ON PARALLEL AND SEQUENTIAL DISSOCIATIONS IN ENERGY SELECTED IONS

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ABSTRACT

JAMES P: KERCHER: On Parallel and Sequential Dissociations in Energy Selected Ions (Under the direction of Tomas Baer)

The ability to extract rate constants and dissociation energies of parallel and sequential dissociation pathways in energy selected ions has been made possible by recent advances in threshold photoelectron photoion coincidence (TPEPICO) spectrometry. The incorporation of velocity focusing optics for improved instrument resolution, the ability to subtract the energetic electron contamination in the threshold signal and a more robust modeling program are the key components in allowing higher energy reactions to be probed. In addition, the recent advances in computational chemistry have allowed the experimental results to be supported quickly and accurately. In many cases it has been used to uncover reaction mechanisms that would otherwise remain hidden.

The work in this thesis is devoted to obtaining kinetic and thermochemical information from higher energy dissociation pathways. Both parallel and sequential reactions are discussed. The broad range molecules for which this technique can be applied makes it both useful and attractive.

Chapter 1 is an introduction to the work presented, dealing with the motivation and methods of obtaining thermochemical properties of molecules. Chapter 2 is the description of the experimental and theoretical methods which are applied. A

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temperature dependant study on the iodine loss in *n*-butyl iodide ions is described in Chapter 3. Modeling this single-step reaction only requires the thermal energy distribution, but it provides a useful place to start, since the first step in parallel and sequential reactions are treated in the same manner. Chapters 4 and 5 deal with the determination of the physical properties of the acetyl ion and radical and well as the propionyl ion and radical from parallel dissociations of several energy-selected ketone ions. The thermochemsitry of six dihalomethanes of the form CH₂XY, where X and Y are any combination of Cl, Br, and I are discussed in Chapter 6. In this analysis of parallel reactions, a complete thermochemical cycle is established to ensure that the results are self-consistent. Chapter 7 deals with the sequential ethane loss channels in a series of energy-selected ethyl phosphine ions. The statistical theory of energy-partitioning is used to extract dissociation onsets. Chapeter 8 is a study on 2-pentanone, an ion very similar to those studied in chapters 3 and 4, but one that dissociates in a much more interesting and complex manner. Although only 3 fragment ions are observed in the TOF distribution, there are 4 parallel and 1 sequential dissociation pathway. The ability to model these reactions clearly illustrates the power of the TPEPICO technique.

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LIST OF ABBREVIATIONS

AE:	Appearance Energy
BE:	Bond Energy
EA:	Electron Affinity
E_{int} :	Ion Internal Energy
hv:	Photon energy
IE:	Ionization Energy
KE:	Kinetic energy
MCP:	Multichannel Plate
PA:	Proton Affinty
PES:	Photoelectron Spectroscopy
TPEPICO:	Threshold Photoelectron Photoion Coincidence
TOF:	Time-of-flight
VUV:	Vacuum ultraviolet
PIMS:	Photoionization Mass Spectrometry

LIST OF SYMBOLS

- $\Delta_{rxn}H^o$: Heat of Reaction
- E_0 : Dissociation Onset at 0K

CHAPTER 1:

Introduction

1.1. Motivation for studying Parallel and Sequential Dissociations

The complex mass spectra with their large number of fragment ion peaks attest to the numerous dissociation paths available to ions excited by moderate energy electron impact. In addition to the lowest energy dissociation pathway, ions fragment via parallel or sequential pathways at higher energies. These parallel and sequential pathways have been investigated for many years in the form of breakdown diagrams, the fractional ion abundance of each species as a function of the parent ion internal energy¹. The ability to extract kinetic and thermochemical information, with well-established error limits, from these reactions is of both practical and fundamental interest.

Ionic reactions provide wonderful examples of dissociations without barriers because of the large ion neutral attractive forces. In many cases, organic ions isomerize prior to dissociation via a rate limiting H-atom transfer step^{2;3}. H-atom transfer steps are often dominated by tunneling^{4;5}, so these reactions provide opportunities to investigate tunneling rates. The methods for modeling tunneling, parallel and sequential reactions are quite different, thus providing a means for testing and developing the statistical theories used to model complex reaction schemes. Of practical importance is the ability to extract accurate dissociation onsets and rate constants which can be used to obtain reliable thermochemical properties. In the experiment described in detail in this dissertation, ions are energy selected by photoionization and the resulting ions are detected by time of flight mass spectrometry. These spectra yield the ion abundances resulting from the dissociation of the energy selected ions. The integrated TOF peak areas for each ion are plotted as a function of the photon energy to obtain a breakdown diagram. At low photon energies, only the parent ion is observed. The parent ion signal drops to zero as the ion internal energy increases past the first dissociation limit. This onset is relatively sharp and can be modeled assuming a room temperature thermal energy distribution. As the photon energy increases, other reaction pathways become available.

Dissociation onsets of higher energy channels are more difficult to establish because the onsets are not sharp. The appearance of the ion in the breakdown diagram blends smoothly into the background. The two classes of high energy dissociation reactions are shown in equations 1.1 and 1.2 as parallel and sequential reactions, respectively. The electron associated with the products are not shown.

$$A^{+} + BC^{\bullet} \leftarrow ABC + hv \rightarrow AB^{+} + C^{\bullet}$$
(1.1)

$$\mathbf{ABC} + \mathbf{hv} \to \mathbf{AB}^+ + \mathbf{C}^\bullet \to \mathbf{A}^+ + \mathbf{B}^\bullet + \mathbf{C}^\bullet$$
(1.2)

In the parallel reaction (1.1), the neutral precursor ABC (in bold) fragments to the AB^+ ion at low energy and the A^+ ion at higher energy. In the sequential reaction (1.2), the ABC precursor fragments into the AB^+ ion and at higher energy the AB^+ ion dissociates further, yielding the A^+ ion. The statistical treatment of the first onset is the same for these two reactions. If the reaction is fast, no transition state parameters need to be adjusted. If the ion internal energy exceeds the dissociation threshold, it will dissociate and if the parent ion has insufficient energy, it will remain a parent ion. However, the second reaction for the formation of the A^+ ion, in the parallel case is in competition with the lower energy pathway.

The A^+ ion yield depends on the relative tightness of the two competing transition states. For the sequential reaction, the yield of the A^+ ion depends on the energy partitioning between the AB^+ ion and the C[•] ligand in the first step. This is modeled by assuming the excess energy is partitioned statistically between the translational, rotational, and vibrational degrees of freedom of the AB^+ ion and C[•] ligand. Thus, the A^+ onset is modeled without reference to the transition state.

1.1.1. Thermochemistry of Stable and Unstable Species

As mentioned above, the practical importance is the ability to determine thermochemical information of ions, neutrals and radicals by measuring the dissociation onset, E_0 , of ionic reactions. The E_0 for a sample reaction, AB + hv \rightarrow A⁺ + B[•] + e⁻, is related to the heats of formation of the products and neutrals by equation 1.3.

$$E_0 = \Delta_f H^o[A^+] + \Delta_f H^o[B^\bullet] - \Delta_f H^o[AB]$$
(1.3)

If two of the three heats of formation are known the third can be determined. In many cases, organometallic complexes such as $Co(CO)_3NO^6$, two of three heats of formation are not known for the first dissociation pathway. However, complete dissociation of the neutral precursor, $Co(CO)_3NO + hv \rightarrow Co^+ + 3 CO + NO$, via higher energy sequential pathways yields products whose heats of formation are well known so that a thermochemical cycle can be used to establish the unknown energies. In order to obtain heats of formation from the complete dissociation of the parent ion, high energy reactions must be modeled accurately and the error limits extracted.

1.1.2. Bond Energies

The energy and conformational changes associated with bond breaking are important concepts found everywhere in chemistry⁷. Traditional synthetic and materials chemists

would benefit by knowing accurate bond energies. Atmospheric and combustion models require accurate energies in order to provide useful results as they afford insight into the stability of radical species. Experimental bond energies also provide a foundation for testing *ab initio* or empirical calculations.

Bond energies are obtained through a thermochemical cycle. For example, the C–H bond energy, BE[C-H], in acetaldehyde is related to the heats of formation, $\Delta_f H^o$, of the products and reactant as illustrated in equation 1.4.

$$BE[C-H] = \Delta_f H^o[CH_3CO^{\bullet}] + \Delta_f H^o[H^{\bullet}] - \Delta_f H^o[CH_3COH]$$
(1.4)

If the heats of formation of all three species are known, the bond energy can be determined. TPEPCIO experiments provide thermochemical information about ions, neutrals and radicals making it a useful tool for determining bond dissociation energies.

1.1.3. Testing the Statistical Theories

The statistical theory of unimolecular reactions has been widely applied to both ionic and neutral systems¹. Most commonly, it is used to model a single reaction step, whose rate has been measured as a function of the internal energy or temperature of the neutral or ionic precursor. The theory, in the framework of neutral thermal reactions, was worked out by Rice, Ramsperger, Kassel and Marcus and is known as RRKM theory. Independently, the quasi-equilibrium theory (QET) was laid out by Rosenstock and Wahrharftig⁸ to address mass spectrometric results. It was later shown that these theories are identical, resulting in what is now known as RRKM-QET theory.

The basis of the original RRK theory is that the dissociation of an energized molecule is statistical⁹⁻¹¹. The reacting molecule is viewed as an ensemble of harmonic oscillators which are free to exchange energy. Dissociation occurs when one oscillator, by chance,

acquires enough energy for reaction. It was here in Chapel Hill where the RRK theory was extended, with the help of Marcus, by incorporating the concept of the transition state¹².

1.2. Measurement of Bond Energies and Heats of Formation

There are several methods used to determine the bond energies and heats of formation of ions and neutrals. They differ not only in the experimental technique but also in their dependence on ancillary themochemical quantities. By using several different methods⁷, weak links in the thermochemical literature can be uncovered and a self consistent set of thermochemical quantities can be obtained. It is for this reason that thermochemical quantities should be measured by more than one method.

1.2.1. Photoionization Mass Spectrometry (PIMS)

The appearance energy, AE_{298K} , of the dissociative reaction RX + hv \rightarrow R⁺ + X[•] + e⁻, can be measured by photoionization mass spectrometry¹³⁻¹⁹. Mass analyzed ions are collected as a function of the photon energy to yield a photoionization efficiency (PIE) spectrum. If the onset is sharp, it can be interpreted as the appearance of the ion in the PIE curve. However, the ion signal often blends smoothly into the background and thus a model is required to extract the dissociation onset. A common procedure is to extrapolate the linear portion of the PIE curve to the baseline and this intercept is called the 298K onset. The 298K onset is converted to a 0K onset, E_0 , by adding the average thermal energy to the AE_{298K}^{16} .

The E_0 is related to the radical ionization energy, $IE[\mathbb{R}^\bullet]$, and bond energy, BE, by equation 1.5.

$$E_0 = BE[\mathbf{R} - \mathbf{X}] + IE[\mathbf{R}^{\bullet}] \tag{1.5}$$

If the $IE[R^{\bullet}]$ can be measured accurately by photoelectron spectroscopy (PES) and an accurate AE is available, the bond dissociation energy is obtained. Although the IEs of small radicals such as CH_3^{\bullet} are known quite well²⁰, it is often difficult to determine the adiabatic ionization energies of large molecules to a high level of accuracy. This is because there can be very large geometry changes between the neutral and ion ground state resulting in poor transition probability due to unfavorable Franck-Condon factors. As pointed out in equation 1.4, *BE*s can be determined directly from radical heats of formation.

The determination of the AE_{298K} for a particular daughter ion from photoionization mass spectrometry is relatively simple if the dissociation is fast. However this is not the case when the activation energy is large or when the ions are large. In the event of slowly dissociating ions, the appearance of the daughter ion signal is shifted to higher energies because the ions do not have time do dissociate during mass selection. This is known as the kinetic shift^{21;22}. Experiments that measure only the ion yield are not sensitive to such effects.

1.2.2. Neutral Kinetics

Accurate thermochemical properties of radicals can be obtained from studies of the kinetics of chemical equilibra^{7;23-25}, such as the reaction of an alkane, RH, with a halogen atom, X^{\bullet} .

$$RH + X^{\bullet} \leftrightarrow RX + H^{\bullet}$$
(1.6)

Absolute rate constants for the forward and reverse reactions, k_1 and k_{-1} , can be obtained from time-resolved experiments if the concentrations of X or R can be generated under controlled conditions. Laser flash photolysis can be used to control [X] and [R] and the rate constants can be measured via atomic fluorescence²⁶⁻³⁰ or PIMS³¹. Once k_1 and k_{-1} are known, K_{eq} is obtained which permits the determination of $\Delta_{rxn}G$, and $\Delta_{rxn}H$. If the heats of formation of any three species are known the fourth can be determined.

Ideally, the forward and reverse reactions are studied separately and the rate constants measured independantly. If k_1 and k_{-1} can be determined accurately as a function of the temperature, then the Arrhenius activation energies, E_1 and E_{-1} , are obtained⁷. $\Delta_{rxn}H$ is determined directly from $E_1 - E_{-1}$ at the midpoint temperature of the study, usually 298K. This is known as the second law method.

If k_1 and k_{-1} can only be obtained at one temperature, usually 298K, $\Delta_{rxn}H$ can still be obtained via the third law method. The equilibrium constant, K_{eq} is given as k_1/k_{-1} and hence $\Delta_{rxn}G$ is known. $\Delta_{rxn}G$ is related to $\Delta_{rxn}H$ and $\Delta_{rxn}S$, so in order to obtain the $\Delta_{rxn}H$, something must be known about $\Delta_{rxn}S$. $\Delta_{rxn}S$ is usually obtained from calculated entropies of the reactants and products using partition functions. If R[•] is a relatively small radical, its structure and vibrational frequencies are known from experiment or *ab initio* methods, permitting a more accurate determination of radical entropies. If the experiment is not done at 298K, the $\Delta_{rxn}H$ and $\Delta_{rxn}G$ at 298K are determined from tabulated heat capacities[Berk18].

Prior to the late 1980's, measured kinetic information for the forward reaction was combined with *assumed* kinetic information for the reverse reaction⁷. This was due to the difficulty in generating known concentrations of polyatomic free radicals. It was generally assumed that the reverse activation energy, E_{-1} , was 0. In the late 1980's, Gutman and co workers developed a method for investigating the reverse reaction by generating the alkyl radicals by pulsed laser photodissociation using a heated tubular reactor couple to a sensitive photoionization mass spectrometer³². It was revealed that the reverse activation energies, E_{-1} ,

were on the order of 1-2 kcal/mol for many of the halide reactions. Many of the radical heats of formation were revised to 1-4 kcal/mol higher than initial thought.

1.2.3. Negative Ion Cycles

Another approach to measuring bond energies or heats of formation is through a thermochemical cycle incorporating negative ions³³. The gas phase acidity³⁴ of RH (1.7) and the electron affinity of R[•] (1.8) are common cycles incorporating negative ions.

$$RH \rightarrow R^{-} + H^{+} \qquad \Delta E = \Delta_{acid} H^{o}[RH] \qquad (1.7)$$
$$R^{-} \rightarrow R^{\bullet} + e^{-} \qquad \Delta E = EA[R^{\bullet}] \qquad (1.8)$$

By adding the above reactions along with the ionization energy of H^{*}, one obtains a reaction for the R-H bond energy, RH \rightarrow R^{*} + H^{*}, where $BE[R-H] = \Delta_{acid}H^o[RH] + EA[R[*]] - IE[H[*]]$. The acidity³⁴, $\Delta_{acid}H^o$, is the enthalpy of proton abstraction for equation 1.7. Although $\Delta_{acid}H^o$ is often measured using flowing afterglow devices or ICR spectrometers, there are several ways to determine $\Delta_{acid}H^o$ using equilibrium measurements, thermochemical cycles, bracketing³⁵, photoion pair formation³⁶, and collision induced dissociation^{37;38}. The electron affinity, *EA*, is the energy required to detach an electron. One method to measure *EA* is to scan the photon energy to find the photodetachment threshold for the destruction of R⁻ ions³⁹⁻⁴¹. A second method to determine *EA* utilizes a fixed frequency laser⁴². One then measures the kinetic energy of the resulting photoelectrons using an electrostatic energy analyser.

1.2.4. Proton Affinites

Radical heats of formation can also be obtained through proton affinity, PA, measurements, such as described by equation 1.8,

$$R=C=O+H^+ \to RCO^+$$
(1.8)

where the ΔE of the reaction is the PA[R=C=O]. In general, the gas phase proton affinity of a molecule is measured using high pressure mass spectrometry under equilibrium conditions. Because it is measured as a relative quantity, the accuracy depends on the knowledge of the PAs of neighboring molecules.

1.2.5. Variations of the PEPICO Technique

Photoelectron photoion coincidence (PEPICO) is a mass spectrometric technique that permits the investigation of energy selected ions in order to obtain dissociation rate contants, k(E), and onsets, E_0 , which can be related to the reaction thermochemisty⁴³⁻⁵¹. The production of ions in a narrow, energy-selected distribution requires more than an energyresolved ionization source. Vacuum ultraviolet (VUV) radiation is an energy-resolved ionization source, but the photon energy is distributed between the ion internal energy, E_{int} , and the kinetic energy of the photoelectron, $KE(e^-)$, as described by equation 1.9.

$$AB + hv \rightarrow E_{int}(AB^{+}) + KE(e^{-}) + IE$$
(1.9)

The principle of PEPICO is to measure only a subset of the ions created, those which are detected in coincidence with energy-selected electrons.

There are two different methods for ion energy selection. The first approach is to use a fixed energy light source, such as a He-discharge lamp, and vary the kinetic energy of the collected electron. The advantage of this method is that it does not require a vacuum monochromator or the pumps to keep it under vacuum. The main disadvantage of this approach is the very low collection efficiency because only a small fraction of electrons are ejected in the direction of the electron energy analyzer.

The other approach is to hold the electron energy constant while varying the photon energy. Although any electron energy can be selected, the most convenient choice is collecting threshold (zero energy) electrons, in the threshold PEPICO approach. The advantages of the TPEPICO technique are that threshold electrons are collected with very high efficiencies because they have no initial velocity. They are easily extracted out of the ionization region with small electric fields. The main disadvantages are 1) a vacuum monochromator is required and 2) the threshold signal is always plagued by energetic electron contamination. Energetic electrons can be discriminated against using electron time-of-flight techniques but this requires a pulsed light source. Our approach is to collect two TOF spectra at each photon energy, one for the threshold plus hot electron contamination siginal and one for energetic electrons⁵². The contribution of energetic electrons can then be subtracted from the threshold spectrum.

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CHAPTER 2:

Experimental Description

2.1. Experimental Apparatus

2.1.1. Threshold Photoelectron Photoion Coincidence (TPEPICO)

The threshold photoelectron photoion coincidence (TPEPICO) mass spectrometer, has been described in detail in several previous publications^{2;52-54}. The TPEPICO apparatus consists of a vacuum ultraviolet light source, a monochromator and an experimental chamber housing either a reflecting or linear time-of-flight mass spectrometer. Room–temperature sample vapor is introduced into the ionization region of the experimental chamber through a small stainless steel capillary such that the chamber reaches a constant pressure of 8x10-6 torr. The sample is ionized with vacuum ultraviolet (VUV) light from a hydrogen discharge lamp dispersed by a 1m normal incidence monochromator. Thus, vacuum ultraviolet light in a continuous energy range from 7-14 eV is obtained in the form of a "many-line" spectrum. The resolution is 9 meV at a photon energy of 10.0 eV. The VUV wavelengths are calibrated by using the Lyman– α and β emissions at 1215.67 and 1025.72 Å, respectively, which are intense lines in the hydrogen lamp spectrum.

The ions and electrons are extracted in opposite directions with an electric field of 20 V/cm. Electrons pass through a second acceleration region where they reach a final energy of 74 eV in the 13 cm long drift region. The applied voltages are designed to

velocity focus threshold electrons onto a 1.4 mm aperture at the end of the electron drift region, where a Channeltron detects them. At the same time, energetic electrons focused to concentric rings around the central hole are collected by a second Channeltron after they pass through a 3x5 mm opening located close to the central 1.4 mm hole. This provides a measure of the hot electron signal which contaminates the threshold signal.

The electron and ion signals provide the start and stop signals, respectively for the time-of-flight measurement. The raw output of the detector (channeltron for electrons, MCPs for ions) is amplified and the noise is suppressed by a discriminator. The amplified signal is sent to a time-to-pulse-height converter and finally on to a data acquisition card. Each channeltron (center collector for threshold electrons and ring collector for energetic electrons) is linked to a separate data acquisition card so that two complete time-of-flight distributions are recorded at each photon energy. The ion stop signal is sent to both acquisition cards simultaneously. The TPEPICO counts are recorded and stored in integer bins or channels in the data acquisition software.

2.1.1.1. Reflecting Time-of-Flight Mass Spectrometer (ReTOF)

The reflecting time of flight (ReTOF) system consists of single acceleration and deceleration fields, in which the ions are accelerated to 100 eV in the first 5 cm long acceleration region and travel 40 cm in the first drift region. The ions are then reflected and travel through another 35 cm second drift region before being collected by a tandem multichannel plate ion detector. The electric fields are determined by the Wiley-McLaren space focusing conditions. The purpose of the long acceleration region is to permit the measurement of ion dissociation rates by modeling the asymmetric TOF distributions. In order to obtain accurate measurements of dissociation thresholds, it is



Figure 2.1. A typical TOF distribution for slowly dissociating ions. The asymmetric peak (light grey) is a result of ions which dissociate as they are being accelerated. The drift peak (grey) is from ions which dissociate in the first field free drift region. The 13C peak is visible at a slight higher TOF. The parent ion is also present (black).

essential to measure the dissociation rate constant as a function of the energy. The experimental rate curve, k(E) can be modeled with the RRKM statistical theory and extrapolated to the E_0 . A typical TOF distribution for a slow dissociation is shown in Figure 2.1. The light grey region highlights ions which dissociate while being accelerated, giving rise to the asymmetry of the peak. If the rate constant is sufficiently low, some ions will not have time to dissociate in the acceleration region, but will do so in the first drift region. Ions that dissociate in the first drift region do not penetrate as deeply into the reflectron as parent ions and will therefore have a shorted time-of-flight. These ions (dark grey) are thus separated from the parent ions (black) and appear as a drift peak; a sharp, symmetric peak just after the corresponding metastable daughter ion peak. The ¹³C peak is also present at a slightly higher TOF (dark grey). The rate constant can be determined from the ratio of TOF peak areas through the equation:

$$\frac{Area(drift)}{Area(total)} = \frac{\int_{\tau_1}^{\tau_2} e^{-kt} dt}{\int_{0}^{\infty} e^{-kt} dt}$$
(2.1)

The main advantage of the ReTOF mass spectrometer is its mass resolution, which is important in hydrogen loss channels, or competing channels were the masses are very similar (ethyl and ethane loss for example). The main disadvantage of the ReTOF is for the case when a parent ion loses a massive neutral fragment, such as the ethene loss $(m/z \ 24)$ from monoethyl phosphine $(m/z \ 62)$. The fragment ions produced during the course of acceleration, or in the first drift region, lose so much kinetic energy as a result of their mass loss that they are no longer efficiently reflected in the ReTOF and are consequently lost. We estimate that if ions lose more than 25% of their kinetic energy,

the daughter ion loss becomes significant. As a result, several of the experiments were carried out in both the ReTOF and the LinTOF systems.

2.1.1.2. Linear Time-of-Flight Mass Spectrometer (LinTOF)

In the LinTOF, ions are accelerated to 100 eV in the first 5 cm long acceleration region and to 280 eV in a short second acceleration region after which they travel 40 cm in the first drift region. The ions are then decelerated and travel through a 7.5 cm second drift region before being collected by a tandem multichannel plate ion detector. The deceleration serves to separate ions which have dissociated in the first drift region from ions which do not dissociate. The drift peak appears as a broad peak at a higher TOF than the parent ion.

2.1.2. Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is a useful tool for the determination of ionization energies and electronic states of ions. Fixed energy light is used to ionize a molecule and the spectrum is obtained by energy analysis of the ejected photoelectrons. When a molecule is ionized, the remaining energy (above the IE) is partitioned between the kinetic energy of the electron and the internal energy of the ion (2.2).

$$E_{int} = h\nu - IE - KE(\bar{e})$$
(2.2)

Thus, the ion spectrum is obtained by measuring the distribution of electron energies. Another approach is to use a tunable light source and collect electrons with a fixed energy. This variation is called threshold photoelectron spectroscopy (TPES).

2.1.2.1. Threshold Photoelectron Spectroscopy (TPES)

In threshold photoelectron spectroscopy (TPES), zero energy electrons are collected while scanning the photon energy. Equation 2.2 reduces to $E_{int} = hv - IE$, so

that the ion internal energy is associated directly with the photon energy. The major advantage of this technique is that zero energy electrons are easily focused to the electron detector while most of the energetic electrons can be suppressed by angular discrimination. Because some energetic electrons have an initial velocity vector directed at the detector there is always a background of energetic electron signal in the real signal. This accounts for a few percent of the real signal.

Energetic electrons can be suppressed by their time-of-flight if a pulsed source is used. Another approach is to subtract the contribution of energetic electrons from the threshold signal. This is done by collecting two spectra, one associated with the threshold signal (center) and one associated with energetic electrons (off-center). The off-center spectrum is used to measure the contribution of energetic electrons in the threshold signal. The true threshold spectrum can be obtained by subtracting a fraction of the off-center signal from the center signal..

2.1.2.2. Ultraviolet Photoelectron Spectroscopy (UPS)

The UPS spectrum is obtained by ionizing the neutral precursor with a fixed frequency laser or discharge lamp. The kinetic energy of the ejected photoelectrons is analyzed in order to obtain the PES. Electrons are typical collected using an electrostatic energy analyzer, and the choice of a specific analyzer depends on the ion source geometry. The main drawback is that the collection efficiency is quite low because only a small solid angle of electrons are directed at the detector.

Radiation from a helium discharge lamp is commonly used. He I (21.2 eV) and He II (40.8 eV) can be obtained by varying the pressure of the helium and the voltage

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applied. The ionization energies of most species fall in the range of 6-20 eV, making He I an ideal choice.

2.2. Detailed information about the TPEPICO experiment

2.2.1. Implementation of a Temperature Controlled Inlet system

The temperature controlled inlet, shown in figure 2.2, is a 1.5"x 1.5"x 5" solid copper block housing which contains a sample line, cooling line and cartridge heater. The sample line is a 1/8" OD copper tube which runs through the center of the block and terminates 2 cm above the VUV light in the center of the ionization region. The tip of the sample line has been flattened to maximize the overlap between the sample vapor and the VUV light. The first extraction plates of the ions and electrons are located approximately 6mm away from the ionization spot. They are each 0.030" copper discs 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 keep them electrically isolated. Cooling is accomplished by flowing ethylene glycol from a circulating Fisher Isotemp bath (model number 9510) through the copper block cooling line. The bath temperature is digitally controlled, with a range from -30 to 120 °C. The bath is positioned to minimize the amount of tubing needed to reach the inlet, thus minimizing the heat gained from the surrounding air, which in turn minimizes temperature fluctuation. Heating is accomplished by using a cartridge heater controlled by a variac. Temperatures in the range of 270K to 400K can be achieved using the isotemperature bath or the heater. Temperatures, lower than 270K, were achieved by flowing the ethylene glycol through a copper coil in an acetone/dry ice bath. The temperature could



Figure 2.2. Schematic diagram of the temperature controlled inlet system. Cold methanol circulated through a channel provides the cooling. The inlet is heated using a cartridge heater. Temperatures in the range of 220 - 400K can be achived.
not be controlled with the Isotemp bath, rather it was monitored and controlled by a hands on approach. In all cases, the temperature was monitored with K type thermocouples at the inlet and outlet of the cooling line as well as directly above the ionization region. The recorded temperature drift is <1 degree over the course of an experiment.

2.2.2. Velocity Focusing

A major problem associated with the selection of threshold electrons is the inability to suppress energetic electrons whose initial velocity vector is in the direction of the detector. Because the ionization region is several millimeters wide, the use of an electrostatic energy analyzer is of limited help. The range of electron energies formed is much wider than the desired 10meV resolution.

Energetic electrons have been successfully suppressed using time-of-flight based approaches with pulsed synchrotron radiation. The main disadvantage here is that very low extraction fields, on the order of 1 V/cm, are unfavorable for ion mass resolution.

Velocity focusing optics have been implemented in the TPEPCIO apparatus⁵², which permits threshold electrons to be focused from a much larger ionization region. Additionally, it allows for much larger extraction fields, on the order of 20 V/cm, which improves ion mass resolution. This has resulted in better threshold electron collection efficiencies and resolution. Electron and ion collection efficiencies are routinely 35% and 20%, respectively. Velocity focusing of the electrons is accomplished by extracting the particles from the ionization through an electrostatic lens, consisting of extraction plates with no grids. By properly adjusting the voltages, threshold electrons are focused to a central spot at the end of the flight tube while energetic electrons are focused to



Figure 2.3. Electron trajectories calculated with the SimION modeling software. Five vertical and three horizontal starting locations were used. Two initial electron energies were used, 0 and 38 meV (both up and down directions).

concentric rings around the central spot. The radius of the rings is determined by the initial off-axis velocity. Figure 2.3 is an illustration of the ionization region and electron drift tube. Electron trajectories for several positions in the ionization region and two initial velocities (0 and 38 meV) were calculated using the SimION modeling program suite. The electrons were launched from five different vertical positions and 3 different horizontal positions. The electrons were given three initial energies as well, 0 and 38 meV in both up and down directions. It is evident from figure 2.3. that the zero energy electrons are tightly focused to the central spot.

2.2.3. Subtraction of Energetic Electrons

The primary TPEPICO experimental data consist of ion TOF distributions at various photon energies. From these we can construct a breakdown diagram, which is the fractional abundance of parent and the various daughter ions as a function of the photon energy. In addition, we analyze the shape of the ion TOF distributions at photon energies where the dissociation rate constants are in the range of $10^3 - 10^7 \text{ s}^{-1}$. The subtraction of the hot electron signal for breakdown diagram as described by Fogleman et al. involves subtracting a fraction of the TOF peak areas in the hot TPEPICO signal from those in the threshold TPEPICO TOF data. The corrected peak areas are then given by:

$$T_n = C_n - F R_n, \tag{2.2}$$

where T_n is the true threshold integrated area of ion n, C_n and R_n represent the integrated areas of ion n, in the center and ring TOF spectra, respectively. The factor F is a constant factor determined by the ratio of center parent ion peak area to the ring parent ion peak area in a TOF distribution well above the dissociation limit. At these high energies, the

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parent ion signal in the center TOF spectrum should be zero and any non-zero area is due solely to hot electron contamination.

For the TOF distributions, the asymmetric peak shape must be conserved, and therefore a point by point subtraction is employed. Because the two spectra have been recorded using two different time-to-pulse-height converters they are not aligned. A second order fitting algorithm is used to align the spectra before the subtraction. This requires selecting three matching peaks in both TOF spectra, *C1, C2, C3, R1, R2*, and *R3*, so that *C1* and *R1* represent the parent ion peak (for example) in the center and ring spectrum, respectively. The TOF spectra are subtracted using a cubic spline algorithm, where the "steps" are along the center channels. The ring channel corresponding to the desired center channel is calculated via equation 2.3,

$$R_{chn} = a(C_{chn})^2 + bC_{chn} + c \qquad (2.3)$$

where *a*, *b*, and *c* are coefficients determined from the selected matching peaks (*C1*, *R1*...)

The determined R_{chn} will not be an integer channel number, so the intensity of the ring signal is determined using the same approach as above. Coefficients *a*, *b*, and *c*, are determined by fitting $I[R_{Ichn-1}]$, $I[R_{Ichn}]$, $I[R_{Ichn+1}]$, R_{Ichn-1} , R_{Ichn+1} , where $I[R_{Ichn}]$ is the intensity (counts) at an integer channel R_{Ichn} . The intensity is then computed via equation 2.4.

$$I[R_{chn}] = a(R_{chn})^2 + bR_{chn} + c$$
(2.4)

A cubic spline algorithm is used to step through the entire TOF spectrum. The same factor is used as in the breakdown diagram.



Figure 2.4. Normalized TOF spectra for the center collecter (black), the ring collector (dark grey) and the subtracted spectrum (light grey filled area). The subtracted spectrum overlaps the center spectrum.

Figure 2.4 shows the normalized TOF spectra for the center (black), ring (dark grey) and subtracted (light grey fill). It is evident from figure 2.4 that parent ion is more abundant in the ring spectrum compared to the center (threshold) spectrum. This is because the total energy available is divided between the kinetic energy of the electron and the internal energy of the parent ion. For center (threshold) electrons, the parent ion retains the total available energy and will therefore have more energy to dissociate.

2.3. Theoretical Approach

2.3.1. Modeling

The data analysis, including RRKM rate constant calculations, requires knowledge of the vibrational frequencies of the starting molecules, the molecular ions, as well as the various transition states. Because the reactions are sequential, the daughter ion and neutral ligand vibrational frequencies are also needed for the calculation of the product energy distribution. All of these calculations were carried out using the Gaussian 03 program suite⁵⁵ provided by the ITS Research computing facility at the University of North Carolina at Chapel Hill. The geometry and vibrational frequencies of all molecules studied were calculated using the Becke 3-parameter exchange functional, the electron correlation functional of Lee-Yang-Parr (B3LYP) with an appropriate basis set. No scale factor was applied to the vibrational frequencies of the stable species. The transition states were determined by the QST3 method, using the same level of theory and basis set. This provides a starting set of frequencies for modeling the data. The four lowest frequencies in the transition state are treated as adjustable parameters, as described below.

2.3.2. Computational Support

2.3.2.1. Ionization Energies

The adiabatic and vertical ionization energies aid in the modeling of the TPEPICO data. The adiabatic ionization energy is the energy from the neutral to ion ground state, while the vertical energy represents a "vertical" transition from the neutral ground state an the ion state with the same geometry. In either case, the *IE* is given by the difference between the ion and neutral energy. The structures and energies for the adiabatic ionization are easily obtained via geometry optimizations at the desired level of theory. The ion structure and energy for a vertical transition was determined by fixing the geometry at the optimized structure of the neutral and removing one electron.

2.3.2.2. Thermochemistry

With the development of computational resources, it is the norm these days to support experimental findings with theoretical calculations. Experimental heats of formation can be calculated through atomization energies, $E_{atomization}$, and isodesmic reactions. The $E_{atomization}$ is the energy required to completely dissociate a target molecule.

$$AB_2C \rightarrow A + 2B + C, E_{atomization} = E[A] + 2E[B] + E[C] - E[AB_2C]$$
 (2.5)

$$E_{atomization} = \Delta_{rxn} H = \Delta_f H[A] + 2\Delta_f H[B] + \Delta_f H[C] - \Delta_f H[AB_2C]$$
(2.6)

This is very advantageous in that the total energies of atoms are easily calculated and the heats of formation are often known to better than 1 kJ/mol. The main disadvantage is that the systematic errors from approximations built into the calculations are not canceled. This limitation lead to the use of isodesmic reactions. An isodesmic reaction is

one in which the number and type of formal bonds on each side of a reaction is conserved. For example,

$$C_2H_6 + C_2H_4 \rightarrow H_3C - CH = CH_2 + CH_4$$
(2.7)

There is one C–C bond, one C=C bond and ten C–H bonds on each side of reaction 2.7. Although the advantage is that systematic errors are canceled, the main disadvantage is that the total energies of four large molecules need to be calculated.

2.3.2.3. Potential Energy Surfaces

In many cases the TPEPICO results do not provide enough information to completely discern the reaction pathway or even the product structures. In this case, calculations along the potential energy surface are used to determine the structures and energetics of stable intermediates or saddle points. The easiest approach is to calculate a DFT reaction coordinate, optimizing the structure or searching for a saddle point. Although this is far and away the easiest method, the energetics, especially those of transition states, are not always accurate to within 10 kJ/mol. In this case, high level coupled cluster calculations are used. These calculations are much more accurate due to the electron correlation. These single point calculations are typical done at the DFT optimized geometry.

CHAPTER 3:

Temperature Controlled TPEPICO Experiments

3.1. Introduction

Photoelectron photoion coincidence (PEPICO) spectroscopy is an established tool for the determination of thermochemical properties of gaseous ions, neutrals and radicals¹⁻¹⁰. PEPICO experiments are most commonly carried out with room temperature samples using a time-of-flight based approach for mass selection. By measuring ions in coincidence with energy selected electrons, the ion internal energy is determined. Time-of-flight (TOF) distributions are collected at several photon energies and the results are easily visualized in the form of a breakdown diagram, which is the fractional abundance of all the ions as a function of the photon energy.

If the dissociation is fast then the 0K onsets, E_0 , can be determined from the disappearance of the parent ion in the breakdown diagram. Only the internal energy distribution of the neutral precursor is required for modeling the breakdown diagram. Any molecular ions with energy above the dissociation threshold will dissociate immediately and those without enough energy remain as parent ions. Integrating over the internal energy distribution, at each photon energy, yields a theoretical breakdown curve to compare with the experimental results. The major assumption in modeling such reactions is that the neutral internal energy distribution is transposed directly to the ion manifold. This assumption has been justified in numerous studies, if the temperature was

adjusted between 290 and 310K¹¹⁻¹³. However, the fit is clearly dependent on the assumed vibrational frequencies so that errors in these values could be compensated for by varying the assumed temperature. The newly developed temperature controlled inlet allows this assumption to be tested at more than one temperature and thus to test this assumption more rigorously.

Investigations of halogen loss reactions from haloalkanes are prominent throughout the literature¹⁴⁻¹⁷. One reasons is that they provide a means to determine gasphase neutral or ionic heats of formation based on the thermochemical relation

$$E_0 = \Delta_f H^o{}_{0K}[\mathbf{R}^+] + \Delta_f H^o{}_{0K}[\mathbf{X}^\bullet] - \Delta_f H^o{}_{0K}[\mathbf{RX}]$$
(3.1)

for the reaction

$$RX + h_{\nu} \to R^{+} + X^{\bullet}$$
(3.2)

where $R = CH_3$, C_2H_5 , etc, and X = Cl, I, or Br. E_0 is the 0K dissociation limit and $\Delta_f H^o_{0K}$ is the 0K heat of formation. The halogen radical heats of formation are well known, so if either of the other species is known, the third can be determined.

The previous studies¹⁸ on these systems uncovered the role of H-atom scrambling in the halogen loss reactions from propyl- and butylhalides. For example, chlorobutane ions dissociate via HCl loss and the four isomers of bromo and iodobutanes (*1-*, *2-*, *iso-*, and *t-*) produce only two product $C_4H_9^+$ isomers. The *1-* and *2-*butylhalides yield the *2*butyl cations (2- $C_4H_9^+$) while the *iso-* and *t*-butylhalides yield the *t*-butyl cation (*t*- $C_4H_9^+$).

3.2. Theoretical Section

The data analysis, including RRKM rate constant calculations, requires knowledge of the vibrational frequencies of the starting molecule, the molecular ion, as well as the transition state. The calculations on these three species were carried out using the Gaussian 03 program suite¹⁹ provided by the ITS Research computing facility at the University of North Carolina at Chapel Hill. The geometry and vibrational frequencies of all molecules studied were calculated using the Becke 3-parameter exchange functional²⁰, the electron correlation functional of Lee-Yang-Parr (B3LYP)²¹ with the 6–311+G* basis set and are listed in Table 3.1. No scale factor was applied to the vibrational frequencies of the stable species. The transition states were determined by the QST3 method, using the same level of theory and basis set. This provides a starting set of frequencies for modeling the data. The four lowest frequencies in the transition state are treated as adjustable parameters, as described below.

Table 3.1. Harmonic vibrational frequencies calculated at the B3LYP/6-311+g* level					
of theory for relevant species.					
Species	Frequencies				
n-C ₄ H ₉ I	84.2 ^a , 104.6 ^a , 125.9 ^a , 225.8 ^a , 236.3, 379.4, 578.8, 746.8, 782.0, 904.5,				
	913.2, 1033.8, 1056.2, 1077.1, 1120.5, 1236.2, 1237.6, 1305.2, 1326.6,				
	1334.9, 1383.1, 1436.7, 1491.7, 1516.3, 1520.4, 1521.0, 1532.4, 3031.5,				
	3035.7, 3058.2, 3074.1, 3112.9, 3114.2, 3127.9, 3129.3, 3195.8				
$n-C_4H_9I^+$	79.7, 102.2, 111.5, 198.2, 222.5, 354.8, 477.6, 760.8, 768.6, 802.3, 928.6,				
-	938.7, 989.5, 1016.8, 1048.3, 1190.0, 1248.0, 1249.2, 1275.2, 1282.0,				
	1310.9, 1406.8, 1442.5, 1466.7, 1506.7, 1512.1, 1521.0, 3007.8, 3069.9,				
	3088.3, 3111.6, 3126.6, 3144.3, 3155.1, 3171.4, 3250.0				
$TS[n-C_4H_9I]^+$	102.2 ^b , 111.5 ^b , 198.2 ^b , 222.5 ^b , 354.8, 477.6, 760.8, 768.6, 802.3, 928.6,				
	938.7, 989.5, 1016.8, 1048.3, 1190.0, 1248.0, 1249.2, 1275.2, 1282.0,				
	1310.9, 1406.8, 1442.5, 1466.7, 1506.7, 1512.1, 1521.0, 3007.8, 3069.9,				
	3088.3, 3111.6, 3126.6, 3144.3, 3155.1, 3171.4, 3250.0				

Table 3.1. a) Denotes neutral frequencies scaled in 275K simulations. b) Denotes frequencies scaled in modeling asymmetric TOF profiles at 298K.

3.3. Results

3.3.1. Ion Time of Flight Distributions

Normalized time-of-flight (TOF) distributions at 9.61 eV for the central electron collector at each temperature are given in Figure 3.1. These spectra have not been corrected for the hot electron contamination and therefore the parent ion is over-represented as compared to the breakdown diagrams. The I-C₄H₉I⁺ parent ion is the symmetric peak centered at 31.3 µs and the 2-C₄H₉⁺ is the slightly asymmetric peak at 17.2 µs. At 220K (black), the TOF distribution is dominated by the molecular ion I-C₄H₉I⁺. The daughter ion, 2-C₄H₉⁺ is hardly visible. The 2-C₄H₉⁺ is more pronounced at 273K (dark grey) and the asymmetry of the peak is observed, but the TOF distribution is still dominated by I-C₄H₉I⁺. By 298K (grey), the 2-C₄H₉⁺ intensity is strong and the peak is clearly, although only slightly, asymmetric. The TOF spectrum at 400K (light grey) shows an equal abundance of both I-C₄H₉I⁺ and 2-C₄H₉⁺.

3.3.2. Breakdown Diagrams

The time-of-flight (TOF) distributions are corrected for the hot electron contamination as described in other publications²² and are plotted as breakdown diagrams, the fractional abundances of all ions as a function of the photon energy. The experimental breakdown curves from 9.45 - 9.8 eV for the four temperatures are given as the solid points for $1-C_4H_9I^+$ and the open points for $2-C_4H_9^+$ in Figure 3.2. The solid lines are the simulated ion abundances. At low photon energies, with the exception of the 400K experiment (triangles), the breakdown curve is predominantly $1-C_4H_9I^+$. As the photon energy increases, the $1-C_4H_9I^+$ signal drops to zero as the $2-C_4H_9^+$ is produced through I^{*} loss. The slope of the decreasing $n-C_4H_9I^+$ signal is sharp for the 220K experiment (diamonds) and becomes more gradual as the temperature is increased to



Figure 3.1. Time-of-flight (TOF) distributions at 9.61 eV for the four different temperatures, 220K (black), 275K (dark grey), 298K (grey) and 400K (light grey). The n-C₄H₉I ion signal at 31.1 µs decreases relative to the n-C₄H₉ ion signal (17.2 µs) as the temperature increase. These spectra have not been corrected for hot electron contamination.



Figure 3.2. The experimental breakdown diagrams for each temperature are plotted as the open points for the ion and the solid points for the ion. The solid lines are the fit. The best E_0 from all four experiments is 9.738 eV.

400K (squares). Additionally, the crossover points, where the $1-C_4H_9I^+$ and $2-C_4H_9^+$ abundances are 50%, shifts to lower photon energies as the temperature increases. Although the shapes of all four breakdown curves differ, the $1-C_4H_9I^+$ signal disappears at the same energy.

3.3.3. Modeling

The first step in modeling the experimental results is the calculation of the *1*-C₄H₉I⁺ internal energy, which is given by the photon energy, hv, plus the thermal energy, $P(E) \approx \rho(E) exp(-E/RT)$, where $\rho(E)$ is the rovibrational density of states. The thermal energy, P(E), is calculated using harmonic vibrational frequencies and the temperature. Once P(E) is obtained, the breakdown curve can be calculated from equations (3.3) and (3.4),

$$P(h\nu) = \int_{0}^{E_{0}-h\nu} P(E)dE \qquad (3.3)$$
$$D(h\nu) = \int_{E_{0}-h\nu}^{\infty} P(E)dE \qquad (3.4)$$

where P(hv) is the parent ion signal, D(hv) is the daughter ion signal, E is the total energy and E_0 is the dissociation onset. The only adjustable parameter is the E_0 . This method works quite well for fast dissociations.

When modeling the asymmetric TOF profiles resulting from slow dissociations, absolute rate information is obtained. In this case, the TPEPICO data are modeled within the RRKM framework using the well known equation:

$$k(E) = \frac{\sigma N^{\mp} (E - E_0)}{h\rho(E)}$$
(3.5)

where *h* is Planck's constant, $\rho(E)$ is the density of states of the molecular ion for a total energy *E*, $N^{\ddagger}(E-E_0)$ is the sum of sates of the transition state at an energy $E-E_0$ and σ is the symmetry number. The RRKM framework is used to account for a kinetic shift associated with slowly dissociating ions. If the ions do not have time to dissociate during mass analysis, then the will appear as parent ions. This results in an overrepresentation of parent ion in the breakdown curve, which would lead to a higher E_0 . By modeling both the breakdown curve and TOF distributions simultaneously, a unique k(E) curve is obtained and the E_0 can be extrapolated to the dissociation onset. The molecular ion density of states, $\rho(E)$, is easily calculated from the vibrational frequencies and is strictly given. Therefore, in order to optimize k(E), the 2 lowest transition state vibrational frequencies are adjusted, along with the E_0 .

3.3.3.1. Room Temperature (298K)

As mentioned earlier, the E_0 can be determined from the disappearance of the parent ion if the dissociation is fast. However, the 2-C₄H₉⁺ peak is slightly asymmetric in the TOF distribution, indicating a possible kinetic shift. The magnitude of the kinetic shift was taken into account by modeling both the breakdown curve and several TOF distributions simultaneously by optimizing the E_0 and transition state frequencies. The latter parameter is adjusted to fit the asymmetric TOF profiles to obtain a unique k(E) curve. This simulation is shown as the solid line going through the experimental points in Figure 3.3. The derived k(E) curve is extrapolated to the E_0 , thus accounting for the kinetic shift. This simulation confirmed that the kinetic shift is negligibly small, i.e. less than 1 meV. The derived 0K dissociation limit, E_0 , was 9.740 \pm 0.009 eV. This rate analysis also showed that the transition state that fits these TOF distribution is "tight", with an entropy of activation of -34 J/K (evaluated at 600 K) That is, the transition state frequencies (see

Table 3.2). This is consistent with a reaction that involves a rearrangement, rather than a simple dissociation reaction.

3.3.3.2. Dry Ice/Acetone (220K)

The breakdown curve at 220K is given as the diamonds in Figure 3.2 and the solid line is the fit. Several temperatures from 210 to 230 K were modeled and the best fit was obtained at 220K with an E_0 of 9.736 \pm 0.017 eV. The much larger error is due to temperature fluctuation during the course of the experiment. As mentioned above, the temperature could not be controlled digitally and thus depended on the acetone/dry ice ratio. Since the fractional abundances of the ions change depending on the temperature, as evident from Figure 3.2, the breakdown curve has more scatter leading to the larger error in the onset determination. Nevertheless, the resulting E_0 agrees to within 4 meV of the room temperature experiment.

3.3.3.3. Ice Water (273K)

The breakdown curve at 275K is given as the squares in Figure 3.2 and the solid line is the fit. The temperature of the isotemp bath was held constant at 273 K, though the temperature at the inlet was 275K. Several temperatures from 260 to 280 K were modeled and the best fit was obtained at 275K with an E_0 of 9.738 ± 0.010 eV.

As described above, only the thermal energy distribution, P(E), is needed when modeling fast dissociations. P(E) is calculated directly from experimental or *ab initio* neutral vibrational frequencies. The major assumption is that P(E) is transposed directly to the ion manifold. By adjusting the calculated neutral frequencies, we can adjust P(E)which in turn effects the simulated breakdown curve. The lowest two calculated frequencies of the neutral corresponded to internal rotations as opposed to vibrations.



Figure 3.3. A TOF distribution at 9.61 eV and 298K. The points represent the experimental TOF distribution and the solid lines are the fits from two different simulations. The solid dark grey line was obtained by modeling only the breakdown curve and using the optimized parameters in a single point TOF calculation. This is referred to as simulation (a) in the text. Simulation (b) was obtained by fitting both the breakdown curve and the TOF distribution simultaneously. The resulting E_{0} s differed by less than 1 meV.

These frequencies, along with one other which corresponded to an internal rotation were scaled by 10%, 20% and 30%. The P(E) distributions for the 3 scaled simulations, as well as the original are given in Figure 3.4. The maximum in the distribution is plotted as the inset in Figure 3.4 from 7.2 to X eV. The separation of the 4 distributions is more clearly visible. The $E_{0}s$ resulting from these simulations range from 9.738 (no scaling) to 9.745 eV (30%). The range of $E_{0}s$ is within the experimental uncertainty, however there is a noticeable worsening of the fit to the breakdown curve when comparing the simulation using the frequencies scaled by 30% to the simulations with the original set of frequencies.

3.3.3.4. Heated (400K)

The breakdown curve at 400K is given as the triangles in Figure 3.2, with the solid line as the fit. Several temperatures from 380 to 410 K were modeled and the best fit was obtained at 400K with an E_0 of 9.738 \pm 0.009 eV. Accurately determining the temperature is done by modeling the experimental curve at low photon energies. In this case, the first experimental point is approximately 50% daughter and parent. This makes determining the temperature a little harder. Nonetheless, the simulated curve fits very nicely over the entire energy range of the breakdown curve and the determined E_0 agrees very nicely with the three other measurements.

3.4. Implications and Discussion

3.4.1. The Role of Thermal Energy in Ionization

The excellent fit of our calculated breakdown diagrams with calculations based on the neutral thermal energy is rather striking. First of all, it means by measuring the



Figure 3.4. Ion internal energy distributions, P(E), at 275K as a function of the total energy minus the ionization energy (*E-IE*). The 4 lowest neutral frequencies were scaled by 0 (black), 10% (dark grey), 20% (grey) and 30% (light grey) in the P(E) calculation. As the distribution shifts to higher energy, the E_0 shifts to higher energy as well, though the difference is only 7 meV.

breakdown diagram for a molecule, it is possible to determine directly its internal energy distribution. There is no other experiment that allows one to measure such a distribution for a large polyatomic molecule. Gas phase heat capacities, which are very difficult to measure, are certainly sensitive to the vibrational modes, but only in an average sense. Similarly, sound velocity depends on $\gamma = C_p/C_v$, which for large molecules approach 1, and are thus very insensitive. The use of breakdown diagrams to determine the internal energy distribution my become useful for very large molecules, especially those having long carbon chains, which have many low frequencies that are difficult to calculate by *ab initio* methods.

We might ask, why ionization process should simply transpose the thermal energy distribution into the ionic manifold. This is rather surprising because the distribution of ionic states should depend on Franck-Condon factors, which vary greatly from mode to mode and molecule to molecule. Consider, for instance, a diatomic molecule whose geometries in the neutral and ionic states are identical. If such a molecule is ionized at the ionization energy, we would expect with equal probability, the following transition: $0 \rightarrow 0', 1 \rightarrow 1', 2 \rightarrow 2'$, etc. where the numbers are the vibrational quantum states in the ground and ionic (primed) states. Under this circumstance, we would expect the thermal energy distribution to be faithfully transposed into the ionic manifold. However, for such a case, all $i \rightarrow j'$ transitions would have zero intensities so that the only ion internal energy distributions that could be prepared would be $hv + E_{th} = IE + E_{th}$. That is, photon energies in excess of the ionization energy would simply yield energetic electrons. The same would happen for a polyatomic molecule in which the neutral and ionic geometries are identical. The fact that we can excite ions at any energy, means that removal of the

electron changes the geometry and permits preparation of the ion at any photon energy, not just at the ionization energy.

Consider now the situation in which the neutral and ion geometries are very different., as is the case in ammonia. The photoelectron spectrum of NH₃ exhibits a long progression of vibrational peaks in the umbrella mode²³. Clearly, the Franck-Condon factors favor production of the high v states, which permits photon absorption to produce more highly excited ionic states by $\Delta v > 0$ transitions. Based on simple diatomic displaced harmonic oscillator Franck Condon factors²⁴, we note that the transition probabilities for a series of v' - v = n (v = 0, 1, 2, ...) excitations permits us to excite ions to higher energies. A series of equal photon energy transitions for a diatomic species in which the neutral has a frequency of 200 cm⁻¹ and the ion 100 cm⁻¹ shows that the Franck-Condon factors are not equal, but that they do not differ wildly. Based on this vibrational mode alone, we would not expect that the thermal energy distribution in the neutral state is faithfully transposed to the ion.

Table 3.2. Iodobutane neutral and ion frequencies (<1000cm ⁻¹) and the contribution to						
the overall thermal energy.						
Freq-N	E-Ave	E-Total	% of Total	Freq-I	Diff	
84.2	166.76	166.7600233	18.32528	79.7	4.5	
104.6	158.1071	324.8671556	35.69969	102.2	2.4	
125.9	149.4226	474.2897293	52.11975	111.5	14.4	
225.8	113.3237	587.6134476	64.57291	198.2	27.6	
236.3	109.9577	697.5711751	76.65617	222.5	13.8	
379.4	71.48306	769.0542303	84.51145	354.8	24.6	
578.8	37.09048	806.1447137	88.58733	477.6	101.2	
746.8	20.44133	826.5860404	90.83363	760.8	-14	
782	17.96548	844.5515192	92.80786	768.6	13.4	
904.5	11.34837	855.8998891	94.05493	802.3	102.2	

Table 3.2. Iodobutane frequencies for the neutral (Freq-N) and ion (Freq-I). E-Ave is the average from the total energy, E-total.

However, in most polyatomic molecules, only a small number of vibrational modes are directly excited. Only those that are symmetric and change significantly from neutral to ion manifold can be excited by $\Delta v = 2, 3, 4$, etc. All other modes follow the Δv = 0 propensity. In Table 3.2, we list all the iodobutane frequencies below 1000 cm^{-1} . These are the ones that provide 95% of the 910 cm⁻¹ total thermal energy at T = 298K. The last column shows the difference in the ion and neutral frequencies. It is evident, that only two frequencies change significantly ($\approx 100 \text{ cm}^{-1}$), and of these only the 578.8 cm⁻¹ neutral frequency is significantly populated at room temperature. This modes then provides the ability to excite the ion to high vibrational levels by $\Delta v > 0$ transitions. All the other frequencies will change by the usual $\Delta v = 0$ propensity and thus simply transpose the thermal energy to the ionic manifold without changing it. It is significant that the lowest five frequencies contribute 75% of the thermal energy. It is because of these low frequencies that carry 75% of the thermal energy and are dominated by $\Delta v = 0$ transitions, that we observe a simple transposing of the neutral thermal energy into the ionic manifold.

3.4.2. Reaction Mechanism

The four measured dissociation onsets (average value of 9.738 ± 0.015 eV) for iodine loss agree to within 4 meV. This value is close to a previous PEPICO measurement by Oliveira et al.¹⁸ of 9.720 eV. In that study, the authors pointed out that the *n*-butyl iodide ion does not dissociate to the *n*-butyl ion, but rather to the lower energy 2-butyl ion. This was concluded on the basis of the dissociation onset, which is about 0.7 eV lower than expected for the *1*-butyl ion. Our tight transition state is in accord with this. In fact, it shows that the H atom transfer must take place at the transition state.

3.5. Conclusions

We report here the first results in which a temperature controlled inlet system is used for TPEPICO studies. Temperatures in the range of 220–400K can be achieved, as illustrate by investigating the iodine loss channel from n-butyl iodide ions. The breakdown diagrams were fitted by assuming that the neutral thermal energy distribution is transposed into the ionic manifold.

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CHAPTER 4:

The Heat of formation of the Acetyl Radical and Ion^a

4.1. Introduction

The heats of formation of the acetyl radical, CH₃CO[•] and its closed shell ion, CH₃CO⁺ are important species because they are related to a number of important thermochemical quantities, such as the C-H bond energy in acetaldehyde and the C-CH₃ bond energy in acetone. It is thus of some importance to establish these quantities to the same level of accuracy as the heats of formation of the related acetaldehyde and acetone molecules. There are several methods for determining bond energies and radical heats of formation, which have been summarized and compared by Berkowitz et al.1 and Blanksby and Ellison.² Among these are negative and positive ion thermochemical cycles as well as methods based on neutral kinetics. All of these approaches for determining a radical or ion heat of formation depend on the accuracy of other The various approaches thus differ not only in their experimental measurements. techniques, but also in their dependence on ancillary thermochemical information. It is thus important to determine these thermochemical quantities by several methods. In this paper we present new experimental data that serve to establish the heats of formation of the acetyl radical and ion to a precision of less than 2 kJ/mol.

The heat of formation of the acetyl ion can be obtained from proton affinity measurements through the reaction:

$$H_2C=C=O + H^+ \rightarrow CH_3CO^+ \qquad \Delta E = PA(H_2C=C=O)$$
(4.1)

The gas-phase proton affinity is generally measured as a relative quantity by equilibrium methods in high-pressure mass spectrometry, and its accuracy depends on a knowledge of the proton affinity of neighboring molecules in the scale.³ The 298 K proton affinity of ketene as listed in the NIST webbook is 825.3 kJ/mol,⁴ a number that was verified by high level ab initio calculations of Smith and Radom⁵ (825.0 kJ/mol). On the basis of the 0 K value of 819.1 kJ/mol and the heat of formation of ketene and H⁺,⁶ the 0 K acetyl ion heat of formation is 664.2 ± 4 kJ/mol. The error limits are difficult to determine because they are based on the reliability of the PA scale in the vicinity of ketene. We estimate it to be 4 kJ/mol.

The acetyl ion heat of formation can also be determined from photoionization of a variety of precursor molecules, $CH_3COX + h\nu \rightarrow CH_3CO^+ + X$. Among the factors that determine the best choice are the accuracy of the $\Delta_r H^o(CH_3COX)$ and $\Delta_r H^o(X)$, the lack of a reverse activation barrier for X loss, and a rapid dissociation reaction that does not involve metastable ions. Finally it is essential that X loss be the lowest energy dissociation channel. Traeger et al.⁷ investigated several precursors, which resulted in a broad range of derived acetyl ion heats of formation. Probably the most reliable precursor is acetone, which had a reported 298 K onset of 10.38 eV. A subsequent evaluation of this onset that takes into account the molecule's thermal energy resulted in a reported $\Delta_r H_{298}(CH_3CO^+)$ of 654.7 ± 1.5 kJ/mol.⁸ However, an earlier photoionization study by Murad and Inghram⁹ had suggested an onset of 10.45 eV, while a more recent study by Trott et al.¹⁰ using a supersonically cooled jet reported an onset of 10.52 eV.

Because the sample usually has a room temperature thermal energy distribution, the onset must be carefully modeled by taking this into account, as suggested by Asher et al.¹¹ This was not done in the previous photoionization studies.

The main information about the CH₃CO[•] radical heat of formation has come from neutral kinetic methods. Niiranen et al.¹² investigated the forward and backward rate constants for the reaction: CH₃CO[•] + HBr \leftrightarrow CH₃CHO + Br[•] as a function of temperature. Knowing the heat of formation of acetaldehyde, HBr, and the bromine atom, permitted them to extract a 298 K acetyl radical heat of formation of -10.0 ± 1.2 kJ/mol. A subsequent critical review of various kinetic methods led Tsang¹³ to propose a 298 K heat of formation of the acetyl radical of -12.0 ± 3 kJ/mol.

In principle, the acetyl free radical heat of formation can be determined through a positive ion cycle. If the acetyl ion heat of formation is known, the radical ionization energy would provide a measure of the radical heat of formation. However, the CH₃CO[•] ionization energy has not been determined and would be rather difficult to measure with great precision unless it was done with a very cold sample and at very high resolution so that the adiabatic ionization energy could be extracted.

In the negative ion cycle, the gas-phase acidity of CH₃CHO is combined with the CH₃CO[•] electron affinity:

$$CH_3CHO \rightarrow CH_3CO^- + H^+ \qquad \Delta E = \Delta_{acid}H^0(CH_3CHO)$$
(4.2)

$$CH_3CO^{\bullet} + e^- \rightarrow CH_3CO^- \qquad \Delta E = -EA(CH_3CO^{\bullet}) \qquad (4.3)$$

When these two reaction are combined with the ionization energy of the hydrogen atom, we obtain the acetaldehyde C-H bond energy: $CH_3CHO \rightarrow CH_3CO^{\bullet} + H^{\bullet}$, which is given by $\Delta_{acid}H^{\circ}(CH_3CHO) + EA(A^{\bullet}) - IE(H^{\bullet})$. An acetaldehyde gas-phase acidity of 1,632 ± 8 kJ/mol was estimated by DePuy et al.¹⁴ in a flowing afterglow instrument. A direct measurement was not reported because the acetyl anion is less stable than the isomeric acetaldehyde enolate anion, so that determining this by reaction kinetics was not possible. The electron affinity of the acetyl radical of 0.423 ± 0.038 eV was reported by Nimlos et al.¹⁵ from the CH₃CO⁻ photoelectron spectrum. Because of the considerable change in the geometry upon electron detachment, the PES consists of a broad band of resolved vibrational peaks in which it is difficult to identify the adiabatic onset from hot bands. Thus the adiabatic EA could be either the published value of 0.423 or 0.481 ± 0.037 eV.¹⁶ Making matters still more uncertain is the heat of formation aceteldhyde, which Pedley¹⁷ lists as -166.1 ± 0.5 kJ/mol, and Wiberg et al.¹⁸ report as -170.7 ± 1.5 kJ/mol. Thus by combining the various possible values, we can obtain 298 K CH₃CO[•] heats of formation ranging from -17.2 to -27.9 kJ/mol. These are all considerably lower than the -10.0 kJ/mol value reported by Niiranen et al.¹²

A final route to the acetyl radical heat of formation is through the dissociative photoionization of butanedione, which yields $CH_3CO^+ + CH_3CO^-$. If the acetyl ion heat of formation is known, then the radical energy can be determined. Traeger et al.⁷ reported the photoionization onset for the acetyl ion to be 9.88 eV, from which Traeger and Kompe⁸ determined the 298 K heat of formation of the acetyl radical to be -11.1 ± 1.8 kJ/mol, which is quite close to the value obtained from the neutral kinetic method.

This review of the experimental acetyl ion heat of formation shows that there is considerable disagreement among the reported values of the acetone dissociative photoionization onsets. However, there seems to be sufficient flexibility in their interpretation that the derived CH_3CO^+ heat of formation can be made to agree with the

value derived from the ketene proton affinity. In the case of the acetyl radical heat of formation, the kinetic methods yield values that are 12 kJ/mol higher than the value from the negative ion cycle. On the other hand the photoionization and kinetic methods agree quite well.

We present in this paper photoionization data that provide new values for these heats of formation with overall error limits of ± 2 kJ/mol. In this study the dissociative photoionization onsets of acetone to give CH₃CO⁺ + CH₃ and butanedione to yield CH₃CO⁺ + CH₃CO[•] are used to establish the acetyl ion and radical heats of formation. The experimental development that has made such a precision in determining the dissociation limits possible is a recently implemented threshold photoelectron photoion coincidence experiment that is free from the contribution of energetic electrons, and thus provides an unambiguous and accurate method for determining the 0K dissociation onset.^{19;20}

4.2. Results

4.2.1. Threshold Photoelectron Spectra

Threshold photoelectron spectra (TPES) of our two molecules were collected in order to determine in which region of the photoelectron spectrum the ions dissociated. Figure 4.1 shows the TPES for acetone. The ring and center electrode signals are plotted as dots and a grey line, respectively. The subtracted spectrum, which represents the true TPES is shown as the heavy solid line. The width of the first peak of 17 meV is nearly limited by the resolution of our instrument (13 meV). The factor by which the center electrode signal was multiplied before data subtraction was determined by collecting a TPEPICO



Figure 4.1. The threshold photoelectron spectrum (TPES) of acetone in the vicinity of its ionization energy. The center spectrum (dark grey) is both threshold electrons and some "hot" electrons, whereas the ring spectrum (light grey) is only "hot" electrons. The subtracted spectrum (black) is the true TPES. The E_0 indicates the dissociation limit for CH_3^{\bullet} loss.

TOF spectrum at an energy of about 11 eV, well above the dissociation limit for ${}^{\circ}CH_3$ loss. At this energy, all parent ion signal in the center spectrum is the result of hot electrons. Thus the factor can be set equal to the ratio of parent ion signal in the ring and central electrode TOF distributions, which is 0.278. The ionization energy of 9.708 ± 0.004 eV agrees perfectly with the most accurate measurement of the acetone ionization energy obtained in a ZEKE/PFI study of Wiedmann et al.²¹ who reported an IE of 9.7080 ± 0.0001 eV. This IE is slightly higher than the 9.703 ± 0.006 eV value listed in the NIST data base,²² and 12 meV higher than the 9.696 ± 0.006 eV reported by Trott et al.¹⁰ on the basis of their molecular beam photoionization study. It is evident that the yield of threshold electrons in the Franck-Condon gap region beyond about 10 eV is very weak, and that most of the center electrode signal is a result of hot electrons. This makes determination of the dissociation onset, which lies in this region, challenging. Indeed, Traeger pointed out the very weak CH₃CO⁺ signal in the vicinity of its appearance energy.^{7,8}

The corrected TPES of butanedione is shown in Figure 4.2. This spectrum differs from the acetone TPES in the very broad first band, which is indicative of a large change in geometry upon ionization. Indeed our ab initio calculations show that the middle C–C bond distance changes from 1.557 Å to 1.981 Å upon ionization. The determination of the adiabatic ionization energy is difficult, and we estimate it to be 9.21 ± 0.05 eV, which is somewhat lower than the values reported reported by Watanabe et al.²³ (9.23 eV) or Traeger et al.⁷ (9.3 eV). The broad peak extends to an energy beyond the derived fragmentation onset, so that the yield of threshold electrons is significant in this critical region.



Figure 4.2. The TPES for butanedione in the vicinity of its ionization energy. The E_0 indicates the dissociation limit for the loss of CH₃CO[•].



Figure 4.3. The TPEPICO time of flight distribution for acetone at 10.45 eV. The CH_2CO^+ peak is slightly asymmetric, characteristic of a slow dissociation, whereas the CH_3CO^+ peak is symmetric. The other three peaks at around 75 µs are due to the ¹³C peak contribution, a metastable peak for CH_2CO^+ formed in the drift region of the reflectron, and a collision induced dissociation peak.

4.2.2. TPEPICO

4.2.2.1. Acetone Results

TOF mass spectra of acetone were collected in the photon energy range from 10.16 to 10.83 eV. In this region, the parent ion, $CH_3COCH_3^+$, and two fragment ions, CH_3CO^+ and CH_2CO^+ , are observed. The latter is a minor fragment associated with a rearrangement that results in the loss of CH₄. The TOF distribution taken at a photon energy of 10.45 eV is shown in Figure 4.3. The center signal is expanded by a factor of 15 in the inset and shows the narrow and symmetric CH_3^{\bullet} loss fragment peak as well as the slightly asymmetric CH₄ loss fragment peak. The asymmetric peak indicates that the production of ketene ion proceeds via a long lived or metastable parent ion. A very slow component that corresponds to dissociation in the first drift region before the reflectron shows up as a peak around 76 μ s. The other two small peaks are a result of the ¹³C isotope and a collision induced dissociation in the drift region of the reflectron. The mechanism for this slow reaction for CH₄ loss has been of considerable interest.^{24;25} A low energy enol ion isomer is certainly involved but a tunneling step associated with the proton transfer may also intervene. Although we could measure the dissociation rate as a function of the ion energy, we choose not to focus on this issue in this study. Rather we simply note that the CH₄ reaction has an onset below that of the CH₃[•] loss and because it is slow, we assume that once the CH₃[•] loss step is energetically accessible, it will dominate the reaction. The CH_3^{\bullet} loss reaction producing the CH_3CO^+ ion results in a symmetric acetyl ion TOF peak, which indicates that it is produced by a fast reaction.

By collecting TOF spectra at various photon (ion internal) energies, and plotting the relative abundance of parent and daughter ions, we obtain the breakdown curve for


Figure 4.4. The experimental breakdown diagram for the acetone ion (points). The solid circles are the parent ion and the solid squares are the CH_2CO^+ data. When these are added together, they yield the open circles (see text for explanation). The open triangles are the CH_3CO^+ points. These data have been corrected for "hot" electron contributions as explained in the text. The solid lines constitute the calculated breakdown diagram at 298 K in which the only adjustable parameter is the 0K dissociation limit, E_0 . The best fit to the data occurs with an E_0 of 10.563 eV

acetone as shown in Figure 4.4. This breakdown diagram has been corrected for hot electrons as described in the experimental section. At low energies, the parent ion has insufficient energy to dissociate so that its fractional abundance is 1. At the same time, the fractional abundance of the CH_3CO^+ ion rises from 0 to 1 at high energies. In between, we also see the CH_4 loss channel rise and decrease between 10.4 and 10.55 eV. However, the CH_2CO^+ signal disappears at the E_0 for the acetyl ion, which shows that when the ion has sufficient energy to produce the acetyl ions, it will do so and will not dissociate via methane loss. The open circles are the combined parent and ketene ion signals, which are summed in order to determine the onset for the acetyl ion.

The solid lines are the calculated breakdown diagram in which the neutral acetone sample internal energy distribution, P(E), is taken into account. All ions that have an energy in excess of the 0 K dissociation limit, E_0 , are assumed to dissociate immediately. Because the ion internal energy is a sum of the photon energy plus the neutral internal energy, the parent and daughter ion curves are given by:

$$B_{P}(hv) = \int_{0}^{E_{0}-hv} P(E)dE \qquad for \ hv < E_{o} \qquad (B_{P}(hv) = 0 \ for \ hv > E_{o}) \qquad (4.4)$$

$$B_D(hv) = \int_{E_0 - hv}^{\infty} P(E)dE \qquad \text{for } hv < E_o \qquad (B_D(hv) = 1 \text{ for } hv > E_o) \qquad (4.5)$$

The thermal rovibrational energy distribution was calculated using both the experimental acetone vibrational frequencies taken form Shimanouchi²⁶ and frequencies calculated at B3LYP/6-311++G** level of theory using the G98 Gaussian package.²⁷ The experimental and unscaled calculated frequencies for the acetone molecule, shown in

Table 1, generally agreed to within 5%. More importantly, the average thermal energy calculated with these two sets of frequencies agreed to within 0.1 kJ/mol. This confirms a finding by Magalhaes and Soares Pinto²⁸ who found that B3LYP/6-311++G** frequencies should not be scaled.

Table 4.1. Calculated Harmonic Vibrational Frequencies			
Species	Vibrational Frequencies		
Acetone Neutral	68, 133, 380, 490, 536, 782, 884, 889, 1083, 1116,		
	1232, 1386, 1387, 1461, 1465, 1472, 1488, 1786,		
	3024, 3031, 3079, 3086, 3139, 3140		
Acetone Ion	75, 134, 335, 367, 475. 688, 893, 899, 1001, 1060,		
	1073, 1299, 1343, 1419, 1423, 1440, 1459, 1625,		
	3025, 3031, 3104, 3110, 3177, 3178		
Butanedione Neutral	39, 103, 106, 238, 348, 360, 519, 546, 617, 682, 910,		
	956, 1012, 1065, 1133, 1272, 1386, 1392, 1456,		
	1456, 1458, 1461, 1782, 1783, 3041, 3041, 3097,		
	3097, 3149, 3149		
Butanedione Ion	11, 92, 99, 195, 200, 303, 340, 466, 482, 511, 882,		
	895, 1002, 1028, 1038, 1041, 1363, 1368, 1423,		
	1428, 1439, 1440, 2003, 2009, 3039, 3039, 3114,		
	3115, 3145, 3147		
Acetyl Radical	110, 469, 855, 956, 1049, 1358, 1453, 1457, 1925,		
	3016, 3108, 3114		
Acetyl Radical	418, 419, 910, 1028, 1028, 1363, 1396, 1396, 2385,		
	2999, 3080, 3081		
Methyl Radical	537, 1402, 1402, 3102, 3282, 3282		

 Table 4.1. Calculated vibrational frequencies of relevant species.

The best fit of the experimental breakdown curve, shown in Figure 4.4, is obtained when the 0K dissociation limit, E_0 , is set at 10.563 ± 0.010 eV. The model reproduces the experimental breakdown curve well over the entire energy range studied. The derived E_0 for this reaction is slightly higher than the 10.52 ± 0.01eV reported by

Trott et al.¹⁰ on the basis of a molecular beam photoionization study. In that study, the onset was determined by extrapolating the CH_3CO^+ signal as a function of the photon energy to the baseline. They also assumed that the molecule was at 0K. However, if the cooling is not complete, the onset would shift toward lower energy. The authors were aware of this and suggested that the E_0 is likely to be 10.54 eV or higher. It is worth noting that the calculated breakdown diagram using calculated frequencies at B3LYP/6-311++G** level of theory is identical to the breakdown diagram using experimental frequencies.

4.2.2.2. Butanedione Results

Figure 4.5 shows the breakdown diagram for butanedione, in which the only fragment observed was the acetyl ion. Because no experimental vibrational frequencies are available for this molecule, we calculated the breakdown diagram for a temperature of 298K using the butanedione vibrational frequencies (Table 4.1) calculated with the B3LYP/6-311++G** level of theory in the G98 Gaussian package.²⁷ When we use our derived ionization energy of 9.21 eV, the best fit to the experimental breakdown diagram is with an $E_0 = 10.090 \pm 0.006$ eV. The value of the ionization energy is important here because this molecule, which is larger than acetone, has a sufficiently large density of vibrational states that the calculated RRKM rate constant at threshold is about 10^3 s⁻¹. The asymmetry of the acetyl ion TOF peak confirms this slow rate. As a result, the observed E_0 is shifted to higher energies by about 10 meV, and the modeling of the breakdown diagram takes into account this slow reaction. Had it not been included, the onset would have been 10.101eV.



Figure 4.5. The experimental breakdown diagram for butanedione (points) and the solid lines represent the calculated breakdown diagram in which the only adjustable parameter is the 0K dissociation limit, E_0 . The best fit to the data occurs with an E_0 of 10.090 eV, indicated by the vertical arrow.

The excellent agreement between the experimental and the calculated 298K breakdown diagram modeled by equations (4.4) and (4.5) justifies the assumption that the ionization process simply transposes the neutral thermal energy distribution into the ion manifold. The validity of this model is fortunate because it means that we are not forced to calculate complicated Franck-Condon factors for each transition connecting rovibrational states in the molecule and ion. The excellent fit with the simple theory appears to suggest that the Franck-Condon factors are the same for all transitions independent of the initial neutral molecule vibrational state. Although this is certainly not correct for individual transitions, it appears to be correct when averaged over the thousands of transitions that are involved. While this model works for 298K TPEPICO experiments, it does not seem to work for cooled samples studied by pulsed field ionization (PFI) PEPICO.²⁹⁻³¹ In those experiments, the pulsed field ionization process seems to favor the product ion channel so that the breakdown diagram cannot be fit by the use of equations (4.4) and (4.5).

4.3. Thermochemistry

The measured 0K dissociation limits obtained from the breakdown diagrams permits us to derive values for the heats of formation of the acetyl ion and free radical. The 0K heat of formation of the acetyl ion is given by:

$$\Delta_{f}H^{o}_{0K}[CH_{3}CO^{+}] = E_{0} + \Delta_{f}H^{o}_{0K}[CH_{3}COCH_{3}] - \Delta_{f}H^{o}_{0K}[CH_{3}^{\bullet}]$$

$$(4.6)$$

The 298K heat of formation of acetone is listed in Pedley¹⁷ as -217.1 ± 0.7 kJ/mol. However, this compilation did not include the work of Wiberg et al.¹⁸ who measured the heats of formation of a number of carbonyl compounds relative to their alcohol counterparts. They list a value of -218.5 ± 0.6 kJ/mol. This number can be transformed to a 0K value by the usual thermochemical cycle using the experimental values for the acetone vibrational frequencies and the known $H^{o}_{298K}-H^{o}_{0K}$ values for the elements as listed in Wagman et al. The transformation, which is given by:

$$\Delta_{f}H^{o}_{0K} = \Delta_{f}H^{o}_{298K} + \sum (H^{o}_{298K} - H^{o}_{0K})_{\text{Elements}} - (H^{o}_{298K} - H^{o}_{0K})_{\text{Molecule}}$$
(4.7)

Table 4.2. Ancillary Heats of formation (kJ/mol)				
Species	$\Delta_{\rm f} {\rm H^o}_{0{ m K}}$	$\Delta_{\rm f} {\rm H}^{\rm o}{}_{298{ m K}}$	$H^{o}_{298} - H^{o}_{0K}{}^{a}$	
CH ₃ COCH ₃	-202.2 ± 0.6^{a}	-218.5±0.6 ^b	16.6	
CH ₃ COCOCH ₃	-310.4 ± 1.2^{a}	-327.1 ± 1.2^{c}	21.6	
CH ₃ •	150.3 ± 0.4^{d}	147.1 ± 0.4^{a}	10.5	
CH ₃ COCH ₃ ⁺	734.5±0.7 ^e	718.8±0.7 ^e	17.2	
CH ₃ COCOCH ₃ ⁺	578.2±5.0 ^f	563.8±5.0 ^f	23.9	
CH ₄	-66.4±0.4	-74.4±0.4 °	9.99	
H•	216.0 ^g	218.0 ^g	6.12 ^g	

Table 4.2. a) Conversion calculated using experimental or ab initio vibrational frequencies from Table 3.1. b) From Wiberg et al.¹⁸ c) From Pedley.¹⁷ d) Determined from $\Delta_{f}H_{0K}(CH_{3}^{+})$ Weitzel et al.³⁰ and IE(CH₃[•]) from Blush et al.³² e) Ionization energy of CH₃COCH₃ from this study. f) Ioization energy of CH₃COCOCH₃ from this study. g) From Wagman et al.⁶

yields a $\Delta_f H^o_{0K}[CH_3COCH_3] = -202.2 \pm 0.6 \text{ kJ/mol}$. These values along with other ancillary heats of formation are listed in Table 4.2. The methyl radical heat of formation is known very accurately as a result of the recently measured 0K onset for: $CH_4 + h\nu \rightarrow$ $CH_3^+ + H^\bullet$ reaction $(14.323 \pm 0.001 \text{ eV})$.³⁰ When this is combined with the even more accurate methyl radical ionization energy of $9.8381 \pm 0.0001 \text{ eV}$,³² we obtain $\Delta_f H^o_{0K}[CH_3^\bullet] = 150.3 \pm 0.4 \text{ kJ/mol}$, in which the error is limited by the methane heat of formation. This results in a $\Delta_f H^o_{0K}[CH_3CO^+]$ of 666.7 ± 1.2 kJ/mol, in which the error is determined mainly by our measured onset. In converting this heat of formation to 298K using equation (4.7), we use the NIST Webbook 0K electron convention in which $(H^o_{298K}-H^o_{0K})_{\text{Electron}}$ is taken to be 0. It differs from the other convention used by the NBS compilation.⁶ To convert the 0K convention to the 298K convention, 2.5RT = 6.2 kJ/mol must be added to the heat acetyl ion heat of formation. The acetyl ion vibrational frequencies used for the 0K \rightarrow 298K conversion are listed in Table 4.1.

The derived acetyl ion heat of formation, which is compared to literature values in Table 4.3, is certainly the most accurate one based on the dissociative ionization of the

Table 4.3. Experimental measurements of $\Delta_f H^o(CH_3CO^+)$ (kJ/mol)					
Method	Measured Value	$\Delta_f H^o_{0K}$	$\Delta_{\rm f} H^{o}_{298K}$	$H_{298} - H_0$	
$CH_3COCH_3 + hv \rightarrow$					
$CH_3CO^+ + CH_3$					
Photoionization (PI) ^a	10.45 eV (0K)				
Photoionization ^b	10.38 eV		654.7±1.1°		
Molecular Beam PI ^d	(298K)				
TPEPICO ^e	10.52 eV (0K)	666.7 ±1.1	659.4±1.1	11.82	
	10.563 eV (0K)				
Ketene proton affinity					
$CH_2CO + H^+ \rightarrow CH_3CO^+$	825.3 (298K) ^f	664.2 ± 2	656.9 ^g	12.0 ^h	

Table 4.3. a) This is an extrapolated 0K value by Murad and Inghram.⁹ b) From Traeger et al.⁷ c) Reevaluation by Traeger and Kompe⁸ in which the thermal energy is taken into account. d) From Trott et al.¹⁰ e) This work. f) From Hunter and Lias.³³ g) Calculated from ketene heat of formation¹⁷ and proton affinity. h) Calculated by Smith and Radom.⁵

acetone molecule because the TPEPICO approach yields directly a 0K dissociation limit that is easily extracted from the data. This is not the case in simple photoionization studies in which the onset is determined from a vanishing acetyl ion signal. The shape of such photoionization signals can be affected by the temperature as well as the photoelectron spectrum in the vicinity of the onset.

The only other route to the acetyl ion heat of formation is through the previously mentioned proton affinity of the ketene molecule, which yields a 0K acetyl ion heat of formation of 664.3 ± 4 kJ/mol. This agrees with our value of 666.7 kJ/mol to within 2.4 kJ/mol, which is within the error of the two measurements. Had we used the acetone heat of formation from Pedley, the discrepancy would have been 3.8 kJ/mol.

The acetone ion C-C bond energy can be determined from the difference in our acetone ionization energy of 9.708 ± 0.004 eV and E_0 of 10.563 ± 0.010 eV. This yields a CH₃CO⁺-CH₃ bond energy of 0.855 ± 0.010 eV or 82.5 ± 1.0 kJ/mol.

Using the above acetyl ion heat of formation from the acetone experiment in combination with results from the photoionization of butanedione gives a 0K heat of

Table 4.4. Experimental measurements of $\Delta_f H^o(CH_3CO^{\bullet})$ (kJ/mol)					
Method	Measured	$\Delta_f H^o_{0K}$	$\Delta_{\rm f} H^{o}_{298K}$	$H_{298} - H_0$	
Neutral Kinetics $CH_3CO^{\bullet} + HBr \leftrightarrow CH_3CHO + Br^{\bullet}$ Critical review	k_f and k_r		-10.0 ± 1.2^{a} -12 ± 3^{b}	12.39 ^a	
Negative Ion Cycle EA(CH ₃ CO) Acidity (CH ₃ CHO)	$0.423 \pm 0.037 \text{ eV}^{c}$ $1632 \pm 8 \text{ kJ/mol}^{d}$		-22.6 ±8.8		
Butanedione Photoionization AE_{298K} CH ₃ CO [•] AE_{298K} CH ₃ CO [•] E_{0K} CH ₃ CO [•]	9.67 eV ^e 9.88 \pm 0.011 ^f 10.090 \pm 0.006 ^h	-3.6±1.8	-11.1 ±1.8 ^g -9.8 ±1.8	12.86	

Table 4.4. a) From Niiranen et al.¹² b) From Tsang.¹³ c) From Nimlos et al.¹⁵ The EA could also be 0.481 eV (see text)¹⁶. d) Estimated acidity from DePuy et al.¹⁴ e) From Murad and Inghram.³⁴ f) From Traeger et al.⁷ with the value given in eV. g) From Traeger and Kompe.⁸ h) This work with the value given in eV.

formation of the acetyl radical. The breakdown diagram of the fragmentation of butanedione to the acetyl radical and acetyl ion was fit with an E_0 of $10.090 \pm 0.006 \text{ eV}$. Using this E_0 and the 298K \rightarrow 0K converted literature value for $\Delta_f H^o_{0K}$ (CH₃COCOCH₃) = $-310.4 \pm 1.2 \ 2 \text{ kJ/mol}$,¹⁷ the 0K heat of formation of the acetyl radical can be determined from:

$$\Delta_{f}H^{o}_{\partial K}(\mathrm{CH}_{3}\mathrm{CO}^{\bullet}) = E_{\partial}(\mathrm{CH}_{3}\mathrm{CO}^{+}) + \Delta_{f}H^{o}_{\partial K}(\mathrm{CH}_{3}\mathrm{COCOCH}_{3}) - \Delta_{f}H^{o}_{\partial K}(\mathrm{CH}_{3}\mathrm{CO}^{+})$$
(4.8)

which yields a $\Delta_f H^o{}_{0K}(CH_3CO^{\bullet}) = -3.6 \pm 1.8 \text{ kJ/mol}$. The conversion to 298K gives a $\Delta_f H^o{}_{298K}(CH_3CO^{\bullet}) = -9.8 \pm 1.8 \text{ kJ/mol}$. The error of 1.8 kJ/mol represents the sum of our appearance energy ($\pm 1 \text{ kJ/mol}$) and the uncertainty in the other heats of formation. The

acetyl radical heat of formation, obtained through our ion cycle and shown in Table 4.4, agrees remarkably well with the values obtained from neutral kinetic measurements, especially the one by Niiranen et al.¹²of -10.0 ± 1.2 kJ/mol. It is interesting, though, that in their calculation of the acetyl radical heat of formation they used $\Delta_{f}H^{o}_{298K}$ [CH₃CHO] = -165.8 kJ/mol, which differs significantly from the Wiberg measured value of -170.7 ± 1.5 kJ/mol.¹⁸ If we were to use the Wiberg heat of formation, the derived Niiranen acetyl radical heat of formation would be -14.9 kJ/mol.

As already pointed out in the introduction, the negative ion cycle is not a good route for determining the acetyl radical heat of formation because of problems with both the electron affinity and the acetaldehyde acidity determinations.

4.4. Conclusions

The heats of formation of the acetyl ion and radical have been measured by dissociative photoionization of acetone and butanedione. The present determination of the 0K acetyl ion dissociation limit from acetone by threshold photoelectron photoion coincidence (TPEPICO) is more reliable than previous photoionization measurements because the 0K onset can be unambiguously established. The derived acetyl ion heat of formation agrees to within 2 kJ/mol with a measurement based on the proton affinity of ketene. The good agreement between these different methods lends support for this value and its error limit.

The acetyl radical has been measured by three methods, neutral kinetics, the negative ion cycle, and the dissociation of butanedione to yield CH_3CO^{\bullet} . The neutral kinetics and our TPEPICO onset for the radical from butanedione agree to within 2

kJ/mol. The negative ion cycle in which the gas phase acidity of acetaldehyde is combined with the radical electron affinity is not a reliable path for determining the acetyl radical heat of formation. This is because the substantial geometry change upon ionization makes determination of the adiabatic ionization energy of CH_3CO^- difficult, and because the heterolytic bond dissociation of acetaldehyde removes the proton from the CH_3^{\bullet} group rather than the CHO group to produce the acetaldehyde enolate ion rather than the acetyl anion.

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CHAPTER 5:

Heat of Formation of the Propionyl Ion and Radical^a

5.1. Introduction

Establishing the heats of formation of radicals, ions, and neutrals by measuring dissociative photoionization onsets is based on the following reaction:

$$AB + h\nu \to A^+ + B \tag{5.1}$$

in which the heats of formation of the three species are related to the threshold energy, E_0 by the thermochemical cycle:

$$E_0 = \Delta_f H^o[A^+] + \Delta_f H^o[B] - \Delta_f H^o[AB].$$
(5.2)

The ideal reaction should meet several criteria, among which are: a) no activation energy for the reverse reaction, b) the heats of formation of two of the three species must be well established, and c) the reaction of interest should in general be the lowest energy dissociation channel. The last requirement is a result of the so-called competitive shift,¹⁻³ which shifts the observed onset for a higher energy channel to higher energies. This is because at the dissociation limit for the second channel, the rate of the lowest energy reaction may be orders of magnitude higher than the rate of the second reaction thereby preventing the observation of products at the dissociation limit. In this paper we utilize the statistical theory of unimolecular decay⁴ to model the experimental data for higher dissociation energy channels in order remove this last limitation to

associated with the photoionization method. The benefit of this analysis is the ability to investigate new species not otherwise accessible.

We have recently studied the heat of formation of the acetyl radical, CH_3CO^{\bullet} , and ion, CH_3CO^{+} through the photoionization of and butanedione.⁵ In the present study, we use two starting molecules and three reactions to establish the heats of formation of the propionyl radical ($C_2H_5CO^{\bullet}$), the propionyl ion ($C_2H_5CO^{+}$), and $C_2H_5COCOCH_3$ (2,3pentanedione). The reactions involved are:

$$\rightarrow C_2 H_5 CO^+ + C H_3^{\bullet} \tag{5.3a}$$

 $C_2H_5COCH_3 + hv$

$$\rightarrow \mathrm{CH}_3\mathrm{CO}^+ + \mathrm{C}_2\mathrm{H}_5^{\bullet} \tag{5.3b}$$

$$\rightarrow C_2 H_5 CO^+ + C H_3 CO^{\bullet}$$
 (5.4a)

 $C_2H_5COCOCH_3 + hv$

$$\rightarrow CH_3CO^+ + C_2H_5CO^{\bullet}$$
 (5.4b)

The heat of formation of butanone is known to within 1 kJ/mol, as are the heats of formation of CH_3^{\bullet} , $C_2H_5^{\bullet}$, CH_3CO^+ , and CH_3CO^{\bullet} .⁵ With the aid of velocity focusing optics for electrons and a method for the subtraction of the "hot" electron contamination in the threshold signal,⁶ we are now able to determine the first dissociation onsets to within 1 kJ/mol, and the second dissociation onset to within 2 kJ/mol. The propionyl ion production channels (5.3a and 5.4a) are the lowest energy dissociation channels whereas the acetyl ion production channels (5.3b and 5.4b) are the second. We can test our ability

to extract the second onset energies by using the known thermochemistry of reaction 5.3b.

The onset of the C₂H₅CO⁺ ion from butanone (reaction 5.3a) was investigated some years ago by Murad and Inghram⁷ as well as by Traeger,⁸ and revisited very recently by Harvey and Traeger.⁹ The latter study yielded a $\Delta_f H^{o}_{298K}$ [C₂H₅CO⁺] of 617.8 \pm 0.9 kJ/mol. In a later paper, Murad and Inghram¹⁰ measured the onsets for reaction 4a to be 9.67 eV but did not assign an onset energy for reaction 5.4b. In the present work, we repeat these measurements and present the first experimentally determined value for the heat of formation of 2,3-pentanedione, as well as a new value for the heat of formation of the propionyl radical. We also show that the effects of the competitive shift can be accounted for in the modeling in order to obtain accurate dissociative onsets for higher energy channels. This ability to model higher energy onsets permits us to utilize reactions 5.4a and 5.4b to extract thermochemical values. That is, we can use the measured onset for 5.4a to obtain a heat of formation of the propionyl radical from the higher energy onset.

5.2. Theoretical Methodology

In support of our data analysis and statistical theory (RRKM) calculations, the geometry and vibrational frequencies of all molecules studied were calculated using Becke 3 parameter exchange¹¹ with the functional of Lee-Yang-Parr correlation $(B3LYP)^{12}$ and the 6-311++G** basis set implemented in the Gaussian 03 program version B04.¹³ The harmonic frequencies of butanone and 2,3-pentanedione were used in

the calculation of the neutral internal energy distribution and are listed in Table 5.1 without scaling. These frequencies were not scaled based on the findings of Magalhaes and Soares Pinto,¹⁴ who found that B3LYP/6-311++G** frequencies should not be scaled. In addition, the analysis of parallel dissociation pathways requires assumptions about the structure of the transition state so that those frequencies were calculated as well. The transition states for all dissociation pathways were calculated using the B3LYP functional and 6-311++G** basis.

Table 5.1. Calculated vibrational frequencies for relevant species			
Species	Harmonic Vibrational Frequencies		
CH ₃ COC ₂ H ₅	53, 102, 198, 247, 401, 475, 590, 753, 762, 941, 955, 1000, 1105,		
	1129, 1185, 1284, 1370, 1387, 1417, 1453, 1467, 1497, 1492,		
	1500, 1783, 3007, 3028, 3031, 3041, 3085, 3103, 3112, 3137		
CH ₃ COC ₂ H ₅ ⁺	53, 117, 228, 239, 340, 404, 470, 565, 742, 806, 938, 966, 1014,		
	1063, 1078, 1246, 1279, 1335, 1406, 1426, 1428, 1449, 1454,		
	1491, 1695, 3008, 3028, 3035, 3082, 3099, 3121, 3141, 3177		
C ₂ H ₅ COCOCH ₃	38, 53, 102, 190, 207, 259, 366, 414, 520, 538, 660, 715, 808, 904,		
	977, 1001, 1045, 1083, 1147, 1247, 1301, 1333, 1389, 1405, 1456,		
	1458, 1470, 1500, 1507, 1775, 1780, 3036, 3041, 3056, 3097,		
	3097, 3106, 3119, 3149		
C ₂ H ₅ COCOCH ₃ ⁺	16, 45, 99, 174, 189, 209, 230, 328, 394, 456, 487, 620, 800, 814,		
	892, 945, 1017, 1036, 1058, 1101, 1260, 1289, 1366, 1413, 1427,		
	1441, 1453, 1486, 1496, 1985, 1997, 3040, 3053, 3058, 3114,		
	3122, 3128, 3144, 3148		
CH ₃ CO ⁺	418, 418, 910, 1028, 1028, 1363, 1396, 1396, 2385, 2999, 3080,		
	3081		
C ₂ H ₅ CO ⁺	188, 193, 419, 599, 771, 833, 930, 1069, 1099, 1252, 1271, 1403,		
	1422, 1487, 1493, 2352, 3007, 3047, 3068, 3154, 3162		
CH ₃ CO [•]	110, 469, 855, 956, 1049, 1358, 1453, 1457, 1925, 3016, 3108,		
-	3114		
C ₂ H ₅ CO [•]	105, 234, 237, 625, 729, 799, 973, 1047, 1081, 1267, 1316, 1410,		
	1445, 1493, 1499, 1917, 3039, 3039, 3064, 3106, 3114,		
CH ₃ •	537, 1402, 1402, 3102, 3282, 3282		
C ₂ H ₅ •	98, 489, 813, 978, 1062, 1190, 1399, 1463, 1481, 1481, 2943,		
	3034, 3078, 3141, 3241		

Table 5.1. Harmonic vibrational frequencies for relevant species calculated at the B3LYP/6-311++ G^{**} level.

High-level calculations were performed to determine the heats of formation of the propionyl ion and neutral free radical. Total atomization energy of the propionyl ion and radical are calculated at the Weizmann-1 (W1) level of theory, where computational methods are outlined by Martin and coworkers in detail.¹⁵ Geometry optimization and vibrational frequency calculations have been performed at the B3LYP/cc-pVTZ level using Gaussian 03 version B04.¹³ All other calculations were carried out using MOLPRO 2002.3.¹⁶

Briefly, the SCF limit was obtained using two point formula¹⁷ using Dunning's augmented correlation consistent n-tuple zeta basis sets, aug-cc-pVTZ (AVTZ) and augcc-pVQZ (AVQZ). Closed shell CCSD¹⁸ with perturbative triple corrections¹⁹ and spin unrestricted RHF-UCCSD(T) open-shell coupled cluster theories²⁰ are used to calculate electron correlation of the propionyl ion and radical, respectively. T-1 diagnostics²¹ for the propionyl radical (0.019) does not suggest a need for a multireference electron correlation procedure. The largest calculations CCSD/AVQZ were carried out using the integral-direct algorithm²² implemented in MOLPRO 2002.3.¹⁶ CCSD and CCSD(T) contributions are obtained using the exponent of 3.22 derived from W2 comparison.¹⁵ The core valence correlations are considered at CCSD(T) level using core correlation basis set, MTsmall.¹⁵ BSSE corrections to core valence correlations²³ are not considered here. Scalar relativistic effects are considered at averaged coupled pair functional $(ACPF)^{24}$ with the MTsmall basis set, which gives essentially the same results to the more accurate one electron Douglas- Kroll approximation^{25;26} at the CCSD(T)/MTsmall level (only 0.2 kJ/mol difference for propionyl radical). Spin orbit coupling is taken into account from CODATA.²⁷ The resulting atomization energy is converted to the heat of



Figure 5.1. Threshold Photoelectron Spectra (TPES) of butanone from 9.25 - 11.25 eV. The true threshold signal is obtained by subtracting the hot electron contribution (ring) from the center (threshold and hot electron contamination) signal. The adiabatic IE (not marked) was determined to be 9.52 ± 0.04 eV. The dissociation onsets for the propionyl ion (E₀1) and acetyl ion (E₀2) are marked. These occur in a Franck Condon gap.

formation using standard formula. The adiabatic ionization energy (IE) is given by 0 K atomization energy difference between the cation and neutral at their optimized geometries.

5.3. Results

5.3.1. Photoelectron Spectra

The threshold photoelectron spectrum (TPES) of butanone was obtained by scanning the photon energy while collecting the zero energy electrons. A fraction of the ring signal (hot electrons) was subtracted from the central electrode signal to yield the true TPES shown in Figure 5.1. The factor is the same in the breakdown diagram and TPES. The derived dissociation onsets are indicated with a vertical arrow. It is apparent that the dissociation limits lie in a Franck-Condon gap, which means that the production of threshold electrons in the region of the dissociation limit is very small. The true threshold electron signal collected at the center electrode comprised only a small portion of the total signal, resulting in a very low yield of propionyl ion signal. The first TPES band of butanone is rather broad, making the assignment of adiabatic ionization energy was determined to be 9.52 ± 0.04 eV.

Uninteresting technical difficulties prohibited the collection of a TPES of 2,3pentanedione. Instead, we show in Figure 5.2 the ultraviolet photoelectron spectrum (UPS) recorded using the ATOMKI ESA 32 instrument, which has been described in detail elsewhere.²⁸ The instrument is equipped with a Leybold-Heraeus UVS 10/35 highintensity gas discharge photon source. The UPS is obtained by ionizing the neutral precursor using a 21.217 eV He(I) lamp and scanning the energy of the ejected



Figure 5.2. Ultraviolet Photoelectron Spectrum (UPS) of 2,3-pentanedione in the energy range of 8 - 16.0 eV. The dissociation onsets for the propionyl (E₀1) and acetyl (E₀2) ion have been marked. The adiabatic IE (not marked) was determined to be 9.10 ± 0.04 eV.

photoelectrons. Electrons were collected using a hemispherical energy analyzer, which has a resolution on the order of 25 meV. The spectrum was calibrated using the Ar ${}^{2}P_{3/2}$ peak. The dissociation onsets for both the propionyl and acetyl ions occur at the end of the first band, where the yield of threshold electrons, although not massive, was nevertheless greater than in the case of butanone. Here, the adiabatic ionization energy was determined to be 9.10 ± 0.04 eV, which is in agreement with the value obtained from photoionization efficiency measurements from Murad and Inghram.¹⁰

5.3.2. Threshold Photoelectron Photoion Coincidence

5.3.2.1. Butanone

Time-of-flight mass spectra were recorded in the photon energy range from 10.0 to 12.0 eV. The breakdown diagram, given in Figure 5.3, is a plot of the ratios of the integrated peak areas for each ion as a function of the photon energy. The breakdown diagram was corrected for the hot electron contamination, which has been described in detail elsewhere.^{5;29} At low energies, only the parent ion is observed. The first dissociation pathway is associated with methyl loss channel producing the propionyl cation. At slightly higher ion energy, the ethyl loss channel producing the acetyl ion appears. The open points represent the experimentally determined ratios of the ion abundances while the lines represent the calculated ratios.

The time-of-flight (TOF) distributions of the propionyl ion ($C_2H_5CO^+$) fragments obtained from butanone were symmetric, which indicates that the products are formed via rapid reactions with rate constants in excess of 10^7 sec^{-1} . The symmetric peaks mean that the observed onset for the first dissociation channel is not shifted to higher energy by the kinetic shift associated with slowly dissociating ions.¹



Figure 5.3. The breakdown diagram of butanone in the range of 10.0 - 12.0 eV. The open points are the experimentally determined ion ratios (circles are parent ion, squares are the propionyl ion, and triangles are the acetyl ion). The lines are the calculated ion ratios. The dissociation onsets for the propionyl ion (E₀1) and acetyl ion (E₀2) are marked.

Because the propionyl ion production is fast, the breakdown diagram for this lowest energy dissociation channel can be modeled with just the thermal energy distribution of neutral butanone. We assume that if the total internal energy of an ion (hv– $IE + E_{th}$, where E_{th} is the thermal energy of the precursor molecule) exceeds the dissociation limit, it will dissociate instantly. If the sample were at 0K where the thermal energy distribution is a delta function, the breakdown diagram would exhibit a step at the dissociation limit. The 298K thermal energy distribution, P(E), broadens this step toward the low energy side. We can calculate the parent and daughter ion curves, $B_p(hv)$ and $B_d(hv)$ respectively, by integrating this distribution as shown in Equations (5.5) and (5.6).

$$B_{p}(h\upsilon) = \int_{0}^{E_{o}-h\upsilon} P(E)dE \qquad (5.5)$$
$$B_{d}(h\upsilon) = \int_{E_{o}-h\upsilon}^{\infty} P(E)dE \qquad (5.6)$$

The thermal rovibrational energy distribution at 298K was calculated using vibrational frequencies obtained at the B3LYP/6-311++G** level of theory. For this reaction the only adjustable parameter is the 0K dissociation onset, which was found to be 10.353 ± 0.012 eV. The degree of uncertainty determined by varying E_0 until the fit was noticeably worse, is limited by the scatter in the data and the photon resolution of 10 meV. This 0K dissociation limit is very close to the onset measured recently by Harvey and Traeger,⁹ whose reported 298K appearance energy in their photoionization experiment converts to 10.347 ± 0.003 eV at 0K. The 0K extrapolated Murad and Ingrahm⁷ value is 10.37 eV.

The modeling of the higher energy acetyl ion onset is somewhat more involved. Unlike the calculation of the breakdown diagram for the lowest energy reaction, the calculation of the second channel requires some assumptions about the transition states for the two competing reactions. The fractional abundance of the two products above the onset energy of the second product is directly proportional to the ratio of the rate constants for their production. These rates are given by the RRKM statistical theory as:

$$k(E) = \frac{N^{\#}(E - E_0)}{h\rho(E)}$$
(5.7)

where $N^{\#}(E-E_0)$ is the sum of internal energy states of the transition state between 0 and $E-E_0$, *h* is Planck's constant, and $\rho(E)$ is the density of states of the molecular ion. The production of the propionyl and acetyl ion proceed from the same molecular ion, therefore their rates differ only through the numerator of equation (5.7). Thus, the ratio of their rate constants is given by the ratio of the sum of states of the transition states, as illustrated by:

$$\frac{k_1(E)}{k_2(E)} = \frac{N_1^{\#}(E - E_1)}{N_2^{\#}(E - E_2)}$$
(5.8)

It can be readily appreciated that when the energy of the ion is just equal to E_2 , there is only one path for dissociation to the acetyl ion (i.e. $N^{\#}_2(0) = 1$) but the value of $N^{\#}_1(E-E_2)$ = 10⁷. This means that the acetyl ion signal cannot compete well with the production of the propionyl ion. As a result, the observed onset is shifted to higher energies by the competitive shift. How rapidly the acetyl ion signal catches up with the propionyl signal is a function of the transition state frequencies for the two reactions. Thus, in addition to the onset energy, E_2 , we need to vary the transition state frequencies for one species.

The breakdown diagram for the higher energy region was modeled as follows. When either CH₃[•] or C₂H₅[•] fragments are lost, a total of six vibrational frequencies are turned into translations or rotations. These frequencies can be identified by carrying out a B3LYP/6-311++G** calculation with the RCO–R' bond stretched from the optimized length in the molecular ion to 4 Å. The reaction coordinate is then identified by the negative frequency and the other five disappearing frequencies by their low values. We chose to use this set of frequencies for the transition state associated with the propionyl ion production. We then found a similar set of five frequencies for the acetyl ion channel. These five frequencies were varied along with the onset energy, E_2 , until the calculated breakdown diagram agreed with the experimental points. Error limits were obtained by varying the frequencies and calculating new best values for the onset energy. The resulting onset energy is 10.475 ± 0.016 eV for the acetyl ion. Murad and Inghram⁷ list this value as 10.5 eV, the lack of significant figures reflecting their level of confidence in obtaining an onset from a slowly rising signal.

This second onset, along with the established heats of formation of butanone and $C_2H_5^{\bullet}$, was used to determine an acetyl ion heat of formation of 665.3 ± 1.8 kJ/mol, which is in agreement with our previously reported value of 666.7 ± 0.9 kJ/mol.⁵ Although the first dissociation in acetone involves the loss of methane, it is a slow reaction that proceeds via tunneling. This channel is effectively blocked once the acetone ion internal energy is above the methyl loss channel because the latter is a fast reaction. Thus the onset for the methyl loss channel in acetone, which leads to the acetyl ion, can

be determined with high precision. The acetyl ion heats of formation obtained from the dissociative ionization of acetone and butanone agree to within 1.2 kJ/mol, which shows that our modeling correctly accounts for the competitive shift associated with higher energy dissociations. This is important to establish because we use this approach for determining the heat of formation of the propionyl radical from the higher energy dissociation pathway in 2,3-pentanedione.

5.3.2.2. 2,3-pentanedione

As shown in equations 5.4a and 5.4b, the 2,3-pentanedione ion dissociates to yield the propionyl ion and at somewhat higher energy the acetyl ion. The breakdown diagram for 2,3-pentandione has been constructed in the same manner as described above. A typical TOF distribution is illustrated in Figure 5.4 and the breakdown diagram is shown in Figure 5.5. The slightly asymmetric propionyl ion peak in the TOF distribution at ~81.5 μ s indicates that this reaction is slow near the dissociation limit. Slow reactions that form products as the parent ions are accelerating in the 5 cm long acceleration region result in asymmetric TOF peaks. Whereas the breakdown diagram is a plot of the relative rate constants over the entire energy range, the absolute rate constant can be extracted from asymmetric TOF profiles.

The TOF distributions and the breakdown diagram for the propionyl ion onset can be modeled by varying the onset energy and the transition state frequencies. This second adjustable parameter is a direct result of the asymmetric TOF distributions, where the lowest 4 frequencies of the transition state are fit to the experimentally determined rate curve. The 4 frequencies adjusted are those which turn into translations or rotations of the departing fragment in the dissocation reaction.



Figure 5.4. A typical time-of-flight (TOF) distribution for 2,3-pentanedione at a photon energy of 9.656 eV. The points are the experimental counts while the solid line is the calculated fit. The molecular ion is the peak at ~107.6 μ s and the propionyl ion is at ~81.1 μ s. The ¹³C peak is also present for the propionyl ion and molecular ion. The simulation indicates the presence of a drift peak, however no peak is observed experimentally. Note the two different scales.

The simulated TOF distribution matches the fast and metastable components nicely, except that a drift peak appears in the simulated TOF distribution which is only weakly present and rather broad in the experimental one. This peak is a result of dissociation in the drift region before the reflectron. The absence of a sharp peak in the experimental TOF distribution is a result of the fact that the reflectron is optimized to pass ions with a certain kinetic energy, namely parent ions or rapidly produced daughter ions. When the 2,3-pentanedione ion loses the acetyl radical sometime in the drift region before entering the reflectron, the remaining propionyl ion retains just 57% of its initial translational energy. As a result, the daughter ion trajectory is altered as it is being reflected and therefore many of these ions never reach the detector. This effect is not noticeable for H or CH₃[•] loss reactions, but becomes increasing problematic as the neutral mass increases. In the case of 2,3-pentanedione, the energy range for metastable ions goes from threshold where the minimum rate is 10^2 s⁻¹ and rises rapidly to 10^4 s⁻¹ within 20 meV. Given that the thermal energy distribution of the molecular ion extends over 200 meV, the metastable ions contribute a negligible fraction to the overall signal. As a result, the error associated with the missing signal near threshold is minor as the good fit of the breakdown diagram demonstrates. The fitting of these TOF distributions along with the breakdown diagram yields an onset of 9.841 ± 0.010 eV for the propionyl ion. Murad and Ingrahm¹⁰ obtained a 298K onset energy of 9.67 eV, which translates to a 0K onset of about 9.86 eV.

With the first onset established, we can keep these parameters fixed, and vary the transition state parameters (in order to fit the relative rate constants for the two competing channels) and the onset energy for the second reaction. That is, we assume the



Figure 5.5. The breakdown diagram of 2,3-pentanedione over the energy range of 9.0 - 11.5 eV. The open points are the experimentally determined ion ratios (circles are parent ion, squares are the propionyl ion, and triangles are the acetyl ion). The lines are the calculated ion ratios. The dissociation onsets for the propionyl ion (E₀1) and acetyl ion (E₀2) are given.

extrapolated rate constant for the first dissociation and adjust the second reaction rate to fit the data as was done for the second reaction in the butanone ion case. This yields an onset for the propionyl radical formation of 10.047 ± 0.023 eV. The error is somewhat larger because the onset is less distinct.

Because the two reaction channels differ only in the location of the charge, the difference in the activation energies, $E_2 - E_1$, is equal to the difference in the ionization energies of the two radicals. That is:

$$E_2 - E_1 = IE[CH_3CO^{\bullet}] - IE[C_2H_5CO^{\bullet}]$$
(5.9)

which is 0.206 ± 0.025 eV.

5.4. The Heats of Formation of C₂H₅CO⁺, C₂H₅CO[•], and C₂H₅COCOCH₃

5.4.1. Experimental

The onset energies for reactions 5.3a, 5.4a, and 5.4b along with the ancillary information in Table 5.2 permit us to derive the heats of formation for the propionyl ion and radical, as well as the neutral 2,3-pentanedione. These values are listed in Table 5.3. For example, the propionyl ion 0K heat of formation is related to the dissociation limit by:

$$\Delta_{f}H^{o}_{0K}[C_{2}H_{5}CO^{\dagger}] = E_{0} + \Delta_{f}H^{o}_{0K}[C_{2}H_{5}COCH_{3}] - \Delta_{f}H^{o}_{0K}[CH_{3}^{\bullet}]$$

$$(5.10)$$

which yields a $\Delta_f H^o_{0K} [C_2 H_5 CO^+]$ of 632.4 ± 1.4 kJ/mol. This value can be converted to 298K through equation (5.11):

$$\Delta_{f}H^{o}_{298K} = \Delta_{f}H^{o}_{0K} - \sum (H^{o}_{298K} - H^{o}_{0K})_{\text{elements}} + \sum (H^{o}_{298K} - H^{o}_{0K})_{\text{molecule}}$$
(5.11)

in which the $(H^{o}_{298K}-H^{o}_{0K})_{\text{elements}}$ values are taken from Wagman et al.,³⁰ and the $(H^{o}_{298K}-H^{o}_{0K})_{\text{molecule}}$ values are calculated using the vibrational frequencies in Table 1. This

conversion results in a 298K heat of formation of 618.6 ± 1.4 kJ/mol, which can be compared to the recent Harvey and Traeger value of 617.8 ± 0.9 kJ/mol.⁹ The difference in the quoted error limits is probably a subjective matter. In principle, the onset derived by the TPEPICO experiment is more accurate, or at least its interpretation is less subject to uncertainties about transition probabilities and Franck-Condon factors. Nevertheless, the derived heats of formation clearly agree within the error of the experiments.

Table 5.2: Ancillary Heats of Formation					
Species	$\Delta_f H^0_{\ 0K} (\text{kJ/mol})$	$\Delta_{f} H^{0}_{298K} \text{ (kJ/mol)}$	$H^{0}_{298K} - H^{0}_{0K}$		
Acetyl radical	-3.6 ± 1.8^{a}	-9.8 ± 1.8^{a}	12.9 ^b		
Acetyl ion	666.7 ± 0.8^{a}	659.4 ± 0.9^{a}	11.8 ^b		
Butanone	-216.1 ± 0.8^{b}	$-238.7 \pm 0.8^{\circ}$	19.8 ^b		
Methyl radical	150.3 ± 0.40^{e}	$147.1 \pm 0.40^{\rm e}$	10.5 ^b		
Ethyl radical	129.3 ± 0.7^{b}	$119.0 \pm 0.7^{\rm f}$	13.0 ^b		
H radical	216.0 ^g	218.0 ^g	6.12 ^b		

Table 5.2. Ancillary heats of formation. a) From Fogleman et al.⁵ b) Conversion calculated by using ab initio vibrational frequencies from Table 4.1. c) From Pedley.³¹ d) From *IE*(butanone) determined in this study and $\Delta_f H^o{}_{298K}$ (butanone) taken from Pedley.³¹ e) Determined from the $\Delta_f H^o{}_{0K}$ (CH₃⁺) from Weitzel et al.³¹ and the *IE*(CH₃[•]) from Blush et al.³² f) Private communication from B. Ruscic. Luo³³ lists 118.8 ± 1.3 kJ/mol and Atkinson et al.³⁴ lists 120.9 ± 1.6 kJ/mol. e) From Wagman et al.³⁰

Table 5.3. Heats of Formation of $C_2H_5CO^+$, $C_2H_5CO^-$, and $C_2H_5COCOCH_3$					
Species	$\Delta_f H^0_{0K}^{a}$	$\Delta_f H^0_{298K}^{a}$	Other Exp.	Theoretical	$H^{0}_{298K} - H^{0}_{0K}$
	·	·	$\Delta_f H^{0}_{298K}$	$\Delta_f H^0_{298K}$	
Propionyl ion	632.4 ±	618.6 ± 1.4	617.8 ^b	617.9 ^c	14.9 ^e
	1.4			618 ^d	
Propionyl	$-18.0 \pm$	-31.7 ± 3.4	$-32.3 \pm 4.2^{\rm f}$	-33.3 ^c	15.7 ^e
radical	3.4		$-34.3\pm8^{\text{g}}$		
2,3-	$-320.7 \pm$	$-343.7 \pm$		-338.3 ^h	24.7 ^e
pentanedione	2.5	2.5		-348^{i}	

Table 5.3. a) From this study. b) From Harvey and Traeger.⁹ c) W1 calculation this study. d) Calculation of Nguyen and Nguyen.³⁵ e) Conversion using calculated ab initio vibrational frequencies from Table 1. f) From Atkinson et al.³⁴ and Luo³³ based on the kinetic measurement of Watkins and Thompson³⁶. g) Kerr and Lloyd³⁷ value corrected for current ethyl radical heat of formation. h) Isodesmic reaction calculated at the B3LYP/6-311++g** level. i) Pedley, Naylor, and Kirby.³⁸

Having determined the propionyl ion heat of formation from the butanone dissociation, we can use it and its onset in reaction 4b to determine the heat of formation of 2,3-pentanedione, as listed in Table 5.3. Finally, we use equation 4b to obtain the propionyl radical heat of formation, $\Delta_f H^o_{298K} [C_2H_5CO^{\bullet}] = -31.7 \pm 3.4 \text{ kJ/mol}$. The larger error bars are a result of cumulative errors in establishing the 2,3-pentanedione heat of formation and the \pm 23 meV uncertainty in measuring the second onset.

5.4.2. Theoretical

In order to support our calculated heats of formation, we also carried out highlevel theoretical atomization energy calculations. The ground state conformers of both the propionyl ion and radical have Cs symmetry at the B3LYP/cc-pVTZ level. Shorter CO and CC bond lengths (1.116 and 1.428 Å) are found for the propionyl ion than for the neutral (1.180 and 1.515A). The OCC bond angle is 178.6 for the propionyl ion. As a consequence of the more rigid structure, the zero point energy (ZPE) for the ion is higher than that of the neutral by 4 kJ/mol. The ZPEs calculated at this level do not affect the atomization energies even for rigid molecule as Martin suggested elsewhere.³⁹ The calculation was tested on the acetyl radical and ion, where we obtained 298K heats of formation to within 1.3 kJ/mol for the acetyl ion and to within 2.7 kJ/mol for the acetyl radical (The experimental values are given in Table 5.2). The theoretical heats of formation of the propionyl ion and radical are listed in Table 5.3. Excellent agreements between theory and experiment are noted for the propionyl ion and propionyl radical in which our calculations differ by only 1.3 and 1.6 kJ/mol from the measured values,

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respectively. Both of these values are well within the experimental uncertainty of 1.4 and 3.4 kJ/mol.

The heat of formation of the 2,3-pentanedione molecule was also calculated using the isodesmic reaction:

$$C_2H_5COCOCH_3 + CH_4 \rightarrow CH_3COCOCH_3 + C_2H_6$$
(5.12)

Because the heats of formation of methane, butanedione and ethane are all well established, we can use the calculated reaction energy to obtain the heat of formation of the 2,3-pentanedione. These low cost calculations were carried out using B3LYP/6-311++G**, and yielded a $\Delta_{\rm f} {\rm H}^{\rm o}_{298}$ of -338.3 kJ/mol, a value is that is close to the -343.7 kJ/mol obtained from the experiment.

5.5. Discussion

The $\Delta_f H^{o}_{298K}$ [C₂H₅CO⁺] as determined in the present study (618.6 ± 1.4 kJ/mol) and by Harvey and Traeger,⁹ (617.8 ± 0.9 kJ/mol) is now well established. As pointed out by Harvey and Traeger,⁹ the propionyl ion heat of formation can be used to obtain the neutral methyl ketene heat of formation through its proton affinity (Equation 5.13).

$$CH_{3}CH=C=O+H^{+} \rightarrow C_{2}H_{5}CO^{+} \qquad \Delta E = PA(CH_{3}CH=C=O)$$
(5.13)

Bouchoux and Salpin⁴⁰ have determined the proton affinity of methyl ketene to be 839.8 kJ/mol through re-evaluation of thermokinetic measurements, which leads to a methyl ketene $\Delta_f H^o_{298K}$ of -71.6 ± 2.3 kJ/mol. This is an updated value from the Hunter and Lias compilation for which the *PA*[CH₃CH=C=O] was listed as 834.1 kJ/mol and is in better agreement with the theoretical value suggested by Nguyen and Nguyen³⁵ of 842 kJ/mol. Another route to the neutral heat of formation of methyl ketene is from the appearance

energy for the production of ionized phenol and neutral methyl ketene from phenyl propionate, which leads to a value of -66.9 ± 4.7 kJ/mol.⁴¹ However, the phenyl propionate heat of formation, upon which this calculation is based, was estimated.

A final pathway to the heat of formation of methyl ketene is through the photoelectron spectrum of methyl ketene reported by Bock et al.,⁴² for which the adiabatic ionization potential was reported to be 8.95 eV. This value can be combined with the $\Delta_f H^o_{298K}$ [CH₃CH=C=O⁺] of 783.5 ± 0.3 kJ/mol obtained by Traeger⁴¹ from the averaged values of the appearance energies of C₃H₄O⁺ from several precursors. This results in a methyl ketene heat of formation of -80.9 ± 1.3 kJ/mol. This value seems out of line with the other two determinations, which led Traeger⁴¹ to suggest that the ionization energy calibration in the photoelectron spectrum of Bock et al. could be off by as much as 0.15 eV. It is evident that the methyl ketene heat of formation remains somewhat controversial.

Kerr and Lloyd³⁷ first reported a heat of formation of the propionyl radical of – $46.0 \pm 8 \text{ kJ/mol}$ back in 1968 based on the kinetics and pressure dependence of the decomposition of azoethane in the presence of propionaldehyde. Cadman et al.⁴³ estimated a $\Delta_{f}H^{o}_{298K}[C_{2}H_{5}CO^{\bullet}]$ of –41.8 kJ/mol based on the Benson group additivity scheme⁴⁴, which is in good agreement with the experimentally determined value for Kerr and Lloyd. In 1973, Watkins and Thompson³⁶ studied the addition of ethyl radicals to carbon monoxide to determine the kinetics and thermochemistry of the propionyl radical, and using the slope of an Arrhenius plot were able to determine a $\Delta_{f}H^{o}_{298K}[C_{2}H_{5}CO^{\bullet}]$ of –44.3 kJ/mol. All of the other entries for the propionyl radical heat of formation in various compilations^{33;34;45-47} are based on these two experiments, although not always
directly referenced. A confusion occurred when Lias et al.⁴⁶ erroneously listed a $\Delta_{f}H^{0}_{298K}[C_{2}H_{5}CO^{\bullet}]$ of +41.5 ± 4 kJ/mol from McMillen and Golden,⁴⁵ which was taken from Watkins and Thompson.³⁶ Unfortunately, the error (it should have been -41.5 ± 4) resulted in an IE listing of 5.7 eV, which they obtained from the difference between the propionyl neutral and an old ion heat of formation.⁸ Nguyen and Nguyen³⁵ then used their calculated value for the propionyl ion (see Table 3) and this erroneous IE value to report a radical heat of formation of 68 kJ/mol. In the meantime the Lias et al. ionization energy has been corrected in the NIST Webbook,⁴⁷ where it is listed as 6.6 eV. More recently Atkinson et al.³⁴ re-evaluated the Watkins and Thompson experimental measurements and using an updated heat of formation for the ethyl radical, listed a $\Delta_{f}H^{0}_{298K}[C_{2}H_{5}CO^{\bullet}]$ of -32.3 ± 4.2 kJ/mol. This is the value that Luo lists in his Handbook of Bond Dissociation Energies.³³ A similarly updated $\Delta_{f}H^{0}_{298K}[C_{2}H_{5}CO^{\bullet}]$ of Kerr and Lloyd is -34.3 kJ/mol.

As shown in Table 5.3, our propionyl radical heat of formation of -31.7 kJ/mol is in good agreement with the previous values based on neutral kinetics, as well as our own theoretical calculation. This value depends on two onset measurements for the 2,3pentanedione ion. The first onset establishes the 2,3-pentanedione heat of formation, and the second onset determines the propionyl radical onset. As already pointed out, the first onset involves a metastable ion anlysis (see fit for asymmetric TOF distribution in Figure 5.4). Distributions at three ion energies were modeled. Our derived value for the 2,3pentanedione heat of formation agrees very well with the theoretical value derived from the isodesmic reaction (5.12), as well as that of the Pedley Naylor, Kirby (PNK) estimation scheme³⁸ (discussed later). It would thus appear that this value is correct. The propionyl radical heat of formation depends on the second onset. Because the two onsets are so close together (0.206 eV) our precision in measuring this onset is good, as it was in the case of butanone, where we obtained consistent results with established heat of formation of the acetyl ion and radical. Thus, it is unlikely that the error in our results is beyond the 3.5 kJ/mol.

With well-established heats of formation for the propionyl cation and radical, the adiabatic ionization energy for the propionyl radical can be obtained through the following relationship:

$$IE = \Delta_f H^o{}_{0K} [C_2 H_5 CO^+] - \Delta_f H^o{}_{0K} [C_2 H_5 CO^\bullet]$$
(5.14)

which yields a values of $6.75 \pm .04$ eV.

The propionyl radical heat of formation can also be used in determining neutral bond energies. These include the C–C bond energies in $CH_3CH_2CO-CH_3$ and $CH_3CH_2CO-COCH_3$, which are summarized in Table 5.4 along with other derived neutral bond energies such as $CH_3CO-COCH_3$.

Table 5.4. Determined 0K Neutral C–C Bond Energies ^a				
Species	BDE _{0K} (kJ/mol)	BDE _{298K} (kJ/mol)		
CH ₃ CH ₂ CO–COCH ₃	299.1 ± 4.5	302.2 ± 4.5		
CH ₃ CH ₂ CO–CH ₂ CH ₃	336.2 ± 3.5	340.7 ± 3.5		
CH ₃ CH ₂ CO–CH ₃	348.4 ± 3.5	354.1 ± 3.5		
CH ₃ CH ₂ -COCH ₃	341.8 ± 3.1	347.9 ± 3.0		
CH ₃ CO–COCH ₃	302.9 ± 2.7	307.2 ± 2.7		

Table 5.4. a) The neutral bond energies have been determined for several species based on the heats of formation of the $C_2H_5CO^{\bullet}$, CH_3CO^{\bullet} , CH_3^{\bullet} , and $C_2H_5^{\bullet}$ listed in Tables 2 and 3, as well as the heats of formation of the molecules taken from Pedley.³¹

The 2,3-pentanedione 298K heat of formation of -343.7 kJ/mol appears to be the first experimental value reported for this molecule. Such heats of formation are often obtained by group additivity schemes such as that of Benson.⁴⁴ The Benson rules work extremely well for determining the heat of formation of butanone, yielding -238 kJ/mol, which is in perfect agreement with the experimental result. (It was probably used to establish the group additivity values.) However, the Benson method yields a $\Delta_f H^{o}_{298K}$ [2,3-pentanedione] of -368 kJ/mol, which is too low by 20 kJ/mol. The group additivity method yields the same -368 kJ/mol for the isomeric 2,4-pentanedione, whereas the experimentally determined value is -382 kJ/mol.⁴⁸ The Benson value is now too high by 14 kJ/mol, but the discrepancy is much less. The method appears to fail due to nearest neighbor interactions that are not accounted for.

The PNK method³⁸ for determining the heat of formation is the sum of the contributions of the various components (like the Benson method) however, group interactions are taken into account. When the PNK method is used, a value of -348.4 kJ/mol is obtained for $\Delta_f H^o_{298K}[2,3\text{-pentanedione}]$ and -380.6 kJ/mol for $\Delta_f H^o_{298K}[2,4\text{-pentanedione}]$. The value of 2,4-pentanedione agrees extremely well with the experimentally determined value of -380 kJ/mol.

5.6. Conclusions

The propionyl ion and radical heats of formation have been determined through the photodissociation of butanone and 2,3-pentanedione. The propionyl ion heat of formation agrees with the value determined by Harvey and Traeger,⁹ as well as with high level calculations. The acetyl ion heat of formation determined from the second loss

channel of butanone agrees with our previously reported value from the lowest energy dissociation in acetone.⁵ This indicates that modeling can correctly account for the effects of the competitive shift associated with high energy dissociations. The results also report on the first experimental measurement of the 2,3-pentanedione heat of formation. These values are important in establishing accurate bond dissociation energies for a number of common molecules such as butanone, propanal, and other ketones.

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CHAPTER 6:

Dihalomethane Thermochemistry^a

6.1. Introduction

The interest in the study of the photoionization and thermochemistry of polyhalomethane molecules has increased considerably in the last years. It is mostly due to the importance of these molecules in atmospheric chemistry, since compounds such as, CH₂Br₂, CH₂I₂, CH₂BrI, CH₂ICl, and others, have been observed in the troposphere, and consequently been considered important sources of reactive halogens in atmosphere¹⁻⁵. From a fundamental viewpoint, dissociative photoionization studies involving polyhalomethane molecules have also attracted recent experimental and theoretical interest due to the different dissociation channels that can be identified upon absorption of VUV photons⁶⁻¹⁰.

Photoionization experiments involving the detection of ions in coincidence with energy-selected electrons, in which the ions are produced in well defined energy states, are known to be of great importance for the study of ion dissociation dynamics as well as for the determination of accurate ion thermochemistry¹¹⁻¹⁴. The aim of this work is to investigate the gas-phase dissociative photoionization and thermochemistry of the dihalomethane compounds, namely CH₂Cl₂, CH₂I₂, CH₂Br₂, CH₂ICl, CH₂IBr and CH₂BrCl, by the use of threshold photoelectron photoion coincidence (TPEPICO) spectroscopy, one of the most precise experimental methods employed to obtain

thermochemical information. The experimental breakdown diagrams obtained, analyzed with the RRKM statistical theory and *ab initio* calculations, provided reliable route on the determination of accurate dissociation onsets, heats of formation and bond dissociation energies for those molecules and their respective ionic fragments. Threshold photoelectron spectra (TPES) have also been recorded in order to obtain accurate ionization energies for the dihalomethanes.

Within the best of our knowledge, except for the CH₂Cl₂ molecule, which has been extensively studied by several experimental and supported by high level theoretical calculations, having quite well established heats of formation, there are no reliable experimental values for heats of formation of the dihalomethane molecules in the literature. Most of the values of neutral and ion heats of formation for those molecules available in the widely used thermochemical tables¹⁵⁻¹⁸ are either estimated values or with error bars as high as 25 kJ/mol. In this sense, our results provide the first accurate and consistent experimental determination of molecular dissociation onsets, derived 0K heats of formation and the $\Delta_f H^0_{298K}$ for this set of molecules.

6.2. Theoretical Methodology

The ab initio calculations were carried out using the Gaussian 03 package¹⁹. The ground state geometries of the neutral and ionic species were fully optimized using density functional theory (DFT), with the Becke²⁰ 3 parameter and Lee, Yang, Parr (B3LYP)²¹ functional, and the 6-311G* basis set. The vibrational frequencies, required for the RRKM analysis of the experimental breakdown curves, were also obtained in these calculations and are listed, without scaling, in table 6.1. The transition state

parameters, required in the fitting of the second dissociation onsets in the mixed dihalomethanes, CH_2BrI , CH_2BrCl and CH_2ICl , were obtained by stretching the carbonhalogen bonds up to 4 Å and calculating the vibrational frequencies in the DFT (B3LYP/6-311G*) level of theory.

Table 6.1. Calculated neutral and ionic vibrational frequencies		
Species	Vibrational frequencies	
CH ₂ Cl ₂	284, 697, 714, 910, 1201, 1323, 1473, 3129, 3208	
$CH_2Cl_2^+$	316, 540, 682, 803, 1071, 1174, 1224, 2850, 2896	
CH ₂ Br ₂	168, 568, 612, 820, 1132, 1239, 1451, 3141, 3228	
$CH_2Br_2^+$	162, 527, 619, 883, 1053, 1202, 1438, 3141, 3257	
CH ₂ I ₂	116, 482, 572, 732, 1075, 1165, 1427, 3144, 3234	
$CH_2I_2^+$	113, 500, 540, 789, 1011, 1127, 1411, 3142, 3257	
CH ₂ BrCl	225, 589, 709, 859, 1172, 1279, 1464, 3136, 3220	
CH ₂ BrCl ⁺	243, 516, 520, 779, 1073, 1150, 1292, 2955, 2963	
CH ₂ ICl	192, 517, 704, 801, 1158, 1242, 1457, 3139, 3223	
CH ₂ ICl ⁺	159, 289, 638, 794, 1109, 1174, 1402, 3064, 3126	
CH ₂ BrI	141, 514, 600, 770, 1111, 1205, 1441, 3143, 3230	
CH ₂ BrI ⁺	130, 506, 594, 831, 1043, 1172, 1430, 3142, 3256	

 Table 6.1. Calculated harmonic vibrational frequencies using DFT theory.

6.3. Results

The integrated peak areas from the center and ring TOF spectra were used in order to generate the breakdown diagrams, which represent the fractional abundances of the parent and fragment ions as a function of the photon energy. The hot electron subtracted breakdown diagram points B(I) for each ion were then obtained by using the equation 6.1:

$$B(I) = \frac{(I_c) - f(I_r)}{(T_c) - f(T_r)}$$
(6.1)

where I_c and T_c are the integrated peak areas of an ion and the total area of the ions associated with the center electrode, respectively. The same holds for I_r and T_r with



Figure 6.1. CH₂I₂ TOF distributions for the center and ring TPEPICO spectra recorded at 10.44 eV.

respect to the ring electrode. The experimental subtraction factor f(0.165), obtained from the ratio of the center and ring TOF distributions for the parent ion at energies above the dissociation limit, was constant for the entire data acquisition. Typical TOF distributions are shown in figure 6.1.

This figure presents the CH_2I_2 TOF distributions recorded from the center and ring electrodes at 10.44 eV photon energy. This photon energy is close to the dissociation limit, so that both parent and fragment ions are observed in the center and ring spectra. The ring spectrum, in which the ions are collected in coincidence with hot electrons, is associated with lower energy ions and thus shows less fragment ions than the corresponding center spectrum, in which the ions are detected in coincidence with essentially threshold electrons. The narrow symmetric peak shapes in the TOF distributions indicate that the dissociation process is rapid. Ion TOF distributions were collected at a number of photon energies from which we obtained the fractional abundance of parent and fragment ions.

The breakdown diagrams obtained for the six dihalomethane molecules in the range from 10 eV to 13 eV are shown in the figures 6.2-6.7. The rapid dissociation character at threshold for these molecules is observed from the shape of the breakdown curves, and is also confirmed by our TOF distributions which present only symmetric ion peaks. The solid lines represent the calculated breakdown curves in which the internal energy distribution, P(E), of the molecules is taken into account²². All ionic species with energy in excess to the 0K dissociation limit, E_0 , dissociate instantly. The vibrational frequencies and rotational constants required in these simulations were obtained at the B3LYP/6-311G* level of theory.



Figure 6.2. The breakdown diagram for CH_2Cl_2 in the 11.7-12.5 eV range. The solid points are the experimental fractional ion abundances of parent and daughter ions and the solid lines represent the best calculated fit to the experimental data, resulting in an E_0 of 12.122 eV.



Figure 6.3. The breakdown diagram for CH_2Br_2 in the 11.0-11.6 eV range. The solid points are the experimental fractional ion abundances of parent and daughter ions and the solid lines represent the best calculated fit to the experimental data, resulting in an E_0 of 11.399 eV.



Figure 6.4. The breakdown diagram for CH_2I_2 in the 10.1-10.7 eV range. The solid points are the experimental fractional ion abundances of parent and daughter ions and the solid lines represent the best calculated fit to the experimental data, resulting in an E_0 of 10.512 eV.



Figure 6.5. The breakdown diagram for CH₂BrCl in the 11-13.2 eV range. The solid points are the experimental fractional ion abundances of parent and daughter ions and the solid lines represent the best calculated fit to the experimental data. The E_0 's have been marked.



Figure 6.6. The breakdown diagram for CH₂ICl in the 10.4-12.2 eV range. The solid points are the experimental fractional ion abundances of parent and daughter ions and the solid lines represent the best calculated fit to the experimental data. The E_0 's have been marked.



Figure 6.7. The breakdown diagram for CH₂IBr in the 10.2-12.6 eV range. The solid points are the experimental fractional ion abundances of parent and daughter ions and the solid lines represent the best calculated fit to the experimental data. The E_0 's have been marked.

In the fitting of the dissociation onset for the non-mixed dihalomethane molecules (CH₂Cl₂, CH₂Br₂, CH₂I₂), the only adjustable parameter is the 0K dissociation limit, in which the approach of the curve to E_0 is determined by the neutral thermal energy distribution. When a second product ion is formed at a higher energy, which is the case of the mixed molecules (CH₂BrCl, CH₂BrI, CH₂ICl), then the fitting can be done in two steps, where the dissociation onset for the first ion is again determined only by a single parameter, E_{01} , however, as shown in the breakdown diagrams of the three mixed molecules, the onset for the second product ion is much less sharp. The reason is that the rate constant for the second halogen atom loss at its onset is $1/h\rho(E_{02})$, whereas the rate constant at that energy for the first halogen atom loss is $N^{\#}(E_{02}-E_{01})/h\rho(E_{02})$, so that the ratio of the two fragments losses is $1/N^{\#}(E_{02}-E_{01})^{23}$. In order to fit the slow rise in the first fragment loss signal and the slow fall of the second loss signal, the transition state frequencies of the two reaction channels are required and were obtained as explained above. The fitting of the second onset is thus determined by two factors, the onset energy, E_{02} , and the TS frequencies of either one of the channels.

6.4. Dissociation onsets and Thermochemistry

The present work is concerned with the determination of the 0K dissociation onsets and the heats of formation for the neutral molecules and fragment ions of the following reactions:

$$CH_2Cl_2 + h\nu \rightarrow CH_2Cl^+ + Cl^{\bullet} + e^-$$
 (6.2)

$$CH_2ClBr + hv \qquad \swarrow \qquad CH_2Cl^+ + Br^{\bullet} + e^{-} \qquad (6.3)$$

$$\sim$$
 CH₂Br⁺ + Cl[•] + e⁻ (6.4)

$$CH_2Br_2 + h\nu \rightarrow CH_2Br^+ + Br^{\bullet} + e^-$$
 (6.5)

$$CH_2BrI + hv \qquad \swarrow \qquad CH_2Br^+ + I^{\bullet} + e^{-} \qquad (6.6)$$

$$\sim CH_2I^+ + Br^{\bullet} + e^{-}$$
(6.7)

$$CH_2I_2 + hv \rightarrow CH_2I^+ + I^{\bullet} + e^-$$
 (6.8)

$$CH_2ICl + hv \qquad \swarrow \qquad \begin{array}{c} CH_2Cl^+ + I^{\bullet} + e^- \qquad (6.9) \\ CH_2I^+ + Cl^{\bullet} + e^- \qquad (6.10) \end{array}$$

Our measured dissociation onsets, presented in figures 6.2-6.7 and summarized in the form of diagram in figure 6.8, are considerably more accurate than the previously published values. If our measurements were perfect, we would be able to obtain the same value for the CH₂BrI energy going in either direction (figure 6.8). The first attempt provided values for the energy of CH₂BrI that agreed within 30 meV, which is the result of accumulated error in the measurements, estimated to be about 10 meV for the first onsets determination and 20 meV for the second ones. By slightly adjusting the three second onsets it was possible to make the difference for the CH₂BrI energies in the cycle vanish. As the total error was only 30 meV, the adjustment per each second onset was only about 10 meV, which is well within the error limits of ± 20 meV.



Figure 6.8. Dissociation onsets diagram connecting all of the reactions in this series of dihalomethane molecules.

Photoionization studies for the CH_2Cl_2 molecule reported by Werner et al.²⁴ attempted to take into account the thermal energy. The published dissociation onset value of 12.14 ± 0.20 eV agrees with the present results within the error margin. Holmes et al.²⁵ reported a value of 12.10 eV for this onset from their monoenergetic electron ionization experiments, however, no error bar was given. Chiang et al.⁶ recently studied the dissociative photoionization of the CH_2Cl_2 using synchrotron radiation, and reported a value of 12.08 ± 0.02 eV for the appearance energy of the CH_2Cl^+ ion. This result is about 40 meV above our value, which we attribute to the non inclusion of the CH_2Br_2 and CH_2I_2 onsets recorded by a TPEPICO apparatus. However, they did not correct for hot electrons. Their onsets of 10.55 ± 0.020 eV and 11.35 ± 0.020 eV, for CH_2I_2 and CH_2Br_2 , respectively, differ from the present results by more than the error margin. More recently, Ma et al.²⁷ reported a Br loss onset from CH_2Br_2 of 11.27 eV. This low value is probably a result of the neglect of the thermal energy.

The activation entropies S^{\ddagger} have also been obtain for the mixed dihalomethanes, from the calculated vibrational frequencies, and the results are listed in figures 6.5-6.7. The ΔS^{\ddagger} values for those molecules, as expected, increase in the order: ΔS^{\ddagger} (CH₂BrI)< ΔS^{\ddagger} (CH₂BrCl)< ΔS^{\ddagger} (CH₂ICl). Besides, the observed positive signals and absolute values of those activation entropies provide the degree of looseness of the transition states of the molecules.

As summarized in table 6.2, all of the dihalomethane molecules have heats of formation listed in the literature. However, the only well established value is that of CH₂Cl₂. The experimental value of $\Delta_t H^o_{298K}$ [CH₂Cl₂] of -95.5 ± 1.3 kJ/mol from the

literature also agrees with recent high level calculations performed by Feller et al.²⁸ We thus used this value of -95.5 kJ/mol, converted to -88.7 kJ/mol at 0K, in order to determine the heats of formation of all other species.

Table 6.2. Summary of the thermochemical results (kJ/mol) for the dihalomethanes					
Species	$\Delta_{f}H^{\theta}_{0K}$	$\Delta_f H^{\theta}_{298K}$	H^{0}_{298K} - H^{0}_{0K} (a)	$\Delta_{f}H^{\theta}_{298K}$ (lit.)	
CH ₂ Cl ₂	-88.7	-95.5 ± 1.3	11.87	$-94.6 \pm 8.3^{(a)}$	
				$-95.7 \pm 0.8^{(b)}$	
				$-95.5 \pm 1.3^{(c)}$	
CH_2Cl^+	961.0	957.0 ± 1.8	10.13	(959.0) ^{* (b)}	
				$949.8 \pm 8.3^{(d)}$	
CH ₂ Br ₂	24.5	3.2 ± 2.7	12.69	$4.7 \pm 8.3^{(a)}$	
				$0.0 \pm 4^{(b)}$	
CH ₂ BrCl	-30.5	-44.6 ± 2.0	12.27	$-44.8 \pm 8.3^{(a)}$	
				$-45.0 \pm 5^{(e,f)}$	
CH_2Br^+	1006.2	994.7 ± 2.6	10.26	(937.0)* ^(b)	
				$974.9 \pm 8.3^{(d)}$	
CH ₂ BrI	70.4	55.0 ± 2.7	12.98	$57.2 \pm 20^{(a)}$	
CH_2I^+	1023.9	1018.2 ± 2.7	10.40	1020.9 ± 8.3 ^(d)	
CH ₂ I ₂	117.0	107.5 ± 3.2	13.25	$117.5 \pm 20^{(a)}$	
				$118.0 \pm 21^{(b)}$	
				119.5 ± 2.2 ^(g)	
CH ₂ ICl	18.8	10.7 ± 1.9	12.47	$13.6 \pm 20^{(a)}$	
				$5 \pm 25^{(h)}$	

Table 6.2. a) For the H^{0}_{298K} - H^{0}_{0K} calculations, the heat capacity of the electron was chosen as 0.0 KJ/mol at all temperatures (Ion Convention¹⁶). Values were obtained using the vibrational frequencies listed in table 1. b) Kudchadker & Kudchadker.¹⁵ c) Lias et al.¹⁶ d) Chase.¹⁸ e) Holmes et al.²⁵ f) Skorobogatov et al.²⁹ g) Seetula.³⁰ h) Pedley.¹⁷ i) Skorobogatov.³¹ * Estimated values (no error margin provided).

The procedure used for determining the heats of formation of the dihalomethanes from the experimental dissociation onsets is explained as follows: By measuring the 0K dissociation onset energy, E_0 , for reaction (6.2) it has been possible to derive the heat of formation of the CH₂Cl⁺ ion, using as start both the CH₂Cl₂ and Cl[•] heats of formation values (which are well established in the literature), and by using equation 6.11.

$$E_0 = \Delta_f H_{0K}^0(CH_2X^+) + \Delta_f H_{0K}^0(X^*) - \Delta_f H_{0K}^0(CH_2XY)$$
(6.11)

where X and Y in equation 6.11 are halogen atoms (Cl, Br or I). The resulting heat of formation of CH_2Cl^+ can be used in reaction 6.3, with the corresponding dissociation onset, to determine the heat of formation of the CH_2ClBr neutral molecule. The CH_2ClBr heat of formation provides a means for determining the heat of formation of CH_2Br^+ from the onset energy for reaction (6.4), which leads to a measurement of the CH_2Br_2 heat of formation via reaction (6.5), and so on.

An important feature in these data is its self-consistency. For instance, by starting with the heat of formation of the CH_2Cl_2 neutral molecule, we were able to determine the heat of formation of the CH_2I^+ fragment by two different routes, which came from the fact that we have nine onset measurements but only eight are unknowns. This determination led to the value 1023 KJ/mol for the 0K heat of formation CH_2I^+ ion from both routes. Finally, the derived 0K heats of formation can be converted to 298K. Table 6.2 lists both the derived 0K and the converted 298 K values, which are compared with literature values at 298K. The conversion for the heat of formation from 0K to 298K and vice-versa can be made by means of the usual thermochemical cycle, given by:

$$\Delta_{f}H_{0K}^{\circ} = \Delta_{f}H_{298K}^{\circ} - [H_{298K}^{\circ} - H_{0K}^{\circ}](molecule/ion) + [H_{298K}^{\circ} - H_{0K}^{\circ}](elements)$$
(6.12)

We used the literature³² $H^{0}_{298K} - H^{0}_{0K}$ values for the atomic elements and the calculated vibrational frequencies and $H^{0}_{298K} - H^{0}_{0K}$ values for the molecules and fragment ions, as listed in tables 6.1 and 6.2, respectively. The $\Delta_{f}H^{0}_{298K}$ values obtained are then compared to the literature values.

Among the neutral dihalomethane molecules, our heats of formation for CH₂BrCl, CH₂Br₂, and CH₂BrI agree very well with the literature values. However, the error limits have been greatly reduced. The heat of formation for the CH₂ICl available in the

literature varies from 5 kJ/mol to 13.6 kJ/mol and with error bars as high as 25 kJ/mol. Our value, 10.7 kJ/mol, agrees within the error margins of the literature values, but again we reduce the uncertainty to less than 2 kJ/mol. The most important disagreement is found in the case of CH₂I₂ molecule, which value should be adjusted downward by approximately 10 kJ/mol, as can be observed from table 6.2. An additional value of 113 kJ/mol for the CH₂I₂ heats of formation, which is closer to our measured 107.5 kJ/mol, is available from the literarature³³, however, no error bar was given. Among the ions, the major literature error found was in $\Delta_f H^o_{298K}$ [CH₂Br⁺], which must be increased by at least 18 kJ/mol.

These new accurate heats of formation provide a new perspective for understanding important atmospheric reactions^{34;35}, for instance, $Cl^{\bullet} + CH_2ICl \rightarrow CH_2Cl_2$ + I[•], among others. They also provide an important route for obtaining heats of formation of other species, including the free radicals, such as CH_2Cl^{\bullet} , CH_2Br^{\bullet} , and CH_2I^{\bullet} . These values can be obtained from the measured ionization energies of the radicals in combination with our corresponding ion heats of formation. Another possible route of obtaining additional thermochemical data is by combining our dihalomethane heats of formation with measured bond dissociation energies.

6.5. Conclusions

Dissociative photoionization and thermochemistry for the set of dihalomethanes, CH₂XY, (X,Y, = Cl, Br, and I), have been studied by threshold photoelectron photoion coincidence (TPEPICO). Accurate information concerning the ionization energies, breakdown diagrams, dissociation onsets, heats of formation and bond dissociation energies have been obtained for those molecules and their respective ionic fragments. By using the known heat of formation of CH₂Cl₂, it has been possible to determine the 0K and 298K heats of formation of CH₂Br₂, CH₂I₂, CH₂BrCl, CH₂BrI, and CH₂ICl, as well as CH₂Cl⁺, CH₂Br⁺, and CH₂I⁺ to a precision better than 3 kJ/mol. Our new results provide the first accurate and consistent experimental determination of heats of formation for this set of molecules which serve to correct the $\Delta_f H^0_{298K}$ literature values by as much as 20 kJ/mol.

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CHAPTER 7:

Dissociation Dynamics of Sequential Ionis Reactions: Heats of Formation of Tri-, Di-, and Monoethyl Phosphine

7.1. Introduction

A cursory literature search for alkylphosphines reveals a decided dearth of quantitative studies aimed at their physical properties¹⁻⁵. The major interest in alkylphosphines is as ligands in organometallic catalysis, where the electron donating power of the phosphorous lone pair electrons results in strong metal – phosphine interactions⁶. This interaction can have profound effects on the catalytic activity, influencing selectivity⁶ and the reaction rate¹. Indeed, it is our prior investigation of the tricarbonylnitrosyl derivatives (Co(CO)₂NOPR₃) ⁵, where R can be CH₃, C₂H₅, etc., that has led us to investigate the physical properties such as heats of formation, ionization energies, and bond dissociation energies of the alkylphosphine series. This started with trimethyl phosphine⁷ and is continuing here with the ethyl phosphines, H_nP(C₂H₅)_{3-n}, where n = 0-2.

A thorough investigation of the phosphine literature reveals a surprising lack of established and reliable thermochemical information about this simple and important series of molecules. For example, the neutral $P(C_2H_5)_3$ heat of formation varies wildly from -225 kJ/mol found in the GIANT compilation of Lias et al.⁸ to -150 kJ/mol listed in Cox and Pilcher's compilation⁹. No reference at all can be found for the monoethyl

phosphine heat of formation. Even the methyl phosphine heats of formation are limited. The one exception to all this is phosphine, PH₃, whose heat of formation is known to within 2 kJ/mol. While preparing this manuscript, a series of high level calculations dealing with the thermochemistry of organophosphorus (III) compounds was published by Dorofeeva and Moiseeva¹⁰. Specifically, they determine a new value of -150.0 kJ/mol for P(C₂H₅)₃ using isodesmic reactions. Additionally, group additivity values were also determined, which yield neutral heats of formation of -88.4 and -36.0 kJ/mol for HP(C₂H₅)₂ and H₂P(C₂H₅), respectively.

One goal in this paper is the experimental determination of the thermochemistry of the ethyl phosphine series, $H_nP(C_2H_5)_{3-n}$ for n = 0-2 by measuring the energetics of the sequential ethene loss channels using dissociative photoionization, and relating it to the reaction thermochemistry as described by equation (7.1).

$$E_0 = \Delta_f H^o{}_{0K}[\mathbf{A}^+] + \Delta_f H^o{}_{0K}[\mathbf{B}] - \Delta_f H^o{}_{0K}[\mathbf{AB}]$$
(7.1)

If the dissociation energy, E_0 , can be measured and two of the three heats of formation are known, the third can be determined. However, the measurement of the dissociation energy is not always straightforward. Factors such as the internal energy distribution^{11;12} of the starting neutral species, a reverse energy barrier in the dissociation, slow dissociation rate constants, and isomerization^{7;13-18} often complicate this determination.

In addition to the lowest energy dissociation channel, ions can fragment via parallel or sequential pathways at higher energies. For parallel reactions, the appearance of the second pathway is shifted to higher energy as a result of the competitive shift.^{19;20} This is because, at the dissociation limit for the second channel, the rate of the lowest energy pathway can be orders of magnitude higher than the rate of the second pathway,

preventing the observation of products at the dissociation limit. Ions may also dissociate in a stepwise or sequential manner at higher energy, such as $ABC^+ \rightarrow AB^+ + C \rightarrow A^+ + B + C$. In this case, the internal energy of the molecular ion, ABC^+ , is partitioned between the fragment ion, AB^+ and neutral C ligand upon the first dissociation. As a result, ion AB^+ has a much broader internal energy distribution which is reflected in the appearance of the final ion, A^+ . We have recently shown^{11;21} that the TPEPICO modeling software can model both competitive and sequential dissociation pathways accurately.

In the case of slowly dissociating ions, the observed fragment ion onset is shifted to energies above the true dissociation limit by the so called kinetic shift^{11;19;22-24} because the ions do not have time to dissociate during mass analysis. Experiments that simply measure the ion yield as a function of the ionizing energy are not sensitive to the effects of a kinetic shift, which is the case for two electron impact studies on the alkylphosphine ions by Wada and Kiser and Bogolyubov et al.³. The TPEPICO experiment, on the other hand, is well suited to study the effects of slowly dissociating ions. The TOF distributions recorded in the TPEPICO experiment can be modeled in terms of the statistical RRKM theory^{11;25;26} and a unique k(E) curve can be obtained by fitting several TOF distributions at various ion internal energies.. The measured rate curve can then be extrapolated to the dissociation threshold, thus accounting for the kinetic shift¹¹.

An additional advantage of measuring the dissociation rate constant is in establishing the absence of a reverse barrier. If the transition state is loose (no reverse barrier), the entropy of activation will be positive. This is an important issue in these reactions which dissociate via a rearrangement rather than a simple bond breaking step. The dissociations of the three ethyl phosphine ions proceed primarily via sequential ethene loss channels, along with a minor methyl loss channel in the case of triethyl phosphine, as described below:

$$\xrightarrow{E_{0}(1p)_{\Gamma}} H_{2}C = P(C_{2}H_{5})_{2}^{+} + CH_{3}$$

$$P(C_{2}H_{5})_{3} + hv \xrightarrow{E_{0}(1)_{T}} HP(C_{2}H_{5})_{2}^{+} + C_{2}H_{4} \xrightarrow{E_{0}(2)_{T}} H_{2}PC_{2}H_{5}^{+} + 2C_{2}H_{4} \xrightarrow{E_{0}(3)_{T}} PH_{3}^{+} + 3C_{2}H_{4}$$

$$HP(C_{2}H_{5})_{2}^{+} + hv \xrightarrow{E_{0}(2)_{D}} H_{2}PC_{2}H_{5}^{+} + C_{2}H_{4} \xrightarrow{E_{0}(3)_{D}} PH_{3}^{+} + 2C_{2}H_{4}$$

$$HP(C_{2}H_{5})_{2}^{+} + hv \xrightarrow{E_{0}(2)_{D}} H_{2}PC_{2}H_{5}^{+} + hv \xrightarrow{E_{0}(3)_{M}} PH_{3}^{+} + C_{2}H_{4}$$

$$(7.2)$$

$$H_{2}PC_{2}H_{5}^{+} + hv \xrightarrow{E_{0}(3)_{M}} PH_{3}^{+} + C_{2}H_{4}$$

$$(7.4)$$

where equations (7.2) are for triethyl, (7.3) for diethyl, and (7.4) for monoethyl phosphine. (Reaction 7.2p is the parallel step.) The E_0 's are the 0K energy differences between the neutral starting molecule and the indicated products, and the subscripts indicate whether the reaction is for the triethyl, diethyl, or monoethyl phosphine. In this series, the first C₂H₄ loss channel in HP(C₂H₅)₂ (equation 7.3) is the same reaction as the second C₂H₄ loss in P(C₂H₅)₃ (equation 7.2) and therefore they must be modeled using the same k(E) curve. The only difference between these two dissociations is the internal energy of the HP(C₂H₅)₂. Similarly, the second dissociation in HP(C₂H₅)₂ is identical to the C₂H₄ loss in H₂P(C₂H₅), so the same k(E) curve is applied to both of those reactions. All in all, the five experimental measurements are modeled with three k(E) curves. This redundancy will provide a valuable check on the calculation of the energy partitioning between the daughter ion and neutral fragment, which has been used extensively in modeling higher energy dissociations.¹²

By determining the three dissociation onsets, the thermochemistry for these six species (three neutral precursors and the corresponding molecular ions) can be determined. The previous work of Wada and Kiser² as well as Bogolyubov et al.³ not only suffered from the poor resolution of their electron impact experiment, no correction

Table 7.1. Calculated harmonic vibrational frequencies of relevant species at the		
B3LYP/6-311+G** level of theory.		
Species	Unscaled Harmonic Frequencies	
P(C ₂ H ₅) ₃	52.1, 71.9, 85.3, 144.7, 161.2, 190.5, 231.2, 251.8, 264.2, 295.1, 346.5, 409.0, 591.9, 646.3, 651.7, 722.7, 755.9, 772.8, 981.7, 982.3, 984.3, 989.3, 995.3, 1021.4, 1053.4, 1059.3, 1066.9, 1260.2, 1267.2, 1277.2, 1280.9, 1287.4, 1297.0, 1411.4, 1412.0, 1414.7, 1463.7, 1464.6, 1471.4, 1497.6, 1499.8, 1501.1, 1504.1, 1504.5, 1509.9, 3015.6, 3017.3, 3022.1, 3023.0, 3023.9, 3027.4, 3052.8, 3056.1, 3056.4, 3079.1, 3079.9, 3080.8, 3089.4, 3091.9, 3099.3	
$P(C_2H_5)_3^+$	43.6, 66.3, 70.5, 130.8, 140.6, 169.1, 229.5, 235.5, 255.6, 289.3, 309.3, 376.1, 585.0, 677.3, 685.9, 725.9, 740.8, 771.0, 970.3, 974.9, 979.6, 984.4, 989.1, 1024.0, 1061.0, 1068.7, 1076.0, 1242.2, 1248.3, 1267.4, 1272.4, 1289.9, 1303.3, 1423.4, 1429.3, 1430.0, 1433.0, 1433.4, 1442.4, 1496.7, 1498.7, 1499.2, 1503.1, 1504.7, 1505.2, 2996.7, 3001.1, 3020.9, 3051.5, 3051.7, 3055.0, 3072.7, 3081.3, 3084.7, 3122.8, 3122.8, 3125.0, 3126.1, 3126.8, 3131.6	
HP(C ₂ H ₅) ₂	64.7, 79.3, 158.4, 225.8, 242.9, 280.1, 363.6, 611.6, 645.1, 692.1, 717.6, 832.1, 866.6, 983.0, 988.1, 1017.8, 1060.2, 1070.6, 1076.0, 1271.4, 1278.1, 1289.5, 1295.2, 1409.7, 1415.0, 1462.5, 1473.8, 1497.1, 1500.1, 1502.4, 1504.1, 2338.2, 3019.9, 3022.3, 3023.8, 3027.7, 3054.8, 3067.4, 3076.0, 3081.3, 3092.5, 3096.7	
$\operatorname{HP}(\operatorname{C_2H_5)_2}^+$	54.9, 59.0, 110.1, 215.7, 220.2, 290.0, 303.1, 496.6, 658.4, 658.9, 698.8, 770.9, 862.8, 965.9, 969.9, 984.2, 1051.9, 1066.2, 1079.1, 1231.5, 1254.8, 1281.6, 1292.3, 1420.6, 1428.3, 1428.5, 1430.2, 1495.1, 1495.7, 1497.7, 1498.0, 2463.6, 2990.0, 2999.1, 3051.1, 3051.1, 3080.1, 3082.7, 3123.2, 3123.3, 3128.3, 3128.3	
H ₂ PC ₂ H ₅	163.7, 232.1, 282.8, 629.1, 698.7, 813.7, 842.7, 988.3, 1060.1, 1085.8, 1114.5, 1273.4, 1289.8, 1417.0, 1478.2, 1500.9, 1504.9, 2367.2, 2373.0, 3023.9, 3039.2, 3074.2, 3085.7, 3097.9	
$H_2PC_2H_5^+$	148.8, 223.6, 263.9, 541.9, 605.6, 693.9, 771.6, 963.0, 1022.1, 1067.6, 1082.9, 1232.5, 1284.7, 1406.5, 1429.5, 1493.2, 1496.2, 2468.4, 2513.2, 2964.8, 3053.2, 3079.5, 3125.8, 3132.4	
C ₂ H ₄	771.8, 882.7, 896.9, 1000.4, 1224.0, 1329.3, 1423.2, 1585.9, 3249.1, 3259.6, 3354.3, 3379.2	
TS[1]	54 ^a , 69 ^a , 80 ^a , 85 ^a , 185.7, 202.3, 244.4, 276.3, 308.0, 328.9, 384.4, 459.0, 637.2, 666.3, 709.1, 721.7, 768.9, 770.0, 954.6, 963.2, 975.7, 981.1, 1000.8, 1001.3, 1041.1, 1050.3, 1075.7, 1103.0, 1194.8, 1213.3, 1253.9, 1269.0, 1276.9, 1298.4, 1426.9, 1428.1, 1436.0, 1441.5, 1450.6, 1463.2, 1498.1, 1498.9, 1504.1, 1505.5, 1675.6, 3027.2, 3030.7, 3047.3, 3047.4, 3080.6, 3084.1, 3090.2, 3117.5, 3117.8, 3118.1, 3120.2, 3120.2, 3144.0, 3226.7	
TS[2]	41 ^a , 48 ^a , 74 ^a , 158 ^a , 287.1, 417.0, 455.3, 587.4, 649.3, 707.6, 747.8, 809.9, 852.2, 970.8, 973.4, 990.2, 1020.9, 1042.2, 1076.0, 1127.5, 1185.0, 1218.1, 1253.2, 1268.7, 1427.4, 1433.5, 1440.8, 1468.5, 1494.9, 1498.3, 1725.8, 2483.8, 3025.2, 3047.8, 3083.9, 3091.7, 3117.5, 3121.6, 3122.2, 3155.8, 3232.6	
TS[3]	15 ^a , 25 ^a , 30 ^a , 40 ^a , 678.2, 738.4, 809.2, 975.3, 1000.2, 1033.8, 1050.1, 1116.7, 1195.6, 1219.5, 1437.4, 1466.3, 1714.9, 2348.0, 2507.5, 3093.4, 3116.8, 3157.1, 3230.3	
TS[1p]	10 ^a , 27 ^a , 45 ^a , 89 ^a , 100.0, 193.9, 218.3, 233.6, 263.7, 287.7, 346.8, 375.5, 587.3, 679.8, 684.6, 728.7, 739.1, 771.4, 881.6, 968.2, 978.8, 981.4, 987.8, 1022.3, 1043.5, 1048.6, 1072.7, 1156.5, 1247.4, 1261.5, 1277.5, 1288.0, 1306.3, 1333.7, 1426.4, 1427.6, 1436.7, 1439.0, 1475.1, 1476.2, 1496.1, 1498.3, 1500.4, 1502.2, 2969.0, 2996.1, 3000.7, 3049.4, 3049.6, 3058.2, 3070.9, 3079.3, 3120.2, 3120.7, 3122.4, 3123.6, 3145.4, 3148.8, 3167.4	

Table 7.1. a) denotes optimized transition state frequency from the analysis of the experimental data.

for the kinetic shift, but also a reliance on estimated heats of formation of the neutral precursor. In our study, the series is anchored to the well-known PH_3^+ heat of formation and the accurately established neutral C_2H_4 heat of formation, these being the two of three known heats of formation needed in the thermochemical energy relation (equation 7.1).

7.2. Theoretical Methodology

7.2.1. Modeling

The data analysis, including RRKM rate constant calculations, requires knowledge of the vibrational frequencies of the starting molecules, the molecular ions, as well as the various transition states. Because the reactions are sequential, the daughter ion and neutral ligand vibrational frequencies are also needed for the calculation of the product energy distribution. All of these calculations were carried out using the Gaussian 03 program suite²⁷ provided by the ITS Research computing facility at the University of North Carolina at Chapel Hill. The geometry and vibrational frequencies of all molecules studied were calculated using the Becke 3-parameter exchange functional²⁸, the electron correlation functional of Lee-Yang-Parr (B3LYP)²⁹ with the 6–311+G** basis set and are listed in Table 7.1. No scale factor was applied to the vibrational frequencies of the stable species. The transition states were determined by the QST3 method³⁰, using the same level of theory and basis set. This provides a starting set of frequencies for modeling the data. The four lowest frequencies in the transition state are treated as adjustable parameters, as described below.

7.2.2. Ionization Energies

The adiabatic ionization energies were calculated at the B3LYP/6-311+G**, G3³¹ and CBSQB3³² levels of theory and the vertical ionization energies at the B3LYP/6-311+G** level of theory for the three neutral precursors. The vertical ionization energy was determined by fixing the geometry at the optimized structure of the neutral and removing one electron. The adiabatic and vertical ionization energies are then given by the difference between the ion and neutral total energies. We have also calculated the adiabatic ionization energies at the B3LYP/6–311+G**, G3, CBSQB3 and W1U levels of theory for PH₃. This is to ensure the thermochemistry is anchored to an accurate PH₃⁺ heat of formation. These results are summarized in Table 7.2.

7.2.3. Thermochemistry

Calculations were carried out using the G2 and G3 methods as described by Curtiss and coworkers.^{31;33-35} These were used in three isodesmic reactions to support the derived thermochemistry of the neutral alkylphosphines. These results are summarized in Table 7.3.

7.2.4. Potential Energy Surfaces

Several key species along the reaction coordinates for ethene loss from all three molecular ions were calculated at the B3LYP/6-311+G** level of theory. This was used to piece together approximate potential energy curves for these reactions. Additionally, single point coupled cluster³⁶ calculations with perturbative triplet excitations, CCSD(T), were carried out using the cc-pVTZ basis set at the B3LYP/6-311+G** optimized geometries of the molecular ions, transition states and products for these reactions as well. This was used to address the issue of reverse energy barriers associated with the hydrogen transfer dissociations, which would affect the derived heats of formation.
Unfortunately, the coupled cluster calculations on the transition states for tri- and diethylphosphine did not converge, so we only present the monoethyl phosphine results.

Table 7.2. Comparison of Experimental and Calculated Ionization Energies ^a							
	IE _{adiabatic}				IEvertical		
Species	Experiment	DFT ^{f,g}	G3 ^{h,f}	CBSQB3 ^{h,f}	W1U ^{h,f}	Experiment	DFT ^{h,f,g}
PH ₃	9.870 ± 0.002^{d}	9.80	9.87	9.86	9.882	10.59 ± 0.05^{d}	10.54
$H_2P(C_2H_5)$	8.80 ± 0.06^{b} 8.50 ± 0.02^{c}	8.79	8.91	8.87		9.50 ± 0.035^{b}	9.41
HP(C ₂ H ₅) ₂	$7.87 \pm 0.02^{\circ}$	8.03	8.17	8.14			8.68
P(C ₂ H ₅) ₃	$\begin{array}{c} 7.50 \pm 0.03^{c} \\ 7.50 \pm 0.03^{e} \end{array}$	7.47	7.64	7.66		8.25 ± 0.03^{b}	8.14

Table 7.2. a) All values in eV. b) UPS measurement in this study. c) TPEPICO result from this study. d) Berkowitz et al. e) Gengelizcki et al. f) Calculated using the Gaussian 03 software suite. g) $B3LYP/6-311++G^{**}$. h) Calulations form this study.

7.3. Synthesis of Monoethyl Phosphine

The synthesis of monoethyl phosphine was carried out as described by Van Hooijdonk et al.³⁷ A 500 mL three–necked round–bottomed flask was equipped with a vacuum/nitrogen inlet, a thermometer, and a magnetic stir bar. With a vigorous flow of nitrogen, 6.9 g of freshly cut Na (0.1 g pieces) were added to 180 ml of dietheneglycol diethyl ether (DIGLYME), followed by 4.7 g of naphthalene. After a few minutes, a slurry of 3.1 g of red phosphorus and 10 ml of DIGLYME was added. The solution was brought to 50°C and allowed to stir for 4 hours. The slurry was cooled to -5°C and 14.8 g of t-BuOH in 30 ml of DIGLYME were added through a dropping funnel over a 20 minute period. The solution was then stirred for another hour. A Vigreux column and condenser were added to the top of the flask in preparation of the addition of alkylhalide. A dry ice/acetone bath was used as 7.5 ml of ethylbromide was added. This procedure yielded 25 g of monoethyl phosphine.

7.4. Results

7.4.1. Determination of Ionization Energies

The TPES of triethyl phosphine, shown in Figure 7.1, exhibits a broad first band, which indicates that the ion and neutral geometries are very different, resulting in a broad Franck–Condon envelope. This situation is reminiscent of both NH₃ and PH₃, making the determination the adiabatic ionization energy difficult. From the TPES we estimate that the upper limit to the adiabatic ionization energy is 7.80 ± 0.050 eV, however, the analysis of the TPEPICO data yields an adiabatic ionization energy of 7.50 ± 0.01 eV, which will be discussed in the TPEPICO results section. The vertical ionization energy of 8.25 ± 0.030 eV is much more easily established since it corresponds to the maximum in the TPES. The calculated vertical ionization energy, at the DFT level, is 8.14 eV which is almost within the measurement error. The calculated adiabatic ionization energies at the DFT, G3, and CBS–QB3 levels of theory are 7.47, 7.64, and 7.66 eV, respectively. These tend to favor the TPEPICO determination of 7.50 eV although the agreement is not as good as one might hope for. The ionization energies are summarized in Table 7.2.

The UPS of monoethyl phosphine is shown in Figure 7.2. The vertical ionization energy was established to be 9.50 ± 0.035 eV, and an adiabatic ionization energy was estimated to be 8.80 ± 0.06 . As in the P(C₂H₅)₃ case, the adiabatic ionization is most likely lower than this value. An adiabatic ionization energy of 8.50 ± 0.01 eV was determined from this TPEPICO analysis, which will be addressed in the discussion section. Calculations at the DFT, G3 and CBSQB3 levels of theory yield adiabatic



Figure 7.1. Threshold photoelectron spectrum (TPES) of triethyl phosphine from 7.5 to 11.0 eV. The TPES arrow (7.80 eV) is the adiabatic ionization energy determined from this spectrum while the TPEPICO arrow (7.50 eV) is the adiabatic ionization energy determined from modeling the TPEPICO data sets. The difference is 300 meV.



Figure 7.2. Ultraviolet photoelectron spectrum (UPS) of monoethyl phosphine from 8.0 to 16.0 eV. The UPS arrow (8.80 eV) is the adiabatic ionization energy determined from the UPS spectrum while the TPEPICO arrow (8.50 eV) is the adiabatic ionization energy obtained from modeling the TPEPICO data sets. The difference is 300 meV.

ionization energies of 8.79, 8.91 and 8.87 eV. The agreement here certainly favors the TPES result over the TPEPICO result, unlike the triethyl phosphine case. The calculated vertical ionization energy at the DFT level is 9.41 eV, a value in good agreement with the experimentally determined one. These values are also summarized in Table 7.2.

7.4.2. TPEPICO Results and Analysis

7.4.2.1. Triethyl Phosphine

The breakdown diagram of $P(C_2H_5)_3$ is given in Figure 7.3 and selected TOF distributions are presented in Figure 7.4. In the breakdown diagram, the points are the experimentally determined ion ratios and the solid lines are the simulated ion ratios. At low energies, only the parent ion is present (squares). At 9.25 eV, the first C_2H_4 loss channel appears, producing the diethyl phosphine ion, $HP(C_2H_5)_2^+$ (triangles).

The TOF distributions at 9.83 and 9.98 eV show these two ions, with the points representing the experimental TOF distribution and the solid lines representing the fit. The $P(C_2H_5)_3^+$ is observed as a sharp peak at 116 µs and the $HP(C_2H_5)_2^+$ is observed over the entire region from 101 –115 µs. The asymmetric peak from 101 – 104 µs is attributed to product ions resulting from parent ion dissociation in the acceleration region. The sharp peak at 105 µs is the drift peak, associated with product ions that are born in the drift region before being reflected. Any ions that dissociate in the reflectron are observed from 105 – 115 µs. Because their numbers are small and because they are spread out over many channels, we do not obtain any rate information from them. Ions that dissociate in the second drift region are observed at 116 µs along with any stable parent ions.



Figure 7.3. The breakdown diagram of triethyl phosphine from 9.0 to 12.5 eV. The open points are the experimentally determined fractional ion abundances and the solid lines are the fit. The E_0 's have been marked.



Figure 7.4. Selected time-of-flight (TOF) distributions for triethyl phosphine using the reflecting TOF mass spectrometer. The points are experimental TOF distributions and the solid lines are the fit.

Because the dissociation is slow, the onset cannot be determined by the disappearance of the parent ion in the breakdown diagram¹¹. This first dissociation step must be modeled by taking into account the RRKM dissociation rate constant, k(E), shown in equation (7.6) in which E and E_0 are the ion energy and the activation energy measured from the ground state of the ion, σ is the reaction symmetry number, and $\rho(E)$ and $N^{\#}(E-E_0)$ are the density of states of the ion and sum of states of the transition state, respectively.

$$k(E) = \frac{\sigma N^+(E - E_0)}{h\rho(E)}$$
(7.6)

Because the ions are produced in a distribution of internal energies, P(E), given by the room temperature sample, we need to take this distribution of energies into account when modeling the data with the microcanonical rates of equation (7.6). The P(E) function is given by equation (7.7) in which E is the neutral molar energy and T the sample temperature of 298K.

$$P(E) = \frac{\rho(E)e^{-E_{RT}}}{\int_{0}^{\infty} \rho(E)e^{-E_{RT}}}$$
(7.7)

Because slowly dissociating ions fragment during the course of their flight to the ion detector, the rate constants can be extracted from the analysis of the asymmetric daughter ion peak shape¹¹. The k(E) function (equation 7.6) was calculated with a density of states fixed by the calculated ion vibrational frequencies, adjusting only the 0K dissociation threshold, E_0 , and transition state transitional vibrational frequencies. There are five transitional frequencies which change during the course of reaction from vibrations to



Figure 7.5. RRKM rate curves as a function of excess ion internal energy for the 3 ethene loss channels used in modeling all five experimental measurements. The grey area is the range in which the daughter ions are metastable, which yields direct kinetic information.



Figure 7.6. Internal energy distributions for the energy selected diethyl phosphine ion (b) compared to the broadened diethyl phosphine energy distribution as a result of the energy partitioning (a). The molecular ion energy relative to the neutral ground state is given on the lower axis, while the daughter ion and neutral product energies referenced to their ground states, are shown on the upper axis.

rotations of the products. We simply multiply these frequencies by a common factor until the data are best fitted. Simultaneously fitting the experimental TOF distributions at various photon energies and the breakdown diagram, by varying the above mentioned parameters, yields a k(E) function (shown in Figure 7.5, curve 1), and a dissociation onset, $E_0(1)_T$ of 9.041 ± 0.014 eV, where the 1 refers to the first C₂H₄ loss and the T to triethyl phosphine. Although this first onset requires two adjustable parameters, the flexibility is limited by the simultaneous fitting of the TOF distributions and breakdown diagram.

The TOF distribution at 10.29 eV shows only the $HP(C_2H_5)_2^+$ peak. Although still asymmetric, the peak is much narrower than in the previous TOF distributions because of the increasing rate constant with increasing energy. At higher energy, the competitive CH_3^{\bullet} loss channel is observed as the sharp, symmetric peak at 108.8 µs in the TOF distributions. The $HP(C_2H_5)_2^+$ (104.5 µs) is also symmetric at this energy, indicating that k(E) is now greater than 5×10^6 s⁻¹. The relative abundance of the CH₃[•] loss ion is given in the breakdown diagram (circles). Because this reaction is in competition with the low energy C_2H_4 loss reaction, the appearance is shifted to higher energy by the so-called competitive shift. The fitting of this onset requires adjusting two parameters, the E_0 and transition state vibrational frequencies of the CH₃[•] loss channel. The latter parameter is adjusted to match the relative rates of the two reactions. How quickly the CH₃[•] loss reaction catches up to the C₂H₄ loss reaction is a function of the transition state vibrational frequencies. This results in a dissociation onset, $E_0(1p)_T$ (p for the parallel step) of 9.698 \pm 0.022 eV for the CH₃[•] loss channel, which is almost 1.5 eV below the appearance of the ion in the breakdown curve.

The sequential C_2H_4 loss channel (diamonds in the breakdown diagram), producing the monoethyl phosphine ion, $H_2PC_2H_5^+$, is observed in the three high energy TOF distributions of Figure 7.4. The dissociation is slow, so the ion appears from 84 -100 μ s in the TOF distributions, with the asymmetric part from 84 – 87.5 μ s, the drift peak at 87.5 μ s and the reflectron dissociation from 87.5 – 100 μ s. Because this is a sequential reaction, the $H_2P(C_2H_5)^+$ is produced from the $HP(C_2H_5)_2^+$, so the modeling involves calculating the product energy distribution between $HP(C_2H_5)_2^+$ and the neutral C₂H₄ ligand³⁸. According to the statistical theory of energy partitioning, this distribution is given by $P(E_{ion}) = \rho_{ion}(E_{ion})\rho_{neutral}(E-E_{ion})$, where the ρ_{ion} is the rovibrational density of states of the product ion, $\rho_{neutral}$ is the rovibrational density of states of the neutral convoluted with the translational density of states associated with the relative translational energy of the ion and neutral fragments, and E is the total energy above the dissociation threshold. The HP(C_2H_5)₂⁺ has a much broader internal energy distribution than its parent ion did, as illustrated in Figure 7.6. The narrow $P(C_2H_5)_3^+$ energy distribution with a width of about 220 meV, is a result of the thermal energy distribution for this room temperature sample selection, with the TPEPICO energy resolution contributing a negligible amount.

The consequence of the broadened internal energy distribution of the $HP(C_2H_5)^+$ ion is a much broader onset of the $H_2P(C_2H_5)_2^+$ ion signal in Figure 6.3. Because the only input in calculating the $HP(C_2H_5)_2^+$ energy distribution are the product vibrational frequencies, we have no adjustable parameters for fitting the slopes at the cross over energy. The excellent fit is simply a demonstration of how well the statistical theory predicts the energy partitioning in the dissociation of a polyatomic ion. The E_0 and transition state vibrational frequencies are adjusted to determine the unique k(E) curve to fit the TOF distributions and breakdown curve, yielding a dissociation onset, $E_0(2)_T$, of 10.740 ± 0.024 eV. The calculated k(E) curve (2) is shown in Figure 7.5. With the determination of this onset, the energy difference between HP(C₂H₅)₂⁺ and H₂PC₂H₅⁺ is established to be 1.70 ± 0.027 eV. The final onset, $E_0(3)_T$ for the production of PH₃⁺ could not be measured because the dissociation was too slow in the energy range of the TPEPICO experiment.

The above dissociation energies were determined with the assumed triethyl phosphine ionization energy of 7.50 eV. This enters into the modeling because the dissociation rate constant is affected by the activation energy. For instance, if the assumed *IE* were reduced the calculated rate constant would be lowered because of the increased E_0 . But, this can be compensated for by raising the TS vibrational frequencies so that the k(E) curve remains approximately constant, but with a change in slope. Because all three k(E) curves can be adjusted in this way, the experimental data were fit with several assumed P(C₂H₅)₃ ionization energies. The best fit to all three data sets (the TOF distributions and breakdown curves for tri-, di- and monoethyl phosphines), is with a triethylphosphine ionization energy of 7.50 ± 0.01 eV.

The activation entropies obtained from the modeling provide valuable insight into the dissociation dynamics. The activation entropies calculated at 600 K are ($\Delta S^{\dagger}_{600K}$), are -10.1 and 2.3 J K⁻¹mol⁻¹ for the first and second ethene loss channels, respectively. These activation entropies are indicative of tight transition states, such as those involving a hydrogen transfer. On the other hand, the $\Delta S^{\dagger}_{600K}$ for the methyl loss channel is 23.5 J/K⁻¹mol⁻¹, indicating a loose transition state associated with homolytic bond cleavage. These entropies will be considered in more detail in the discussion.

7.4.2.2. Diethyl Phosphine

The TOF distributions for diethyl phosphine are given in Figure 7.7. Because the parent ion loses 40% of its mass upon dissociation (in the second step), this experiment was done on the linear TOF mass spectrometer so that the appearance of the TOF distributions is different. Not only are the total time-of-flights much shorter, but the drift peak appears at 22.7 μ s, a longer TOF than the parent ion. This is because of the deceleration after the first drift region, as explained earlier in the experimental section. The parent ion is observed at 22.3 μ s, and the asymmetric daughter ion from 18.2 – 20.0 μ s. The breakdown diagram data (open points) and simulated ion abundances (solid lines) are presented in Figure 7.8.

The first C_2H_4 loss channel in $HP(C_2H_5)_2$ produces the monoethyl phosphine ion, $H_2PC_2H_5^+$ as illustrated below,

$$HP(C_{2}H_{5})_{2} + h\nu \to HP(C_{2}H_{5})_{2}^{+} \to H_{2}PC_{2}H_{5}^{+} + C_{2}H_{4}$$
(7.9)

where the first step represents the adiabatic ionization energy, and the second the energy difference between HP(C₂H₅)₂⁺ and H₂PC₂H₅⁺. This energy difference has already been established from the P(C₂H₅)₃ measurements, as has the transition state for C₂H₄ loss, so that the k(E) curve must be the same. The only adjustable parameter is the adiabatic ionization energy of HP(C₂H₅)₂, which serves to establish the total energy scale. The best fit to the data is achieved with an adiabatic ionization energy of 7.870 ± 0.013 eV, resulting in a dissociation onset, $E_0(2)_D$ of 9.568 ± 0.015 eV.



Figure 7.7. Selected time-of-flight (TOF) distributions for the diethyl phosphine ion recorded using the linear TOF mass spectrometer. The points are experimental TOF distributions and the solid lines are the fit.



Figure 7.8. The breakdown diagram for diethyl phosphine from 9.5 to 13.5 eV. The open points are the experimentally determined fractional ion abundances and the solid lines are the fit.

One of the major assumptions in modeling sequential unimolecular dissociations is that the internal energy of the molecular ion is redistributed statistically between the daughter ion and neutral fragment. It has been shown by Sztáray and Baer³⁸ that the energy partitioning can be modeled precisely and the confidence and the validity of this model is further enhanced by its successful application to several molecules^{5;38}. Here, a more rigid check can be employed because two sets of dissociation reactions differ only by the internal energy distribution of the dissociating species. Figure 7.6 illustrates the difference. On the right-hand side (7.6b) is the internal energy distribution of the energy selected HP(C_2H_5)₂⁺ ions. This narrow energy distribution, with a FWHM of 0.2 eV, can be compared to the same ion's energy distribution obtained from the first dissociation of $P(C_2H_5)_3^+$, as shown in 7.6a, with a width of 1 eV. The excess energy above the dissociation limit for $P(C_2H_5)_3^+$ is partitioned between the internal energy of the C_2H_4 neutral ligand plus two degrees of relative translation energy and the internal energy of $HP(C_2H_5)_2^+$. (We use two degrees of freedom for the translations as is done in phase space theory.) Other than the internal energy distribution, the two reactions are the same so they must be modeled using the same k(E) curve.

The second C₂H₄ loss in HP(C₂H₅)₂⁺ is modeled in the same manner as described above for the second onset in the triethyl phosphine reaction. The E_0 and the five transition state frequencies were adjusted until the best fit was obtained, resulting in k(E)curve 3 in Figure 7.5. The dissociation onset, $E_0(3)_D$, was determined to be 11.870 ± 0.019 eV. The energy difference between H₂PC₂H₅⁺ and PH₃⁺ is 2.302 ± 0.025 eV, given by the difference between the two measured E_0 s.



Figure 7.9. The breakdown diagram for monoethyl phosphine from 10.5 to 11.1 eV. The open points are the experimentally determined fractional ion abundances and the solid lines are the fit.



Figure 7.10. Selected time-of-flight (TOF) distributions for the monoethyl phosphine ion recorded using the linear TOF mass spectrometer. The points are experimental TOF distributions and the solid lines are the fit.

The activation entropy, $\Delta S^{\ddagger}_{600K}$, for the final ethene loss channel is 76.0 J/Kmol, which is indicative of a very loose transition state. When compared to the first two ethene loss channels, the activation entropies increase from $-10.1 \text{ J K}^{-1}\text{mol}^{-1}$ for the first, 2.3 J K⁻¹mol⁻¹ for the second and now 76.0 J K⁻¹mol⁻¹ for the third ethene loss. This trend will be discussed later.

7.4.2.3. Monoethyl Phosphine

The breakdown diagram of monoethyl phosphine, $H_2PC_2H_5$, is presented in Figure 7.9 and selected TOF distributions are given in Figure 7.10. Since the ion loses 40% of its mass upon dissociation, the experiment was also done on the LinTOF. The sharp symmetric peak at 17.8 µs is the parent ion, and the asymmetric peak that ranges from 13.1 - 14.2 µs is the PH₃⁺. The slightly broadened drift peak is present at 18.2 µs.

The onset for this C₂H₄ loss channel is the same as the second C₂H₄ loss channel in diethyl phosphine, therefore, k(E) curve 3 is used to model this reaction. The only adjustable parameter is the adiabatic ionization energy which serves to set the total energy scale. The best fit, resulting in an E₀(3)_M of 10.802 ± 0.025 eV, is achieved with an optimized adiabatic ionization energy of 8.500 ± 0.025 eV. The determined E_0 s are summarized in Table 7.3.

In estimating errors for the derived dissociation onsets, some of the parameters were varied in order to obtain an overall best fit for the data from all three molecules. In summary, the adjusted variables were the energies of the three starting molecules as well as the ion energies for the di- and monoethyl phosphine, and three transition state vibrational frequencies. (We ignore the CH_3^{\bullet} loss, which is a minor channel that does not affect the analysis of the sequential loss reactions.) With these eight parameters, it was

possible to fit absolute rates and relative rates at high energies for five reactions, two each from the tri– and di-, and one from the monoethylphosphine. Because each of these reactions requires two parameters, E_0 and the transition state frequencies, the number of unknowns is ten. Thus, our six variables have successfully modeled a ten parameter data set.

Table 7.3. Dissociation onsets for the C_2H_4 loss channels			
Reaction	TPEPICO E ₀ (eV)	Literature AE (eV)	
$\mathbf{P}(\mathbf{C}_{2}\mathbf{H}_{5})_{3} \rightarrow \mathbf{HP}(\mathbf{C}_{2}\mathbf{H}_{5})_{2}^{+} + \mathbf{C}_{2}\mathbf{H}_{4}$	9.041 ± 0.014^{a}	$10.7 \pm 0.3^{\circ}$	
$P(C_2H_5)_3 \rightarrow H_2PC_2H_5^+ + 2 C_2H_4$	10.740 ± 0.022^{a}	$12.7 \pm 0.2^{\circ}$	
		12.3 ± 0.3^{d}	
$P(C_2H_5)_3 \rightarrow PH_3^+ + 3 C_2H_4$	13.020 ± 0.043^{b}	14.7 ± 0.2^{c}	
		14.2 ± 0.3^{d}	
$HP(C_2H_5)_2 \rightarrow H_2PC_2H_5^+ + C_2H_4$	9.568 ± 0.015^{a}	10.9 ± 0.3^{d}	
$\mathrm{HP}(\mathrm{C_2H_5})_2 \rightarrow \mathrm{PH_3}^+ + 2 \ \mathrm{C_2H_4}$	11.870 ± 0.019^{a}	12.8 ± 0.3^{d}	
$\mathrm{H_2PC_2H_5} \rightarrow \mathrm{PH_3}^+ + \mathrm{C_2H_4}$	10.802 ± 0.025^{a}	$11.2 \pm 0.2^{\circ}$	

Table 7.3. a) Measured TPEPICO onset. b) Calculated onset from known heats of formation of PH_3^+ , C_2H_4 and $P(C_2H_5)_3$. c) Wada and Kiser. d) Bogolyubov, Grishen et al.

7.5. Thermochemistry

The measured dissociative photoionization onsets permit us now to establish the heats of formation of all three neutral ethyl phosphines and their ions by anchoring the energy scale to the $\Delta_f H^o{}_{0K}[PH_3^+]$ of 966.2 \pm 2.0 kJ/mol. The latter value is determined from the $\Delta_f H^o{}_{298K}[PH_3]$ of 5.4 \pm 1.7 kJ/mol, based on the heats of explosive decomposition of Gunn and Green³⁹ and an experimental adiabatic ionization energy of 9.869 \pm 0.002 eV from Berkowitz et. al.⁴⁰ Our own W1U calculation of the adiabatic ionization energy of 9.882 eV supports the experimental measurement to within 1.3 kJ/mol. The thermochemistry also relies on the well–known $\Delta_f H^o{}_{0K}[C_2H_4]$ of 61.05 \pm 0.4 kJ/mol, listed in several of the major compilations^{8;41}. The resulting thermochemistry,

which was obtained using equation 7.1 is summarized in Table 7.4. Figure 7.11 summarizes the 0K thermochemistry and the measured ionization and dissociative ionization onsets.

Table 7.4. Heats of formation for the ethylphosphine ions and neutrals					
	TPEPICO Exp. (kJ/mol)		Lit. and The		
Species	$\Delta_{f}H^{o}_{298K}$	$\Delta_{f}H^{o}_{\theta K}$	$\Delta_{f} H^{o}_{298K}$	$\Delta_{f}H^{o}_{\theta K}$	$H_{298K} - H_{0K}^{e}$
P(C ₂ H ₅) ₃	-152.7 ± 2.8	-109.0 ± 2.8	$\begin{array}{r} -225^{a} \\ -145.4^{b} \\ -159^{c} \\ -150.0 \pm 7.0^{d} \end{array}$	-101.8 ^b	31.5
$P(C_2H_5)_3^+$	571.6 ± 4.0	614.7 ± 4.0	561 ^a		32.1
HP(C ₂ H ₅) ₂	-89.6 ± 2.1	-56.7 ± 2.1	-102^{a} -88.7 ^b -88.4 ^d	- 55.9 ^b	23.3
$\mathrm{HP}(\mathrm{C_2H_5)_2}^+$	669.9 ± 2.5	702.3 ± 2.5	736 ^a 820 ^c		23.7
H ₂ PC ₂ H ₅	-36.5 ± 1.5	-15.0 ± 1.5	-50.2° -38.7° -36.0°	-17.2 ^b	15.6
$H_2PC_2H_5^+$	784.0 ± 1.9	805.2 ± 1.9	962.3°		16.1

Table 7.4. a) Estimate in Lias et al. b) Isodesmic reactions as described in paper. c) These values from Wada and Kiser.² are severely outdated and are only included for completeness. d) Calculated using the G3X method from Dorofeeva and Moiseeva. e) Calculated using harmonic vibrational frequecies from DFT calculations described in the text.

7.6. Discussion

The derived thermochemistry would be affected if a reverse energy barrier were present in the ethene loss reactions. Because such a barrier is quite plausible for a reaction that involves a hydrogen transfer step, we need to consider this possibility. As a starting point, the structures and energies for several structures along the reaction path were calculated at the B3LYP/6-311+G** level of theory. In all three ions, a tight transition state corresponding to a hydrogen transfer from the carbon to phosphorus atom separated the starting structure and a stable intermediate, which is a four-coordinated central phosphorous atom where the positive charge is located. At the DFT level, the



Figure 7.11. Summary of the derived heats of formation for the ethyl phosphine series. The solid lines represent the 5 measured dissociation onsets and the adiabatic ionization energies.

energy of this intermediate relative to the dissociated products was -150, -110, and -100kJ/mol for the mono- di-, and tri-ethyl phosphine ions, respectively. The hydrogen transfer barrier was found to be 10 and 4 kJ/mol below the dissociation product energies for the case of the mono- and diethyl phosphine ions. However, for the case of the triethyl phosphine, the barrier was located 5 kJ/mol *above* the energy of the dissociated products. To verify these barries, we also carried out higher level calculations on these reactions. For the H₂P(C₂H₅) reaction at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** level, the transition state energy decreased to 50 kJ/mol below the onset for the production of PH_3^+ and C_2H_4 . The results are summarized in Figure 7.12, where the points (a-d) are the coupled cluster calculated values and the line is present to guide the We conclude that the monoethyl phosphine ion (a) rearranges to a stable eve. intermediate (c) by passing through the tight transition state (b). The stable intermediate (c) has 3 hydrogens and the ethene bound to the phosphine atom. From (c) the ion can dissociate via a loose transition state (not shown) to the products (d). This picture agrees with the experimental results in that the third ethene loss reaction is modeled nicely without taking a reverse barrier into account yielding an activation entropy of 76 J/Kmol, which is consistent with a loose transition state and barrierless dissociation.

Calculations at the coupled cluster level of theory for the tri- and diethyl phosphine were attempted, however the transition states, analogous to (b) in Figure 7.12, did not converge. As a result, we do not know for certain whether these barriers would also descend with higher level calculations. However, based on the activation entropies and the agreement between the experimental and calculated thermochemistry, we conclude that the H atom transfer barriers in the case of the di- and triethyl phosphines are very



Figure 7.12. Schematic potential energy diagram for the ethene loss reaction from monoethyl phosphine. The points labeled a–d have been calculated at the $CCSD(T)/cc-pVTZ//B3LYP/6-311++G^{**}$ level of theory. The curve has been added to guide the eye.

close to the dissociation limit. This would account for the negative activation entropy in the triethylphosphine case. It is quite likely that the H atom tunnels through the isomerization barrier. But, because our rates are measured well above the dissociation limit in the triethylphosphine case, we are not sensitive to tunneling. For diethyl phosphine, the influence of the first transition state is not as drastic as in the case of triethyl phosphine, which is reflected in the activation entropy that lies between the two others.

The derived heats of formation for the three alkylphosphines in Table 7.4 are compared to calculated values using the following isodesmic reactions.

$$P(C_2H_5)_3 + CH_4 + C_2H_6 \to P(CH_3)_3 + 2C_3H_8$$
(7.10)

$$3 \operatorname{HP}(C_2H_5)_2 + 6 \operatorname{CH}_4 \to \operatorname{PH}_3 + 2 \operatorname{P}(\operatorname{CH}_3)_3 + 6 \operatorname{C}_2H_6$$
(7.11)

$$3 H_2 P C_2 H_5 + 3 C H_4 \rightarrow 2 P H_3 + P (C H_3)_3 + 3 C_2 H_6$$
(7.12)

The heats of reaction were calculated at the G2 and G3 levels of theory and the average of the two methods was used in conjunction with the established values of the alkanes, PH₃ and P(CH₃)₃, listed in Table 7.5, yielding 298K heats of formation for P(C₂H₅)₃, HP(C₂H₅)₂, and H₂PC₂H₅ of -145.4, -88.7, and -38.7 kJ/mol respectively, in good agreement with the experimental results. The least well established value of the ancillary species is the trimethyl phosphine with a quoted error of 5 kJ/mol. The largest disagreement between the calculated and experimental values is for the case of the triethyl phosphine, in which the calculated value is about 7 kJ/mol (70 meV) higher than the experimental value, a value outside our experimental uncertainty. We cannot attribute this discrepancy to the uncertainty in the P(CH₃)₃ heat of formation because the error does not appear in the di- and monoethyl phosphine determinations.

Independent verification of the neutral heats of formation comes from the work of Dorofeeva and Moiseeva¹⁰, who used a series of isodesmic reactions computed at the G3X of theory. They report a 298K heat of formation of -150.0 ± 7.0 kJ/mol for triethyl phosphine, which is in excellent agreement with our measured and calculated values. Additionally, using the group additivity values provided by Dorofeeva and Moiseeva¹⁰, the 298K heats of formation of -88.4 and -36.0 are obtained for HP(C₂H₅)₂ and H₂P(C₂H₅), respectively. These are in excellent agreement with our measured, -89.6 and -36.5, and calculated, -88.7 and -38.7, values as well.

Table 7.5. Ancillary	thermochemical data		
Species	$\Delta_{f}H^{o}_{298K}$ (kJ/mol)	$\Delta_{f}H^{o}_{OK}$ (kJ/mol)	$H_{298K} - H_{0K}^{d}$
PH ₃	5.02 ± 1.00^{a}	13.97 ± 1.00^{a}	10.1
P(CH ₃) ₃	-101 ± 5.0^{b}	-76.3 ± 5.0^{b}	20.4
C_2H_4	$52.5 \pm 0.4^{\circ}$	61.05 ± 0.4^{d}	10.5
C ₂ H ₆	$-83.8 \pm 0.4^{\circ}$	-68.0 ± 0.4^{d}	11.7
C ₃ H ₈	$-104.7 \pm 0.5^{\circ}$	-82.2 ± 0.5^{d}	14.5

 Table 7.5. a) Gunn and Green. b) Lias et al. c) Pedley. d) Calculated using harmonic vibrational frequencies.

So far, we note that our experimentally derived energies are in good agreement with both sets of calculated ones and it would appear that these ethyl phosphine heats of formation are now reliably established. However, the implication for the ionization energies is a bit more problematic. Aside from the heat of formation of the $P(C_2H_5)_3^+$, all of the thermochemistry in Table 7.3 was obtained from the dissociative photoionization experiments. Because we have determined both the neutral and the ion energies, we know directly the adiabatic ionization energies of the diethyl and monoethyl phosphines, which can be compared to those obtained from the ab initio calculations, and those derived from the photoelectron spectra in Figure 7.2.

The arrows in Figures 7.1 and 7.2 point to the experimental ionization energies for the triethyl and monoethyl phosphines. It is evident that the TPEPICO derived adiabatic IE's are considerably below what might be called the phenomenological adiabatic IE's. But, as already pointed out, the large change in the geometry upon ionization, from an out of planar PC₃ angle of 30° to 15° and the low vibrational frequency associated with this umbrella mode, makes the experimental adiabatic IE difficult to establish. The calculated IE's listed in Table 7.1 do not offer much resolution. They agree with the lower TPEPICO value for the case of the triethyl phosphine, but agree better with the phenomenological IE of the monoethyl phosphine. Support for the 7.50 eV value of the triethyl phosphine *IE* comes also from the study of Gengeliczki et al. who measured the collision induced dissociation onsets for $CoP(C_2H_5)_3^+$ ion, which resulted in the production of the $P(C_2H_5)_3^+$ ion at a collision energy some 0.38 eV below that of the Co⁺ ion. With the assumption that this energy difference is the difference in the ionization energies of Co (7.881 eV^{42}) and P(C₂H₅)₃, they concluded that the latter's adiabatic IE is 7.50 ± 0.30 eV, which is in perfect agreement with our TPEPICO result. In support for our low IE value for the monoethyl phosphine, we note that the 8.50 eV TPEPICO value is shifted about equally to lower energy from the phenomenological adiabatic ionization energy as it is in the trimethyl phosphine case.

7.7. Conclusions

We have used three k(E) curves to model five sets of experimental data on C₂H₄ loss reactions in a series of energy selected ethyl phosphine ions and have determined their dissociation onsets. Coupling these measured onsets with reliable ancillary thermochemical values, new heats of formation for several ions and neutrals have been determined. These new accurate and reliable values can be applied to phosphine containing systems such as derivatives of transition metal carbonyls to help solidify the thermochemistry of those system. The redundancy has provided a valuable check of the calculation of the internal energy distribution as well as the energy partitioning between the ion and the neutral fragment.

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CHAPTER 8:

On the Dissociation of the 2-Pentanone Ion^a

8.1. Introduction

The low energy dissociation channels of acetone¹ and butanone² ions have been well studied by photoionization and offer excellent routes for the determination of the acetyl and propionyl ion heats of formation. At low ion internal energies, these $\text{RCOR}^{\prime+}$ ions, where R and R' can be any combination of CH_3^{\bullet} and $\text{C}_2\text{H}_5^{\bullet}$, predominantly dissociate to produce carbonyl ions and neutral free radicals as described by the equations (8.1):

$$\operatorname{RCOR}' + \operatorname{hv} \to \operatorname{RCO}^+ + \operatorname{R}' \qquad E_0(1)$$
 (8.1a)

$$\rightarrow$$
 R + COR⁺ $E_0(2)$ (8.1b)

These reactions have provided the major source of accurate heats of formation for the acetyl and propionyl ions through use of the energy equation such as:

$$E_0(1) = \Delta_f H^o[\mathbf{R}'] + \Delta_f H^o[\mathbf{R}^{\mathrm{CO}^+}] - \Delta_f H^o[\mathbf{R}^{\mathrm{COR}'}]$$
(8.2)

If two of the heats of formation are known, the third can be determined. The only complication is a minor side reaction in the case of acetone ions, in which it loses $CH_4^{1;3;4}$. In contrast, the 2-pentanone ion dissociates in a much more complex and interesting manner. Ethylene loss leads to the formation of the propen-2-ol (acetone enol) ion, a reaction first used by Holmes and Lossing⁵ and then by Traeger⁶ to obtain the heat of formation of the acetone enol ion. In addition, Murad and Inghram⁷ used photoionization with deuterated samples to show that methyl loss can take place from both ends of the ion.

The problems associated with the extraction of thermochemical information from such disssociative photoionization onsets are well known. These include reactions with reverse activation barriers that lead to onsets higher than the thermochemical value. Another is the kinetic shift,⁸ which results from slow reaction rates that shift the observed onsets to higher energies. In the case of parallel reactions, the higher energy onset is invariable shifted to higher energy because of the competitive shift^{8;9} with respect to the first dissociation channel. Experiments that simply measure the ion yield as a function of the ionizing energy, either by photoionization or by electron impact, are not sensitive to such effects and thus can lead to errors.

We have recently improved our threshold photoelectron photoion coincidence (TPEPICO) experiment by effectively suppressing the influence of hot electrons^{2;10;11}. In combination with advances in the data analysis, which include incorporation of the thermal energy distribution and all of the various competitive and sequential dissociation channels, we can now model reactions of energy selected ions to very high energies.

In this study, we have collected new data on the 2-pentanone ion dissociation and have modeled the four parallel dissociation channels as well as a sequential reaction. Because much of the thermochemistry is fairly well established, this system provides an excellent test of our data and its analysis.

8.2. Theoretical Methodology

The data analysis, including RRKM rate constant calculations, requires knowledge of the vibrational frequencies of the starting molecule, the 2-pentanone ion, as

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well as the various transition states. These are best obtained from ab initio calculations,

which were

Table 8.1. Calculated Vibrational Frequencies				
Species	Vibrational Frequencies at B3LYP/6-311++g**			
2-pentanone ^b	48.5, 89.2, 97.1, 179.9, 250.5, 351.1, 410.2, 497.2, 616.6, 754.5, 851.5, 868.5, 938.8			
1	,999.7, 1017.7, 1087.3, 1169.6, 1184.0, 1225.1, 1301.0, 1372.2, 1379.5, 1437.9,			
	1450.7, 1469.3, 1507.6, 1523.1, 1533.9, 1549.1, 1558.4, 1566.0, 1849.7, 3111.5,			
	3132.5, 3136.5, 3144.4, 3157.5, 3178.5, 3203.3, 3204.6, 3205.6, 3257.3			
2-pentanone ⁺	70.7, 138.3, 158.9, 219.1, 288.5, 315.9, 422.3, 485.8, 581.3, 682.8, 783.7, 869.7,			
-	910.9, 924.0, 1003.7, 1030.5, 1078.6, 1107.2, 1130.4, 1207.3, 1256.0, 1326.8,			
	1377.0, 1392.2, 1430.3, 1449.2, 1481.9, 1491.2, 1491.3, 1513.3, 1529.5, 1735.3,			
	2921.2, 3050.5, 3122.4, 3152.0, 3174.3, 3180.9, 3225.9, 3233.7, 3234.7, 3300.6			
But-3-en-2-	54.2, 128.0, 283.8, 430.0, 454.0, 584.7, 633.0, 712.7, 834.9, 991.6, 1007.2, 1043.9,			
ol ⁺	1078.5, 1093.8, 1166.3, 1330.4, 1366.5, 1386.2, 1439.4, 1456.6, 1493.6, 1555.6,			
	1655.0, 3023.4, 3075.6, 3132.7, 3156.3, 3199.5, 3253.8, 3721.3			
CH ₃	537.0, 1402.4, 1402.4, 3103.2, 3282.9, 3283.0			
TS 3a	100 ^a , 185 ^a , 273 ^a , 356 ^a , 261.5, 215.5, 230.4, 259.0, 347.7, 420.3, 557.9, 757.7,			
	801.2, 880.1, 888.7, 938.8, 1031.2, 1124.4, 1160.9, 1275.6, 1283.6, 1369.0, 1405.6,			
	1455.9, 1459.9, 1461.8, 1479.0, 1548.7, 1550.0, 1558.9, 2417.7, 3127.0, 3158.8,			
	3180.6, 3184.2, 3204.8, 3221.5, 3240.5, 3245.0, 3385.4, 3389.2			
TS 3b	35 ^a , 46 ^a , 122 ^a , 153 ^a , 445.7, 466.6, 531.0, 575.2, 707.9, 784.5, 869.3, 897.2, 934.9,			
	1012.6, 1041.9, 1081.8, 1120.6, 1161.3, 1192.6, 1244.8, 1262.0, 1283.5, 1393.0,			
	1422.9, 1430.4, 1481.0, 1494.9, 1497.3, 1519.7, 1529.2, 1538.9, 1694.7, 3092.3,			
	3115.6, 3139.4, 3197.6, 3208.8, 3210.1, 3223.4, 3285.9, 3297.7			
TS 3c	65 ^a , 70 ^a , 83 ^a , 84 ^a , 96.7, 245.2, 254.5, 312.3, 355.1, 375.1, 761.5, 792.9, 915.4,			
	930.3, 935.3, 997.8, 1046.7, 1076.4, 1141.9, 1242.7, 1349.8, 1358.1, 1416.8, 1452.6,			
	1457.5, 1457.7, 1524.4, 1546.9, 1548.9, 1566.5, 2365.7, 3112.5, 3135.8, 3156.1,			
	3178.8, 3198.1, 3221.6, 3233.0, 3238.8, 3239.4, 3343.0			
TS 3d	40 ^a , 50 ^a , 90 ^a , 100 ^a , 261.5, 215.5, 230.4, 259.0, 347.7, 420.3, 557.9, 757.7, 801.2,			
	880.1, 888.7, 938.8, 1031.2, 1124.4, 1160.9, 1275.6, 1283.6, 1369.0, 1405.6, 1455.9,			
	1459.9, 1461.8, 1479.0, 1548.7, 1550.0, 1558.9, 2417.7, 3127.0, 3158.8, 3180.6,			
	3184.2, 3204.8, 3221.5, 3240.5, 3245.0, 3385.4, 3389.2			
TS 3e	260 ^a , 300 ^a , 400 ^a , 500 ^a , 574.7, 731.9, 848.4, 857.5, 910.7, 988.4, 1084.2, 1118.6,			
	1230.2, 1237.3, 1318.1, 1352.7, 1404.5, 1425.3, 1490.6, 1491.5, 1500.3, 2344.7,			
	3007.7, 3043.3, 3050.2, 3068.9, 3106.0, 3121.2, 3128.6			

Table 8.1. a) denotes adjusted frequencies in the transition states. b) Scaled as described in text

carried out at the DFT, G3B3 and CBS-QB3 levels of theory using the Gaussian 03 program suite¹² provided by the ITS Research computing facility at the University of North Carolina at Chapel Hill. The geometry and vibrational frequencies of all molecules studied were calculated using the Becke 3 parameter exchange functional¹³, the correlation functional of Lee-Yang-Parr (B3LYP)¹⁴ with the 6-311+G** basis set. The

harmonic frequencies of 2-pentanone, used in the calculation of the neutral internal energy distribution, are listed in Table 8.1. These frequencies were scaled as suggested by Andersson and Uvdal¹⁵ who found that in B3LYP/6-311+G** calculations, the low frequencies (below 100 cm⁻¹) should be scaled by 1.01, whereas the other vibrational frequencies should be scaled by 0.9679. The analysis of competitive dissociation pathways requires assumptions about the structure of the transition state. Those vibrational frequencies were also calculated at the B3LYP / 6-311+G** level of theory.

Finally, high level calculations at the G3B3 and CBS-QB3 level of theory were used to confirm the measured onsets for the known product ions, to provide insight into the products of each reaction, and to create isodesmic reactions which are used to support the derived thermochemistry.

8.3. Results

8.3.1. Time-of-Flight Distributions and the Breakdown Diagram

Time-of-flight (TOF) mass spectra were recorded in the energy range of 9.6 – 12.2 eV and selected TOF distributions are shown in Figure 8.1. The solid lines through the experimental points are the simulated TOF profiles. At low energies, 10.289 eV, both the butanoyl ion (90.7 μ s) and the propen-2-ol (82.0 μ s) have slightly asymmetric peak shapes, which arise from parent ions that dissociate as they are being accelerated in the 5 cm acceleration region. The asymmetric peak shape indicates that the reaction rate is slow at the dissociation threshold, and that the rate constant is between 10³ s⁻¹ and 5x10⁶ s⁻¹. It is in this range that the absolute rate constant can be extracted from the asymmetric TOF profile. The simulated TOF distributions given by the solid lines, and described


Figure 8.1. Selected time-of-flight (TOF) distributions. At 10.289 eV, both the butanoyl ion (90.8 μ s) and the propen-2-ol ion (82.0 μ s) peaks are asymmetric. At 10.668 eV the acetyl ion peak has appeared at 70.7 μ s as a symmetric peak. The butanoyl and propen-2-ol ions are now symmetric. At 11.808 eV, the acetyl ion (70.7 μ s) is now asymmetric, indicating a sequential reaction pathway is energetically accessible.



Figure 8.2. The breakdown curve of 2-pentanone. The open points are the experimentally determined ion ratios, the dashed lines are the simulated methyl loss abundances, the dotted lines are the simulated acetyl ion abundances. Adding the dashed lines together and the dotted lines together produces the solid fit.

later, match these metastable profiles. There are also two small peaks at 91.9 and 85.0 μ s, which result from dissociation of the parent ions in the drift region before the reflectron, which are also fitted.

The TOF spectrum at 10.688 eV in Figure 8.1 shows the butanoyl and propen-2ol ion peaks to be symmetric, indicating that the rate constant is now greater than 5×10^6 s⁻¹. The acetyl ion peak, formed by the loss of the n-propyl radical, has also appeared at 70.7 µs. This peak is symmetric as well, because it is in competition with the other two fast channels. According to Murad and Ingrahm⁷ the second methyl loss channel is now energetically accessible, but we are unable to distinguish the resulting ion from the butanoyl ion because they have the same mass. Because all the peaks are symmetric, no direct kinetic information is obtained at this ion internal energy.

The TOF distribution at 11.808 eV in Figure 8.1 shows that the acetyl ion peak at 70.7 μ s is now slightly asymmetric, a rather unexpected situation in that rate constants are expected to increase with ion energy, rather than decrease! This indicates that a new dissociation channel has opened for the production of the acetyl ion. If this pathway were in competition with the lower energy channels, the rate constant would need to be greater than 5×10^6 s⁻¹, and the peak would be symmetric. Because it is asymmetric, this dissociation channel cannot be in competition with the four lower energy pathways. We ascribe it instead to a sequential reaction. We propose that it results from the further or sequential dissociation of the ion produced from the second methyl loss channel, the but-3-en-2-ol ion, which can lose ethylene to produce the acetyl ion.

With the addition of a fifth dissociation pathway, the reactions, in order of increasing onset energy, along with the mass of the resulting ions are given below:

2-pentanone
$$\rightarrow$$
 CH₃CH₂CH₂CO⁺ (71) + CH₃[•] (8.3a)

$$\rightarrow CH_3COH = CH_2^{+} (58) + C_2H_4 \tag{8.3b}$$

$$\rightarrow CH_3CO^+(43) + C_3H_7$$
 (8.3c)

$$\rightarrow CH_3COHCHCH_2^+(71) + CH_3^{\bullet}$$
(8.3d)

$$\rightarrow \mathrm{CH}_3\mathrm{CO}^+(43) + \mathrm{CH}_3^{\bullet} + \mathrm{C}_2\mathrm{H}_4$$
 (8.3e)

The most interesting point is that the five dissociation pathways yield three distinguishable mass peaks. There are two parallel methyl loss channels (8.3a and 8.3d), resulting in the formation of two different ions, both of mass 71, and there are two different pathways for the production of the acetyl ion (8.3c and 8.3e).

Table 8.2. Experimental and Calculated Dissociation Onsets ^a					
Reaction Products	Exp. <i>E</i> _θ	Lit. E_{θ}	CBS-QB3 E_{θ}		
Butanoyl ion + CH ₃	10.239 ± 0.015	10.207 ^{b,e}	10.18 ^d		
Propen-2-ol ion + C ₂ H ₄	10.259 ± 0.019	10.248 ^{b,e}	10.24 ^d		
		10.257 ^{c,e}			
		$10.207 \pm .05^{g}$			
Acetyl ion + C ₃ H ₇	10.483 ± 0.025	$10.52^{\rm f}$	10.47 ^d		
TS to ENOL	10.540 ± 0.033		10.20 ^d		
Acetyl ion + $CH_3 + C_2H_4$	11.482 ± 0.037	11.486 ^h	11.42 ^d		

Table 8.2. a) All values are given in eV. b) From Murad and Inghram. c) From Holmes and Lossing. d) Calculated E_0 at the CBS-QB3 level of theory. e) AE converted to 0K using $AE_{298K} = E_0 - \langle E_{rot} \rangle - \langle E_{vib} \rangle$. f) Fogleman et. al. g) Traeger. h) based on known 0K thermochemistry of the products and neutral 2-pentanone.

The breakdown diagram, given in Figure 8.2, is a plot of the fractional ion abundance as a function of the photon energy. The points are the experimentally determined ion ratios, whereas the solid lines are simulated fits using the same parameters as employed in the TOF fitting. The dashed lines are the simulated curves that would be observed if the 2 methyl loss channels (8.3a and 8.3d) were distinguishable and the dotted thin lines are for the 2 acetyl ion production channels (8.3c and 8.3e).

Summing the 2 methyl loss channels together and the 2 acetyl ion channels together produces the solid lines. The 0K dissociation energies, E_0 , obtained from the fits to the data are given in Table 8.2.

8.3.2. Simulation of Experimental Results

The solid line fits to the experimental data in Figures 8.1 and 8.2 were obtained by taking into account the thermal energy distribution of 2-pentanone at the experimental temperature of 305K as well as the photon and electron energy resolution of our instrument (15 meV). The ion internal energy distribution was calculated using the 2pentanone vibrational frequencies obtained from the ab initio calculations. The fit to the experiment was obtained by varying the assumed dissociation energies as well as the transition state vibrational frequencies. Varying the frequencies was necessary to model the slow dissociation rate of the methyl and ethylene loss reactions, as well as the sequential channel. It is often helpful to adjust the parameters in a sequential manner beginning with the first onset. Because the first two dissociation onsets are very close together, their fitting is not entirely independent so that they were fit together by adjusting the onset energy and the lowest four transition state vibrational frequencies for each reaction.

The extracted 0K onsets for the butanoyl and propen-2-ol ions were determined to be 10.239 ± 0.015 eV and 10.259 ± 0.019 respectively. The errors were determined by fixing the onsets at various energies in the vicinity of the optimum value and allowing the other parameters to vary. The error was then determined by noting at what energy a noticeable worsening of the fit was obtained. Because two reactions with very similar

onset energies compete, the error limits are somewhat larger than ones obtained when only a single reaction dominates¹⁶. Both of these onsets were determined by previous experiments in which the fragment ion onset was measured as a function of the ionization energy for room temperature samples without taking into account the possible kinetic shift due to the slow reaction. We can convert these 298K onsets to 0K in an approximate manner by adding the rotational and vibrational energy to the 298K onset. The Murad and Inghram⁷ photoionization onset of 10.03 eV for the butanoyl onset converts to 10.207 eV at 0K, which is some 32 meV lower than ours. Both Murad and Inghram⁷ using photoionization and Holmes and Lossing⁵ using mono energetic electron ionization measured onsets for the higher energy propen-2-ol product, reporting converted 0K onsets of 10.248 ± 0.08 and 10.257 ± 0.08 eV, respectively, which are both quite close to our more accurate value of 10.259 eV. Traeger⁶ reported a 298K onset of the propen-2-ol ion to be 10.03 ± 0.05 eV, which converts to 10.207 eV at 0K. This value is lower than the other three by 41, 50, and 52 meV respectively, though it is within the experimental error of each.

The acetyl ion production channel, associated with the loss of the n-propyl radical, is modeled by adjusting the E_0 and four lowest frequencies of the transition state. Although this reaction is fast in the energy region where it is observed, it must compete with the two lower energy channels so that its transition state frequencies must be adjusted. That is, these two parameters are varied to fit the relative rate of the acetyl ion production with respect to the other two channels. How rapidly the acetyl ion production channel catches up with the two lower energy dissociation channels is a function of the transition state frequencies. The resulting onset for the acetyl ion is calculated to be

 10.483 ± 0.025 eV. Because this is a higher energy dissociation channel, the acetyl ion signal does not show a sharp onset, but rather blends smoothly into the background noise. This is because at its onset, the acetyl ion rate is several orders of magnitude smaller than the combined rates of the first two channels. Our fitting program takes all of this into account.

The second methyl loss channel associated with the methyl group on the long hydrocarbon chain is more complicated. Its only manifestation is in the breakdown diagram in which the flat topped profile from 10.5 to 11.4 eV suggests two processes. In fact, it was impossible to fit this profile by assuming a single methyl loss reaction. Because the onset of this ion was obscured by the lower energy butanoyl ion, the range of energies that provided a reasonable fit is wider. The E_0 and four lowest transition state frequencies were adjusted until the best fit over the entire energy range of the breakdown diagram was achieved, yielding an onset of 10.540 ± 0.033 eV. Although there are several adjustable parameters, the degree to which these parameters can be varied to reproduce a good fit over the entire energy range of the breakdown diagram is limited because there are three other competing channels, two of which are associated with asymmetric TOF distributions that yield direct kinetic information. That is, the amount of experimental information provides severe restraints on the range of the parameters. Based on ab initio calculations, we conclude that the ion produced in this reaction is the but-3-en-2-ol ion, rather than the higher energy ketone (but-3-en-2-one). The mechanism is discussed further in the next section.

As previously pointed out, the appearance of the slow acetyl ion reaction at higher energies must be attributed to a reaction that does not compete with the lower energy

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Table 8.3. Ancillary	Thermochemical Valu	ies ^a	
Species	$\Delta_{\rm f} {\rm H^o}_{0{ m K}}$	$\Delta_{\rm f} {\rm H}^{\rm o}{}_{298{ m K}}$	$H_{298K} - H_{0K}^{c}$
2-pentanone	$-230.2 \pm 1.1^{\circ}$	-258.8 ± 1.0^{b}	23.3
•CH ₃	150.3 ± 0.4^{d}	147.1 ± 0.4^{h}	10.5
CH ₄	-66.8°	-74.4 ^b	9.99
C ₂ H ₄	$61.05 \pm 0.4^{\circ}$	52.5 ± 0.4^{b}	10.5
C ₂ H ₆	$-68.0 \pm 0.4^{\circ}$	-83.8 ± 0.4^{b}	11.7
CH ₃ CO ⁺	666.7 ^g	659.4 ^g	11.8
C ₃ H ₆	$35.7 \pm 0.8^{\circ}$	20.0 ± 0.8^{b}	15.7
°C ₃ H ₇	118.0 ^c	100.2^{i}	15.5
C ₃ H ₈	$-82.2 \pm 0.5^{\circ}$	-104.7 ± 0.5^{b}	14.5
CH ₃ COCH ₃	$-202.2 \pm 0.6^{\circ}$	-218.5 ± 0.6^{e}	16.6
CH ₃ OH ⁺	846.0 ^f	856.9 ^f	11.5
CH ₃ NH ₂	$-8.3 \pm 0.5^{\circ}$	-23.0 ± 0.5^{b}	11.5
C ₃ H ₇ NH ₂	$-42.2 \pm 0.4^{\circ}$	-70.2 ± 0.4^{b}	17.6

Table 8.3. a) All values given in kJ/mol. b) Pedley. c) Converted using calculated vibrational frequencies from Table 1. d) Determined from the $\Delta_f H^o_{0K}[CH_3^+]$ from Weitzel et. al. and the IE['CH_3] from Blush et. al. e) From Wiberg et. al. f) From $\Delta_f H^o 0K[CH_3OH]$ from Pedley and IE[CH_3OH] from Tao et al. g) Fogelman et. al. h) Weitzel et. al³¹. i) Tsang.

reactions. This new channel is also evident in the breakdown diagram in which the acetyl ion yield increases at 11.4 eV, rather than leveling off as would be expected for a single source reaction. This increase in the acetyl ion abundance is at the expense of the methyl loss channel. It is for this reason that we conclude that the but-3-en-2-ol ion (8.3d) further dissociates to the acetyl ion. The acetyl ion production rate is dependent on the energy partitioning between the but-3-en-2-ol ion and the neutral methyl ligand. Therefore the modeling requires knowledge of the ion and neutral structures as well as their vibrational frequencies. If reaction 8.3e were fast, the only adjustable parameter would be E_0 , and the shape of the breakdown diagram would be governed solely by the energy partitioning in reaction 8.3d, which has no adjustable parameters¹¹. Because the reaction is slow, the transition state frequencies are also adjusted. This is done to fit the measured reaction rate as observed in the TOF distributions. The onset for the acetyl ion from the sequential reaction is 11.482 \pm 0.037 eV. Because the final products (acetyl ion



Figure 8.3. Comparison of the experimental and calculated onset energies for all 5 dissociation pathways. All stable species were calculated at the CBS-QB3 level of theory from the $B3LYP/6-311+g^{**}$ optimized structure. The transition state was calculated at the $B3LYP/6-311+g^{**}$ level of theory.

+ CH_3^{\bullet} + C_2H_4) have well established heats of formation shown in Table 8.3, we can calculate this onset to be 11.489 eV, an energy that agrees perfectly with the best fit to the data.

8.4. Theoretical Results for Product Identification

All reaction products were calculated at various levels of theory. Figure 8.3 shows the potential energy diagram and compares the experimental dissociation onsets (dotted lines) and the calculated onsets (solid) at the CBS-QB3 level of theory. The transition state is calculated at the B3LYP/6-311+G** level of theory. The measured and calculated onsets (Table 8.2) for the butanoyl ion, propen-2-ol ion and acetyl ion agree very nicely, differing by 5.3, 1.8 and 0.9 kJ/mol, respectively. In addition, the sequential reaction for the formation of the acetyl ion agrees with the calculated value to within 5.8 kJ/mol. The only true disagreement is the fourth onset (8.3d), which does not agree with either the calculated but-3-en-2-one onset (too low by 50 kJ/mol) or the calculated but-3en-2-ol onset (too high by 40 kJ/mol). The only reasonable explanation, confirmed by DFT calculations, is that the measured onset is associated with the transition state for the isomerization of the ketone to its enol structure. The QST3 method using B3LYP/6-311+g** was used to find the transition state, and the resulting energy differs from the measured onset by about 13 kJ/mol. Therefore, the measured onset must be associated with the isomerization barrier to the enol form of the ion. The lowest energy dissociation pathway from the enol is for the production of the but-3-en-2-ol ion $(CH_3COHCH=CH_2^+)$, which lies approximately 90 kJ/mol below the but-3-en-2-one ion onset. It is the but-3-en-2-ol ion that dissociates further via an ethylene loss channel to produce the acetyl ion.

8.5. Experimental and Theoretical Thermochemistry

The 298K heat of formation of neutral 2-pentanone was determined by Harrop and Head¹⁷ and is listed in Cox's Thermochemical compilation¹⁸ as -259.1 ± 1.1 kJ/mol. This has been updated in Pedley's¹⁹ recent compilation to -258.8 ± 1.0 kJ/mol. Because the determination of the thermochemistry hinges on the 2-pentanone heat of formation, we have used four homodesmotic reactions to verify the neutral 2-pentanone heat of formation. These reactions are summarized below:

2-pentanone + methane \rightarrow butanone + ethane	(8.4a)
2-pentanone + ethane \rightarrow butanone + propane	(8.4b)
2-pentanone + ethene \rightarrow butanone + propene	(8.4c)
2 nontanona mathylamina acatona propylamina	(9.14)

2-pentanone + methylamine
$$\rightarrow$$
 acetone + propylamine (8.4d)

The reaction energy for these four reactions were calculated at the G3B3 and CBS-QB3 levels of theory, and the 2-pentanone heat of formation obtained by using well known heats of formation of all the other species (Table 8.3). The results of these calculations yielded an average $\Delta_{H}^{o}{}_{0K}$ [2-pentanone] = -230.6 ± 0.3 kJ/mol, which compares nicely with the experimental heat of formation of -230.2 ± 1.1 kJ/mol.

The onset energies for the various fragment ions are related to the heats of formation of the reactants and products. The least well established heats of formation are those of the butanoyl ion and the propen-2-ol ion (enol of acetone). Because these are the first two onsets, and the associated neutral species (CH_3° , C_2H_4 , and 2-pentanone) are

well known, we can use our analysis to establish accurate heats of formation for these two ions. For instance, the onset for the butanoyl ion (first CH_3^{\bullet} loss reaction) at 10.239 ± 0.015 eV is related to reactant and product heats of formation as shown in equation 6.

$$E_0 = \Delta_f H^o{}_{0K}[\text{butanoyl ion}] + \Delta_f H^o{}_{0K}[\text{CH}_3^{\bullet}] - \Delta_f H^o{}_{0K}[2\text{-pentanone}]$$
(8.6)

This yields a butanoyl ion 0K heat of formation of 606.7 ± 2.1 kJ/mol, which can be converted to a 298K value, using equation 8.7,

$$\Delta_{f}H^{o}_{298K} = \Delta_{f}H^{o}_{0K} - \sum (H^{o}_{298K} - H^{o}_{0K})_{\text{elements}} + \sum (H^{o}_{298K} - H^{o}_{0K})_{\text{molecule}}$$
(8.7)

in which the $(H^{o}_{298K}-H^{o}_{0K})_{elements}$ values are taken from Wagman et al.²⁰ and the $(H^{o}_{298K}-H^{o}_{0K})_{molecule}$ values are calculated using the vibrational frequencies in Table 8.1. This conversion results in a 298K heat of formation of 586.9 ± 2.1 kJ/mol.

Similarly, the measured onset for reaction 8.3b, along with the ancillary heats of formation of 2-pentanone and ethylene in Table 8.3, yields a 0K heat of formation for the propen-2-ol ion of 697.9 \pm 1.8 kJ/mol, which converts to 680.7 kJ/mol at 298K. It is interesting that Holmes and Lossing⁵, although obtaining the same measured onset as we do here, reported a $\Delta_f H^{o}_{298K}$ [propen-2-ol ion] to be 661 kJ/mol, which is some 20 kJ/mol lower than our value. This result, which is listed in the NIST²¹ website as the heat of formation of the acetone ion enol ion, is obtained by using the phenomenological 298K onset along with 298K heats of formation for the 2-pentanone and ethylene without taking into account the proper treatment of such onsets²² (a commonly committed error in the early 1980's). This was noted by Turecek and Crammer²³, who applied the correction to the original Holmes and Lossing⁵ value, resulting in a 298K heat of formation of 684 kJ/mol. Turecek and Crammer²³ used a G2(MP2) ab initio study to obtain a $\Delta_f H^{o}_{298K}$ [propen-2-ol ion] of 677 kJ/mol. Traeger⁶ also determined the $\Delta_f H^{o}_{298K}$ [propen-

2-ol ion] from the dissociative photoionization of a series of methyl ketones, including 2pentanone. The resulting $\Delta_f H^o_{298K}$ [propen-2-ol ion] from 2-pentanone was determined to be 676.9 kJ/mol, while the mean average of the four measurements is 676.6 ± 0.7 kJ/mol.

Because the experimentally measured propen-2-ol ion heats of formation vary by \sim 8 kJ/mol, we have determined it using high level calculations with the isodesmic reaction:

propen-2-ol⁺ + methane \rightarrow methanol⁺ + propene (8.9)

With the well established heats of formation of methane, propene and the methanol ion,(see Table 8.3) the calculated 0K G3B3 and CBS-QB3 enol ion heats of formation were 698.8 and 698.4 kJ/mol, respectively. At 298K, these values of 682.3 and 681.8 kJ/mol, respectively, agree extremely well with our measured value of 680.7 ± 1.8 kJ/mol for the $\Delta_f H^o_{298K}$ [propen-2-ol ion]. Using other alcohols in the isodesmic reaction can lead to error, because the adiabatic ionization energies of most the other alcohols are not well established because Franck-Condon factors do not favor the adiabatic transition. This is because of the large geometry change between the neutral and ion ground states.

Trikoupis et. al.²⁴ recently calculated the acetone enol to be 42.2 kJ/mol more stable than the acetone radical cation using the CBS-Q/DZP level of theory. This supports the B3LYP/cc-pVTZ level theory calculation of Nummela and Carpenter⁴, who reported an energy difference of 42 kJ/mol. If we assume an acetone ion heat of formation at 0K of 734.5 kJ/mol, obtained from the ionization energy reported by Fogleman et al.¹ and the heat of formation of neutral acetone from Wiberg et al.²⁵, the Nummela Carpenter⁴ enol ion heat of formation, after being converted to a 298K value is

675.8 kJ/mol, which is 6 kJ/mol lower than our measurement, and is in much better agreement with the value of 676.6 reported by Traeger.

8.6. Discussion

On the basis of our measured methyl loss onset, which confirms the Murad and Inghram⁷ measurement, the heat of formation of the butanoyl ion is now well established. This ion heat of formation will be used in our current TPEPICO study of 2,3-hexanedione. The 2,3-hexanedione ion dissociates to produce the butanoyl ion and acetyl radical at low energies, followed by the acetyl ion and butanoyl radical at higher energies, as shown below.

$$CH_{3}COCOCH_{2}CH_{2}CH_{3} \rightarrow CH_{3}CO + COCH_{2}HC_{2}CH_{3}^{+} \qquad E_{0}(1) \quad (8.8a)$$
$$\rightarrow CH_{3}CO^{+} + COCH_{2}CH_{2}CH_{3} \qquad E_{0}(2) \quad 8.8b)$$

 $E_0(1)$ can be used with acetyl radical and butanoyl ion heat of formation to determine the 2,3-hexanedione neutral heat of formation, which can then be applied with $E_0(2)$ and the acetyl ion heat of formation to yield the butanoyl radical heat of formation. Because the 2,3-hexanedione ion dissociation is made complicated by a sequential reaction of the butanoyl ion to produce the acetyl ion, a full analysis of the dissociation dynamics and onset energies will be reported in a subsequent paper.

The propen-2-ol ion heat of formation derived from the 2-pentanone ion dissociative ionization onset has now been measured by Murad and Inghram, Holmes and Lossing, Traeger, and ourselves. Three of the experiments agree on the higher value, and Traeger's onset is lower by about 50 meV. The competition between the two dissociation channels and the fact that the onsets occur in a Franck-Condon gap present some

problems in establishing a reliable onset. Under these circumstances, our TPEPICO experiment is ideally designed to establish an accurate onset so that we favor our value of 680.7 ± 1.8 kJ/mol for the $\Delta_f H^o_{298K}$ [propen-2-ol ion]. The various calculations also disagree. Turecek and Cramer and Numella and Carpenter obtain values that are about 5 kJ/mol lower, around ~677 kJ/mol. As with the discrepancies among the experimental values, we favor our own value, which is carried out at a higher level than the others and also agrees with our experimental finding.

An interesting finding in this study is the high energy acetyl ion onset energy, which proceeds via a sequential loss of the methyl radical followed by an ethylene loss step. The fact that this onset is identical to the thermochemically expected one indicates that there is no barrier to this ethylene reaction. However, on energetic grounds, the acetyl ion could equally well go via an ethylene loss from 2-pentanone ion to form the acetone enol ion, followed by a methyl loss. Yet, the breakdown diagram shows that the second onset for the acetyl ion comes at the expense of the methyl loss channel (see breakdown diagram in Figure 8.2). By contrast, the ethylene loss channel in Figure 8.2 follows the pattern expected for simple reaction, with no evidence for a sequential loss of the methyl radical.

The fact that the enol ion of acetone does not readily lose a methyl radical is well known. The only way for the enol to dissociate to the acetyl ion is by isomerizing to the keto form of acetone²⁶. Chava Lifshitz was one of the first to point out that this involves a barrier²⁷. This conclusion was based on a non-statistical energy distribution caused by a 150 kJ/mol reverse barrier. More recent calculations of Numella and Capenter indicate

an even higher barrier of 159 kJ/mol. The barrier is a result of the difficult H atom transfer via a 4-center transition state.

The interesting question that remains is: why is there no barrier in the acetyl ion formation from the but-3-en-2-ol ion? This enol must also transfer its H atom prior to ethylene loss. A major difference between this ion and the acetone enol ion is that the double bond is one carbon atom removed from the carbonyl C atom [C-C(OH) -C=C] rather than adjacent to the carbonyl group in the acetone enol ion.

8.7. Conclusions

The dissociation of 2-pentanone ions is both interesting and complex. The parent ion can undergo ethylene loss, n-propyl loss and two competing methyl loss channels. The higher energy methyl loss channel involves isomerization into an enol well. In addition it dissociates further via ethylene loss. The breakdown diagram and TOF distributions have been modeled in terms of the RRKM framework and the 0K dissociation onsets have been determined. Quantum chemical calculations have been used widely to support the measured onsets and derived thermochemistry and to identify the product ion structure.

We report on the heats of formation of the butanoyl and propen-2-ol ions. We have shown that the measured onsets for the higher energy dissociation channels can be determined accurately. In addition to the derived thermochemistry, the photodissociation of the 2-pentanone ion has illustrated the clever ways in which these ions can dissociate, via rearrangements and enol wells. Our TPEPICO data have illuminated the hidden dissociation channels, which if unaccounted for can lead to large errors in the determined

onsets which propagate to the derived thermochemistry. Even in this complicated reaction, the statistical theory within the RRKM framework can be applied successfully.

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