( f \) depends upon both the relative
Figure 2-4 Velocity focusing of electrons. When the velocity focusing condition is met, electrons without velocity perpendicular to the extraction axis are focused onto a central spot. Electrons with velocity perpendicular to the extraction axis are focused into concentric rings with radius corresponding to their velocity in this direction.
areas of the electron detectors, which is determined by the apertures through which electrons must travel to be detected, and the efficiencies of the two detectors. These efficiencies are hard to determine \textit{a priori} therefore $f$ is determined empirically. At high photon energies, well above the dissociation limit, the parent ion abundance in the center TOF spectrum must be due to hot electrons. $f$ is thus determined by setting $fH_i = C_i$.

Figure 2-5 shows adequate hot electron correction by the dissemination of the parent at 13.6 eV, 4.5 eV above the ionization energy. This photon energy also corresponds to a region of low intensity in the PES (\textit{i.e.} a Franck-Condon gap) where few threshold electrons are formed thereby causing hot electrons signal to be significant. Figure 2-5 demonstrates the effect of the factor $f$ on the breakdown diagram for chlorobenzene. The red curve indicates $f=0$ or no correction and the blue curve represents adequate correction for the hot electrons. If rate information is present in the TOF distribution, (\textit{i.e.} $10^3 < k(E) < 10^7$) then the asymmetric peak shape must be preserved during correction of the center spectrum for hot electrons. In order to do this, the spectra are subtracted channel by channel. Because two different TPHCs and MCPHAs are used to collect the center and hot electron TOF spectra, the time width of a single channel is different for the two TOF spectra. As a result, the off-axis spectrum must be scaled to align with the center spectrum using the equation below.

$$i'_H = \sum_{n=1}^{s} a_i i_c^{n-1}$$

Where $s$ is the number of peaks used to align the two spectra and is usually 2 or 3, $i'_H$ is the channel number of the hot electron (H) TOF spectrum that corresponds to the channel number of the cold electron (C) TOF spectrum $i_c$, and $a_i$ are fitting parameters used to align the two spectra. The scaled off axis channel numbers $i'_c$ will be non-integer.
Figure 2-5 Effect of hot electron correction in breakdown diagram of chlorobenzene.
channel numbers. To determine these intensities the ring spectrum is interpolated using a cubic spline algorithm. The scaled and interpolated hot electron spectrum can be subtracted from the center spectrum using eq. 2.1 where $i$ now refers to center spectrum channel number.

2.2 iPEPICO Apparatus

The recently built imaging photoelectron-photoion coincidence (iPEPICO) spectrometer located at the X04DB VUV beam line at the Swiss Light Source Synchrotron of the Paul Scherrer Institute has been described in detail recently.$^{5,6}$ Pure sample is effusively introduced at room temperature into the ionization region through a Teflon tube. A needle valve is used to control the flow of sample gas into the experimental chamber so that the pressure was between $5 \times 10^{-6}$ and $1 \times 10^{-5}$ mbar. Synchrotron radiation ionizes the sample in a 2 x 4 mm interaction region after passing through an inline monochromator and gas filter which filters higher order harmonics. The well known Ar 11s$^\prime$-14s$^\prime$ and Ne 13s$^\prime$,14s$^\prime$, 12d$^\prime$, and 13 d$^\prime$ autoionization lines are used to calibrate the photon energy. Upon ionization, a 40-80 V•cm$^{-1}$ electric field accelerates the electrons and ions in opposite directions. The electrons travel vertically into a 26.5 cm flight tube. Velocity map imaging is used to focus the electrons onto a 40 mm diameter DLD40 Roentdek position sensitive delay-line detector. At 80 V•cm$^{-1}$, threshold electrons were focused to a spot size of 0.9 mm x 0.4 mm which corresponds to 0.2 meV, much less than the photon resolution of 1 meV at 10 eV. After acceleration, the ions pass through a second acceleration region followed by a linear time of flight mass analyzer and are space focused onto a Jordan TOF C-726 MCP detector.
Electron and ion signals as well as electron positions are recorded in the triggerless mode of a high performance time to digital converter card. The electron and ion hit times are measured relative to a master clock. All ions detected within a defined time window of an electron are correlated to obtain time-of-flight distributions. This multiple start/multiple stop data acquisition scheme enables data acquisition at ionization rates in excess of 100 kHz, which is beneficial at a high intensity light source, such as the synchrotron.

The experimental data may be analyzed and plotted in many ways: at a single photon energy, the radial distribution of electrons positions on the image in Figure 2-6 yields a portion of the photoelectron spectrum (PES); the threshold electron signal as a function of the photon energy yields a TPES; the threshold electron signal detected in coincidence with an ion in a particular TOF range yields a mass-selected TPES; the total ions in coincidence with all electrons as a function of photon energy yields the total ion curve; and the fractional ion abundances in the TOF spectra as a function of the photon energy yield the breakdown diagram.

Similar to TPEPICO, contamination of the threshold electron signal from hot electrons must be subtracted. Figure 2-6 shows the regions on the electron image that are defined as the center and energetic electron background or ‘ring’. The TPES is corrected for hot electrons by subtracting the number of counts in the ring region of the image multiplied by the same factor discussed in section 2.1.3.3 from the number of electron counts in the center region. With the imaging detector however, the efficiencies of the threshold and background regions are identical and therefore \( f \) is determined exclusively by the ratio of the center and ring areas. The ions that are in coincidence with
the electrons defined as either center or ring are used to generate center and ring TOF spectra. Threshold TOF spectra can then be generated using eq. 2.1 where \( i \) corresponds to channel number. Because hit times for both the ring and center electrons are recorded on a master clock and corresponding TOF spectra from these data post acquisition using software, the channel/TOF calibrations are the same for the center and ring TOF spectra and therefore do not require alignment prior to correction as described in section 2.1.3.3. Using this scheme, the energy resolution was ultimately limited by the photon energy resolution of 2.5 meV.

2.3 Modeling of experimental data

In order to determine reaction energetics and kinetics as precisely as possible, we model the experimental PEPICO data. Our approach to determining reaction energetics depends upon whether the ions dissociate rapidly on the timescale of our apparatus \((k(E) > 10^7 \text{ s}^{-1})\) or the ions dissociate slowly \((k(E) < 10^7 \text{ s}^{-1})\). If the dissociation is fast, then only the breakdown diagram is required to determine \(E_0\). For slow dissociations, the individual TOF distributions are modeled to determine the \(k(E)\) curve. In both cases, ions are produced from a room temperature sample of neutral molecules and therefore have a distribution of internal energies. It is approximated that the neutral internal energy distribution is transposed to the ionic manifold. To determine the ion internal energy distribution, the electron energy resolution, the spectral width of our light source \((ca \ 12 \text{ meV})\) and the energy distribution of our room temperature sample \((30 \text{ to more than 140 meV depending on the number of degrees of freedom of the molecule})\) were convoluted with the thermal energy distribution.

2.3.1 Fast dissociation

When the dissociation rate is fast, the \(E_0\) for the lowest energy dissociation pathway is located at the energy at which the parent ion disappears. (See Figure 1-1)
Figure 2-6 Electron image with defined threshold (blue, center) and energetic background (red, ring) regions.
However, for large ions with many vibrational degrees of freedom, the internal energy distribution is broad and the precise energy at which the parent ion disappears is poorly defined. As a result, modeling is necessary to determine this 0 K dissociation energy.

The ion internal energy, relative to the ground state of the ion, is given by \( E_{\text{ion}}(h \nu) = h \nu - IE + E_{\text{th}} \), where \( IE \) is the adiabatic ionization energy and \( h \nu \) is the photon energy. If \( f_{\text{Th}}(E) \) is the normalized internal energy distribution of the ion, then the relative abundance of the parent ion, \( BD_{\text{parent}}(h \nu) \), is determined by the portion of the ion internal energy distribution that lies below the 0 K dissociation threshold \( E_0 \):

\[
BD_{\text{parent}}(h \nu) = \int_0^{E_0-h \nu} f_{\text{Th}}(E) dE \quad \text{for } h \nu < E_0
\]  

(2.3)

The relative fragment ion abundance is then

\[
BD_{\text{fragment}}(h \nu) = 1 - BD_{\text{parent}}(h \nu)
\]

(2.4)

When the photon energy exceeds \( E_0 \), the fractional parent and daughter ion signals remain 0 and 1, respectively. The neutral sample temperature is measured at the ionization region by a thermocouple. Thus, the \( E_0 \) can be determined by varying only a single parameter.

2.3.2 Slow dissociation

For slow dissociations, kinetic information available in the TOF spectra, (see Figure 2-1 and Figure 2-2) is modeled to determine the \( E_0 \). The ion internal energy distribution \( f_{\text{Th}}(E_{\text{th}}) \) is taken into account when determining the relative abundances of the peaks in the TOF spectra as well as the asymmetric shape of the fragment peak.

Figure 2-7 shows that at a given photon energy the amount of parent detected slowly decreases as the ion internal energy, \( E_{\text{th}} \), and therefore \( k(E) \), increases. The fractional
The relative abundances of parent and fragment ion are determined by both the ion internal energy distribution \( f_{Th} \) and the rate curve \( k(E) \). At a specific ion internal energy the parent abundance is determined by \( k(E) \). To determine the \( k(E) \) and relative abundances for all ion internal energies at a certain photon energy, these abundances are weighted by the internal energy distribution and summed. (eq. 2.6)
abundances, \( A \), are determined by summing the parent ion decay and fragment ion growth over \( E_{Th} \), weighted by \( f_{Th}(E_{Th}) \) as is shown by eq. 2.5 and 2.6.

\[
A_{\text{parent}, \tau} = \int_0^\infty f_{Th}(E_{Th}) \exp\left[-k(h\nu + E_{Th} - IE)\tau\right] dE_{Th}
\]

\[
A_{\text{fragment}} = 1 - A_{\text{parent}} = \int_0^\infty f_{Th}(E_{Th}) \left(1 - \exp\left[-k(h\nu + E_{Th} - IE)\tau\right]\right) dE_{Th}
\]

Where \( k(E) \) is the dissociation rate as a function of the ion internal energy measured relative to the ground state of the ion and \( \tau \) is the time that the parent ion, after being formed, has to dissociate and still be detected as a fragment (i.e. the time required for the parent ion to travel from the ionization region to the end of the first drift region).

In the TOF spectra, the asymmetric fragment peak is modeled by calculating the TOF spectrum denoted by \( F(E_t, t) \), for each \( k(E) \) over range of \( f_{Th}(E_{Th}) \) and summing these spectra weighted by \( f_{Th}(E_{Th}) \). The summed TOF spectrum, \( F_{\text{eff}}(h\nu, t) \), is given by

\[
F_{\text{eff}}(h\nu, t) = \int_0^\infty f_{Th}(E_{Th}) F(h\nu + E_{Th} - IE_t, t) dE_{Th}
\]

The \( E_0 \) is determined by adjusting the parameters that determine \( k(E) \) which, as is discussed in detail in chapter 4 depend upon the rate theory employed, to fit the experimental TOF distributions and breakdown diagram.

2.4 Computational Methods

2.4.1 Modeling

Molecular parameters used in the modeling of experimental data such as vibrational frequencies, rotational constants and geometries used in this paper were determined using the Gaussian 03 computer software. Geometry optimizations and
normal mode analyses, unless otherwise specified, were determined using the B3LYP hybrid functional with the 6-311++G(d,p) basis set for H, C, N, Cl and Br, and 6-311G(d,p) for iodine.\textsuperscript{9,10} A scaling factor of 1 was used\textsuperscript{11} for vibrational frequencies and anharmonicity corrections. For the molecules where internal rotations may have significant contributions to the molecular heat capacity, the Ayala-Schlegel\textsuperscript{12} method was used to determine a correction to the harmonic treatment of these modes when determining $H_{298}-H_0$. Thermochemical values were calculated using the G3, W1, and CBS-APNO methods.

2.4.1.1 Ionization Energies

The adiabatic IE is the energy difference between the ground state of the ion and the ground state of the neutral. For fast dissociations, the $IE_{ad}$ is not necessary because, as shown by eq. 2.3, the parent ion abundance is determined by the integral of $f_{Th}(E_{Th})$ from 0 to $E_0-h\nu$. For slow dissociations however, $k(E)$ must be calculated, where $E$ is the ion internal energy relative to the ground state of the ion (i.e. $h\nu-IE_{ad}+E_{Th}$). Often an experimental value is available but sometimes the adiabatic IE must be calculated. Optimized the periodic table. The difference between the atomization energies of the ground and neutral states provides the adiabatic IE.

2.4.1.2 Calculated thermochemistry from isodesmic reactions.

We have supported several of our reported $\Delta H$ using high level energy calculations. The calculated atomization energies of molecules and ions of interest can be converted to heats of formation. However, there is some error in these values due to approximations built into the calculations. This error can be diminished using isodesmic
reactions. An isodesmic reaction is one where the products and reactants have the same number of the same types of bonds, an example is shown in eq. 2.8.

\[
\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5^+ \rightarrow \text{CH}_3^+ + \text{C}_2\text{H}_5\text{Cl}
\]

In eq 2.8, both products and reactants have 8 H-C bonds, 1 C-Cl bond, and 1 C-C bond. This sort of “symmetry” results in a cancellation of the intrinsic error when the heat of reaction is determined. This heat of reaction is used in combination with experimentally determined heats of formation for the constituents to determine the heat of formation of the species of interest. By cleverly selecting reaction constituents that can be calculated to a high precision and also have high precision thermochemistry available, uncertainty in the desired heat of formation can be minimized.


CHAPTER 3: Photodissociation of $\text{C}_3\text{H}_8^+$ observed by iPEPICO:

Accurate Heats of Formation of $i$-$\text{C}_3\text{H}_7^+$, $i$-$\text{C}_3\text{H}_7\text{Cl}$, $i$-$\text{C}_3\text{H}_7\text{Br}$, and $i$-$\text{C}_3\text{H}_7\text{I}$

3.1 Introduction

Due to its stability, the isopropyl ion is a common product of the dissociative photoionization of alkanes. However, a reliable high accuracy determination of its heat of formation has yet to be determined. One route to determining $\Delta H(i$-$\text{C}_3\text{H}_7^+)$ is via dissociative photoionization:

$$i$-$\text{C}_3\text{H}_7X + h\nu \rightarrow i$-$\text{C}_3\text{H}_7^+ + X + e^-(X=\text{H, Cl, Br, I})$$

3.1-1

It is known that these systems have stable parent ions that rapidly dissociate to form $i$-$\text{C}_3\text{H}_7^+$ which makes determination of their photoionization onset relatively easy.

The 298 K photodissociation of $\text{C}_3\text{H}_8$ to form $i$-$\text{C}_3\text{H}_7^+$ was first observed by Steiner et al.\textsuperscript{1} in 1961 and measured again by Chupka and Berkowitz\textsuperscript{2} in 1967 using photoionization mass spectrometry (PIMS). The 298 K appearance energy ($AE_{298}$) of 11.53 ± 0.01 eV reported by Steiner\textsuperscript{1} appears to be quite reasonable, however the extrapolated $AE_0$ was significantly underestimated in both of these studies. The photodissociation of the isopropyl halides have been reported several times but the derived $\Delta_h H(i$-$\text{C}_3\text{H}_7^+)$ are scattered over nearly 10 kJ·mol$^{-1}$\textsuperscript{3-6} The first study was by
Traeger\textsuperscript{3} in 1980 using PIMS which yielded a value for $\Delta H_{298}^\circ (i$-$C_3H_7^+)$ of 802.5 ± 1.7 kJ$\cdot$mol$^{-1}$\textsuperscript{7}. However, the onsets in these measurements are poorly defined and the uncertainty is believed to be underestimated. In 1982, Rosenstock \textit{et al} used photoelectron-photoion coincidence (PEPICO) spectroscopy to report a $\Delta H_{298}^\circ (i$-$C_3H_7^+)$ of 798.8 ± 2 kJ$\cdot$mol$^{-1}$ from the 0 K photoionization onset of $i$-$C_3H_7$Br\textsuperscript{4}. In this study, it was reported that the dissociation was metastable which has not been observed in subsequent studies. Accounting for a nonexistent kinetic shift would certainly cause the determined $\Delta H_{298}^\circ (i$-$C_3H_7^+)$ to be underestimated. In 2000, the 0 K dissociation onsets ($E_0$) of isopropyl ion from isopropyl chloride, isopropyl bromide and isopropyl iodide were measured using pulsed field ionization-photoelectron photoion coincidence spectroscopy (PFI-PEPICO) by Baer \textit{et al}\textsuperscript{5} to be 11.085 ± 0.005 eV, 10.505 ± 0.008 eV and 9.851 ± 0.025 eV. This resulted in a composite $\Delta H_{298}^\circ (i$-$C_3H_7^+)$ of 807.7 ± 1.5 kJ$\cdot$mol$^{-1}$. However, as pointed out recently\textsuperscript{8}, these experiments were plagued by dimers which caused the reported onsets to be too high. In 2004 Brooks \textit{et al}\textsuperscript{6} reported a value of 803.9 ± 1.5 kJ$\cdot$mol$^{-1}$ using threshold photoelectron-photoion coincidence spectroscopy (TPEPICO) to determine the photoionization onset of isopropyl ion from isopropyl chloride. In this study, the sample was not cooled in an expansion, eliminating the possibility of dimer formation. However, it was recently determined that the photon energies of the isopropyl chloride data were not properly calibrated and, as a result, reported a 0K dissociation onset (and therefore $\Delta H^\circ (i$-$C_3H_7^+)$) that was 0.030 meV too low.

Another possible route to $\Delta H^\circ (i$-$C_3H_7^+)$ is measurement of the ionization energy of the isopropyl radical. In 1979 Houle and Beauchamp measured the $IE(i$-$C_3H_7)$ to be
7.36 ± 0.02 eV. This value was later confirmed by Dyke et al.\textsuperscript{10} Beauchamp, relying upon $\Delta_{f}H^\circ(i\text{-}C_{3}H_{7})$, reported a value of 783 ± 4.6 kJ mol\textsuperscript{-1} for $\Delta_{f}H^\circ(i\text{-}C_{3}H_{7}^+)$. A value for $\Delta_{f}H^\circ(i\text{-}C_{3}H_{7})$ that was too low, in combination with the $IE(i\text{-}C_{3}H_{7})$ being underestimated due to hot bands in the observed photoelectron spectra, caused Beauchamp’s reported value for $\Delta_{f}H^\circ(i\text{-}C_{3}H_{7}^+)$ to be lower than subsequent photoionization studies by nearly 20 kJ mol\textsuperscript{-1}.

The proton affinity of propene plays an important role in calibrating the proton affinity scale. The heats of formation of $H^+$ and $C_{3}H_{6}$ are very well known.\textsuperscript{11} Most of the uncertainty in $PA(C_{3}H_{8})$ is therefore due to the $\Delta_{f}H^\circ_{298}(i\text{-}C_{3}H_{7}^+)$. As a result of the scatter in $\Delta_{f}H^\circ_{298}(i\text{-}C_{3}H_{7}^+)$, $PA(C_{3}H_{8})$ has oscillated between 746 kJ mol\textsuperscript{-1} and 743 kJ mol\textsuperscript{-1}.

Calculations can also be used to determine $\Delta_{f}H^\circ_{0,K}(i\text{-}C_{3}H_{7}^+)$. Lau and Ng\textsuperscript{12} have recently determined values of 90.0 and 806.4 kJ mol\textsuperscript{-1} for the isopropyl radical and ion 298 K heats of formation at the CCSD(T)/CBS level. These values appear to be within the scatter of previously reported values. The 0 K values provide an ionization energy of 7.437 eV, significantly higher than the experimentally observed IE.\textsuperscript{9,10}

3.2 Results

The data are shown in the forms of threshold photoelectron spectra (Figure 3-3 through Figure 3-4) and breakdown diagrams (Figure 3-5 through Figure 3-8) for $C_{3}H_{8}$, $i\text{-}C_{3}H_{7}Cl$, $i\text{-}C_{3}H_{7}Br$ and $i\text{-}C_{3}H_{7}I$. It is shown in Figure 3-5 that the formation of $i\text{-}C_{3}H_{7}^+$ is the lowest energy dissociation channel for propane. The breakdown diagrams for the isopropyl halides (Figure 3-6 through Figure 3-8) show that the only fragment ion formed over the energy range of interest is $i\text{-}C_{3}H_{7}^+$. For all compounds studied it was
Figure 3- 1 Propane TPES
Figure 3-2 $i$-$\text{C}_3\text{H}_7\text{Cl}$ TPES
Figure 3- 3 TPES of $i$-C$_3$H$_7$Br
Figure 3-4 TPES of i-C₃H₇Br
Figure 3-5 Breakdown Diagram for $\text{C}_3\text{H}_8^+$. The open circles indicate the $\text{C}_3\text{H}_8^+$ abundance and the solid squares represent $i\text{-C}_3\text{H}_7^+$ abundance. The inset is an expanded view of the breakdown diagram near the $E_0$. 
Figure 3-6 Breakdown Diagram for \( i-C_3H_7Cl^+ \). The open circles indicate the of the \( i-C_3H_7Cl^+ \) abundance and the solid squares represent \( i-C_3H_7^+ \) abundance. The inset is an expanded view of the breakdown diagram near the \( E_0 \). The grey line indicates the threshold photoelectron spectrum (arbitrary units).
Figure 3- 7 Breakdown Diagram for \(i\)-C\(_3\)H\(_7\)Br\(^+\). The open circles indicate the of the \(i\)-C\(_3\)H\(_7\)Br\(^+\) abundance and the solid squares represent \(i\)-C\(_3\)H\(_7^+\) abundance. The inset is an expanded view of the breakdown diagram near the \(E_0\). The grey line indicates the threshold photoelectron spectrum (arbitrary units).
Figure 3-8 Breakdown Diagram for $i$-C$_3$H$_7$I$^+$. The open circles indicate the of the $i$-C$_3$H$_7$I$^+$ abundance and the solid squares represent $i$-C$_3$H$_7^+$ abundance. The inset is an expanded view of the breakdown diagram near the $E_0$. The grey line indicates the threshold photoelectron spectrum (arbitrary units).
observed that the $i$-$C_3H_7^+$ peaks in the TOF spectra were symmetric at low energies, indicating that the dissociation rates for $i$-$C_3H_7^+$ formation were faster than the timescale of our apparatus ($k(E) > 10^7$ s$^{-1}$).

The improved energy resolution of the iPEPICO apparatus reveals some structure in the breakdown diagrams for $i$-$C_3H_7Br$ and $i$-$C_3H_7I$. Similar features have been observed in the case of CH$_3$I.$^8$ In Figure 3-7 and Figure 3-8 the $i$-$C_3H_7Br$ and $i$-$C_3H_7I$ abundance is lower than expected in the region of the Franck-Condon gaps in the TPES. The production of threshold electrons in Franck-Condon gaps is not well understood. Guyon et al.$^{13}$ and Chupka et al.$^{14}$ proposed a mechanism that relies upon the existence of long-lived neutral Rydberg states. Because there is a quasi continuum of these Rydberg states converging to various ion states, it is possible for the neutral molecule to absorb a photon and access these neutral Rydberg states in regions where the probability of direct ionization is low ($i.e.$ a Franck-Condon Gap). From these states the neutral molecule can cross over to a neutral dissociative surface. As the molecule dissociates the molecule may cross over to a lower energy ion state, generating a threshold electron. Because energy must be conserved, the kinetic energy of the dissociating neutral fragments becomes vibrational energy in the ion. It was suggested in the study of CH$_3$I that the warmer ion internal energy distribution observed as an increase in fragment ion abundance, is a result of this process being aided by rotational excitation.$^8$ A similar effect appears operatie in the isopropyl halide ion dissociation. Observed in Figure 3-8 are peaks in the $i$-$C_3H_7Br$ abundance that coincide perfectly with peaks in the TPES. Most notable is the peak at 10.35 eV. When a neutral molecule is excited to a Rydberg state that is close in energy to an ion state, the Rydberg molecule can autoionize and generate a threshold electron.
However rotationally excited neutral molecules can also begin to dissociate, the majority of which will not form a threshold electron. This results in a warmer ion internal energy distribution observed as an increase in fragment ion abundance. It is important to mention that, because the dissociation is fast, these features do not shift the location of the $E_0$.

When the dissociation rate is fast, the $E_0$ for the lowest energy dissociation pathway is located at the energy where the parent ion disappears. To precisely determine the $E_0$, modeling is necessary. The ion internal energy, relative to the ground state of the ion, is given by $E_{\text{ion}}(h\nu) = h\nu - IE + E_{th}$, where $IE$ is the adiabatic ionization energy and $h\nu$ is the photon energy. If $P(E)$ is the normalized thermal energy distribution of the ion, then the relative abundance of $i$-$C_3H_7X^+$, $BD_{C_3H_7X}(h\nu)$, is determined by the portion of the ion internal energy distribution that lies below the 0 K dissociation threshold $E_0(i$-$C_3H_7^+)$ (See Figure 1-1):

$$BD_{C_3H_7X}(h\nu) = \int_0^{E_0-h\nu} P(E) dE \quad \text{for} \ h\nu < E_0$$

(3.2)

The relative fragment ion abundance is then

$$BD_{C_3H_7}(h\nu) = 1 - BD_{C_3H_7X}(h\nu)$$

(3.3)

When the photon energy exceeds the $E_0$, the fractional parent and daughter ion signals remain 0 and 1, respectively. We use the neutral frequencies here to determine the ion internal energy distribution. The internal energy distribution of the neutral molecule is often faithfully transposed to the ionic manifold upon ionization. However, this is not always the case and the temperature is therefore used as a fitting parameter. The best fit onset for $C_3H_8$ was $11.639 \pm 0.002$ eV with a Temperature of $270 \pm 15$ K. For $i$-$C_3H_7Cl$ and $i$-$C_3H_7Br$, the best fit onsets were $11.064 \pm 0.004$ and $10.454 \pm 0.008$
eV with best fit temperatures of 305 ±10 K and 298 ± 20 K, respectively. The larger uncertainty in the temperature for \( i-C_3H_7\)Br is due to the enhanced structure in the breakdown diagram. For \( i-C_3H_7\)I, the best fit \( E_0 \) and temperature was 9.812 ± 0.008 eV and 320 ± 15 K. The elevated temperature of the ion internal energy distribution may be a result of the Franck-Condon gap coinciding with a large portion of the breakdown diagram. The reported \( E_0 \) for \( i-C_3H_7\)I is within the experimental error of the previous TPEPICO measurement by Baer et al\(^{16} \) (9.818 ± 0.010 eV) and slightly lower than the laser based MATI value of 9.818 ± 0.004 eV.\(^{17} \) Table 3-1 summarizes the current and previously measured onset energies.

**Table 3-1. Comparison of \( E_0 (i-C_3H_7^+) \) with previous values.**

<table>
<thead>
<tr>
<th></th>
<th>( E_0 )</th>
<th>( AE_{298} )</th>
<th>( AE_{0}-AE_{298} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3H_8 )</td>
<td>11.64 ± 0.03(^a)</td>
<td>11.58 ± 0.03(^b)</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>11.63 ± 0.01(^c)</td>
<td>11.52 ± 0.02(^d)</td>
<td></td>
</tr>
<tr>
<td>( i-C_3H_7)Cl</td>
<td>11.05 ± 0.02(^a)</td>
<td>10.92(^e)</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>11.085 ± 0.005(^f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.036 ± 0.010(^g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( i-C_3H_7)Br</td>
<td>10.47 ± 0.02(^a)</td>
<td>10.33(^e)</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>10.42 ± 0.01(^e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.505 ± 0.020(^f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( i-C_3H_7)I</td>
<td>9.84 ± 0.02(^a)</td>
<td>9.7(^e)</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>9.77 ± 0.02(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.851 ± 0.025(^f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.8180 ± 0.0036(^i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( i-C_3H_7)I</td>
<td>9.818 ± 0.010(^d)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)These values were converted from an \( AE_{298} \) by adding \( AE_{0}-AE_{298}=<E_{rot}>+<E_{vib}> \).  
\(^b\)Steiner et al. 1961; \(^c\)Chupka 1967; \(^d\)This work; \(^e\)Traeger 1980; \(^f\)Baer et al 2000; \(^g\)Brooks et al 2004; \(^h\)Rosenstock et al 1982; \(^i\)Kim et al.
3.3 Derived Thermochemistry of \(i\)-C\(_3\)H\(_7^+\), \(i\)-C\(_3\)H\(_7\)Cl \(i\)-C\(_3\)H\(_7\)Br and \(i\)-C\(_3\)H\(_7\)I

In the absence of a reverse barrier, the \(E_0\) is equal to the thermochemical onset. That is,

\[
E_0 = \Delta_f H^o_{0K}(i\text{-C}_3\text{H}_7^+) + \Delta_f H^o_{0K}(X) - \Delta_f H^o_{0K}(i\text{-C}_3\text{H}_7X)
\]

(3.3)

where \(X = \text{H, Cl, Br, and I.}\) Thus, the uncertainty in \(\Delta_h(i\text{-C}_3\text{H}_7^+)\) is dependent upon the uncertainty in the \(\Delta_h(i\text{-C}_3\text{H}_7X), \Delta_h(i\text{-C}_3\text{H}_7)(X),\) and \(E_0\). The 298 K heats of formation of C\(_3\)H\(_8\), \(i\)-C\(_3\)H\(_7\)Cl, \(i\)-C\(_3\)H\(_7\)Br, and \(i\)-C\(_3\)H\(_7\)I reported in the literature must be converted to 0 K heats of formation. This requires the \(H_0-H_{298}\) of the constituents of the formation reaction. The \(H_0-H_{298}\) for \(H_2(g), \text{Cl}_2(g), \text{Br}_2(g), \text{I}_2\) and \(\text{C}(s)\) are reported by Chase,\(^\text{11}\) but the \(H_0-H_{298}\) for \(i\)-C\(_3\)H\(_7X\) must be calculated. Usually, \(H_{298}-H_0\) is calculated using the harmonic oscillator-rigid rotor approximation. However these molecules contain two methyl groups which should be treated as hindered rotors. To account for this we use the method outlined by Ayala and Schlegel\(^\text{18}\) to calculate a correction to the \(H_0-H_{298}\) determined using the rigid rotor-harmonic oscillator approximation. These corrections were 0.34, 0.24, 0.24, and 0.22 kJ\(\cdot\)mol\(^{-1}\) for C\(_3\)H\(_8\), \(i\)-C\(_3\)H\(_7\)Cl, \(i\)-C\(_3\)H\(_7\)Br, and \(i\)-C\(_3\)H\(_7\)I. The values determined for \(H_0-H_{298}\) and \(\Delta_h H^o_{0K}(i\text{-C}_3\text{H}_7X)\) are listed in Table 3-2. From \(i\)-C\(_3\)H\(_7\)Cl, \(i\)-C\(_3\)H\(_7\)Br, and \(i\)-C\(_3\)H\(_7\)I the \(\Delta_h H^o_{0K}(i\text{-C}_3\text{H}_7^+)\) was determined to be 823.9 ± 1.4 kJ\(\cdot\)mol\(^{-1}\), 819.3 ± 2.5 kJ\(\cdot\)mol\(^{-1}\), and 821.3 ± 3.9 kJ\(\cdot\)mol\(^{-1}\) respectively. The value for \(\Delta_h H^o_{0K}(i\text{-C}_3\text{H}_7^+)\) determined from propane is known better than the heats of formation of the isopropyl halides. We can therefore use Eqn. 3.3 and the reported \(\Delta_h H^o_{0K}(i\text{-C}_3\text{H}_7^+)\) to determine more precise values for these molecules. These values are determined to be \(-144.2 ± 0.7\) kJ\(\cdot\)mol\(^{-1}\), \(-94.1 ± 0.9\) kJ\(\cdot\)mol\(^{-1}\), and \(-37.0 ± 0.9\) kJ\(\cdot\)mol\(^{-1}\) for \(i\)-C\(_3\)H\(_7\)Cl, \(i\)-C\(_3\)H\(_7\)Br, and \(i\)-C\(_3\)H\(_7\)I respectively.
Table 3-2 Derived and Ancillary Thermochemical Values (kJ•mol\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>(\Delta H_{298K})</th>
<th>(\Delta H_{0K})</th>
<th>(H_{0}^\circ H_{298})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)H(_8)</td>
<td>-104.7 ± 0.5(^b)</td>
<td>-82.4 ± 0.5</td>
<td>14.70</td>
</tr>
<tr>
<td>i-C(_3)H(_7)Cl</td>
<td>-144.2 ± 0.7(^a)</td>
<td>-123.4 ± 0.7</td>
<td>16.57</td>
</tr>
<tr>
<td>i-C(_3)H(_7)Br</td>
<td>-94.1 ± 0.9(^a)</td>
<td>-66.2 ± 0.9</td>
<td>17.07</td>
</tr>
<tr>
<td>i-C(_3)H(_7)I</td>
<td>-37.0 ± 0.9(^a)</td>
<td>-15.0 ± 0.9</td>
<td>17.32</td>
</tr>
<tr>
<td>H</td>
<td>216.035(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>119.621(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>117.92(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>107.161(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(^+)</td>
<td>1530.049(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-C(_3)H(_7)</td>
<td>20.0 ± 0.7(^e)</td>
<td></td>
<td>15.86</td>
</tr>
<tr>
<td>i-C(_3)H(_7)(^+)</td>
<td>807.4 ± 0.5(^af)</td>
<td>824.6 ± 0.5(^af)</td>
<td>15.57</td>
</tr>
</tbody>
</table>

\(PA_{298}(C_3H_6) = 742.7 ± 0.8\(^a\)\)

\(^a\)This Work; \(^b\)Pittam 1972; \(^c\)Pedley 1994; \(^d\)Chase 1998; \(^e\)Seakins et al 1992; \(^f\)Determined using the convention that excludes the enthalpy of an electron at room temperature.

3.3.1 Isodesmic Calculations of i-C\(_3H\(^7\)\(^+\)

In support of the experimentally derived i-C\(_3H\(^7\)\(^+\) heat of formation, we calculated the G3, CBS-APNO, and W1 energies for the following isodesmic reactions:

\[
C_3H_8 + \left( \frac{CH_3^+}{C_2H_5^+} \right) \rightarrow (i-C_3H_7^+) + \left( \frac{CH_4}{C_2H_6} \right)
\]

\[
(i-C_4H_{10}) + \left( \frac{CH_3^+}{C_2H_5^+} \right) \rightarrow (i-C_3H_7^+) + \left( \frac{C_2H_6}{C_3H_8} \right)
\]

The i-C\(_3H\(^7\)\(^+\) heat of formation is determined from the calculated reaction energy and the experimental heats of formation for the other reaction constituents. The methane heat of formation\(^23\) and the corresponding \(E_0(CH_4 \rightarrow CH_3^+ + H)\)\(^24\) are very well known and
provide a value of 1099.37 ± 0.1 kJ•mol⁻¹ for $\Delta_f H^0_{\text{ok}}(\text{CH}_3^+)$. The heats of formation of the neutral hydrocarbons are all reported by Pedley²⁰ to within 1 kJ•mol⁻¹.

Table 3-3 shows the $\Delta_f H^0_{\text{ok}}(i$-$\text{C}_3\text{H}_7^+)$ determined by calculations of the above isodesmic reaction energies. The G3 values are the least expensive calculation and provides results that agree with each other to within 4 kJ•mol⁻¹, yielding an average value of xxx. The W1 and CBS-APNO results provide values in better agreement with each other as well as in much better agreement with the experimental value of 823.9 ± 1.4 kJ•mol⁻¹. The average of the W1 and CBS-APNO calculations is 825.1± 1.0 kJ•mol⁻¹.

These results rely upon the accuracy of the experimentally determined heats of formation of the reaction constituents. It is observed that the values for $\Delta_f H^0_{\text{ok}}(i$-$\text{C}_3\text{H}_7^+)$ determined for Y=C₂H₅ are 1kJ•mol⁻¹ higher than the values determined for Y=CH₃. The methyl ion heat of formation is known much better than the ethyl. As a result, the ethyl ion heat of formation may require further study. This value is difficult to obtain experimentally due to the dearth of systems that dissociate simply to form ethyl ion. This ion is small and is closed shell, thus making it a good candidate for state of the art ab initio calculations such as W4²⁵ or HEAT²⁶.

<table>
<thead>
<tr>
<th>Y</th>
<th>Method</th>
<th>X = H</th>
<th>X = CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>G3</td>
<td>828.8</td>
<td>828.0</td>
</tr>
<tr>
<td></td>
<td>CBS-APNO</td>
<td>823.5</td>
<td>825.3</td>
</tr>
<tr>
<td></td>
<td>W1</td>
<td>824.7</td>
<td></td>
</tr>
<tr>
<td>C₂H₅</td>
<td>G3</td>
<td>824.0</td>
<td>824.0</td>
</tr>
<tr>
<td></td>
<td>CBS-APNO</td>
<td>826.2</td>
<td>826.0</td>
</tr>
<tr>
<td></td>
<td>W1</td>
<td>825.2</td>
<td></td>
</tr>
</tbody>
</table>
3.3.2 Ionization Energy of \( i\text{-C}_3\text{H}_7 \) and Proton Affinity of \( \text{C}_3\text{H}_6 \)

The adiabatic ionization energy of the \( i\text{-C}_3\text{H}_7 \) can be determined from the 0 K heats of formation of the isopropyl ion and radical. Bodi et al.\textsuperscript{27} reported the \( \Delta H^\circ_{298K}(i\text{-C}_3\text{H}_7) \) to be \( 90 \pm 1.7 \) kJ \( \cdot \) mol\(^{-1} \). With a hindered rotor correction\textsuperscript{18} of \( -0.31 \) kJ\( \cdot \)mol\(^{-1} \) the \( H_0-H_{298} \) was calculated to be \( 15.57 \) kJ\( \cdot \)mol\(^{-1} \). Using this value, a \( \Delta H^\circ_{0K}(i\text{-C}_3\text{H}_7) \) of \( 106.9 \) kJ\( \cdot \)mol\(^{-1} \) is determined. Using the experimentally determined value for \( \Delta H^\circ_{0K}(i\text{-C}_3\text{H}_7^+) \) the IE(\( i\text{-C}_3\text{H}_7 \)) was determined to be \( 7.438 \pm 0.020 \) eV. This is in excellent agreement with the theoretical IE(\( i\text{-C}_3\text{H}_7 \)) of \( 7.436 \) eV calculated by Lau and Ng\textsuperscript{12}. This value disagrees, however with previous attempts to measure the adiabatic ionization energy from photoelectron spectra by Houle and Beauchamp\textsuperscript{9} and by Dyke et al.\textsuperscript{10}. This is not surprising as the first peak in the PES of isopropyl radical is very small and broad due to poor Franck-Condon factors at threshold.

The absolute proton affinity of propene can be determined by converting the 0K heat of formation of the isopropyl ion to 298 K. The hindered rotor correction was determined to be \( 0.32 \) kJ\( \cdot \)mol\(^{-1} \) with a value of \( H_{298}-H_0 \) of \( 15.57 \) kJ\( \cdot \)mol\(^{-1} \), the \( \Delta H^\circ_{298K}(i\text{-C}_3\text{H}_7^+) \) is determined to be \( 806.7 \pm 1.4 \) kJ\( \cdot \)mol\(^{-1} \). Using this value, we calculate a \( PA_{298}(\text{C}_3\text{H}_6) \) of \( 743.4 \pm 1.5 \) kJ\( \cdot \)mol\(^{-1} \). This value is in excellent agreement with the composite value reported by Meot-Ner\textsuperscript{28} of \( 743.4 \pm 1.3 \) kJ\( \cdot \)mol\(^{-1} \) who took a simple average of relative PA\textsuperscript{298}’s reported by Szulejko and McMahon,\textsuperscript{29} Meot-Ner and Sieck,\textsuperscript{30} and Smith and Radom.\textsuperscript{31}
3.4 Conclusions

\[ \Delta_f H^{0}_{298K}(i-C_3H_7^+) \] has been determined to be 824.6 ± 0.6 kJ\( \cdot \)mol\(^{-1} \) from measurement of the \( E_0(i-C_3H_7^+) \) by modeling TPEPICO breakdown diagram of propane. Breakdown diagrams were also modeled for \( i-C_3H_7Cl, i-C_3H_7Br, \) and \( i-C_3H_7I \) and the \( E_0(i-C_3H_7^+) \) was determined for each species. Using the currently determined value for \( \Delta_f H^{0}_{298K}(i-C_3H_7^+) \), \( \Delta_f H^{0}_{298K}(i-C_3H_7Cl) \), \( \Delta_f H^{0}_{298K}(i-C_3H_7Br) \) and \( \Delta_f H^{0}_{298K}(i-C_3H_7I) \) were determined to be -144.9 ± 0.7 kJ\( \cdot \)mol\(^{-1} \), -94.1 ± 1.0 kJ\( \cdot \)mol\(^{-1} \) and -37.0 ± 1.0 kJ\( \cdot \)mol\(^{-1} \), respectively. The new value for \( \Delta_f H^{0}_{298K}(i-C_3H_7^+) \) corresponds to an IE\((i-C_3H_7)\) of 7.438 ± 0.020 eV which is in good agreement with the theoretical value of Lau and Ng.\(^{12} \) Using the \( \Delta_f H^{0}_{298K}(i-C_3H_7^+) \), the PA\(_{298}(C_3H_6)\) was determined to be 742.7 ± 0.9 kJ\( \cdot \)mol\(^{-1} \).


CHAPTER 4: Specific Rate Constants $k(E)$ of the Dissociation of the Halobenzene Ions: Analysis by Statistical Unimolecular Rate Theories

4.1 Introduction

Unimolecular dissociation reactions provide an important access to the threshold energies $E_0$ for bond breaking. The specific rate constants $k(E)$ of these reactions (apart from some fine structure) decrease with decreasing energy $E$ and approach their minimum value as $E \rightarrow E_0$. In order to derive $E_0$ from $k(E)$, this quantity must be measured experimentally at energies close enough to $E_0$ that a unique extrapolation is feasible. In addition to the limited range of specific experimental methods, in dissociations with rate constants at threshold slower than about $10^2 \text{ s}^{-1}$ it is not possible to directly measure these low energy rates due to competition from radiative decay.\(^1\),\(^2\) In these cases, the difference between the experimental appearance energy of the fragments and the bond energy $E_0$, the so-called “kinetic shift”\(^3\),\(^4\) needs to be determined by fitting the measured part of $k(E)$ to a model from unimolecular rate theory.\(^5\) Larger molecules have minimum rate constants well below $10^2 \text{ s}^{-1}$ and thus require rate constants to be accurate over several orders of magnitude to correctly extrapolate to $E_0$. For energy selected reactants, a commonly used model for the specific unimolecular rate constants ($k(E)$) is the Rice-Ramsperger-Kassel-Marcus (RRKM) equation:\(^5\)

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where \( N^\dagger(E-E_0) \) is the sum of states of the transition state, \( \rho(E) \) is the ion density, \( \sigma \) is the reaction degeneracy, and \( h \) is Planck’s constant. In evaluating \( N^\dagger(E-E_0) \), it is useful to separate conserved vibrational modes from the transitional modes, which are converted from vibrations into rotational and translational degrees of freedom as the reaction coordinate \( R \) goes to infinity. Differences arise in the various rate theories from their treatment of these transitional modes in calculating \( N^\dagger(E-E_0) \).

Phase space theory (PST) as advanced by Light, Pechukas, Klots, Chesnavich and Bowers\(^6\)\(^-\)\(^10\) treats \( N^\dagger(E-E_0) \) by locating the transition state at either \( \infty \) along the reaction coordinate \( R \), or at the centrifugal barrier. In our treatment we assume the low \( J \) limit, for which both models place the transition state at \( R = \infty \), at which point the transitional modes have become rotations. Thus, \( k(E) \) is determined by the phase space available to the products. This treatment is appropriate for reactions where the interaction potential between the products is isotropic at large separations. At the other extreme is rigid activated complex RRKM theory (RAC-RRKM), in which the transitional modes are treated as vibrations with fixed frequencies. This is appropriate for reactions with real barriers, in which the transition state structure is located at this barrier and does not change with internal energy. However, it is well known that for reactions with no barrier, the effective transition state, which is related to an entropic minimum, shifts from \( R = \infty \) when \( E = E_0 \) to progressively smaller values as the energy is raised.\(^5\) Several statistical unimolecular rate models have been developed to account for this feature.
In variational transition state theory (VTST), the entropic minimum mentioned above is found by locating the global minimum in the sum of states $N(E-V(R))$ along the reaction coordinate.\textsuperscript{11-13} Depending on the implementation of the model, two minima may be found, corresponding to a tight transition state (TTS) at smaller values of $R$ and an orbiting transition state (OTS) at large $R$.\textsuperscript{14} Both minima shift inward as the energy increases, but at some energy an abrupt switch from OTS to TTS may occur. There has been some debate as to whether this transition state switching is physically meaningful in a single-well ionic dissociation, or if only the more gentle transition state shifting occurs, and the two entropic wells are merely an artifact of the approximations used in the interpolation.\textsuperscript{15}

An alternative approach to this problem is the statistical adiabatic channel model (SACM) in which the rovibrational quantum states of the reactant are treated as invariant throughout the dissociation by following adiabatic potential curves linking the reactant states and the equivalent product states. Each potential curve has a barrier, the maximum of which moves inward along the reaction coordinate as the energy and angular momentum of the channel increase.\textsuperscript{5} A full implementation of either VTST or SACM requires considerable computational effort. Rate constants derived from a full SACM-classical trajectory (SACM-CT) treatment however, have been shown to be reproduced by the much simpler PST with suitable rigidity factors incorporated.\textsuperscript{16} Such simplified versions of SACM (SSACM) require no more effort than PST as will be demonstrated below.

It has become clear that in barrierless neutral-neutral dissociations the inward movement of the transition state is significant and RAC-RRKM and PST are insufficient
to model the reaction rate.\textsuperscript{17} Instead, the extra effort of VTST or SACM is required. The need is less clear, however, in barrierless ionic dissociations. The stronger long range attraction due to ion-induced dipole interactions causes the transition state to be located at larger values of $R$. The question then arises whether PST is still insufficient to accurately model the rates.

Troe et al\textsuperscript{16} recently showed that RAC-RRKM fails to predict accurate $E_0$’s in the case of the dissociations of the benzene and butylbenzene cations. However these systems are not ideal for an analysis of kinetic shifts. The former involves a Renner-Teller type avoided curve-crossing between a ground $^2\text{B}_1$ and an electronically excited $^2\text{A}_1$ state of $\text{C}_6\text{H}_6^+$.\textsuperscript{16,18,19} For the latter system, experimental data\textsuperscript{20,21} only exist at higher rates ($k(E)>10^5$ s$^{-1}$) which require a large extrapolation to $E_0$. Additionally, the structure of $\text{C}_7\text{H}_7^+$ is not known with certainty and the energetics are thus not firmly established.

For this reason, we have chosen to investigate other systems which are more suitable for an analysis of kinetic shifts and for the study of energy dependences of specific rate constants $k(E)$. Such systems should fulfill a number of conditions: (i) $k(E)$ should be measurable over a large range; (ii) the thermochemistry of the system should be established sufficiently well by other than kinetic means; (iii) the potential along the dissociating bond should correspond to a simple bond fission, and not show complications such as avoided crossings, small barriers, or reefs.

The halobenzene ion dissociations (2) appear to be suitable systems for the described analysis.

$$\text{C}_6\text{H}_5X^+ \rightarrow \text{C}_6\text{H}_5^+ + \text{X}^* \quad (X = \text{Cl, Br, and I})$$

(4.2)
The dissociation does not involve a curve crossing although both singlet and triplet states of \( \text{C}_6\text{H}_5^+ \) may be produced. Experimental values of \( k(E) \) can be measured over sufficiently large ranges, in the present work over 3–5 orders of magnitude, and the thermochemistry of the reactions is relatively well known. Additionally, the polarizability of the halogens, and therefore the strength of the long-range attraction in the dissociation, increases from Cl to Br to I.

Previous measurements of halobenzene ion dissociation rates have been obtained by numerous workers\textsuperscript{22-35} with varying methods, precisions, and ranges of \( k(E) \). In this paper we use threshold photoelectron-photoion coincidence (TPEPICO) to accurately measure the dissociation rate constants over a large range for these three ions and then compare the modeling of these rates with the statistical theories mentioned above in order to determine which methods are appropriate to extrapolate the measured rate constants to their dissociation thresholds.

### 4.2 Experimental Results

Examples of TOF distributions corrected for hot electrons are shown in Figure 4-1. The isotopic pattern of the parent ion peaks for chlorobenzene is clearly evident at 12.806 eV, where the two chlorine isotopes (35 and 37) as well as the \(^{13}\text{C}\) peaks are fully resolved. At higher energies, the subtraction of the hot electron TOF spectrum eliminates these parent ions (in some cases imperfectly because of the sharp peaks). The broad peak to the right of the parent ion is due to fragment ions that were born in the long drift region.

To extend the experimental range of the bromobenzene data, spectra were taken using a temperature-controlled inlet\textsuperscript{36} set to 256 K and an extraction field of 50 V cm\(^{-1}\).
The lowered temperature and steeper gradient improved mass resolution and decreased the time spent in the first acceleration region where we obtain our kinetic information allowing for rates as fast as $10^7 \text{s}^{-1}$ to be observed for bromobenzene. Threshold photoelectron spectra of argon were taken to ensure that the electron energy resolution was not significantly reduced by the increased extraction fields.

4.3 Thermochemistry of the Dissociations of Halobenzene Ions

Before presenting and analyzing our kinetic data, we briefly inspect the available thermochemical data for the reactions described in equation 4.2. Assuming that there are no energy barriers for the reverse reactions, the $E_0$’s of the halobenzene dissociations are derived from known heats of formation of the participating species through

$$E_0 = \Delta H^0_{f,0K}(X*) + \Delta H^0_{f,0K}(C_6H_5^+) - \Delta H^0_{f,0K}(C_6H_5X^+)$$

The heats of formation of the neutral halobenzene molecules $C_6H_5X$ are given in Table 4-1. They are accurate to ±1.3 kJ •mol$^{-1}$ (±13 meV) for chlorobenzene and somewhat less certain for bromo- and iodobenzene. The ionization energies for all three halobenzenes have recently been determined by ZEKE spectroscopy$^{37}$ and are accurate within 0.05 kJ mol$^{-1}$. The values for the halogen atoms are well established.$^{38}$ The heat of formation of the phenyl cation was obtained from the Active Thermochemical Tables (ATcT)$^{39,40}$ by private communication$^{41}$ as 1149.1 ± 1.8 kJ•mol$^{-1}$. This value is in good agreement with a derived value of 1148.5 ± 3.4 kJ•mol$^{-1}$ determined from the heat of formation of the phenyl radical$^{42}$ and a phenyl ionization energy calculated by Lau and
Figure 4-1a-c: Time of flight distributions for the three halobenzene ions at selected photon energies. All spectra have been corrected for energetic electron contamination which accounts for the noise in the region of the parent peak at higher energies. The peak at 28.5 μs in 2c is due to remnant bromobenzene in the sample line, however the bromobenzene ion does not dissociate at these photon energies and does not affect the fragment peak area.
Figure 4-2 Breakdown curves for bromobenzene. Experimental points indicate abundance of ions dissociating to $\text{C}_6\text{H}_5^+$ within 8.2 $\mu$s (squares) or within 26.3 $\mu$s (circles). The respective open points indicate the relative abundance of ions that did not dissociate within that time window. Lines are obtained by fitting the experimental fragment peak shape and relative ion abundances at each photon energy using RAC-RRKM theory at 8.2 $\mu$s (---) and 26.3 $\mu$s (—) at each photon energy.
Ng\textsuperscript{43}. On the basis of these data, the values $E_0 = 3.381 \pm 0.038$, 2.812 \pm 0.046, and 2.382 \pm 0.064$ eV are obtained for the dissociations of chloro-, bromo- and iodo- benzene ions, respectively.

<table>
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<tr>
<th>Molecule</th>
<th>$\Delta_f H_{298K}$ $^{\circ}$</th>
<th>$\Delta_f H_{0K}$ $^{\circ}$</th>
<th>IE (eV)</th>
</tr>
</thead>
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<tr>
<td>C$_6$H$_5$Cl</td>
<td>52.0 ± 1.3$^{44}$</td>
<td>66.42 ± 1.3</td>
<td>9.0728(6)$^{37}$</td>
</tr>
<tr>
<td>C$_6$H$_5$Br</td>
<td>105.4 ± 4.9$^{44}$</td>
<td>127.0±4.1</td>
<td>8.9976(6)$^{37}$</td>
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<tr>
<td>C$_6$H$_5$I</td>
<td>164.9 ± 5.9$^{44}$</td>
<td>180.7 ± 5.9</td>
<td>8.7580(6)$^{37}$</td>
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<td>Cl$^-$</td>
<td>121.302(6)$^{38}$</td>
<td>119.621(6)$^{38}$</td>
<td>117.92(6)$^{38}$</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>111.86(6)$^{35}$</td>
<td>107.16(4)$^{58}$</td>
<td>1149.1 ± 1.8$^{41}$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>106.76(4)$^{38}$</td>
<td>110.76(4)$^{58}$</td>
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<tr>
<td>C$_6$H$_5^+$</td>
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### 4.4 Experimental Determination of Specific Rate Constants $k(E)$

The specific rate constants $k(E)$ of the dissociation determine both the abundance of dissociated ions and the shape of the asymmetric fragment peak in the TOF spectrum. However, while our photon resolution is as narrow as 12 meV, our “energy-selected” ions are produced from a room temperature sample of neutrals and therefore correspond to a room temperature thermal energy distribution. Consequently, our experimentally observed dissociation rates are averages over the internal energy distributions of the ions such as illustrated in Figure 4- 3. In order to extract the rate constants as a function of ion internal energy, we convoluted an assumed $k(E)$ function with the thermal energy distribution.
At the lowest experimental energies little information is available from the shape of the fragment peak in the TOF distribution because this distribution is very flat (see Figure 4-1). At these energies, the rate is mainly determined from the relative peak areas of the parent ions, the asymmetric peak, and the drift peak after the parent ion. However, at higher energies the asymmetric shape of the first peak provides the bulk of the rate information. The largest range of rate constants was accessible for the bromobenzene ion because there are large Franck-Condon factors in the photoelectron spectrum over the full range, which permitted us to obtain rate constants over almost 5 orders of magnitude. In the case of the chlorobenzene ion, the experimental range was limited at high energies by a Franck-Condon gap and the low photon intensity of our light source. At low energies, the range was less than for bromobenzene because of the shorter chlorobenzene ion time of flight.

The convolution of the \( k(E) \) function with the spectral width of our light source (\( ca \ 12 \) meV) and the energy distribution of our room temperature sample (\( ca \ 140 \) meV) was carried out for the TOF distribution and the relative abundances of parent and fragment ions. Denoting a calculated TOF distribution at an energy \( E \) by \( F(E,t) \) and the thermal internal energy distribution by \( f_{th}(E_{th}) \), the convoluted TOF distribution \( F_{eff}(h\nu,t) \) is given by

\[
F_{eff}(h\nu,t) = \int f_{th}(E_{th}) F(h\nu + E_{th}, t) dE_{th}
\]

(4.4)

The TOF distribution \( F(h\nu + E_{th}, t) \), where \( t \) is the ion TOF, is directly given by the specific rate constants \( k(E) \) at an energy \( E = h\nu + E_{th} \), while \( F_{eff}(h\nu,t) \) is the observable.
The fractional abundances $A$ of the parent and fragment ions observed up to a time $\tau$, are given by

$$A_{\text{parent}} = \int_0^\infty f_{\text{th}}(E_{\text{th}}) \exp\left[-k(h\nu + E_{\text{th}})\tau\right] dE_{\text{th}}$$

(4.5)

and

$$A_{\text{fragment}} = 1 - A_{\text{parent}} = \int_0^\infty f_{\text{th}}(E_{\text{th}}) (1 - \exp[-k(h\nu + E_{\text{th}})\tau]) dE_{\text{th}}$$

(4.6)

$k(E)$ has to be chosen in such a way that the convoluted TOF distributions $F_{\text{eff}}(h\nu, t)$ and the fractional ion abundances from the experiment are reproduced in an internally consistent manner. We achieve this by using an RRKM trial function for $k(E)$ which is locally optimized around the energy of the data point. The procedure provides a unique and correct $k(E)$ at an energy that corresponds to the peak of the thermal energy distribution (Figure 4-3) and is independent of the trial function. As an example of the analysis of our experimental data, Figure 4-4 shows a comparison of measured and fitted TOF distributions in the bromobenzene system for a series of excitation energies.

The reported rate constants are those evaluated at the peak of each ion internal energy distribution. They are shown, along with their uncertainties, in Table 4-2, Table 4-3, and Table 4-4 and in Figure 4-5 and Figure 4-6. The given errors were established by observation of the fit to the experimental TOF distributions and breakdown diagrams.

The larger errors in the chlorobenzene rates from 3.893 to 4.163 eV and in the
Figure 4-3 Depiction of the ion thermal energy distribution ($f(E_{Th})$) and corresponding variation in the dissociation rate at a single photon energy. Experimental $k(E)$ for a single ion internal energy are determined from the RRKM $k(E)$ evaluated at the most probable (MP) energy in the ion internal energy distribution ($h\nu - IE + E_{MP}$) as described in the text where $E_{MP} = 56$ meV, 61 meV, and 61 meV for chloro-, bromo-, and iodobenzene.
bromobenzene rates from 3.136 to 3.323 eV reflect a discrepancy between the rate
constants derived from the fragment peak shapes and those derived from the relative
areas of the fragment and parent peaks. Before comparing the measured rate constants to
the calculated dissociation rate constants, it is important to establish whether at low
energies the ions could be stabilized by IR emission. Such an emission would effectively
stabilize the parent ions and yield a daughter to parent ratio that is too low. The IR
emission rates, calculated using the method described by Dunbar$^{45}$ with frequencies and
IR emission intensities calculated using Gaussian 03,$^{46}$ were similar for all three systems
and ranged from about 100 photons s$^{-1}$ at 2.4 eV internal energy to 450 photons s$^{-1}$ at 5
eV. Although IR emission is competitive with dissociation at the lowest experimental
energies, the effect on the extracted rate constants is much smaller than the reported error
bars.

The measured rate constants range from $3 \times 10^2$ s$^{-1}$ to $10^7$ s$^{-1}$, a range of over 4
orders of magnitude. A number of groups have previously determined halobenzene ion
dissociation $k(E)$ rates using a variety of techniques and covering selected regions of the
$k(E)$ curve (Figure 4-5).$^{22-33,35,47}$ Baer et al$^{22}$ reported rate constants for all three
molecular ions that were obtained by fitting the TPEPICO TOF distributions for the
room temperature sample with a single exponential decay. These points have rates that
are too high. In a subsequent paper$^{35}$ the rates for the bromobenzene ion were analyzed in
terms of a distribution of single exponential decays over the thermal energy distribution,
resulting in rate constants that are in agreement with the current measurements. In a
series of three papers, Rosenstock et al.$^{23-25}$ measured $k(E)$ for the three ions by fitting an
RRKM curve to breakdown diagrams obtained by TPEPICO at two ion extraction times.
Figure 4-4 Experimental and modeled fragment peaks for bromobenzene at various photon energies.
Table 4-2. Experimental and Calculated \(\log(k(E)) / s^1\) for chlorobenzene.

<table>
<thead>
<tr>
<th>(h\nu)</th>
<th>(E(eV))</th>
<th>(\text{exp.}^a)</th>
<th>RRKM</th>
<th>PST</th>
<th>SSACM</th>
<th>VTST</th>
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<td>12.753</td>
<td>3.736</td>
<td>2.70^{0.10}_{0.09}</td>
<td>2.80</td>
<td>2.34</td>
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<td>3.35</td>
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^aThe superscripts and subscripts represent the upper and lower uncertainties in the experimental values respectively.
Table 4-3 As in Table 4-2 except for bromobenzene.

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<tr>
<th>$h\nu$</th>
<th>E(eV)</th>
<th>exp.$^a$</th>
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<th>PST</th>
<th>SSACM</th>
<th>VTST</th>
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<td>6.88</td>
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<td>6.76</td>
<td>7.03</td>
<td>6.79</td>
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<tr>
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<td>7.14</td>
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<td>7.12</td>
<td>7.44</td>
<td>7.15</td>
<td>7.11</td>
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$^a$The superscripts and subscripts represent the upper and lower uncertainties in the experimental values respectively. $^b$Measurements taken at 40 V/cm and 256 K.
Table 4-4. As in Table 4-2 except for Iodobenzene

<table>
<thead>
<tr>
<th>( \text{hv} )</th>
<th>( E(\text{eV}) )</th>
<th>( \text{exp.}^a )</th>
<th>RRKM</th>
<th>PST</th>
<th>SSACM</th>
<th>VTST</th>
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<td>11.188</td>
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<td>2.45</td>
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<td>3.21</td>
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<td>11.326</td>
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<td>4.00</td>
<td>3.94</td>
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<td>6.80</td>
<td>6.92</td>
<td>6.79</td>
<td>6.67</td>
</tr>
</tbody>
</table>

*The superscripts and subscripts represent the upper and lower uncertainties in the experimental values respectively.*
Figure 4-5 Comparison of current experimental data with previously reported data. SSACM curves are calculated using the parameters that best describe the data presented in this paper. The names in the legend are those of the corresponding authors who reported the data and superscripts refer to their citations. For a detailed discussion of previous data see text. All $k(E)$ data have been adjusted to reflect the most current ionization energies reported in table 1.
These rate constants, which extend between 2 to 3 orders of magnitude, agree well with the current data. In 1984, Durant et al.\textsuperscript{27} used a supersonically cooled sample of chlorobenzene to investigate the ion dissociation rates in the vicinity of $k(E)\approx 10^6$ s$^{-1}$ by multi-photon ionization time of flight mass spectrometry. A few years later, Castleman \textit{et al.}\textsuperscript{28} used a similar technique to study the chlorobenzene ion dissociation over a similarly limited range of rate constants by varying the reflector voltage in a reflectron-time of flight apparatus. None of these investigations reported rate measurements below about $5\times 10^4$ s$^{-1}$, which means that they were not very useful for extrapolating the rate measurements to the dissociation threshold. However, Lifshitz \textit{et al.}\textsuperscript{30,31} performed a series of measurements using an ion trap, which could store the ions for up to milliseconds and could thus explore the critical low rate constant region for the case of bromo- and iodobenzene. Although the ions were not energy selected, the ion internal energy distribution obtained by single photon ionization was modeled and the ratios of the fragment and parent ions as a function of both photon energy and ion extraction time where reproduced using RRKM rate curves. This provided rates in the $10^2$ to $10^5$ s$^{-1}$ range, which as shown in Figure 4-5, agree quite nicely with our reported rate constants. Finally, Kim \textit{et al.}\textsuperscript{32,33,48} measured the $k(E)$s of iodo-, chloro-, and bromobenzene by mass-analyzed ion kinetic energy spectrometry (MIKES) in which ions prepared by charge transfer were photodissociated as they were traveling at high velocity toward an electric sector of a double focusing mass spectrometer. With the exception of one measurement for bromobenzene at a rate of $10^7$ s$^{-1}$, which agrees with our rate constants, this yielded rates in the region of about $k(E)\approx 10^8$ s$^{-1}$, which for bromo- and chlorobenzene are clearly higher than the extrapolated rate constants using the SSACM
model. Because we did not measure rate constants up to $10^8$ s$^{-1}$, we cannot be certain that the Kim rate constants are in error. However, it is worth mentioning that ion energy selection by charge transfer depends upon the assumption that the ionizing ion (Xe$^+$ for chlorobenzene and CS$_2^+$ for bromo- and iodobenzene) be in the ground state and that the charge transfer process is strictly resonant so that no energy is lost to translation.

4.5 Modeling the Rate Constants $k(E)$ by Statistical Unimolecular Rate Theories

The lowest energy rate points measured are between 0.1 and 0.4 eV above $E_0$. In order to extrapolate the rate curves down to threshold we model the dissociations using several forms of statistical unimolecular rate theory: RAC-RRKM, PST, SSACM, and VTST (Figure 4-6). These approaches all use the same density of states in the denominator of Eq. (4.1), but differ in the manner in which the sum of states is calculated. We have made the assumption that the various excited electronic states initially populated in the ionization process rapidly interconvert to the ground ionic state, thereby converting their electronic energy into vibrational energy of the ground state. However, ions are free to interconvert electronic and vibrational energy among the several electronic states that lie below the dissociation limit. We tested the contribution of the excited electronic state to the total density of states and found that even for the case of chlorobenzene, in which the upper spin orbit state lies only 100 meV above the ground state, the contribution is less than 10%. Such small differences are negligible and are generally compensated by assumed transition state frequencies.
4.5.1 Rigid Activated Complex RRKM Theory (RAC-RRKM):

In RAC-RRKM\textsuperscript{5} theory, $N^\ddagger$ is a function of just the vibrational frequencies of the transition state, which we express by means of the calculated equilibrium frequencies of the halobenzene ion. The frequency corresponding to the C-X stretch is assumed to correspond to the reaction coordinate and is omitted from the transition state. The 27 vibrational modes of the phenyl ring are assumed to be conserved along the reaction coordinate, and the frequencies of the remaining 2 modes, corresponding to C-X bends, are scaled by a common factor. Two parameters, this frequency scaling factor and $E_0$, are optimized to find a best-fit to the experimental data.

The molecular parameters and the parameters used in the fitting are summarized in the Appendix. One should note that there are ambiguities even in this simple RAC-RRKM approach because, apart from the uncertainties in the frequency set, the contribution of anharmonicity can only be guessed. An energy-independent anharmonicity factor $F_{anh} = 1.4$ was adopted by Klippenstein et al\textsuperscript{18} for the case of H loss from benzene ions. However, this ignores the fact that $F_{anh}$ is energy dependent\textsuperscript{5}. Here we take $F_{anh} = 1.0$ and include the effects of anharmonicity in the fitted transition state frequency scaling parameter. The experimental $k(E)$ curves can be fit well by this RAC-RRKM modeling, however, the resulting bond energies underestimate the chloro- and bromobenzene thermochemical values from section 3 by 0.13 eV, well outside the thermochemical uncertainties. Of the fitted values, only the iodobenzene value is within the uncertainty of the literature value. Tables 2-4 compare the RAC-RRKM $k(E)$ results with the experimental data.
The good agreement between the RAC-RRKM derived $E_0$ and the thermochemical value for the iodobenzene ion dissociation is the result of the low $E_0$ which causes the minimum rate $k(E_0)$ to be larger and therefore the kinetic shift to be smaller. For bromobenzene, in addition to inaccurately predicting the $E_0$, the described RAC-RRKM modeling was unable to provide good agreement simultaneously at the upper and lower extremes of the data set. The results for chlorobenzene demonstrate most clearly the shortcomings of the RAC-RRKM method. The experimental chlorobenzene data set extends over the smallest experimental range (three orders of magnitude), and requires the largest extrapolation to $E_0$. These two factors allow for a ‘worst case scenario’ where the modeling in Figure 4-6 reproduces the chlorobenzene data deceivingly well over the entire data set but nevertheless predicts a dissociation energy that is too low by 0.13 eV.

4.5.2 Phase Space Theory (PST)

The underestimation of $E_0$ by RAC-RRKM theory agrees with the observations made by Troe et al.,\textsuperscript{16} namely that RAC-RRKM fails because it treats the activated complex with a set of vibrational oscillators, resulting in a $k(E)$ function with too weak an energy dependence. One then might think that PST is more appropriate for ionic dissociations, because it considers the activated complex at $R = \infty$, where the transitional modes are rotations and the energy dependence of $k(E)$ is much stronger. In this case, the activated complex frequencies are those of the phenyl product ion. The density of states of these “conserved oscillators” is then convoluted with the relevant number of states $N_{\text{orb}}(E)$ of the orbital motion of the fragments. We simplify any rotational effects by using only $k(E,J=0)$ for which $N_{\text{orb}}(E) \approx (E-E_0)/B_{\text{eff}}$ and $B_{\text{eff}} = (ABC)^{1/3}$,\textsuperscript{49} thereby treating the phenyl ion as a spherical top. The $J$-dependence of $k(E,J)$ in this case is known to be
small and can practically be neglected if $E$ is identified with the vibrational energy.\textsuperscript{16} However, it must be accounted for through $E_0(J)$ when thermal rate constants for dissociation or the reverse combination are calculated. We again neglect anharmonicity ($F_{anh} = 1.0$) and note that there are considerable uncertainties in the frequencies of the phenyl cation (see Appendix). The two frequency sets determined by Klippenstein\textsuperscript{19} lead to differences in $k(E)$ by about a factor of 2. Regardless of this ambiguity, using the frequencies determined here, the PST $k(E)$ (Figure 4-6) provides a good fit to the iodobenzene ion experimental $k(E)$, but not to the chloro- or bromobenzene ion data. The only parameter, $E_0$, is varied in order to fit the PST rates at an energy near the middle of the experimental data set. This leads to values of $E_0$ that are larger than the thermochemical values. Apart from the uncertainties in the frequency set and the anharmonicity factor, the PST model of $k(E,J=0)$ is a single-parameter fitting approach which provides upper limits of $E_0$. We note that the PST rate curve anchored at the literature value of $E_0$ provides a good fit to the experimental rates below $10^5 \text{ s}^{-1}$ for the bromobenzene ion and below $10^4 \text{ s}^{-1}$ for the chlorobenzene ion, but significantly overestimates the higher energy rates.

The overestimation of $k(E)$ by PST, if the true $E_0$ is chosen, is a general phenomenon which, within the framework of the SACM, is attributed to the anisotropy of the potential energy surface and is characterized by a “rigidity factor” $f_{\text{rigid}}$ being smaller than unity. One might try to represent this effect by an increased value of $B_{\text{eff}}$ in $N_{\text{orb}}(E)$, which corresponds to an energy-independent value of $f_{\text{rigid}}$ such as was proposed in the simplest version of a “simplified SACM” (SSACM)\textsuperscript{50}. Adopting this approach here and fitting the scaling factor of $B_{\text{eff}}$ in the middle of the experiments still overestimates the true $E_0$. Although this approach accounts for some rigidity of the activated complexes, it
does not do this in an adequate manner when large energy ranges are considered. A more realistic procedure requires energy-dependent rigidity factors such as discussed in the following section. Alternatively variational transition state theory (VTST) may be used such as also described in the following. In these models, there will be a gentle “shifting” or a more abrupt “switching” of the effective transition states from larger fragment distances at lower energies to smaller distances at higher energies. As a result, $k(E)$ with increasing energy falls increasingly below the PST values.

### 4.5.3 Simplified SACM (SSACM) for Ion Dissociation

Rigidity factors $f_{\text{rigid}}(E)$ reflect the anisotropy of the potential and, in addition, the subtle interplay between the anisotropic and attractive properties of the potential, i.e. they are specific for particular types of potential energy surfaces of the dissociation process. In some cases, like ion fragmentations dominated by long range ion-permanent dipole forces, $f_{\text{rigid}}$ is energy independent, but strongly depends on angular momentum $J$. In other cases like ion fragmentations governed by a superposition of polarizability and permanent dipole contributions, $E$- and $J$-dependences of $f_{\text{rigid}}(E,J)$ arise. Energy-dependent rigidity factors $f_{\text{rigid}}(E)$ are also typical for ion fragmentations which at short range are dominated by valence forces and at long range by comparably weak ion-induced dipole forces. A detailed SACM/CT treatment was applied to systems of this type. The results could approximately be described by a functional form of $k(E)$ in which $N_{\text{orb}}(E)$ is used from PST and is multiplied by an energy-dependent rigidity factor given approximately by

$$f_{\text{rigid}}(E) = \exp\left[-(E-E_0)/c\right]$$

This version of a SSACM was shown to mimic the transition state shifting or switching and found to reproduce quite well the results of the full SACM/CT calculations.
on modelled potential energy surfaces for the fragmentations of benzene and n-butylbenzene cations.

Similar to RAC-RRKM theory, this version of SSACM contains two adjustable parameters, $E_0$ and $c$. In order to determine the best-fit $E_0$ and the corresponding uncertainty, we calculate a least-linear squares error between the calculated and experimentally determined rate curves for all reasonable combinations of $E_0$ and $c$. The results are recorded in Figure 4-5 and Figure 4-6 and Table 4-2, Table 4-3, Table 4-4, and Table 4-5. Our best fits correspond to values of $E_0 = 3.355^{0.030}_{0.040}$, $2.783^{0.026}_{0.029}$, and $2.415^{0.020}_{0.027}$ eV, where the superscripts and subscripts respectively correspond to the upper and lower uncertainties, and $c = 71$, $77$, and $194$ meV for chloro-, bromo-, and iodobenzene, respectively. The meaning of the $c$ parameter will be discussed later.

We obtain the error limits for the onset energies by calculating a least squares error between the calculated and experimentally determined rate curves for all reasonable combinations of $E_0$ and the fit parameter $c$ (Figure 4-7). The reported $E_0$ corresponds to the best fit value, while the uncertainties correspond to the limits of a goodness-of-fit contour (Figure 4-7, bold contour) beyond which the agreement of the rate curves is determined to be poor. The relationship between $E_0$, the fit parameter $c$ and the resulting error bars are plotted in Figure 4-8 for the three halobenzenes. Figure 4-7 and Figure 4-8 show the origins of the sometimes asymmetric error bars. The nearly vertical line in the case of iodobenzene indicates that, within the experimental window, $k(E)$ is independent of $c$ and is therefore described well by PST.
4.5.4 Microcanonical Variational Transition State Theory (VTST)

Microcanonical VTST locates the transition state at the minimum in the $N(E,R)$ along the reaction coordinate $R$, which moves to shorter bond distances with increasing $E$. Obtaining $N(E,R)$ requires knowledge of both the interaction potential and transitional modes along $R$. Below is a simplified approach to obtaining $N(E,R)$ proposed by Chesnavich et al.\textsuperscript{14} For this version of VTST, the potential is approximated by

$$V_{cs}(R) = \frac{D_e}{c_1} \left[ 2(3 - c_2) \exp[c_1(1 - X)] - (4c_2 - c_1c_2 + c_1)X^{-6} - (c_1 - 6)c_2X^{-4} \right]$$ \hspace{1cm} (4.8)

where $X$ is the reduced length, $X = R/R_e$, of the dissociating bond, $D_e$ is the dissociation energy corrected for the zero point energy, $c_2 = \alpha q^2/2R_e^4D_e$ with the polarizability $\alpha$ of the halogen atoms, $q$ is the ionic charge, and $c_1$ is determined by the force constant of the C-X stretch. These quantities are calculated and given in the Appendix. We note that the corresponding quantum-chemical potentials for chloro- and bromobenzene\textsuperscript{19} are more repulsive than this empirical potential in the important region between 3 and 5 Å. We will return to this point below and highlight the relative unimportance of an accurate reaction coordinate potential in the VTST scheme.

The contribution of the transitional modes, which for the halobenzene dissociation are the two C-X bending modes, to $N_{tot}(E,R)$ was determined using a hindered rotor potential of the form

$$V(\theta) = \frac{V_0(r)}{2} (1 - \cos 2\theta)$$ \hspace{1cm} (4.9)

The rotational barrier $V_0$ is a function of the bond length $R$ of the form

$$V_0(r) = V_e \exp[-\alpha(R - R_e)^3]$$ \hspace{1cm} (4.10)
where \( a \) is a fit parameter that determines how quickly the rotational barrier decays as a function of bond length, and therefore the rate of “loosening” of the transitional modes. The equilibrium barrier heights \( V_e \) were calculated from the geometrical means of the equilibrium C-X bending frequencies and were derived to be 7.85, 5.92, and 4.85 eV for chloro-, bromo-, and iodobenzene, respectively. The exponent in (10) differs from the Gaussian form proposed by Chesnavich and used in previous studies.\(^{14,29}\) In modelling the \( k(E) \) data with VTST, we found that raising the \((R-R_e)\) function to the third power provided a better fit over the full range of the data, and more importantly, provided a much tighter fit (with uncertainties of \( \pm 3 \) kJ mol\(^{-1}\) as opposed to \( \pm 7 \) kJ mol\(^{-1}\)). Energy levels for the transitional modes, \( E_i \), were calculated using a harmonic oscillator \( E_i < V_{eq}(R) \) and a Pitzer rotor model for \( E_i > 0.75 \) \( V_0(R) \). \( N_{tot}(E,R) \) was determined by convoluting the phenyl cation density of states with the contribution from the transitional modes. In all three reactions we found two minima of \( N(E,R) \) along the reaction coordinate \( R \), an outer TS at very large bond distances \((r > 15\AA)\), where \( N(E,R) \) is independent of the parameter \( a \), and a tight TS in the range \( 3 < r < 5 \) Å where \( N(E,r) \) strongly depends on \( a \). At small \( E \), the outer minimum is the global minimum, as \( E \) increases, the inner minimum increases at a slower rate and eventually determines the rate.

We obtained an optimum fit to the experimental \( k(E) \) with the parameters \( E_0 = 3.401^{0.017}_{0.062}, 2.829^{0.012}_{0.030}, \) and \( 2.420^{0.010}_{0.011} \) eV and \( a = 0.38, 0.28, \) and \( 0.22 \) Å\(^{-2}\) for chloro-, bromo-, and iodobenzene, respectively. The VTST results are plotted with experimental \( k(E) \) for comparison in Figure 4-6 and listed in and Table 4-2, Table 4-3, Table 4-4, and
Table 4-5. The uncertainties in $E_0$ were determined in the same way as for the present SSACM, and are included in Figure 4-8.

Table 4-5 compares the $E_0$ values obtained by the different approaches. In the cases of chloro- and bromobenzene, RAC-RRKM extrapolates to too low a barrier, PST extrapolates to too high a barrier, while both VTST and SSACM extrapolate to barriers within mutual uncertainty of the literature values. All four methods correctly the uncertainty of the literature value of the iodobenzene ion dissociation.

| Dissociation energies $E_0$ (eV) for $C_6H_5X^+$ $\rightarrow$ $C_6H_5^+$ + X (see text) |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| **Reference** | **$E_0$** | **RRKM**<sup>a</sup> | **PST</sup>† | **SSACM</sup> | **VTST</sup>† |
| $C_6H_5Cl^+$ | 3.381 ± 0.023 | 3.253 ± 0.05 | 3.457 | 3.355<sup>0.030 0.040</sup> | 3.401<sup>0.017 0.062</sup> |
| $C_6H_5Br^+$ | 2.812 ± 0.046 | 2.684 ± 0.06 | 2.874 | 2.783<sup>0.026 0.029</sup> | 2.829<sup>0.012 0.030</sup> |
| $C_6H_5I^+$ | 2.382 ± 0.070 | 2.387 ± 0.05 | 2.435 ± 0.01 | 2.415<sup>0.020 0.027</sup> | 2.420<sup>0.010 0.011</sup> |

<sup>a</sup>The superscripts and subscripts represent the upper and lower uncertainties in the experimental values respectively. †Due to poor fits to the experimental data, uncertainties are not reported for chlorobenzene and bromobenzene.

4.6 Discussion

Neither the RAC-RRKM nor PST approaches correctly extrapolate to the reaction barriers for the chloro- and bromobenzene ion dissociations explored here or the benzene and $n$-butylbenzene ions previously studied. Of particular concern is the fact that the RAC-RRKM theory is perfectly capable of fitting data over a broad range of rates from $10^3$ to $10^7$ s$^{-1}$ and provides no clues about its inability to extrapolate to the onset. Thus, if the predicted kinetic shift is greater than about 0.2 eV, it is best not to apply RAC-RRKM for extrapolation. In contrast, both the VTST approach correctly determines the $E_0$ for not only the iodobenzene but also the chloro- and bromobenzene ion dissociations.
Figure 4-6. Comparison of rate curves predicted by several models (see text) of statistical unimolecular dissociation fit to experimentally determined rate points. Literature dissociation thresholds ($E_0$) are indicated by black arrows. Dotted vertical lines for iodo and bromobenzene are to guide the eye from lowest $k(E_0)$ point to the horizontal axis. The determination of errors bars in rate points and $E_0$ is described in the text.
Figure 4-7 The two-parameter $c$ versus $E_0$ plot used to determine the best fit SSACM $k(E)$ curve for the experimental rate constants for iodobenzene. The bold contour represents the maximum error that defines an acceptable fit.
Figure 4-8. Combinations of $E_0$ and fitting parameter (see text) determined by VTST (black, left axis) and SSACM (gray, right axis) that yield an acceptable fit to the experimentally determined rate curves. Points are the best fit parameters and the limits of the whiskers are the derived uncertainties in $E_0$. 
while SSACM determines the $E_0$ to within the uncertainty of bromobenzene and is just outside the limit of uncertainty for the chlorobenzene $E_0$.

The VTST and SSACM models produce nearly identical rate curves over the experimental range, along with similar $E_0$s and uncertainties. The VTST calculation requires knowledge of the potential energy surface along the entire reaction coordinate, whereas the SSACM requires only the product vibrational and rotational frequencies. Additionally, the SSACM rate curve can be calculated using 2 orders of magnitude less computational effort than our VTST curve. In fact, it requires no more effort than the RAC-RRKM method.

What physical insight does the functional form of eq. 4.7 and the values of the parameter $c$ provide? The energy-dependence of $f_{\text{rigid}}(E)$ signals a potential with changing anisotropy character, being strongly anisotropic at short range where valence forces dominate and being nearly isotropic at long range where ion-induced dipole forces are relevant. The values of the parameters $c$, being 71, 77, and 194 meV for chloro, bromo, and iodobenzene, respectively, are of the same order as observed in benzene and n-butylbenzene cation dissociations. In an intricate manner they reflect the transition from the anisotropic to the isotropic region of the potential. The larger value of $c$ for iodobenzene indicates that the relative contribution of the isotropic long range part of the potential in comparison to the anisotropic short range part is larger than for chloro- and bromobenzene, due to the smaller value of $E_0$. However, a more quantitative connection to details of the potential would require the full SACM/CT treatment on the complete potential energy surface. This is beyond the scope of our present work.

It might appear that our version of VTST provides more dynamical information than SSACM because we identify the entropy bottle neck directly by minimizing the sum
of states. However, we found that our empirical potential, fitted to some of the molecular properties of the ion, does not correspond well with a DFT calculated interaction potential. Furthermore, when we replace the empirical potential with a DFT calculated curve, or even a simple Morse potential, the $a$ parameter changes, but the overall fit of the rates to the data and its ability to extrapolate to the onset is not affected. This means that our approach is simply a procedure that reproduces the data using an adjustable parameter. The empirical VTST approach also does not lend much insight into the question of transition state switching versus a smooth transition from PST at low energy to RRKM at high energy. For instance, we observe an abrupt transition-state switch at $10^4$ s$^{-1}$ for chlorobenzene and at $10^5$ s$^{-1}$ for the bromobenzene ion dissociations. However, the energy at which the switch occurs is highly dependent on the specifics of the model. The data can be well fit and the switch occur inside the experimental range, outside that range, or not at all depending on the treatment of the transitional modes (i.e. the value of the $a$ parameter and the form of eq. 4.10). Further insight about the issue of transition state switching can be found in discussions by Klippenstein$^{19}$ and Hase$^{15}$. On the basis of our results, we conclude that the $a$ parameter is effectively a catch-all fitting parameter, much like the c parameter in the SSACM or the frequency scaling factor in RAC-RRKM. On the one hand this robustness lends confidence in the results of the calculation in that incorrect assumptions about the potential energy surface do not bias the results, but on the other hand, it means that $a$ does not have a precise meaning.

Because both VTST and the SSACM provide similar results and similarly limited physical insight into the dissociations, the considerably simpler SSACM is the preferred approach. Although VTST and SSACM both predict $E_{0S}$ that are within the experimental error, the error limits are smaller than those of the experiment, and the two theories
systematically differ in that the VTST approach yields slightly lower $E_0$s than does the
SSACM, and their predictions in the case of chloro- and bromobenzene are just beyond
the error of each method. Both methods predict a considerably higher $E_0$ for
iodobenzene, which means that the experimental values for the heat of formation of
iodobenzene should probably be lowered by 3 kJ mol$^{-1}$. If the precision of the
thermochemistry of the halobenzene ion dissociations could be improved, it could decide
whether VTST or SSACM approaches are more accurate. Finally, it is worth noting that
the version of SSACM used is essentially a first order correction to the PST and is thus
most accurate at low energies. As the energy is increased, the employed rigidity factor
decreases faster than the PST $k(E)$ increases and the calculated reaction rates become too
slow, even decreasing at higher energies, which is clearly not in accord with experiment.
This can be corrected for by adding a small energy independent term to eq. 4.7. The
VTST rate curves do not suffer from this same problem, however their accuracy at higher
energies are untested.

Whether the VTST or SSACM method is used, the accuracy of the derived $E_0$
values is highly dependent on the quality and range of the experimentally determined rate
curves. The uncertainties in $E_0$ scale roughly linearly with the uncertainties in the
experimental rates and are very sensitive to the range of the experimental data. For
chlorobenzene, excluding rates below $10^4$ s$^{-1}$ from our analysis doubles the uncertainty in
the derived $E_0$ and excluding rates below $10^5$ s$^{-1}$ increases the uncertainty beyond
reasonable limits. However, the effect of increasing the experimental range at higher
energies is marginal. Excluding all rates above $10^4$ s$^{-1}$ only doubles the uncertainty. The
VTST analysis of Lifshitz et al.\textsuperscript{29} of the bromobenzene ion dissociation illustrates this
point. The modeled rate curve, fit to experimental PIE data ranging from $10^3$ s$^{-1}$ to $10^5$ s$^{-1}$
is wholly inaccurate at higher rates, but the extrapolated $E_0$ is nearly as accurate and precise as the results presented here.

**4.7 Conclusions**

Rate constants for energy selected dissociation of the halobenzene ions have been measured by TPEPICO over four orders of magnitude from $4 \times 10^2$ to $9 \times 10^6$ s$^{-1}$. Rate curves calculated by RAC-RRKM, PST, SSACM, and VTST were fitted to the experimental rate data and used to extrapolate the rates down to the threshold energy, $E_0$. The derived dissociation onsets were compared to the known $E_0$s as determined from literature thermochemical values. While RAC-RRKM provided good fits to the experimental rate curves, the predicted $E_0$s were significantly lower than the literature values for the chloro- and bromobenzene ion dissociations. PST provided neither good fits to the experimental rate curves for chloro- and bromobenzene, nor the correct $E_0$s. Although both models correctly predict the $E_0$ of the iodobenzene ion dissociation, PST and RAC-RRKM should not be used for barrierless ionic dissociations. Both simplified 2-parameter versions of VTST and SSACM properly fit the experimental rate curves and extrapolate to the correct $E_0$ for all three halobenzene ion dissociations with VTST appearing to do better for the case of chlorobenzene. However, SSACM is significantly simpler to employ.

Finally, the range and quality of the experimental rate points are critical to any method of extrapolating the rate curve down to threshold. The uncertainty in the derived $E_0$ scales approximately linearly with the uncertainty in the experimental data points, while extending the experimental range to the lowest rates possible is vital for an accurate determination.
Reference List


CHAPTER 5: The heats of formation of C₆H₅⁺ C₆H₅⁺ and C₆H₅NO by TPEPICO and Active Thermochemical Tables Analysis

5.1 Introduction

The development of the active thermochemical tables, in which the directly measured reaction energy differences are used to determine optimal heats of formations for the relevant species, has reinforced the importance of alternative routes that relate the various species. In this study we focus on the nitrosobenzene molecule, which dissociatively ionizes to form C₆H₅⁺. The monosubstituted benzenes are often difficult systems to study by dissociative photoionization (C₆H₅X + hν → C₆H₅⁺ + X) because of slow dissociation near threshold and/or large uncertainties in the thermochemistry of the constituents. The active thermochemical tables¹² provide a reasonably accurate value for Δ₀H(C₆H₅⁺) and Δ₀H(C₆H₅) and the neutral bond dissociation energy has been measured for nitrosobenzene.³ Figure 5-1 shows that by measuring E₀(C₆H₅⁺) from nitrosobenzene, new values for IE(C₆H₅) and Δ₀H(C₆H₅NO) can be determined.

A precise ionization energy of the phenyl radical has been difficult to determine experimentally. This is due to the poor Franck-Condon factors associated with the adiabatic transition from the ground electronic state of the radical to the ground singlet state of the phenyl ion. Difficulties in determining the phenyl radical and cation heats of formation have hindered thermochemical determination of IE(C₆H₅). As a result, the two
Figure 5-1 Energy diagram showing that the phenyl radical ionization energy is the difference between the onsets for $C_6H_5$ and $C_6H_5^+$. 
previously reported measurements of the adiabatic $\text{IE}(C_6H_5)$ differ by 200 meV, well outside of their mutual uncertainty.\textsuperscript{4,5} The first attempt to directly measure $\text{IE}(C_6H_5)$ was in 1972 by Sergeev et al.\textsuperscript{4} who measured the appearance energy of the phenyl ion from the phenyl radical, generated by pyrolysis of azobenzene, by photoionization mass spectrometry to be $8.1 \pm 0.1$ eV. In 1987, Butcher et al.\textsuperscript{5} determined the best experimental value to date using photoelectron spectroscopy to measure an $\text{IE}(C_6H_5)$ of $8.32 \pm 0.04$ eV. Low intensity due to low concentrations of the phenyl radical and poor Franck Condon factors limited the precision of this measurement.

Previous attempts to calculate the $\text{IE}(C_6H_5)$ have also been inconclusive in determining the $\text{IE}(C_6H_5)$. In 1997 Hrusak et al. calculated, using single point CCSD(T) calculations on B3LYP optimized geometries of the phenyl radical and cation, an $\text{IE}$ of $8.1 \pm 0.1$ eV,\textsuperscript{6} identical to the experimental value by Sergeev et al.\textsuperscript{4} However, Lau and Ng recently calculated a value of $8.261$ eV\textsuperscript{7} with an estimated uncertainty of $0.035$ eV by CBS extrapolation using the CCSD(T)/6-311++G method. This value is in mutual agreement with the photoionization value reported by Butcher et al yet is well outside the uncertainty of the value by Sergeev et al. Clearly this value merits further study.

Figure 5-1 demonstrates that the $\text{IE}(C_6H_5)$ can be determined from the neutral bond dissociation energy $E_D(C_6H_5)$ and phenyl ion dissociation onset $E_o(C_6H_5^+)$ from the same precursor. This has the advantage of not being dependent upon the thermochemistry associated with the phenyl radical and ion or the benevolence of Franck-Condon factors. The neutral BDE of nitrosobenzene ($C_6H_5NO$) has been determined by Park et al. to be $226.8 \pm 2.1$ kJ\textsm{mol}\textsuperscript{-1}.\textsuperscript{3} It is possible to determine $E_o(C_6H_5^+)$ using photoelectron-photoion coincidence spectroscopy. However, the homolytic dissociation to the phenyl ion from
C₆H₅NO is immeasurably slow at threshold, requiring an extrapolation to determine E₀(C₆H₅⁺). This extrapolation requires the use of unimolecular rate theory. It has recently been shown that for the dissociation of the benzene, butyl benzene, and halobenzene cations, which also have immeasurably slow rate constants at threshold and no well defined transition state, the extrapolated zero Kelvin dissociation onset (E₀) is strongly dependent upon the rate model used.⁸,⁹ For these systems Rice-Ramsperger-Kassel-Marcus (RRKM) theory, although capable of fitting the data over 4-5 orders of magnitude, significantly underestimates the E₀, while phase space theory (PST) does not fit the data very well, and tends to overestimate the E₀. On the other hand, a semi-empirical variational transition state theory (VTST)¹⁰ and the simplified statistical adiabatic channel model (SSACM)¹¹,¹² both were both capable of fitting the data and predicting the correct onset. However, the SSACM was found to be much easier to employ and is used here. More recent studies¹³,¹⁴ have successfully employed this model to extrapolate accurate E₀ for both kinetic and competitive shifts.

Figure 5-1 shows that, in addition to using E₀(C₆H₅⁺) to determine IE(C₆H₅), we can use the experimentally determined E₀(C₆H₅⁺) and ΔƒH°₀ₚₖ(C₆H₅⁺) from the active thermochemical tables¹⁵ to determine a new value for ΔƒH°₀ₚₖ(C₆H₅NO). Prior to this study, the only route to ΔƒH°₀ₚₖ(C₆H₅NO) has been by reported measurement of the bond dissociation energy of neutral C₆H₅NO.³,¹⁶ Large uncertainties in both the BDE(C₆H₅NO) and ΔƒH°₀ₚₖ(C₆H₅)¹⁷ have limited the uncertainty in ΔƒH°₀ₚₖ(C₆H₅NO) to about 3 kJ•mol⁻¹.

5.2 Thermochemistry and Energetics
Determining absolute thermochemistry of the constituents of the cycle in Figure 5-1 requires a species with known thermochemistry for calibration. Furthermore, the
uncertainty in that calibration species will propagate to any derived thermochemistry. Until recently, the uncertainty in \( \Delta_H^{0\text{K}}(\text{C}_6\text{H}_5^+) \) has been too large (± 4 kJ•mol\(^{-1}\)) to significantly improve the thermochemistry of this cycle by measuring the \( E_0 \). However, a value of 1149.8 ± 2.1 kJ•mol\(^{-1}\) has been obtained by private communication\(^{15}\) of results obtained using the Active Thermochemical Tables (ATcT).\(^{1,18}\) Additionally, ATcT provides a value for \( \Delta_H^{0\text{K}}(\text{C}_6\text{H}_5) \) of 350.5 ± 0.8 kJ•mol\(^{-1}\).\(^{15}\) Lastly, the \( \Delta_H^{0\text{K}}(\text{NO}) \) is well known and is reported by Chase\(^{19}\) to be 89.77 ± 0.17 kJ•mol\(^{-1}\).

Figure 5-1 shows that the \( E_0 \) can be determined from the sum of IE(\( \text{C}_6\text{H}_5 \)) and \( E_D(\text{C}_6\text{H}_5) \). Using the ATcT values for \( \Delta_H^{0\text{K}}(\text{C}_6\text{H}_5^+) \) and \( \Delta_H^{0\text{K}}(\text{C}_6\text{H}_5) \), in combination with the \( E_D \) determined by Lin et al., an \( E_0 \) of 10.584 ± 0.032 eV is obtained.

5.3 Results

Figure 5-2 shows the threshold photoelectron spectrum for \( \text{C}_6\text{H}_5\text{NO} \). A detail of the first band shows some vibrational structure with a spacing of 205 cm\(^{-1}\) which we ascribe to a single vibrational mode. The reason for this is that if two or more modes had significant Franck-Condon factors for \( \Delta v > 1 \) transitions, the structure would disappear due to dephasing of the two or more slightly different vibrational modes. The electronic configuration of the ion is produced predominantly by the loss of the nobonning lone pair electron from the nitrogen atom. This is confirmed by the calculated C-N-O bending mode which changes from 257 to 221 cm\(^{-1}\) and the corresponding angle change 116 to 134 °. The experimentally measured spacing of the PES peak is 200 cm\(^{-1}\), which is close to the calculated ion frequency of 221 cm\(^{-1}\). We therefore rely upon the IE predicted
Figure 5-2 TPES of nitrosobenzene with zoom in of threshold region in inset. The red line corresponds to the modeled TPES (see text) and the arrow corresponds to the IE calculated by CBS-APNO with an estimated uncertainty of ±0.05 eV.
to the calculated ion frequency of 221 cm\(^{-1}\). We therefore rely upon the IE predicted using CBS-APNO determined to be 8.50 ± 0.05 eV. As a check, we have taken a linear combination of Gaussian functions with widths and centroids optimized to fit the experimental TPES. The coefficients were determined by assuming that each peak corresponds to a single transition (i.e. the peaks at 8.475 eV and 8.525 eV are due solely to the \(v_I \rightarrow v_0\)' and \(v_0 \rightarrow v_I\)' transitions respectively) and that the Franck-Condon factors for \(v_I \rightarrow v_J\)' transitions are equal to \(v_J \rightarrow v_I\)' transitions. This allows us to predict the intensity of the hot bands independent of the Franck Condon factors by taking the ratio of the \(v_I \rightarrow v_J\)' peak intensity to the \(v_J \rightarrow v_I\)' intensity. The results from this approach are shown in the inset of Figure 5-2. It is observed that this method somewhat underestimates the hot band intensities which may be due to the assumption that each peak corresponds to a single transition. Performing a similar analysis assuming a higher energy IE results in a worse fit while a lower IE results in a better fit to the TPES. However it is not clear whether this is due to an incorrect IE assignment, faulty assumptions in the model, or the fact that at lower IE’s the fit is less sensitive. A more sophisticated analysis of the TPES may eliminate this ambiguity but is outside of the scope of this paper. We account for the uncertainty in the IE(C\(_6\)H\(_5\)NO) by assigning a somewhat large error bars of 0.05 eV. This error will be used in the modeling of the dissociative photoionization of the C\(_6\)H\(_5\)NO.

Figure 5-3 shows representative TOF distributions of the parent fragment ions of C\(_6\)H\(_5\)NO\(^+\) at various photon energies, corrected for contamination from ionization events that generated energetic electrons. The parent peak (C\(_6\)H\(_5\)NO\(^+\)) is observed at 24.0 μs. The shoulder at slightly longer times of flight, observed in the TOF distribution at 10.58
Figure 5-3 TOF distributions for nitrosobenzene over experimental window. Black Dots represent the experimental TOF distributions that have been corrected for ions that generated energetic electrons. Red lines indicate simulated TOF distributions.
eV, is due to the $^{13}$C isotope peak. The rapidly dissociated fragment ions have a TOF of 20.32 μs. Slowly dissociating fragment ions in the first acceleration region show up as asymmetric daughter ion time of flight distributions as shown in the data for the top three TOF distributions in Figure 5-3. If the parent ion lives sufficiently long to enter the first drift region, it will produce a fragment ion that has the same velocity, but a lighter mass, thus less kinetic energy. These daughter ions are separated from their parent ions by slowing them down in the last 10 cm of the drift region. Their reduced translational energy causes them to be slowed down more than the parent ions and results in the daughter ion peak at 24.5 μs. By analyzing the whole TOF distribution, it is possible to derive a dissociation rate constant, which can be measured in the range between $10^3$ and $10^7$ s$^{-1}$.

Figure 5-4 shows the relative abundances of the fragment and parent peaks from 10.30 to 10.9 eV. The C$_6$H$_5$NO$^+$ intensity remains zero at photon energies greater than 10.8 eV. The two breakdown diagrams plotted in Figure 5-4 differ in how the fragment peak at 24.5 μs is treated. In one case, labeled ‘7.0 μs’, this drift peak is added to the parent peak area. The drift peak area is added to the fragment ion peak for the breakdown diagram labeled ‘19.5 μs’. These two breakdown diagrams differ in the time scale of the experiment.

5.3.1 Modeling of the TOF distributions and the breakdown diagrams.

The experimental data are modeled using experimental parameters and either RRKM or SSACM. For both RRKM and SSACM the vibrational frequencies of the ion were used to determine density of states, $\rho(E)$. For the RRKM treatment, the vibrational frequencies of the ion equilibrium geometry were used for transition state frequencies
Figure 5-4 Breakdown diagram for nitrosobenzene. The points represent the experimental relative abundances of the parent (open) and fragment (solid) ion at each photon energy. The lines are the simulated results. The squares and dashed lines consider all fragment ions formed after 7 μs to be parent while the circles and solid lines consider fragment ion formed after 19.5 μs to be parent.
less the C-N stretching mode. In addition to the $E_0$, the 4 vibrational frequencies corresponding to the transitional modes were scaled to fit the data. For SSACM, the product vibrational frequencies and rotational constants are used to determine the phase space theory transition state. The rotational contribution to the transition state sum of states is scaled by an energy dependent rigidity factor $f(E)$:

$$f(E) = e^{-\left(\frac{E - E_0 + IE}{c}\right)}$$

(5.1)

In addition to the $E_0$ and the IE, the variable, $c$, which is determined by the anisotropy of the interaction potential between the leaving neutral and fragment ion, was optimized to fit the data and to extract the limits of uncertainty for $E_0$. The modeled RRKM and SSACM curves are shown in Figure 5-5. The time of flight distributions are modeled by taking into account the thermal energy distribution of the room temperature sample. The RRKM and SSACM rate curves are essentially identical throughout the experimental window which extends over 4 orders of magnitude, but diverge at both higher and lower energies. At lower energies, the SSACM transition state is at the phase space limit and therefore has much stronger energy dependence than does the RRKM, so that SSACM predicts a higher $E_0$ than RRKM. Figure 5-5 also shows the calculated ion internal energy distribution for a single photon energy, which is obtained by assuming that the neutral thermal energy distribution is transposed to the ionic manifold. Because the ion internal energy distribution covers nearly the entire experimental window, it is impossible to obtain accurate $k(E)$ information without accounting for the ion internal energy distribution. This is done by calculating TOF distributions at each ion internal energy and combining them, weighted by the ion internal energy distribution. The extrapolated
Figure 5-5 RRKM and SSACM rate curves and ion internal energy distribution used to fit the experimental data. The arrow indicates the location of the $E_0$ determined from current literature values (see text). The error bars represent uncertainties in the extrapolated onset by SSACM and RRKM.
$E_0$s are 10.533 ± 0.02 eV and 10.607 ± 0.02 eV for RRKM and SSACM respectively. For both rate models, the somewhat large uncertainty in IE($C_6H_5NO$) was taken into account when computing the uncertainties in the $E_0$’s. However, because the ionic dissociation energy ($E_0$-IE($C_6H_5NO$)) changes to offset changes in the IE($C_6H_5NO$), this had a negligible effect on the uncertainty in $E_0$. SSACM fits to the data were obtained with a fitting parameter $c$ of 100 meV. For RRKM, fits were obtained by scaling the transitional frequencies by 0.12, indicating a very loose transition state with an entropy of activation of 66 J/mol•K. Although good agreement between the two models is observed within the experimental window, they extrapolate to different $E_0$’s. Previous studies have shown that the RRKM model extrapolates to $E_0$ values that are too low, and so we utilize the SSACM results for extracting thermochemical information.

5.3.2 The heat of formation of $C_6H_5NO$

The determined $E_0$ (10.607 ± 0.02) provides access to the $\Delta H(C_6H_5NO)$ from the known $C_6H_5^+$ and NO heats of formation. Using these values we obtain a $\Delta H_{0K}(C_6H_5NO)$ of 216.1 ± 2.6 kJ•mol$^{-1}$. This value is within mutual uncertainty of the $\Delta H(C_6H_5NO)$ derived from the neutral BDE of $C_6H_5NO$ and $C_6H_5$ and NO heats of formation of 213.5 ± 2.25 kJ•mol$^{-1}$ and the higher value determined by Choo et al. of 218.3 ± 4.2 kJ•mol$^{-1}$.

5.3.3 The ionization energy of $C_6H_5$

According to Figure 5-1, there are two paths for determining the IE($C_6H_5$). The first route is to take the difference between the Active Tables heats of formation of the phenyl radical and ion. Using the values reported in Table 5-1 results in an IE($C_6H_5$) of 8.284 ± 0.023 eV. The second route is by taking the difference between the $E_0$ and the
neutral BDE reported by Lin et al., which results in an IE(C₆H₅) of 8.257 ± 0.029 eV. These values are independent of one another, we can therefore reduce the uncertainty in the ΔfH(C₆H₅NO) by taking an uncertainty weighted mean of the two values using the equation below.

\[
\bar{x} = \frac{\sum_i x_i \sigma_i^{-2}}{\sum_i \sigma_i^{-2}} \quad (5.2a)
\]

\[
\sigma = \left(\sum_i \sigma_i^{-2}\right)^{-\frac{1}{2}} \quad (5.2b)
\]

Where \(x_i\) corresponds to the individual values of IE(C₆H₅) and \(\sigma\) are the uncertainties in those values. This method results in an IE of 8.273 ± 0.018 eV. This value is within mutual uncertainty of the IE(C₆H₅) determined by Butcher et al⁵ and in good agreement with the IE(C₆H₅) calculated by Lau and Ng.⁷

Table 5-1. Derived and Ancillary Thermochemistry and Energetics.

<table>
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<tr>
<th></th>
<th>ΔH₀K (kJ•mol⁻¹)</th>
<th>ΔH₂⁹₈K (kJ•mol⁻¹)</th>
<th>H₂⁹₈-H₀ (kJ•mol⁻¹)</th>
<th>IE (eV)</th>
<th>E₀ (eV)</th>
<th>D₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅NO</td>
<td>216.1 ± 2.6⁶</td>
<td>198.8 ± 2.6</td>
<td>18.8</td>
<td>8.50 ± 0.05⁶</td>
<td>10.607 ± 0.02⁶</td>
<td>2.350 ± 0.022⁶</td>
</tr>
<tr>
<td>C₆H₃</td>
<td>350.5 ± 0.8⁷</td>
<td>337.2 ± 0.8</td>
<td>15.7</td>
<td>8.273 ± 0.018⁷</td>
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<td></td>
</tr>
<tr>
<td>C₆H₅⁺</td>
<td>1149.8 ± 2.1⁸</td>
<td>1138.0 ± 2.1</td>
<td>14.2</td>
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<tr>
<td>NO</td>
<td>89.775 ± 0.17⁹</td>
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</tbody>
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⁶ Determined in the present study.
⁷ Calculated using CBS-APNO
⁵ Park 1997³
¹⁵ ATcT value
¹⁹ Chase 1998¹⁸

5.4 Conclusion

The 0 K dissociation onset for nitrosobenzene has been determined by SSACM modeling of data obtained by TPEPICO to be 10.607 ± 0.02 eV. Using this value the heat of formation of nitrosobenzene has been determined to be 216.1 ± 2.6 kJ•mol⁻¹. Using the E₀ determined in this study and the previously determined neutral bond energy
of nitrosobenzene, in combination with the ATcT values for $\Delta_f H_{0K}(C_6H_5)$ and

$\Delta_f H_{0K}(C_6H_5^+)$, a new value for the phenyl radical IE has been determined to be 8.273 ± 0.018 eV. This is in good agreement with the value calculated by Ng. et al and with mutual uncertainty of the IE experimentally determined by Butcher et al.
Reference List


CHAPTER 6: Dissociative Photoionization Study of Neopentane: A path to an accurate heat of formation of the \( t \)-butyl ion, \( t \)-butyl iodide, and \( t \)-butyl hydroperoxide

6.1 Introduction

The \( t \)-butyl cation is a very stable ion, yet a high precision (\( \pm 1 \text{-} 2 \text{ kJ} \cdot \text{mol}^{-1} \)) direct determination of its heat of formation, \( \Delta H(\text{t-}C_4\text{H}_9^+) \), has proven to be difficult. An attractive route for obtaining ionic heats of formation is via dissociative photoionization, \( t\text{-BuR} + h\nu \rightarrow t\text{-Bu}^+ + \text{R} + e^- \). If the precursor molecule, \( t\text{-BuR} \), and the neutral fragment, \( \text{R} \), have known energetics, an onset energy can be used to obtain the heat of formation of \( t\text{-Bu}^+ \). However, the high stability of the ion actually causes a complication in that the parent ion is in many cases unbound, causing the dissociative photoionization onset to reflect only the ionization energy of the neutral.

Another approach involves measuring the ionization energy of the \( t \)-butyl radical\(^{1,2} \) and obtaining the ion heat of formation using the \( t \)-butyl radical as the anchor. However, the large geometry change from tetrahedral to trigonal planar causes the Franck-Condon factors for the \( v_i \rightarrow v'_i \) transition to be very weak, thus enhancing hot band transitions. Making matters even worse, the \( t \)-butyl radical is typically formed via

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pyrolysis at temperatures in excess of 800 K, thus making an accurate determination of
the IE of the \( t \)-butyl radical problematic. These difficulties are illustrated in the various
reported IE’s which are, in chronological order, 6.58\( \pm \) 0.01 eV,\(^1\) 6.70 \( \pm \) 0.03 eV,\(^2\) and a
recent unpublished result of 6.77 \( \pm \) 0.02 eV\(^3\).

The final route to the \( t \)-butyl ion heat of formation is via calculations.\(^4\) Its closed
shell structure makes this an attractive alternative to experimental approaches. However,
in order to improve upon experimental values for \( \Delta_fH^0_{\text{0K}}(t-C_4H_9^+) \), such calculations
would have to be reliable to within 2.5 kJ\( \cdot \)mol\(^{-1}\). Such precision would require the
highest level of theory (\textit{e.g.} W4\(^5\) or HEAT\(^6\) methods). To date no such calculations have
been reported.

The best experimental measurements of the \( t \)-butyl ion heat of formation have
come from dissociative photoionization measurements with neopentane,\(^7,8\) \( t \)-butyl
iodide,\(^9\)-\(^11\) and possibly isobutane,\(^8,12\) all of which have stable parent ions and yield \( t \)-
butyl ions as products. The first such measurement was reported by Steiner et al.\(^7\) in
which they measured the onset of the \( t \)-butyl ion from neopentane at various temperatures
using photoionization mass spectrometry (PIMS). The problem with such experiments is
that the onset energy is ill defined because the shape of the PI curve is a function of the
molecule’s thermal energy, the shape of the photoelectron spectrum, the rate at which the
ion dissociates, and competition with lower energy dissociation channels. Usually, a
“straight line” portion of the fragment ion PI signal is extrapolated to intersect with the
energy axis. This phenomenological appearance energy must then be related to the 0 K
dissociation limit. By observing the shift in this appearance energy with temperature,
Steiner et al. derived a 0 K CH\(_3\) loss onset energy of 10.56 \( \pm \) 0.020 eV. The lower energy
CH₄ loss onset was reported as 10.39 ± 0.020 eV.⁷ A rather strange finding in these neopentane data was that the onsets hardly shifted as the temperature was varied. In the case of the CH₃ loss reaction, The 0 K onset of 10.56 ± 0.02 eV was extrapolated from the 10.53 (150°C) and 10.55 (28°C) eV onsets. As they pointed out, this 15 meV shift was only 11% of the expected shift if all the neopentane thermal energy were available for dissociation. The only other PIMS study of neopentane was carried out by Traeger⁸ in 1996 who reported 298 K onsets of 10.38 ± 0.02 and 10.33 ± 0.01 eV for CH₃ and CH₄ loss steps. It is instructive to note that the 0.17 eV discrepancy between the Inghram and Traeger 298 K methyl loss onsets stems from the choice of the straight line portion of the PIMS curve chosen by the two groups. However, because Traeger used the full thermal correction, whereas Inghram et al. used their measured extrapolation, the two 0 K values (10.56 and 10.54 eV, respectively) end up being quite similar. Neither group took into account any correction for the interference of the lower energy CH₄ loss channel.

For a number of years, the isobutene proton affinity (PA) accepted by the thermochemical community¹³ was based on the 1979 Houle and Beauchamp² adiabatic ionization energy of the t-butyl radical (6.70 ± 0.03 eV) by HeI photoelectron spectroscopy (PES), and a 1979 PIMS study of the H loss reaction from isobutane.¹² Their derived heats of formation of 681.5 ± 5 kJ•mol⁻¹ and 678.5 ± 3 kJ•mol⁻¹ agreed to within their mutual uncertainty. However, a decade later Radom and co-workers undertook an extensive theoretical study defining the PA scale using the G2 method.¹⁴ The study noted a significant and systematic discrepancy between calculated and experimental values, which would be rectified were the accepted isobutene PA anchor too positive by roughly 20 kJ•mol⁻¹. Further G2 calculations suggested a t-butyl cation
298 K heat of formation of 716 kJ mol⁻¹,⁴ prompting a reevaluation of the experimental results. Apparently, an uncertain IE measurement of the t-butyl radical coupled with an even less certain t-butyl radical heat of formation caused the resulting t-butyl ion heat of formation to be in error. The PIMS measurement on isobutane, later corrected by Traeger,⁸ suffered from t-C₆H₉Cl contamination in addition to the fact that the H loss reaction accounts for less than 1% of the yield because of competition with methane loss, which makes its PIMS onset determination very unreliable.

In search of another route for establishing the t-butyl ion heat of formation, Keister et al.¹⁰ used a supersonically cooled beam of t-butyl iodide and collected threshold photoelectron photoion coincidence (TPEPICO) spectra at energies near the dissociation limit for I atom loss. They extracted a 0 K onset energy of 9.180 ± 0.015 eV, which yielded a 298 K t-butyl cation heat of formation of 711 ± 3.6 kJ mol⁻¹, in good agreement with the calculated G2 results for Radom. However, this analysis was marred by low signal level due to the molecular beam, a significant contribution of hot electrons to the spectrum, and the ± 3.3 kJ mol⁻¹ uncertainty in the t-butyl iodide heat of formation. Although the data were modeled by taking into account the contaminating hot electrons, the derived onset is less than firm. More recently, Kim et al.¹¹ determined the I loss onset from t-butyl iodide ions by mass analyzed threshold ionization (MATI) in which t-butyl iodide cooled in a molecular beam was ionized by a vacuum UV laser and the parent and daughter ion signals monitored as a function of the laser energy. Although the data are somewhat less than convincing, they derived an onset of 9.176 ± 0.004 eV, which agrees well with the 9.180 ± 0.015 eV TPEPICO onset of Keister et al.¹⁰ These two measurements are probably the most consistent and best values for determining the t-
butyl ion heat of formation. However, the $t$-butyl iodide heat of formation is known to only $3.3 \text{ kJ} \cdot \text{mol}^{-1}$, an uncertainty that is then transferred to the $t$-butyl ion. So, this route is also not optimum for obtaining an accurate value for the $t$-butyl ion heat of formation.

The fundamental problem in establishing an accurate heat of formation of the $t$-butyl ion by dissociative photoionization is that of the few systems that dissociate simply to form $t\text{-C}_4\text{H}_9^+$ (i.e. no lower energy pathways, stable parent ion, etc.) none have established heats of formation. Two reactions, the previously mentioned $t$-butyl iodide and the not yet investigated $t$-butyl hydroperoxide, yield the $t$-butyl ion fall into this category. On the other hand, neopentane has a very well established heat of formation of $167.9 \pm 0.8 \text{ kJ} \cdot \text{mol}^{-1}$, which is based on a bomb calorimetry measurement. In addition, high level quasi W4 level calculations by Karton et al. on a variety of hydrocarbons, including neopentane, have reported a value of $-166.0 \text{ kJ/mol}$, which agrees reasonably well with the experimental value of Good. However, the methyl loss reaction for this ion is in competition with a lower energy methane loss, which makes the extraction of the higher energy onset difficult. Fortunately, recent progress in our laboratory in modeling complex dissociation paths involving both parallel and sequential reactions gives us the opportunity to extract a high quality onset for the methyl loss reaction in the presence of the slightly lower energy methane elimination. An accurate heat of formation for the $t$-butyl ion then allows us to obtain an accurate heat of formation of the $t\text{-C}_4\text{H}_9\text{I}$ and $t\text{-C}_4\text{H}_9\text{OOH}$, as well as a more reliable proton affinity of the isobutene molecule.
6.2 Results

We begin with the more easily analyzed t-butyl iodide and t-butyl hydroperoxide results. Both dissociations proceed through a single channel at a rate much faster than the microsecond time scale of the experiment.

6.2.1 t-Butyl Iodide

The relative abundances of the parent and fragment peaks are plotted as a function of photon energy in Figure 6-1 for t-C₄H₉I (i.e. a breakdown diagram). The only product ion observed over this energy range is the t-C₄H₉⁺ ion. Additionally the t-C₄H₉⁺ peak is symmetric at low energies, indicating that the dissociation rate is faster than the timescale of our apparatus (>10⁷ s⁻¹).

When the dissociation rate is fast, the $E₀$ for the lowest energy dissociation pathway is located at the energy at which the parent ion disappears. However, for large ions with many vibrational degrees of freedom, the precise energy at which the parent ion disappears is poorly defined and modeling is necessary to determine this 0 K dissociation energy. The ion internal energy, relative to the ground state of the ion, is given by $E_{\text{ion}}(h\nu) = h\nu - IE + E_{Th}$, where $IE$ is the adiabatic ionization energy and $h\nu$ is the photon energy. If $P(E)$ is the normalized thermal energy distribution of the ion, then the relative abundance of $t$-C₄H₉⁺, BD$_{t\text{-C₄H₉I}}(h\nu)$, is determined by the portion of the ion internal energy distribution that lies below the 0 K dissociation threshold $E₀(t$-C₄H₉⁺): 

$$BD_{t\text{-C₄H₉I}}(h\nu) = \int_{0}^{E₀-h\nu} P(E)dE \quad \text{for } h\nu < E₀$$  \hspace{1cm} (6.1)

The relative fragment ion abundance is then

$$BD_{t\text{C₄H₉I}}(h\nu) = 1 - BD_{t\text{C₄H₉I}}(h\nu)$$  \hspace{1cm} (6.2)
When the photon energy exceeds $E_0$, the fractional parent and daughter ion signals remain 0 and 1, respectively.

It is often possible to assume that the internal energy distribution of the neutral molecule is faithfully transposed to the ionic manifold upon ionization. However, this assumption may fail when the ion and neutral geometries are significantly different. This geometry change causes low Franck-Condon factors for $v_i \rightarrow v_j$ transitions and therefore a different internal energy distribution for the ion. Such a case was found in the ionization of SiCl$_3$H for which the ion structure has an elongated Si-H bond and a nearly planar SiCl$_3$ subgroup, relative to the neutral. As a result, the ion vibrational modes are much looser, and the ion internal energy distribution is best described by a temperature 22 K higher than that of the neutral. Similar results are observed for all three systems studied here. Unfortunately, we are unable to describe these changes quantitatively in order to predict the ion energy distribution and must treat the distribution as an additional fitting parameter. This extra parameter increases the uncertainty in the $E_0$ by about a factor of two for the case of $t$-butyl iodide. The best fit $E_0$ (Figure 6-1) was $9.170 \pm 0.007$eV with an optimized temperature of 280 K for the nominal temperature of 260 K. This is within the experimental error of the previous TPEPICO measurement by Keister et al. ($9.18 \pm 0.015$ eV) as well as the laser based MATI value of $9.176 \pm 0.004$ eV. Table 6-1 summarizes the current and previously measured onset energies.

### 6.2.2 $t$-Butyl hydroperoxide

The breakdown diagram for $t$-C$_4$H$_9$OOH is shown in Figure 6-2. As with $t$-C$_4$H$_9$I, eq. 6.1 can be used to determine $E_0(t$-C$_4$H$_9^+)$. The B3LYP optimized structures of the ion
Figure 6-1 $t$-butyl iodide breakdown diagram acquired at 260 K. Points are experimentally measured ion abundances. Solid line is the best-fit simulation of the data (see text); dashed lines are the simulated fits at the edges of the reported uncertainty. The inset graph is an expanded view of the breakdown diagram in the energy range of the determined onset.
Table 6-1 Comparison of $E_0(t$-$C_4H_9^+)$ (in eV) with previously determined studies.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Ion</th>
<th>$AE_{298K}$</th>
<th>$E_0$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$-$C_4H_9$I</td>
<td>$t$-$C_4H_9^+$</td>
<td>8.98$^a$,$^c$</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.99$^b$,$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.16$^d$</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.18$^e$</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.176$^f$</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.170$^g$</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>$t$-$C_4H_9$OOH</td>
<td>$t$-$C_4H_9^+$</td>
<td>9.904$^g$</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>$t$-$C_4H_9$</td>
<td>$t$-$C_4H_9^+$</td>
<td>10.55$^h$</td>
<td>10.56$^h$</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.38$^b$</td>
<td>10.53$^i$</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.564$^g$</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_4$C</td>
<td>$t$-$C_4H_9^+$</td>
<td>10.37$^h$</td>
<td>10.39$^h$</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.33$^b$</td>
<td>10.48$^i$</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.397$^g$</td>
<td>0.010</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ McLoughlin and Traeger 1979; $^b$ Traeger 1996; $^c$ These values reflect the ionization energy of $t$-$C_4H_9$I and were therefore not converted to $E_0$; $^d$ Oliveira, Olesik, Almoster Ferreira and Baer 1988; $^e$ Keister, Riley and Baer 1993; $^f$ Park, Kim and Kim 2001; $^g$ These values were obtained in the current study; $^h$ Steiner, Giese and Inghram 1961; $^i$ Only $AE_{298}$ values were reported, an $E_0$ was determined by adding the neutral internal energy ($<E_{vib}>+<E_{rot}>$) of 0.15 eV to $AE_{298}$ and neutral molecules show a change in ion geometry where the central carbon moves into the same plane as the methyl groups and the C-O bond length increases. As with $t$-butyl iodide, the temperature used to fit the experimental breakdown diagram was higher than the neutral temperature. The determined $E_0$ was 9.904 ± 0.012 eV with a temperature of 330 K for a nominal temperature of 298 K.
6.2.3 Neopentane

TOF spectra of \((\text{CH}_3)_4\text{C}\) taken at 223 K (LinTOF), 260 K (Re TOF), and 298 K (LinTOF) are shown in Figure 6-2. Spectra taken with the ReTOF with its resolution of 350 have clearly resolved m/Z 56 \((\text{C}_4\text{H}_8^+)\) and m/Z 57 \((t-\text{C}_4\text{H}_9^+\text{ and }^{13}\text{C}_4\text{H}_8^+)\) peaks. Spectra taken with the LinTOF mass analyzer, resolution of 100, have these peaks less well resolved so that the peak areas are determined by fitting the spectra with a linear combination of Gaussian functions.

The breakdown diagrams corresponding to the three different temperatures for neopentane are shown in Figure 6-3. Because the dissociation is fast, the breakdown diagrams are not dependent upon the total flight time, and therefore independent of which apparatus (the LinTOF or the ReTOF) was used. Poor Franck-Condon factors and low photon intensity at the ionization threshold cause the increased scatter at lower photon energies observed in the breakdown diagrams.

Figure 6-3 shows that the appearance of \(t-\text{C}_4\text{H}_9^+\) is slightly higher in energy than \(\text{C}_4\text{H}_8^+\). This means that in order to obtain \(E_0(t-\text{C}_4\text{H}_9^+)\), both dissociation channels must be modeled simultaneously. Methane loss is the lowest energy channel and as a result the 0K dissociation energy, \(E_{\text{CH}_4}\), is obtained as was described above for \(t-\text{C}_4\text{H}_9\text{I}\). However, the higher energy competitive loss of the methyl group is more complicated because there
Figure 6-2  Experimental neopentane mass spectra acquired at various temperatures. The 260 K spectrum used a ReTOF analyzer at a photon energy of 10.365 eV while spectra acquired at 220 K and 298 K used the LinTOF mass analyzer at 10.345 and 10.373 eV. The 260 K spectrum has been scaled so that the masses are aligned with the linear TOF spectra.
Figure 6-3 Breakdown Diagrams for neopentane acquired at 220 K, 260 K and 300 K. The arrows indicate the best fit E0(t-C4H9+) and the whiskers indicate their uncertainties. The dotted line indicates the weighted average of the three E0(t-C4H9+). The dashed lines represent the upper and lower limits of acceptability of the fit to the data.
is no feature in the breakdown diagram (e.g. the energy at which the parent ion disappears) from which the $E_0$ (t-C$_4$H$_9^+$) can be directly measured. Instead, the breakdown diagram reflects only the relative rates of the competing dissociation channels. Using the statistical theory, the branching ratio at an ion energy, $E$, measured relative to the ground state ion, can be calculated using eqn. 6.3:

$$\frac{[C_4H_8^+]}{[t-C_4H_9^+]} = \frac{k_{C_4H_8^+}(E)}{k_{t-C_4H_9^+}(E)} = \frac{\sigma_{C_4H_8}N^t(E - E_{CH_4} + IE)}{\sigma_{t-C_4H_9}N^t(E - E_0(t-C_4H_9^+) + IE)}$$

(6.3)

where the $IE$ is assumed to be 10.21 eV, $\sigma$ represents the reaction symmetry numbers, which are 3 and 1 for C$_4$H$_8^+$ and t-C$_4$H$_9^+$ formation, respectively, and $N^t$ is the transition state sum of states for the two dissociation pathways. Because the branching ratio is known over the experimental range, if $k(E)$ for C$_4$H$_8^+$ formation is known then, according to eqn. 6.3, the $k(E)$ over the same energy range for t-C$_4$H$_9^+$ is also known.

The best fit $E_{CH_4}$’s were 10.396 ± 0.014, 10.391 ± 0.019 and 10.408 ± 0.021 eV with optimized temperatures of 280 ± 20 K, 300 ± 30 K and 370 ± 30 K for the nominal temperatures of 220 K, 260 K, and 298 K respectively. The uncertainties in the $E_{CH_4}$ were obtained by varying the assumed temperatures by the indicated amounts. The $E_{CH_4}$ and the assumed temperature are quite independent of each other in that changing $E_{CH_4}$ translates the modeled curve, while the temperature varies its slope. These uncertainties are somewhat larger than those obtained for the t-butyl iodide and t-butyl hydrogen peroxide because of the scatter in the parent ion abundance at low energies. However, we can reduce the uncertainty in the derived onset energy by treating the three experiments as independent. We obtain a weighted average value and uncertainty using equations 6.4a and 6.4b.
where \( x_i \) represents the experimental onset energy and \( \sigma_i \) is the uncertainty in that value.

The average value of \( 10.397 \pm 0.010 \text{ eV} \), shown in Table 6-1, agrees very nicely with the 0K value of 10.39 eV of Steiner et al., but differs considerably from the Traeger value of 10.48 ± 0.010 eV.

The heats of formation of both \( \text{C}_4\text{H}_8^+ \) and methane co-products are well known from which we can calculate the thermochemical dissociation threshold to be 9.91 eV, which is well below the observed onset of 10.397 eV. The methane-loss channel must have a significant reverse barrier, a conclusion supported by DFT calculations (Figure 6-4). It is evident from this figure why the methyl reaction, which is in competition with the lower energy methane loss reaction, will not have a sharply defined onset. At its energy threshold, the number of open channels via the methane loss reaction will be huge so that the methyl loss signal is negligibly small. Its threshold energy thus requires fitting the breakdown diagram with eq. 6.3 for which we need to know the sum of states for both channels. Although we do not have experimental information about the absolute rates, we can calculate the methane loss reaction rate constant using RRKM theory if the transition state for this reaction can be established. The geometry of the transition state at the top of this barrier was found using the STQN method at the B3LYP/6-311++G(d,p) level. The vibrational frequencies for this tight transition state were thus used to calculate \( N^J(E) \) for the \( \text{CH}_4 \) loss reaction. It is possible for tunneling to contribute significantly to the dissociation rate, including at higher energies where

\[
\bar{x} = \frac{\sum x_i \sigma_i^2}{\sum \sigma_i^2} \tag{6.4a}
\]

\[
\bar{\sigma} = \left( \sum \sigma_i^2 \right)^{\frac{1}{2}} \tag{6.4b}
\]
Figure 6-4. Experimental energies and calculated structures of neopentane ion dissociation.
accurately modeling the $C_4H_8^+$ rate is critical to determining the $C_4H_9^+$ rate. We attempted to model the methane-loss channel including tunneling through an Eckart barrier treating critical frequency as an optimizable parameter,\textsuperscript{25} however no acceptable fit to the data could be found except at conditions where the tunneling contribution was negligible. The calculated rate curve ignoring tunneling and using the calculated transition state frequencies appears in Figure 6-5. To account for uncertainty in the calculated frequencies, rate curves were calculated with the transition state frequencies scaled by 0.8 and 1.2 when determining the upper and lower limits of uncertainty in $E_0(t$-$C_4H_9^+)$. 

With the methane loss reaction rate constant established, we can use the experimentally determined branching ratios to determine the methyl loss reaction rate using eqn. 6.3. In so doing, we must again take into account the full thermal energy distribution of the neopentane ion. The 0 K dissociation onset can then be obtained by extrapolating the methyl loss rate constant to its threshold energy. The formation of $t$-$C_4H_9^+$ occurs via homolytic bond cleavage without a barrier along its dissociation path. As a result, there is no fixed location and energy for the transition state that leads to $t$-$C_4H_9^+$. It has been shown\textsuperscript{26,27} that the use of a fixed transition state with RRKM theory fails to accurately extrapolate to the $E_0$. More appropriate treatments are variational transition state theory\textsuperscript{28,29} or the statistical adiabatic channel model,\textsuperscript{25} however both require arduous calculation and ultimately, for larger molecules, require some sort of fitting parameter. An alternative is the simplified statistical adiabatic channel model (SSACM) which has recently been shown\textsuperscript{26,27} to accurately model the specific rate curves of several barrierless ionic dissociations. Details of the model may be found
Figure 6-5 $k(E)$ for C$_4$H$_8^+$ and $t$-C$_4$H$_9^+$ formation from neopentane. The dotted lines represent the limits of uncertainty determined by fitting the experimental data. The transition state frequencies for C$_4$H$_8^+$ formation were scaled by 0.8 and 1.2.
elsewhere. In brief, SSACM is a first-order correction to the orbiting transition state phase space theory, accounting for anisotropy along the reaction coordinate by scaling the number of states of the transitional modes by an energy dependent rigidity factor \( f_{\text{rigid}} \) and then convoluting this with the density of states of the rest of the molecule to get a total transition state sum of states. Troe et al. have suggested various forms for the rigidity factor including:

\[
f_{\text{rigid}} = \left[ 1 + \left( \frac{E - E_0 + IE}{c} \right) \right]^{\frac{2}{3}}
\]  

(6.5)

where \( c \) is a fitting parameter used to model the branching ratios. SSACM tends to underestimate dissociation rates at ion internal energies well above threshold, the form of \( f_{\text{rigid}} \) used in (5) appears to mitigate this issue relative to other functional forms. Using the \( N^f(E) \) defined by SSACM, the branching ratios can be calculated using eqn.6.3.

\( E_0(t-C_4H_9^+) \) and ‘c’ are varied to determine the best fit to the data. To determine the overall uncertainty in the derived \( E_0(t-C_4H_9^+) \), the temperature, \( E_{CH_4} \), and CH\(_4\) loss transition state frequencies were all varied. The best fit \( E_0 \)'s for the three data sets were \( 10.560 \pm 0.036 \) eV, \( 10.560 \pm 0.043 \) eV, and \( 10.582 \pm 0.059 \) eV, which, using equations 4a and 4b result in an average 0 K onset energy of \( 10.564 \pm 0.025 \) eV. It is interesting that this value does not differ much from the previous determinations, in which the quoted error limits were smaller (see Table 6-1). However, the current value is much more trustworthy as it has been determined using the statistical theory with lower energy dissociation channels taken into account and error limits that reflect a more realistic uncertainty.
6.2.4 Derived t-C₄H₉⁺, t-C₄H₉I, and t-C₄H₉OOH heats of formation

The three 0 K onset energies for t-C₄H₉⁺ formation from t-C₄H₉I, t-C₄H₉OOH, and (CH₃)₄C can now be used in the thermochemical cycle below.

\[
E_0(t-C_4H_9^+) = \Delta_f^0 H_{0K}^0(t-C_4H_9^+) + \Delta_f^0 H_{0K}^0(R) - \Delta_f^0 H_{0K}^0(t-C_4H_9R)
\]  

(6.6)

The precision with which we can determine \(\Delta f^0 H_{0K}^0(t-C_4H_9^+)\) using the neopentane cycle is better than the uncertainty in the heats of formation of t-C₄H₉I and t-C₄H₉OOH. We will therefore use the t-C₄H₉⁺ heat of formation determined from neopentane in the other 2 cycles to obtain better values for the t-butyl iodide and t-butyl hydroperoxide heats of formation.

The first task is to establish the 0 K heat of formation for neopentane. We must therefore determine \(H_{298}^0-H_0\) for the constituents of the formation reaction. \(H_{298}^0-H_0\) for the reactants, C(s) and H₂(g), are reported by Chase.\(^{24}\) Although the \(H_{298}^0-H_0\) for neopentane is listed in the 1974 compilation of Scott\(^{31}\) as 23.2 kJ/mol, there is no indication as to whether this is an experimental value or calculated on the basis of assumed vibrational frequencies. This is troubling because neopentane, as well as a number of other molecules in this study, has multiple methyl rotors, whose motion should be considered in terms of hindered rotors rather than vibrations. Karton et al.\(^{16}\) recently reported a theoretical \(H_{298}^0-H_0\) value corrected for internal rotations based on the method described by Ayala and Schlegel\(^{32}\) which is 3 kJ/mol lower than the Scott value. This discrepancy must be primarily due to the assumed vibrational frequencies of neopentane because the hindered rotor correction is only 0.5 kJ/mol. The average deviation of the \(H_{298}^0-H_0\)
calculated by Karton et al from those reported by Scott for the other 16 linear and branched isomers of alkanes containing 4-8 carbon atoms was 0.25 kJ • mol\(^{-1}\). Because we have no way of knowing on what basis the Scott conversion for neopentane was reported, and because other calculations in the same study by Karton et al. were shown to be quite reliable, we choose to adopt the theoretical \(H_{298} - H_0\) value. The \(\Delta_{\text{f}H}^o(\text{CH}_3)_4\text{C}\) is therefore -132.2 ± 0.8 kJ • mol\(^{-1}\).

These 0 K heats of formation can now be used in Eqn. 6.6 to determine a \(\Delta_{\text{f}H}^o[\text{t-C}_4\text{H}_9^+]\) of 737.1 ± 2.5 kJ • mol\(^{-1}\). Converting this value to 298 K requires the calculation of \(H_{298} - H_0\) for the t-butyl ion, which we did using the same method as described by Karton et al., which yielded a 298 K value of 714.3 ± 2.5 kJ • mol\(^{-1}\). We used the stationary electron convention in which the electron energy is 0 regardless of temperature. This t-butyl ion heat of formation is somewhat higher than the 1993 PEPICO study of t-butyl iodide,\(^{10}\) which reported the generally accepted value for \(\Delta_{\text{f}H}^o(\text{t-C}_4\text{H}_9^+)\) of 711 ± 3.6 kJ • mol\(^{-1}\). The new t-C\(_4\)H\(_9^+\) heat of formation with realistic error limits, and which is firmly based on neopentane as an anchor, can now be employed to obtain the heats of formation of the t-butyl iodide and t-butyl hydroperoxide, which are listed in Table 6-2. The t-butyl iodide value of -68.5 ± 2.6 kJ • mol\(^{-1}\) is considerably lower than the Pedley value of -72.1 ± 3.3 kJ • mol\(^{-1}\), although it falls within the combined error limits. The heat of formation for the t-butyl hydroperoxide of -233.2 ± 2.5 kJ • mol\(^{-1}\) complements a 1964 heat of combustion measurement by Kozlov and Rabinovich\(^{33}\) of -246. ± 5.0 kJ • mol\(^{-1}\). The NIST Chemistry WebBook\(^{34}\) lists a second value of -234.9 kJ • mol\(^{-1}\) with no error limits quoted by Khursan and Marten`yanov.\(^{35}\) This value is taken from a compilation in preprint form by Komissarov, whose book we cannot find.
A new and preliminary value for $IE_{ad}$ ($t$-C$_4$H$_9$) of 6.77 ±0.02 eV has been determined by Fischer et al$^3$ from a threshold photoelectron spectrum using supersonically cooled $t$-butyl radicals formed from the pyrolysis of di-$t$-tert-butylidiazine seeded in argon. This value is significantly higher than previous values (6.58$^1$ and 6.70 eV$^2$), indicating perhaps that the radicals are colder than in the other experiments. However, when our new t-C$_4$H$_9^+$ heat of formation is combined with the accepted value for the radical $\Delta H^o_{298K}(t$-C$_4$H$_9$) of 51.5 ± 1.3 kJ•mol$^{-1}$, we predict an adiabatic IE of 6.87 ± 0.02 eV, which is a 0.10 eV (10 kJ/mol) higher still. What is clearly required is a vibrationally resolved PES of the t-butyl radical.

**Table 6-2 Derived and Ancillary Thermochemical values. (kJ•mol$^{-1}$)**

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^{o}_{298K}$</th>
<th>$\Delta H^{o}_{0K}$</th>
<th>$H^{298K-H_0}$</th>
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</thead>
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<tr>
<td>(CH$_3$)$_4$C</td>
<td>-168.0 ± 0.8$^a$</td>
<td>-132.2 ± 0.8</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>-166.0$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t$-C$_4$H$_9$I</td>
<td>-68.5 ± 2.8$^c$</td>
<td>-40.5 ± 2.6</td>
<td>20.9</td>
</tr>
<tr>
<td>$t$-C$_4$H$_9$OOH</td>
<td>-233.2 ± 2.8$^c$</td>
<td>-203.3 ± 2.8</td>
<td>24.3</td>
</tr>
<tr>
<td>$t$-C$_4$H$_9^+$</td>
<td>714.3 ± 2.5$^{c,f}$</td>
<td>737.1 ± 2.5</td>
<td>19.0</td>
</tr>
<tr>
<td>OOH</td>
<td></td>
<td>15.2 ± 0.3$^d$</td>
<td></td>
</tr>
<tr>
<td>CH$_3$</td>
<td></td>
<td>149.9$^d$</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td></td>
<td>107.2$^d$</td>
<td></td>
</tr>
<tr>
<td>H$^+$</td>
<td></td>
<td>1530.0$^e,f$</td>
<td></td>
</tr>
<tr>
<td>i-C$_4$H$_8$</td>
<td>-16.9 ± 0.9$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$PA(i$-C$_4$H$_8^+)$</td>
<td>798.8 ± 2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Good, W. D. 1970$^{15}$  $^b$ Karton, Gruzman, and Martin, 2009$^{16}$  $^c$ These values were obtained in the current study; $^d$ Pedle 1994$^{37}$  $^e$ Chase 1998$^{24}$  $^f$ Obtained using the convention that excludes the enthalpy of the electron at room temperature.
6.3 Isodesmic Calculations of the t-C$_4$H$_9^+$ heat of formation

In support of the experimentally derived t-C$_4$H$_9^+$ heat of formation, we calculated the G3 and CBS-APNO energies for the following isodesmic reactions:

\[
(t - C_4H_{10}) + \left(\frac{CH_3^+}{i - C_3H_7} \right) \rightarrow (t - C_4H_9^+) + \left(\frac{CH_4}{i - C_4H_9} \right)
\]

\[
((CH_3)_4C) + \left(\frac{CH_3^-}{i - C_3H_7} \right) \rightarrow (t - C_4H_9^+) + \left(\frac{C_2H_6}{i - C_4H_{10}} \right)
\]

The t-C$_4$H$_9^+$ heat of formation is determined from the calculated reaction energy and the experimental heats of formation for the other reaction constituents. The methane heat of formation\(^{38}\) and the corresponding \(E_0(CH_4 \rightarrow CH_3^+ + H)\)\(^{39}\) are very well known and provide a value of 1099.37 ± 0.1 kJ•mol\(^{-1}\) for \(\Delta fH_0^o(CH_3^+)\). Using \(\Delta fH_0^o(i-C_3H_7Cl)\)\(^{37}\) and a recently measured photoionization onset for the isopropyl ion from \(i-C_3H_7Cl\) of 11.065 ± 0.003 eV,\(^{40}\) which is very close to a calculated value reported by Brooks et al. of 11.061 eV,\(^{41}\) the \(\Delta fH_0^o(i-C_3H_7^+)\) has been determined by us to be 824.1 ± 1.3 kJ•mol\(^{-1}\). The heats of formation of the neutral hydrocarbons are all reported by Pedley\(^{37}\) to within 1 kJ•mol\(^{-1}\).

Table 6-3 shows the \(\Delta fH_0^o(t-C_4H_9^+)\) determined by calculations of the above isodesmic reaction energies. The scatter in the G3 values is somewhat high, however the average of 738.7 kJ•mol\(^{-1}\) is in excellent agreement with the experimental value of 737.1 ± 2.5 kJ•mol\(^{-1}\). The higher level CBS-APNO method provides results that exhibit less scatter and whose average value of 736.2 kJ/mol agrees equally with the experimental value. When we take the average of the G3 and CBS-APNO values, we obtain a
\( \Delta H_{0K}(t-C_4H_9^+) = 737.5 \text{ kJ/mol} \). These calculated results thus provide strong support of the new experimental t-butyl ion heat of formation.

**Table 6-3** \( \Delta H_{0K}(t-C_4H_9^+) \) determined from *ab initio* isodesmic reaction energies. (kJ•mol\(^{-1}\))

<table>
<thead>
<tr>
<th>( t-C_4H_9-X + Y^+ \rightarrow t-C_4H_9^+ + XY )</th>
<th>Y=</th>
<th>( t-C_4H_9-X + i-C_3H_7-G3 )</th>
<th>( t-C_4H_9-X + CH_3-CBS-APNO )</th>
<th>( t-C_4H_9-X + i-C_3H_7-CBS-APNO )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>740.0</td>
<td>735.8</td>
<td>736.6</td>
<td>734.8</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>741.5</td>
<td>737.6</td>
<td>737.4</td>
<td>736.1</td>
</tr>
</tbody>
</table>

### 6.4 Proton Affinity of isobutene

The proton affinity of isobutene and its use as an anchor for the proton affinity scale has played an important role in the history of the \( t-C_4H_9^+ \) heat of formation. Using the currently reported value of the \( \Delta H_{298K}(t-C_4H_9^+) \) provides a value for \( PA_{298K}(C_4H_8) \) of 798.8 ± 2.5 kJ•mol\(^{-1}\). This value is outside of the uncertainty of the previously accepted value of 801.7 ± 1.4 kJ•mol\(^{-1}\).\(^8\) However, it is probable that these uncertainties were significantly underestimated.

### 6.5 Conclusion

\( \Delta H_{298K}(t-C_4H_9^+) \) has been determined to be 714.3 ± 2.5 kJ•mol\(^{-1}\) from measurement of the \( E_0(t-C_4H_9^+) \) by modeling TPEPICO breakdown diagrams of neopentane at 220 K, 260 K, and 300 K. The higher than previously reported uncertainty reflects the true uncertainty in the value rather than sensitivity of fit as reported in PIMS measurements. Breakdown diagrams were also modeled for \( t \)-butyl iodide and \( t \)-butyl hydroperoxide and the \( E_0(t-C_4H_9^+) \) was determined for both species. Using the currently determined value for \( \Delta H_{298K}(t-C_4H_9^+) \), \( \Delta H_{298K}(t-C_4H_9I) \) and \( \Delta H_{298K}(t-C_4H_9OOH) \) were determined to be -68.5 ± 2.6 kJ•mol\(^{-1}\) and -233.2 ± 2.8 kJ•mol\(^{-1}\), respectively. A
new proton affinity of isobutene is $798.8 \pm 2.5$ kJ\textbullet mol$^{-1}$. These new results do not remove the discrepancy between the well established $\tau$-C$_4$H$_9$\textbullet radical heat of formation and its ionization energy. Two PES and one TPES measurement of this radical yield adiabatic IE’s that are about 0.1 eV below the predicted value. This problem will probably not be resolved until a vibrationally resolved photoelectron spectrum is collected.
Reference List


CHAPTER 7: Conclusions

The work described in this dissertation deals with the dissociation energetics and dynamics of three types of ionic reactions, which include a case of a fast dissociation, two systems in which the dissociation rates are slow compared to the experimental time scale, and one case where competing dissociation paths required the use of detailed modeling of the reaction rates. The data for the fast dissociation of halogen loss from 2-propyl halide ions was one of the first experimental data sets determined at the new iPEPICO end station at the VUV beamline of the Swiss Light Source (SLS). These results have resolved a long standing conflict in the literature concerning the dissociative photoionization onsets. The slow dissociation of halobenzene ions were used to test various unimolecular dissociation rate theories. This required careful measurement of reaction rates over a range of 4-5 order of magnitude. A special effort was made to extend this range to very slow rates, to about $3\times10^2$ s$^{-1}$. These results have shown clearly that flexible transition state models such as VTST and SACM are required to reliably model the rates of homolytic bond cleavages. In chapter 5, SSACM was used to
extrapolate to the $E_0$ for the formation of phenyl ions from nitrosobenzene. The $E_0$ was then used to determine more precise values for the ionization energy of the phenyl radical and the heat of formation of nitrosobenzene. In chapter 6, RRKM was appropriate for the CH$_4$ loss which occurs via rearrangement and SSACM was used for the homolytic CH$_3$ loss. The bond energy for CH$_3$ loss was then used to determine the heat of formation of the $t$-butyl ion which is used to anchor the gas phase proton affinity scale.

A different form of the rigidity factor was used in chapter 6 from the one in chapters 4 and 5. Both forms of the rigidity factor as well as a third have been previously reported in the literature by Troe. The functional form is chosen based on which one best describes the data. Because the rigidity factor has little to no effect at low internal energies, changing the functional form of the rigidity factor results in a similar value for the extrapolated $E_0$ but with a larger uncertainty and worse fit to the data. However, a significant improvement to this model would be an a priori method of determining the most appropriate functional form of the rigidity factor.
Reference List