Spring 5-31-2013

Photoionization Mass Spectrometry and Photoelectron-Photoion Coincidence (PEPICO) Spectroscopy Studies of Select Biofuel Molecules

Joseph G. Czekner
jczechner@gmail.com

Follow this and additional works at: https://repository.usfca.edu/thes

Part of the Physical Chemistry Commons

Recommended Citation

https://repository.usfca.edu/thes/206
Photoionization Mass Spectrometry and Photoelectron-Photoion Coincidence (PEPICO) Spectroscopy Studies of Select Biofuel Molecules

A Thesis Presented to the Faculty of the Department of Chemistry at the University of San Francisco in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

Written by

Joseph Czekner
Bachelor of Science in Chemistry
California University of Pennsylvania
2016
Photoionization Mass Spectrometry and Photoelectron-Photoion Coincidence (PEPICO) Spectroscopy Studies of Select Biofuel Molecules

Thesis written by Joseph Czekner

This thesis is written under the guidance of the Faculty Advisory Committee, and approved by all its members, has been accepted in partial fulfillment of the requirements for the degree of

Master of Science
in Chemistry
at
the University of San Francisco

Thesis Committee

Giovanni Meloni, Ph.D.
Research Advisor

Lawrence Margerum, Ph.D.
Professor

William Melaugh, Ph.D.
Professor

Marcelo Camperi, Ph.D.
Dean, College of Arts and Science
Acknowledgement

First and foremost, I would like to thank my research advisor, Dr. Giovanni Meloni for his guidance, motivation and his infectious enthusiasm for chemistry. I have learned so much from him and I am grateful he always listened to my ideas and corrected me without judgement, no matter how wrong I was. I also need to thank my committee, Dr. Lawrence Margerum and Dr. William Melaugh for their constructive comments and critiques of this work. I am also indebted to the staff in the chemistry department, specifically Deidre Shymansky and Jeff Oda for their help with paperwork and experiments.

I have to thank my friends and lab mates at USF, especially Ken, Nick, AJ, Matt, and Maggy, along with everyone else from the department. Without the (sometimes necessary) distractions I would not have become the person I am today. I am grateful for the time with all of my friends from outside the chemistry department who enriched my life outside of science.

I owe much to my family who always shows support for all of my endeavors, no matter how difficult they may be. I also need to thank my extended family, The Blackburns, who provided a roof over my head for the last few months of my time at USF, which kept me from being homeless. Lastly, to my girlfriend Courtney, I cannot express how glad I am that you are in my life. I could not have done any of this without you and I cannot wait to see where the future will take us.
Table of Contents

1. Introduction
   1.1 Combustion 1
   1.2 Engine and Biofuel Technology 2
   1.3 Atmospheric Pollution 4
   1.4 Projects 5
   1.5 References 8

2. Experimental Instrumentation
   2.1 Advanced Light Source (ALS) 11
      2.1.1 ALS Beamlines 12
      2.1.2 ALS Components 12
      2.1.3 End Station 9.0.2.3 – Multiplex Apparatus for Combustion Experiments 17
   2.2 The Swiss Light Source (SLS) 23
      2.2.1 Available Beamlines of the SLS 24
      2.2.2 Features of the SLS at the VUV Endstation 25
      2.2.3 SLS Components 25
      2.2.4 iPEPICO Instrumentation, Electron, and Ion Optics 29
   2.3 References 32

3. Theoretical Concepts and Methodology
   3.1 Photoionization 34
   3.2 Franck-Condon Principle 35
   3.3 Threshold Photoelectron Spectra (TPES) and Photoionization Efficiency (PIE) Curves 36
   3.4 Photoionization Cross Sections and Branching Fractions 37
   3.5 Computational Methods 39
      3.5.1 Density Functional Theory (B3LYP and UB3LYP) 40
5.2.1 Fundamental Low Temperature Oxidation Chemistry of Oxygenates and Bimolecular Reactions  83
5.3 Experimental  84
5.4 Computational Methods  85
5.5 Results and Discussion  85
  5.5.1 Photoionization Behavior of Ethyl Butyrate  85
  5.5.2 Experimental Results – Product Identification  87
  5.5.3 Comparison between Theory and Experiment – HO₂-Elimination Reactions from EB Radicals  89
  5.5.4 Comparison between Theory and Experiment – Observation of Formaldehyde and Acetaldehyde  94
5.6 Conclusions  99
5.7 Acknowledgments  100
5.8 References  101
6. Photoelectron-Photoion Coincidence Spectroscopy (PEPICO) Study of Potential Biofuel Additives
  6.1 Abstract  109
  6.2 Introduction  109
  6.3 Experimental  110
  6.4 Computational Techniques  112
    6.4.1 Ab Initio Calculations  112
    6.4.2 Statistical Modeling  112
  6.5 Results and Discussion  114
    6.5.1 Mesitylene  114
    6.5.2 γ-Valerolactone  118
6.6 Conclusion 123
6.7 Acknowledgements 123
6.8 References 124
Abstract

This thesis is the culmination of numerous experiments, performed on two different continents, investigating the spectroscopic and thermodynamic properties of several biofuels and fuel additives. It will start with an introduction about the motivation behind these experiments. The second chapter will outline the experimental details of the apparatus at the Advanced Light Source (ALS) in Berkeley, CA, followed by the Swiss Light Source (SLS) in Villigen, Switzerland. Third, the theoretical concepts and data analysis methods will be discussed in detail.

Chapter 4 will be the start of the newly obtained data. It presents some photoionization mass spectrometry studies on γ-valerolactone (GVL). The photoionization cross section of GVL and some suspected combustion products are measured. In addition, several dissociative ions are determined. Theoretical calculations are used to support all alignments. This data is vital to product identification and branching fraction calculations in time- and energy-resolved photoionization experiments. The fifth chapter will investigate the chlorine-initiated reactions of methyl butyrate (MB) and ethyl butyrate (EB) in the presence of oxygen. Ethyl crotonate is found to be a major product in the EB reaction. Formaldehyde and acetaldehyde are both formed in the EB and MB reactions. Both products are suspected to be produced by the RO₂-HO₂ radical-radical reaction and ab initio calculations are performed to analyze the reaction mechanisms. Finally, chapter six will discuss the photoelectron-photoion coincidence (PEPICO) spectroscopy of two biofuel additives (GVL and mesitylene). This technique is used to measure various thermodynamic quantities, such as heats of formation, entropies of activation, and bond strengths. In addition, dissociation rates will also be obtained with the use of two statistical models, Rice-Ramsperger-Kassel-Marcus (RRKM) theory and the Simplified Statistical Adiabatic Channel Model (SSACM).
Chapter 1

Introduction

Today’s society could not function without reliable fuels. This also means that the fuels used need to be plentiful and renewable so there a crisis, such as a fuel shortage, does not happen. In addition, the past few generations have been becoming increasingly aware of their environmental impact. This makes the development of biofuels interesting and difficult due to the complexity of creating a fuel that is not only more efficient and renewable, but also cleaner burning.

1.1 Combustion

During the industrial revolution, coal/steam powered engines were implemented to improve the efficiency in manufacturing and transportation. Not only was the mining and deforestation detrimental to the environment, but the burning of very impure coal lead to even more damage with the release of sulfur and nitrogen oxides. These engines operated on the simple and ideal reaction shown below.\(^1\)

\[
\text{Fuel} + \text{Air} \rightarrow \text{Heat} + \text{CO}_2 + \text{H}_2\text{O} \quad (1.1)
\]

The internal combustion engine was also invented based on the same reaction, but instead of coal, liquid gasoline fuels purged from petroleum products were used. This greatly improved the efficiency of automobiles and made it practical for more people to own and operate one. During this time, researchers were only looking for ways to improve the engine efficiency without worrying about other problems, such as pollution and renewable resources. Additives such as organoleads,\(^2\) and methyl tertiary butyl ether (MTBE)\(^3\) were an attempt to increase efficiency, which had a severe impact on the environment. It was not until the 1970’s that concerns about climate change started to emerge and people began to question what these fuels were doing to the environment.\(^4\)

It is now understood that combustion mechanisms could have several hundred, or even thousands, of pathways depending on the molecule that is being burned. Even the simplest hydrocarbon, methane, has a complex combustion mechanism, which is shown in Figure 1.1. As the diagram shows, pollutants such as formaldehyde, ethane, and many others can be formed through the burning of methane. These pollutants can become even more prominent in the combustion of larger molecules.
1.2 Engine and Biofuel Technology

New technology is making it possible to derive renewable fuels from plant and bio-mass using enzyme or chemical methods. In addition, the study of their combustion mechanism can provide insight to the use of these fuels within a homogeneous charge compression ignition (HCCI) engine. The difference in HCCI engines versus spark-ignition (SI) and diesel engines are there are multiple ignition points within the combustion chamber as shown in Figure 1.2. The advantage of having multiple ignition points are that there is a more complete combustion due to a better fuel to air ratio over the entire combustion chamber. This allows the engine to combust at cooler temperatures, which greatly reduces the amount of nitrogen oxides (NO<sub>x</sub>) pollution. In addition, the multiple ignition points allow for a more complete combustion due to the more even temperature distribution.

One current problem to overcome with HCCI engine before they can be implemented, is finding the correct temperature and pressure for the fuel to achieve autoignition as shown in Figure 1.3. Recent studies have seemed to suggest that the best way to implement autoignition engines is to have a varying blend of fuels with adjustable autoignition properties.

Figure 1-1. The combustion mechanisms of methane in a premixed methane-air flame.
This will allow for operation at low (start-up) temperatures and high (operational) temperatures. This means that significant studies will need to be done to determine the autoignition properties of fuels and then engines can be built to accommodate these conditions. One such device is a variable valve timer, which can release different amounts of fuels based on programmable conditions.

**Figure 1-2.** Basic schematic of a gasoline spark-ignition, diesel, and HCCI engine (left to right).

**Figure 1-3.** A sample graph of the ideal autoignition range as a function of temperature and vapor concentration.
1.3 Atmospheric Pollution

The study of chlorine radical initiated reactions are also important in understanding the formation of pollutants in both the stratosphere and troposphere. Chlorine radicals have been found from both natural and anthropogenic sources in the aforementioned parts of the atmosphere. Understanding how chlorine radicals react with gaseous emissions in the atmosphere could easily be the first step of understanding how to clean the air and slow the formation of ozone in the troposphere and depletion of the ozone layer in the stratosphere.

The ozone layer in the stratosphere is able to prevent damaging UV radiation from reaching the surface of Earth. It can be produced through what it commonly referred to as the Chapman Mechanism (shown below). Here, oxygen gas is photolyzed with UV radiation that is less than 242 nm. The oxygen atoms that are produced can then react with a second O₂ molecule to form ozone. The M represents any third molecule that is present to absorb excess heat from the reaction. The ozone formed is then able to absorb UV or visible radiation and dissociate into an oxygen radical and O₂. Finally oxygen radicals are able to react with ozone and form oxygen gas and allow the whole process to repeat.

\[
\begin{align*}
O_2 + h\nu (~<242 \text{ nm}) & \rightarrow 2 \cdot O \\
O\cdot + O_2 + M & \rightarrow O_3 + M \\
O_3 + h\nu (UV/visible) & \rightarrow O\cdot + O_2 \\
O_3 + O\cdot & \rightarrow 2 \cdot O_2
\end{align*}
\]

Also in the stratosphere, chlorofluorocarbons (CFCs) are still present due to their past use as propellants in aerosol sprays and refrigerants. CFCs have since been banned in numerous countries, but the effects of their damage are still being realized. Ultraviolet radiation from the sun that normally is absorbed by the ozone layer is capable of photolyzing CFCs and producing chlorine and fluorine radicals. These halogen radicals are highly reactive, especially with ozone. The reaction between ozone and a halogen radicals can disrupt the Chapman mechanism. The reaction of ozone with a chlorine radical is shown below. The Cl• radical can remove an oxygen atom to produce •ClO and O₂. An example of one reaction that •ClO can
undergo is reacting with an O• radical to produce O₂ and a Cl• radical. This reaction directly interferes with the Chapman cycle and is one reason the ozone layer has been damaged.\textsuperscript{12}

\[
\text{Cl•} + \text{O}_3 \rightarrow \text{•ClO} + \text{O}_2
\]  
(1.6)

\[
\text{•ClO} + \text{O•} \rightarrow \text{Cl•} + \text{O}_2
\]  
(1.7)

Many other reactions are possible in the stratosphere due to the abundance of high energy photons, exotic radicals, and low pressures. The mechanisms presented here are some simple examples showing how a radical can interfere with a natural cycle to produce ozone.

Two of the largest sources of halogen radicals in the troposphere are the oceans and burning of biomass (mostly in tropical areas).\textsuperscript{12} Both processes mainly produce methyl halides, such as CH₃Cl, CH₃Br, and CH₃I. These species can be broken down directly through photolysis or reactions with other radicals, e.g. hydroxyl radicals (•OH) formed through combustion. Another source of halogen radicals are aerosol mists of ocean water along coasts that can directly create Cl• and Br• radicals.\textsuperscript{13} Once the halogen radicals are in the troposphere, there are numerous species that they could react with. One group of molecules of particular interest are volatile organic compounds (VOCs). VOCs include organic compounds with a relatively high vapor pressure and low boiling point at room temperature, such as benzene, gasoline, methylene chloride, and many others. Chlorine radicals can react with VOCs through hydrogen abstraction to create organic radicals, that can further react in the atmosphere.\textsuperscript{14}

1.4 Projects

Atmospheric and combustion chemistry still have many unexplored areas. The focus of this thesis will be on a wide range of concepts, including photoionization (PI) cross-section measurements, product determination of chlorine initiated reactions, and thermodynamic and rate measurements of dissociation reactions. Briefly, chapter 2 will outline all of the experimental methods used and chapter 3 will describe the theoretical methods and data analysis techniques. Chapters 4 through 6 will present the results obtained.

Chapter 4 will describe PI cross-section measurements of γ-valerolactone (GVL) and some of the potential products of its combustion. It is well established that when studying reactions using PI mass spectrometry, the PI cross-sections of the starting material and products must be known accurately.\textsuperscript{15-23}
Measurements of the PI cross-sections for this thesis were performed with the time- and energy-resolved photoionization mass spectrometer at the chemical dynamics beamline at the Advanced Light Source (ALS).\textsuperscript{15-16} We will first confirm our measurements are accurate by measuring the photoionization cross-sections of some furanic compounds that are well established in the literature. In addition, adiabatic ionization energies and appearance energies of daughter ions will be presented and compared to theoretical calculations.

The next project (Chapter 5) will discuss the chlorine radical initiated reactions of two esters, methyl butyrate (MB) and ethyl butyrate (EB) in an excess of oxygen gas. Both esters have been proposed as renewable additives to increase the octane number of gasoline fuels.\textsuperscript{24-25} Initiating reactions with chlorine radicals allows us to make direct comparisons to atmospheric reactions as described above. However, chlorine radicals also react in a similar mechanism (hydrogen abstraction) as hydroxyl radicals, which are present in combustion reactions. Different reaction rates may be observed when comparing chlorine and hydroxyl radicals, but the main focus of this project will be on product determination. These experiments were performed using the time- and energy resolved photoionization mass spectrometer at the ALS.\textsuperscript{15-16} The main reaction products observed were formed through Cl\textsuperscript{•} initiated hydrogen abstraction, followed by formation of an oxyradical that can internally abstract a hydrogen atom and finishing with the elimination of a •OOH. This leads to the formation of an unsaturated carbon chain. Formaldehyde was also observed in significant quantities after each reaction.

The final project (Chapter 6) will focus measuring dissociation rates and appearance energies of daughter ions using photoelectron-photoion coincidence spectroscopy (PEPICO). Three fuel additives are studied, which are mesitylene, GVL, and MB. Ions were prepared with a specific internal energy using the vacuum ultraviolet (VUV) beamline at the Swiss Light Source.\textsuperscript{26-27} Subsequent dissociations of the ions allow us to combine experiments and theoretical calculations to deduce bond dissociation energies if the reaction is barrierless and only a single bond breaks. Mesitylene has one dissociation in the photon energy range that was investigated, and that is the loss of one methyl group. The bond dissociation energy and dissociation rates were calculated for this reaction. GVL first loses a neutral CO\textsubscript{2} group. The reaction is
slow enough that the dissociation rates could be determined. Quantum chemical calculations are used to locate the transition state to the dissociation products that is used in the reaction modeling. Finally, the experimental barrier height is found to be in good agreement with the calculated value.
1.5 References


Chapter 2

Experimental Instrumentation

This chapter describes the major details of the experimental facilities at the Advanced Light Source (ALS) of the Lawrence Berkeley National Labs and Swiss Light Source (SLS) of the Paul Scherrer Institute, along with basic information regarding synchrotron radiation. For organizational purposes, section 2.1 will describe the ALS and 2.2 will describe the SLS. The experimental apparatuses at the end stations 9.0.2 at the ALS and the VUV station of the SLS are presented together with background information about time-of-flight mass spectrometry and photoelectron spectroscopy.

2.1 Advanced Light Source (ALS)

Some experiments were performed at the Advanced Light Source of Lawrence Berkeley National Laboratories in Berkeley, CA (Figure 2-1).

Figure 2-1. The ALS floor diagram.

The ALS is a third generation synchrotron facility. Synchrotron light is the electromagnetic radiation produced from the oscillations of charged particles (in this case electrons) traveling near the speed of light through magnetic fields. Electrons are kept in a circular orbit using bending magnets and radiation
is generated via specific devices, such as bending magnets, undulators, or wigglers, ranging from radio waves to gamma-rays depending on the selected oscillation period.

### 2.1.1 ALS Beamlines

The ALS has 43 available beamlines that are used for a variety of techniques such as, Infrared Spectromicroscopy, Magnetic Spectroscopy, Macromolecular Crystallography (MX), Polymer Scanning Transmission X-Ray Microscopy (STXM), and Ultrafast/Femtosecond Dynamics Soft X-Ray (Figure 2-2). Research areas include molecular environmental science, structurally integrated biology for life sciences (SIBYLS), photoemission of highly correlated materials, and high resolution atomic, molecular, and optical physics. Our experiments were performed at beamline 9.0.2 Chemical Dynamics, which is able to deliver photons between 7.8 and 25 eV. This is the ideal energy range for studying combustion chemistry, atmospheric chemistry, and detecting free radicals or other intermediate species.

### 2.1.2 ALS Components

The ALS consists of an electron gun to produce electrons, the linear particle accelerator, a tubular ultra-vacuum chamber with radiofrequency cavities (RF) as the booster ring, and the storage ring that is also under ultra-vacuum conditions using bending magnets to direct the electrons around the ring and undulators and wigglers to produce synchrotron radiation.

![ALS Beamlines](image)

**Figure 2-2.** The available beamlines at the ALS.
2.1.2.1 Linear Particle Accelerator

Linear particle accelerators (LINACs) are simply electron guns. Electrons are produced, bunched, and accelerated down a tube towards its target. At the ALS the electrons are generated using a heated barium aluminate cathode and pulled down the LINAC, shown in Figure 2-3, using an anode gate pulsing at 500 MHz, which loosely bunches electrons every 500 millionths of a second. These electrons are then further bunched by a Klystron buncher that delivers powerful microwave bursts and produces tighter bunches of electrons while speeding them up to 60% the speed of light before injection into the booster ring.$^1$

![Figure 2-3. A simplified diagram of a linear particle accelerator (LINAC).$^1$](image)

2.1.2.2 Booster and Storage Ring

Electrons are injected from the LINAC into a 1.9 GeV booster ring that uses RF cavities to accelerate the electrons further to 99.999994% the speed of light under ultra-vacuum conditions. Next, the electrons are injected into the storage ring, which is also under ultra-vacuum conditions, where the synchrotron radiation is produced by undulators, wigglers, or bending magnets. The system shown in Figure 2-4 uses bending magnets (B), quadrupoles (QFA, QDA, QF, and QD), and sextupoles (SF and SD) to guide the electrons around the ring rather than the linear path they would take otherwise. The energy lost from the small amounts of radiation emitted from the path change caused by the bending magnet is replenished by a RF cavity to increase the life of the particles.
Periodically, electrons must be replaced due to collisions with the ring walls and residual gas molecules in order to produce enough radiation to run experiments. The ALS is equipped with a top-off injection mode to allow for almost continuous operation. This top-off injection mode means that electrons can be added to the storage ring after acceleration without interrupting the production of radiation.

2.1.2.3 Undulators and Wigglers

Undulators, wigglers, and bending magnets create magnetic fields that are used to oscillate electrons in the storage ring. A general schematic is shown in Figure 2-5. These oscillations are caused by a series of strong magnets with alternating poles. The difference between undulators and wigglers is explained by the $K$ parameter, which is mathematically defined by the equation below, where $e$ is the charge of the electron, $B_0$ is the amplitude of oscillation, $\lambda_H$ is the period of oscillation, $m_0$ is the rest mass of the electron, and $c$ is the speed of light:\(^2\)

$$
K = \frac{eB_0\lambda_H}{2\pi m_0 c}
$$

(2.1)

$K$ corresponds physically to the product $\varepsilon\sigma_M$, where $\varepsilon$ is the energy of each electron (about 1.5 GeV at the ALS) and $\sigma_M$ is the maximum deflection angle of the undulator or wiggler. Due to the larger amplitudes of oscillation, the undulators cause the electrons to enter a relativistic motion, which means the frequencies emitted can be calculated by Equation 2.2:\(^2\)

$$
\nu_n = n\nu_1 \approx \left(\frac{n(2\gamma^2)}{\lambda_H}\right)\left(\frac{1 + K^2}{2 + \gamma^2 \theta^2}\right)^{-1} \quad n = 1, 2, 3, \ldots
$$

(2.2)
Here $n$ is the harmonic number of the wave in question and theta is the angle at which the photon is being emitted. For a small collection cone (like what is produced in the undulator used), only odd number harmonics are emitted. For an undulator, the magnetic field is weaker than a wiggler and $\alpha_M < \gamma^1$. Gamma$^1$ is the amplitude of the cone emission of radiation and alpha is the deflection angle caused by the undulator as shown in Figure 2-6.

![Diagram showing the relation of the angle of divergence of radiation ($\gamma^1$) compared to the maximum deflection angle ($\alpha_M$).]

The undulator used at beamline 9.0.2 has a 10-cm-period and is called the U10.0. It produces a brightness of about $10^{16}$ and $10^{17}$ photon/sec/0.1% BW mm$^2$ mrad$^2$ in the 5-15 eV range (Figure 2-7) before being further filtered through the gas filter and monochromator.$^3$
Figure 2-7. Brightness of the U10.0 undulator at various photon energies before being filtered through the monochromator and gas filter.\(^3\)

The synchrotron radiation is filtered in the 9.02 beamline through a windowless gas filter filled with 30 Torr of argon, krypton, or neon to remove higher harmonics of the synchrotron radiation. Argon, krypton, and neon are ionized at 15.8 eV, 14.0 eV, and 21.6 eV, respectively. This means that nearly all resonance frequencies above 14.0 eV will be removed by the filter and all lower energy photons will pass through unaffected. Finally, the beam energy band is further narrowed through a 3-m off-plane eagle monochromator. The brightness after the filter and monochromator is reduced to \(10^{14}\) photons/s/0.1% BW mm\(^2\) mrad\(^2\) at the ionizing region at T3 (endstation 9.0.2.3). Figure 2-8 shows the schematic of the whole chemical dynamics end station (9.0.2.) and location of the gas filter and monochromators.\(^1\)

Figure 2-8. A schematic of the synchrotron radiation as it is directed into the gas filter and monochrometer to T3, which is end station 9.0.2.3.\(^1\)
2.1.3 End Station 9.0.2.3 – Multiplex Apparatus for Combustion Experiments

Experiments performed at the ALS were done using a multiplex photoionization energy- and time-resolved time-of-flight mass spectrometer (Figure 2-9). The three main parts of the instrument are the reactor tube, the time-of-flight mass spectrometer, and detection system.

2.1.3.1 The Reactor Tube

The reactor is a 62 cm quartz slow flow tube with a 1.27 cm outer diameter and 1.05 cm inner diameter. The slow flow allows an even distribution of radicals and reactants throughout the tube, which consents an accurate measure of the time traces without a bulk sample size. Reactants and inert gases are flown through the reactor tube using individually calibrated flow controllers. The pressure in the reactor cell is measured with a capacitive manometer that controls a throttle valve connected to a Roots pump (discussed in section 2.1.3.2). Experiments can be performed at pressures of 3-10 Torr. Temperature in the tube is monitored by a thermocouple 3 cm downstream of the pinhole and is controlled with nichrom tape wrapped in a layer of square weave yttria-stabilized zirconia cloth (ZYW-15, Zircar Zirconia, Inc.).

Figure 2-9. Schematic of the reactor tube and multiplex photoionization energy-resolved time-of-flight mass spectrometer using tunable VUV radiation from the ALS.
The cloth is surrounded by two halves of a gold plated copper sheath to hold it in place and to keep the temperature stable. Experiments can be performed between 298 and 1000 K. Gasses effuse through a 650 μm pinhole on the side of the reactor tube into the source chamber that is pumped by a 3200 L s\(^{-1}\) oil free turbomolecular pump (discussed in section 2.1.3.2). Gasses are then directed into the ionizing region with the use of a 0.15 cm skimmer that is 0.2–0.3 cm downstream of the pinhole. The ionizing region is pumped with a turbomolecular pump with a pumping speed of 1600 L s\(^{-1}\) and the detector region is pumped with a turbomolecular pump with a speed of 700 L s\(^{-1}\). Both pumps are backed by oil free scroll pumps (discussed in section 2.1.3.2).\(^4\)

### 2.1.3.2 Vacuum System

In order to have accurate results, all of the components of the apparatus must be under vacuum to ensure there is no contamination. The three types of vacuum pumps used are roots pumps (reactor tube), turbomolecular pumps (ionization region and detector), and oil free backing scroll pumps (ionization region and detector).\(^4\)

Roots pumps consist of a pump housing that holds two lobes rotating in opposite directions that are interlocked. While the lobes rotate, they trap gas on the sides of the housing pump and eventually expel it as shown in Figure 2-10. Roots pumps typically rotate at 1000–3000 rpm and can reach pressures as low as \(10^{-4}\) Torr.\(^5\)

\[\text{Figure 2-10. Cutaway of a Roots pump showing the operation cycle (1-5).}\] \(^5\)
Scroll pumps are used first to pump down the source chamber, ionization region, and detector. They have the distinct advantage of being oil free, which is crucial to avoid any contamination of experiments. Scroll pumps operate with two opposite spirals where one is orbiting inside of the other that is fixed (Figure 2-11). They typically operate at speeds of 12–25 cubic feet per minute and also have the advantages of simple structure, low cost, and easy maintenance. Typically, pressures of $10^{-4}$ Torr can be achieved.

**Figure 2-11.** Simple schematic of a scroll pump.⁷

Turbomolecular pumps are used to pump the source chamber, ionization region, and detector with pumping speeds of $3200 \text{ L s}^{-1}, 700 \text{ L s}^{-1},$ and $1600 \text{ L s}^{-1}$, respectively. Turbomolecular pumps work through a series of turbines rotating in opposite directions to force gases to move in a desired direction (Figure 2-12). The collisions with the turbines, which have a decreasing angle down the pump housing, force the gas molecules out and can reach pressures as low as $10^{-8}$ Torr.⁸

**Figure 2-12.** Cutaway view of a turbomolecular pump showing the opposite spinning turbines and decreasing angles.⁸
2.1.3.3 Excimer Laser and Radical Sources

The main source of radicals in the experiments to be discussed later is Cl₂. A mixture of 1% Cl₂ in He is used as a radical precursor to produce Cl atoms. Other possible radicals include OH (from H₂O₂) and CH (from CHBr₃).

A typical laser system consists of a lasing medium that is used to generate light. In the case of an excimer (excited dimer) laser, the medium is a high pressure cell filled with a noble gas (Ar, Kr, or Xe), fluorine gas (F₂), and a buffer gas (He). An electrical pulse is used to create a charged noble gas atom (xenon in this example) and dissociate the fluorine gas as shown as step “E” in the simplified schematic (Figure 2-13). These charged atoms can then react quickly to form the excited dimer XeF∗ (4 → 3). The recombination of F‾ and F (4 → 1) is slow relative to the formation of the XeF∗, which creates an abundance of excited dimers that is more commonly referred to as population inversion. In this process, the lifetime of state 3 is much longer than that of state 4. Therefore, the system gets trapped in state 3 and creates a system where there is a higher population of excited molecules than ground state molecules. This excited state will slowly decay though radiative transition (3 → 2) that produces the UV pulse of 351 nm along with the ground state noble gas and two fluorine atoms. The fluorine atoms finally recombine (2 → 1) to form the starting species and finishing a single pulse generation cycle. The UV pulses can easily be collimated in the cavity and directed towards the laser output. The main advantage of using an excimer laser is the low spectral bandwidth of the pulse (typically less than 0.001 nm), which means there is no need for a monochromator. In addition, the simplistic design of the cavity allows beam to be focused easily so the divergence is very small (3 x 1 mrad).

The UV pulses are focused into the reactor tube to create radicals through photolysis. The available wavelengths are 193 nm (ArF excimer), 248 nm (KrF excimer), and 351 nm (XeF excimer). The choice of the wavelength is based on selected radical. The unfocused laser has a fluence of 10-60 mJ cm⁻² and a pulsewidth of 20 ns. Its repetition rate can be changed up to 10 Hz, but our experiments are typically carried out at 4 Hz.
Figure 2-13. A simplified schematic showing reaction to form UV pulses in an excimer laser. The initial electrical pulse (E) creates charged species that react to form an excited dimer. These dimers relax through a radiative process before recombination to the original species.

2.1.3.4 Time-of-Flight Mass Spectrometer

Experiments at the ALS were performed using a multiplexed time-of-flight mass spectrometer (TOF-MS). A multiplex apparatus allows the simultaneous detection of multiple properties that in our case are both the reaction time and photon energy dependence of the detected species. The molecules that effuse from the source chamber are ionized by the synchrotron radiation and sent into the TOF-MS. After ionization, the ions pass through a small slit to reduce the spread of the beam into an electric field that accelerates the particles into the drift region. Since the ions have the same kinetic energy while enter the drift region, and the same electric field is applied to all particles (+150 V pushing and -150 V pulling), the velocity of each ion can be calculated by Equation 2.3, where $z$ is number of charges on the ion, $e$ is the electron charge, $E$ is the electric field in volts, and $m$ is the mass of the ion. In the investigated photon energy range the ions all have a charge of +1 and therefore $m$ is mathematically equal to $m/z$, the mass-to-charge ratio.

$$v = \sqrt{\frac{2zeE}{m}} \quad (2.3)$$

Substituting the path length to the detector ($l$) and time ($t$) for the velocity and rearranging for time, yields Equation 2.4 below:
Through experiments with a calibration gas, a square-root relationship can be obtained between time of flight and \( m/z \) below, where \( \alpha \) and \( \beta \) are found empirically (Equation 2.5). \( \beta \) is dependent on the electric field and path length (Equations 2.6):

\[
t = \alpha + \beta \sqrt{m/z}
\]

\[
\beta = \frac{i}{\sqrt{2zeE}}
\]

While traveling through the drift region ions with smaller masses move faster and reach the detector first, whereas the heavier ions will reach it later, which allows us to discriminate the masses and identify different products. A voltage of +150 V is used to push and the -150 V is used to pull the positive ions through the drift region perpendicularly with respect to the initial direction towards the detector.\(^4\) After traveling through the drift region the ions are detected by a 44 mm chevron-plate-style microchannel plate configuration.\(^4\)

### 2.1.3.5 Microchannel Plates

Microchannel plates (MCPs) are used to amplify the signal of particles. They consist of a stack of photomultiplier tubes that are normally coated with an electron emitting substance like silicon dioxide over conductive lead oxide with a positive potential to force electrons down the path as shown in Figure 2-14.\(^{15}\) In simple terms, the MCPs act as a gain medium to increase the signal of the reaction products and decrease data acquisition times. This is accomplished using photomultiplier tubes, which create a spray of scattered electrons when a particle strikes inside the tube (Figure 2-14). The scattered electrons are then detected as an output current on an anode (Figure 2-15) that can be analyzed using a computer coupled with an oscilloscope or digitizer.\(^{15}\)
A single microchannel plate can have a gain of up to $10^4$, but by stacking plates at alternating angles it is possible to increase gains to $10^6$–$10^7$ (Chevron stack) with two MCPs stacked or $10^8$ (Z-stack) for 3 MCPs stacked as shown in Figure 2-15. Our experiments use a time sensitive 44 mm chevron-plate-style microchannel array that increases gains about $2 \times 10^7$.

2.2 The Swiss Light Source (SLS)

The SLS is a third generation synchrotron facility located at the Paul Scherrer Institut in Villigen, Switzerland. Figure 2-16 shows the basic layout of the building.
Figure 2-16. The building floor layout of the SLS at the Paul Scherrer Institut. (1) is an office building with control room, labs, and offices for 80 people on 3 levels. (2) is a technical gallery with power supplies and RF-stations. (3) is the tunnel with concrete shielding walls, which holds the storage ring, LINAC, and booster ring. (4) is the beamline area. (5) is the outer ring with 60 pillars, transport lane, and air inlet system to maintain a temperature around 25 °C.16

2.2.1 Available Beamlines of the SLS

There are 17 available beamlines at the SLS with photons ranging from infrared to hard X-rays as shown in Figure 2-17. Techniques such as X-ray absorption (XAS) and emission spectroscopy (XES), Infrared (IR) spectroscopy, Photoemission and Atomic Resolution Laboratory (PEARL), and others are used. Our experiments were performed in the 7–20 eV photon energy range, which is ideal for imaging photoelectron–photoion coincidence spectroscopy (iPEPICO) techniques.

Figure 2-17. The available beamlines at the SLS and the types of magnets used for each beamline.
2.2.2 Features of the SLS at the VUV Endstation

Synchrotron radiation is produced from a bending magnet. Wavelengths are selected using a monochromator and focused into a differentially pumped gas chamber to filter higher resonance harmonics. The photon flux is $10^{11} - 10^{12}$ s$^{-1}$ at a resolving power of 1:2500–10000 in the range of 5–20 eV with a horizontal exit slit of 100 μm–1 mm. The maximum interaction area in the PEPICO instrument is large due to the ionization region being 50 cm downstream and the divergence of the beam being 4 x 8 mrad.$^{16}$

2.2.3 SLS Components

Like the ALS, the SLS consists of 3 major components, which are the LINAC, the booster ring, and the storage ring. Within the storage ring, there are undulators and bending magnets that produce synchrotron radiation. At the VUV endstation, wavelengths are selected and filtered by monochromators and gas filters.$^{16}$

2.2.3.1 Linear Accelerator

Like the ALS LINAC, the SLS consist of 3 parts, the electron source, the buncher, and the accelerator. The electron source is a standard EIMAC cathode YU-171, which is a 90 kV conventional electron source (Figure 2-18).$^{17}$

![Figure 2-18. Simplified schematic of the EIMAC cathode YU-171.]

The electrons are fired in a maximum of 1 ns burst. The pulse can be decreased by a factor of 40 for additional tunability. Multibunch modes make use of a 499.652 MHz RF cavity to allow for the top-off injection method. The bunching section of the LINAC consists of a 500 MHz subharmonic prewave
buncher, a 4 cell travelling wave buncher, and a 16 cell travelling wave buncher shown in Figure 2-19. Electrons are then injected into the booster ring.

**Figure 2-19.** Simplified schematic of the entire bunching system.

### 2.2.3.2 Booster and Storage Ring

The booster ring can operate at a maximum energy of 2.7 GeV (Figure 2-20). It is mounted on the inner walls of the storage ring tunnel at the same height of the storage ring, which has the advantages of saving space, low field magnets with small apertures, simple stainless steel vacuum chambers, low power consumption, flexible repetition rates and field operating modes (including the option of acting as a storage ring at < 1.7 GeV), low emittance beam, clean injection into the storage ring, and simple booster line transfer.

**Figure 2-20.** Simplified schematic of the injection systems of the SLS.
The downside of this design is the large number of components needed, including 93 combined function magnets, 18 quadropoles, 18 sextupoles, 108 correction magnets, and 97 pumping stations.\textsuperscript{19}

The SLS storage ring can be filled in 2–3 minutes when empty. This design is able to provide an emittance of 4.8 nm rad at 2.4 GeV with dispersion free sections and $\approx$4 nm rad when allowing for some dispersion.\textsuperscript{18}

2.2.3.3 Bending Magnets and Undulators

The bending magnets and undulators operate on the same principles described in section 2.1.2.3. The VUV light is produced from bending magnet X04DB collimated using a copper mirror with a platinum coating. The measured photon flux is $10^{12}$ s$^{-1}$ @ $10^4$ BW (400 mA ring current) with a beam diameter of 2x1 mm to 2x4 mm. The resolution is $10^{-4}$ eV and photons between 3–150 eV can be produced, but only 5–21 eV are harmonic free.\textsuperscript{16}

2.2.3.4 Monochromator and Gas Filter

Two silicon gratings are available with 600 and 1200 mm\textsuperscript{-1} line density for 5–15 and 15–30 eV energy ranges, respectively (Figure 2-21).\textsuperscript{20} There is currently a third grating available, which is a new ruled 150 groove/mm gold coated grating blazed at an angle of 1.29$^\circ$. This new grating is mainly used for pyrolysis experiments because it shows an increase in photon flux of 6-8 times in the energy range of 8-10 eV, which is normally the range to detect radicals and intermediates.\textsuperscript{21} The monochromator is a custom made “turn-table” style with a pitch angle scanning range of $\pm 15^\circ$, roll angle adjustment of $\pm 1.5$ mrad ($\pm 6$ $\mu$rad precision), and a yaw adjustment of $\pm 2.5$ mrad ($\pm 3$ $\mu$rad precision).\textsuperscript{21} This monochromator decreases the amount of out-of-vacuum alignment requirements, allows for easy grating exchange, and switching between gratings under vacuum conditions. After the monochromator selects the wavelength, a mirror is used to direct the radiation into the gas filter.\textsuperscript{21} The gas filter (Figure 2-22) is windowless and consists of 7 identical chambers (sections 2-8).\textsuperscript{22} The bore sizes range from 1 mm (section 7 to 9) to 3.9 mm (between sections 1 and 2).\textsuperscript{22}
Sections 1-5, 8, and 9 are each connected to a set of turbomolecular vacuum pumps and vacuum gauges. The pumps will be described below. Section 1 is slightly longer to allow the attachment of a viewport for alignment purposes. Section 7 is equipped with a vertical and horizontal slit to adjust the spot size in the ionization region of the PEPICO instrument. Section 6 is fitted with a flow meter and vacuum gauge to monitor the pressure of the gas filter to ensure it is below 30 mbar. The typical operating pressure during experiments is 10 mbar. If the pressure exceeds 30 mbar a pneumatic VAT series 75.2, DN40 fast valve, 3 m upstream from the gas filter, is shut to ensure no gases leak into the storage ring. Section 9 is a differential pumping section and connects to the iPEPICO endstation.

Sections 1 and 2 are pumped with two 75 L s⁻¹ TMU 071 P turbopumps. The other sections are pumped with three TMH-261-250-010 P splitflow turbopumps (280 L s⁻¹ sections 3 and 9, 205 L s⁻¹ sections 4 and 8, and 10 L s⁻¹ sections 5 and 7) supplied by Pfeiffer Vacuums.
2.2.4 iPEPICO Instrumentation, Electron, and Ion Optics

The iPEPICO instrument consists of two main parts shown in Figure 2-23. The source chamber where the sample is inserted and the ionizing region where the electron and ion optics are located.

![Image of iPEPICO instrument](image)

**Figure 2-23.** The iPEPICO instrument at the VUV beamline of the SLS. On the left is the source chamber where the sample is inserted and the synchrotron radiation enters in the back of the machine. The chamber on the right is another source chamber that is used in pyrolysis experiments.

2.2.4.1 iPEPICO Instrumentation

The samples are placed in a vial that is pumped and flushed with argon. A needle valve is used to control the sample flow into the source chamber that is kept at a pressure between $10^{-5}$-$10^{-4}$ mbar during operation. This is performed using a 5000 L s$^{-1}$ cryogenic Leybold COOLVAC CL pump driven by a compressor unit backed with an Adixen ACP 40 G series Roots pump.$^{21}$ The cryogenic pump is also backed by an Adixen ACP 28 G series 2 Roots pump.$^{21}$ All of these pumps are also backed by an oil-free foreline system.$^{20}$ The source chamber is continuously effusing through a skimmer that is held 2 mm from the ionizing beam.$^{21}$ The ionizing region is pumped using a 1500 L s$^{-1}$ Leybold COOLVAC 1500 CL cryogenic pump with the same compressor and roots pump as the 5000 L s$^{-1}$ cryogenic pump described above, and a 500 L s$^{-1}$ turbomolecular pump that is also backed with a roots pump.$^{20}$ Again, all of these pumps are backed with an oil-free foreline system.$^{20}$ Typical operation pressures in the ionization region are $2-6 \times 10^{-6}$ mbar.$^{21}$

29
2.2.4.2 Electron and Ion Optics

The set-up used is known as symmetric double velocity map imager because the same time and position sensitive detection plates (Roentdek DLD40) are used for both the electron and ion detections (Figure 2-24). The extraction field ranges between 20-160 V cm$^{-1}$ across three electrodes that are spaced 12 mm apart with openings of 8, 20, and 15 mm. The third electrode was added based on SIMION simulations that showed the velocity map focusing conditions would be greatly improved with the third plate to decrease the spot size of threshold coincidences. The electrons and ions are sent into their respective drift regions that are both encased in $\mu$-metal to ensure there are no interactions with any external magnetic fields. The electron detector is not completely surrounded in $\mu$-metal but experiments have shown it does not affect the image quality.

![Figure 2-24. A general diagram of the ionization region and detector layout of the iPEPICO instrument.](image)

Figure 2-25 shows the general layout for the ion and electron detectors. The mask plate is used to shield a majority of the “hot” ions and electrons with excess kinetic energy and elongate the life of the MCPs. The MCPs are stacked in a chevron configuration as describe earlier. The two detector plates each have four delay lines ($x_1$, $x_2$, $y_1$, and $y_2$) that are processed after constant fraction discrimination by an 8-channel ATR19 unit and recorded by a HPTDC8-PCI card. The positions are found by the differences of the $x_1$, $x_2$, $y_1$, and $y_2$. 

and $y_1, y_2$ positions and the event time stamp corresponds to the average of these four values.\textsuperscript{21} Using this information it is possible to subtract the zero kinetic energy electrons and ions from the hot electrons and ions to get an accurate threshold electron spectrum of the parent molecules and dissociative fragments.\textsuperscript{24} This process will be explained in chapter 3.

\textbf{Figure 2-25.} A general diagram showing the layout of the detector set-up. The mask is used to shield excess hot coincidences, the two MCPs are in a chevron configuration, and the collector is the Roentdek DLD40 delay line detector.\textsuperscript{23}
2.3 References


12. Thomas, V. R.; Schreiner, A. F.; Xie, T.-y.; Chen, C.-L.; Gratzl, J. S., Photolytic Dechlorination of 4-Chlorophenol in O2-Saturated Aqueous Solutions in the Absence of Photocatalysts or Additives Using


Chapter 3

Theoretical Concepts and Methodology

In this chapter, concepts such as the photoelectric effect, photoionization, and the Franck-Condon Principle will be discussed along with computational and analytical techniques. The programs used in the data collection and analysis will be also discussed.

3.1 Photoionization

Photoionization is based on the photoelectric effect, where a molecule absorbs a photon and ejects an electron. The energy to remove an electron is known as the ionization energy (IE) and can be determined by equation 3.1.

\[ M + h\nu \rightarrow M^+ + e^- \]  \hspace{1cm} (3.1)

In this equation M is the molecule under study, h\nu is the photon, M\(^{+}\) is the cationic state of the molecule, and e\(^{-}\) is the electron. From this expression, it can easily be determined that \( \Delta H_{\text{rxn}} = \text{IE}. \) The two types of ionization energies that will be discussed are the adiabatic ionization energy (AIE) and vertical ionization energy (VIE). Adiabatic ionization energies refer to the electronic transition between the lowest energy electronic, rotational, and vibrational (rovibronic) state of the neutral molecule to the lowest energy rovibronic cation state. Vertical ionization energies are the electronic transitions between the lowest energy rovibronic state of the neutral molecule to a vibrationally excited state of the cation with an identical configuration of the neutral state. Because of this, the Franck-Condon overlap will be the greatest (see section 3.2) yielding the highest intensity.

When a photon with enough energy is absorbed by a molecule, it may cause certain bonds to break within the molecule. This is known as dissociative ionization. Figure 3-1 shows the potential energy surfaces of a neutral and cationic state of a molecule along with the photon absorption to increase the internal energy past the dissociation threshold.
The energy to reach this threshold is known as the appearance energy (AE). Using the reaction (3.2) and equation 3.3, it is possible to calculate the appearance energy (if no barrier for dissociation is present) where AB is the neutral molecule, A$^+$ is the cation fragment, B is the neutral fragment, e$^-$ is the electron, and $E_{CBS-QB3}$ are the calculated CBS-QB3 energies of A$^+$, B, and AB (see section 3.5.2 for a description of CBS-QB3 calculations).

\[
AB \rightarrow A^+ + B + e^- \quad (3.2)
\]

\[
AE = E_{CBS-QB3}(A^+) + E_{CBS-QB3}(B) - E_{CBS-QB3}(AB) \quad (3.3)
\]

3.2 Franck-Condon Principle

The Franck-Condon Principle states that because the nuclei are so much more massive than electrons, electronic transitions take place on a much faster time scale than the nuclei can move.\(^3\) This means that during photoionization the transition is vertical. This can be described quantitatively by the degree of overlap of the wave functions, otherwise known as the Franck-Condon factor.\(^3\)
Quantitatively, the Franck-Condon factor can be determined from the dipole moments as follows.\(^3\)

\[
\mu_{\varepsilon_f \varepsilon_i} S(\nu_f, \nu_i) = -e \sum_i \int \psi_{\varepsilon_f}^* r_i \psi_{\varepsilon_i} d\tau \int \psi_{\nu_f}^* \psi_{\nu_i} d\tau
\]

(3.4)

Here, \(\mu_{\varepsilon_f \varepsilon_i}\) is the matrix element of the electric dipole moment arising from the redistribution of the electrons, \(S(\nu_f, \nu_i)\) is the Frank-Condon factor for the final and initial vibrational states \((\nu)\), \(r_i\) is the bond distance, and \(\psi\) and \(\psi^*\) are the wave functions and its complex conjugate for the initial and final electronic and vibrational states.\(^3\) If the overlap is perfect, \(S = 1\) and if there is no overlap, \(S = 0\).

### 3.3 Threshold Photoelectron Spectra (TPES) and Photoionization Efficiency Curves (PIE Curves)

Photoelectron spectroscopy studies the transitions of electrons excited and ejected out of various molecular orbitals using photons of known energy.\(^3\) Each electron that is ejected obeys the equation below where \(h\nu\) is the photon energy, \(I_i\) is the ionization energy of an orbital \(i\), \(m_e\) is the mass of the electron, and \(v\) is the velocity of the electron.\(^3\)

\[
h\nu = \frac{1}{2} m_e v^2 + I_i
\]

(3.5)

Once the photon energy is equal to or larger than the ionization energy, all electrons will have a total kinetic energy greater than or equal to zero. The electrons can be accelerated through a drift tube and then collected by a detector. If the proper deflectors are used to direct the electrons to the detectors, a mask (see section 2.2.4.2) can be placed in front of the micro channel plates to separate electrons with zero kinetic energy from “hot” electrons with excess kinetic energy.\(^4\) The subtraction of these two signals, shown in Figure 3-2, can provide a threshold photoelectron spectrum (TPES) that corresponds only to the electrons detected with zero kinetic energy and therefore relate directly to the molecular orbital energy.\(^4\) The procedure for this subtraction will be discussed in depth in section 3.7.2.
In a similar process, after photoionizing a molecule, the cation can be accelerated towards a detector with the same process as described for the electrons. With this technique the total counts of ions are used. The counts plotted against the photon energy will provided the photoionization efficiency curve (PIE curve) or photoionization spectrum. Every molecule will have its own distinct ionization energy and Franck-Condon factors so the PIE curve can be used for identification, which will be discussed in section 3.7.1.

### 3.4 Photoionization Cross Sections and Branching Fractions

In addition to qualitative analysis using PIE curves, quantitative results can be obtained if the photoionization cross sections of the starting material and products are known. Photoionization cross sections are the area over which the photo-radiation can ionize a molecule. Units are typically given in Megabarn (Mb) ($1 \text{ Mb} = 10^{18} \text{ cm}^2$).

Cross sections can be found in the literature and used as long as they are measured in the same photon range of interest. If the cross section is not reported in literature, it can be measured. This is done by determining the concentration of the starting material and comparing it to a reference with a well-known...
photoionization cross section, such as ethene, propene, or 1-butene.\textsuperscript{7} Equation 3.6 shows the relation of the signal intensity ($S(E)$), the cross section at a specific energy ($\sigma(E)$), the concentration ($C$), and the mass discrimination factor ($\alpha$). The mass discrimination factor has been found empirically through the use of many known gas mixtures to be $(m/z)^{0.643\pm0.086}$.\textsuperscript{8} Rearrangement to equation 3.7 provides the photoionization cross section of the target molecule ($t$) compared to the reference ($r$).\textsuperscript{9}

\begin{equation}
\frac{S_t(E)}{S_r(E)} = \frac{\sigma_t(E)C_t\alpha_t}{\sigma_r(E)C_r\alpha_r}
\end{equation}

\begin{equation}
\sigma_t(E) = \frac{S_t(E)\sigma_r(E)C_r\alpha_r}{S_t(E)C_t\alpha_t}
\end{equation}

The concentration of the target and reference are calculated based on the selected flow into the reactor cell, mix percent, and total pressure.\textsuperscript{9} The uncertainty of the measured cross sections can be determined by considering the uncertainty of each individual quantity in equation 3.7. The uncertainty of the mass discrimination factor has been experimentally determined to be ±0.086 as stated above.\textsuperscript{8} The uncertainty of the photoionization cross section of the target molecule is either given in the literature or determined from previous experiments. Uncertainty of the concentrations are determined under the assumption that 100% of the molecules in the beam are ionized and detected. Equation 3.8 shows how the number densities (concentrations) of the molecular beam are calculated. Here, $P_T$ is the pressure of the reactor tube, $T_T$ is the temperature of the reactor tube, $M_i$ is the percentage of species $i$ in the cylinder, and $I_{Flow}$ and $T_{Flow}$ are the flow rates of species $i$ and the total flow, respectively, and all remaining quantities are constants required for unit analysis.

\begin{equation}
C_i = \frac{P_T}{62.364 \times T_T} \frac{M_i I_{Flow}}{T_{Flow}} \frac{6.022 \times 10^{23}}{1000}
\end{equation}

The uncertainties of the individual quantities are all dependent on the measuring devices. The pressure transducers have an uncertainty of ±5% of the measurement (for $P_T$ and $M_i$), all flow transducers have an error of ±1%, and temperature probe has an uncertainty of ±0.1%. Lastly, because the apparatus counts single ions, Poisson Statistics must be used.\textsuperscript{10} The standard deviation of the signal intensity can then be related to the mean ion counts of all laser shots by $\sigma = \mu^{0.5}$.\textsuperscript{10} If a compound does not have a reported cross
section in the literature, and it cannot be purchased or synthesized easily, then the photoionization cross section is approximated by using a known cross section of a similar molecule.

Once the cross sections are known or estimated, branching fractions are calculated as the ratio for the amount of product formed against the total amount of starting material reacted as shown in equation 3.9. In this equation, $S$ is the signal intensity of the starting material ($s$) and product ($p$), $\sigma$ is the cross section of $s$ or $p$, and $\alpha$ is the mass discrimination factors of $s$ or $p$. The mass discrimination factors are the same as defined above.

$$\text{Branching Fraction} = \frac{S_s \sigma_p \alpha_s}{S_p \sigma_s \alpha_p}$$

(3.9)

The branching fractions are calculated for each primary product. Primary products are the products that form at the same rate as the depletion of the starting material. If all primary products are account for then the sum of all branching fractions should be 100 %.

### 3.5 Computational Methods

Computational calculations are performed in the Gaussian 09 program suite\textsuperscript{11} and visualized in Gaussview 5.0.9.\textsuperscript{12} The Gaussian software allows for the use of different semi-empirical and \textit{ab initio} methods. These techniques are extremely useful for the prediction of many molecular parameters including harmonic vibrational frequencies, rotational constants, force constants, ionization energies, appearance energies, and many others.\textsuperscript{2}

Semi-empirical methods take parameters from experimental data to simplify calculations and estimate molecular properties of the species in question.\textsuperscript{2} In contrast, \textit{ab initio} methods use various approximations to solve the Schrödinger equation (3.10).\textsuperscript{2,3} Below, $\hat{H}$ represents the Hamiltonian operator, $E$ is the total electronic energy, and $\psi$ is the wave function of the system.

$$\hat{H}\psi = E\psi$$

(3.10)

Two computational methods were employed throughout this work. Density Functional Theory (DFT) was used to optimize structures and obtain harmonic vibrational frequencies for modeling breakdown diagrams and obtaining dissociation rates in PEPICO studies. Second, the Complete Basis Set
(CBS-QB3) composite method was used to obtain zero-point corrected energies for energetics calculations. This includes ionization energies, appearance energies (as described in section 3.1), and enthalpies of reaction and formation.

### 3.5.1 Density Functional Theory (B3LYP and UB3LYP)

The level of theory used for calculating vibrational frequencies of all neutral closed shell species for the PEPICO studies is the Becke-3-Lee-Yang-Parr (B3LYP) theory. This theory uses semi-empirical combination of an exchange-correlation energy functional\(^{13}\) with the local-spin-density exchange-correlation approximation\(^{14}\) and gradient correction terms\(^{15}\) proposed by Becke. It is used in combination with the Lee-Yang-Parr correlation functional\(^{16}\). The unrestricted B3LYP theory (UB3LYP) uses the same method but wave functions are unrestricted to remove the unwanted mixing of electronic states to eliminate the possibility of spin contamination\(^{17}\). This method is only applied to open shell molecules, such as cations and radicals. The reason for using this method is that it provides fairly accurate geometry and frequency optimizations with relatively low computational cost. For the PEPICO studies, only accurate vibrational and rotational frequencies are needed to calculate the internal energy distribution, so DFT is ideal since we do not need to spend time calculating accurate energetics.

In addition to the choice in level of theory, a basis set must also be chosen. A basis set defines the space that the electrons can occupy when optimizing a structure. A larger basis set will not constrain the electrons as much and the approximations will be smaller, which should lead to more accurate computations. The only basis set used with the B3LYP and UB3LYP calculations is the 6-311+G(d,p).\(^{18}\) The “G” means Gaussian functions are used and the numbers “6”, “3”, and the “1’s” represent the number of Gaussian functions that describe the core (1s), inner (2s), and outer atomic orbitals (valence). The “+” means diffuse orbitals are used since open shell molecules typically have a very large HOMOs where the unpaired electron is localized. Lastly, the “(d,p)” represents the orbitals to apply these calculations to. Only d and p orbitals are needed for the first and second row elements.
3.5.2 Complete Basis Set Composite Method (CBS-QB3)

For calculations on the energetics of molecules, a composite method is used. This method is the Complete Basis Set (CBS-QB3) developed by Montgomery et al.\textsuperscript{19,20} It is chosen because of the accurate results combined with the relatively low computational cost.

CBS-QB3 begins by optimizing the geometry and vibrational frequencies using the B3LYP level of theory with the 6-31G basis set. Then, further optimizations are performed with the MP2/6-31G theory and basis set. Next, the energies are extrapolated using the UMP2/6-311G(3d2f,2df,2p) theory followed by MP4(SDQ)/6-31+G(df,p) and CCSD(T) with the inclusion of experimental atomic spin-orbit interactions. Typical energies are calculated with a total error of 4-5 kJ mol\textsuperscript{-1}.

Because this method performs optimizations with increasingly stringent levels of theory using the previously optimized structure, it saves on computational cost while ensuring accurate results. Before using calculated values, the vibrational frequencies should be checked to ensure there are no negative (imaginary) frequencies. The lack of imaginary frequencies means the molecule is at a minimum on the potential energy surface and is therefore a “stable” molecule rather than a transition state.

3.6 Statistical Rate Theories - Rice-Ramsperger-Kassel-Marcus Theory (RRKM)

Dissociations are by definition unimolecular. This means the rate of dissociation can be defined by equation 3.11, where [A] is the concentration of a species “A”, \( k \) the dissociation constant, and \( dt \) the time of interest. This equation can be integrated to give the expression below where [A\textsubscript{o}] is the initial concentration.

\[
\frac{d[A]}{dt} = k[A] \tag{3.11}
\]

\[
[A] = [A_o]e^{-kt} \tag{3.12}
\]

There are a few other factors to take into consideration in case of unimolecular dissociation reactions caused by photons, such as the initial state produced by the excitation, how fast the products produced are, the products identity, and the energy states of the products.\textsuperscript{21} Since the rate is dependent on the energy of all of the states, rate theories are defined in terms of energy and temperature.\textsuperscript{22} This is shown in equation 3.13.
where $k(T)$ is known as the canonical rate constant, $P(E,T)$ is the distribution of internal energies at a temperature $T$, and $k(E)$ is the microcanonical rate constant.\textsuperscript{21} Equation 3.13 is integrated over all energies above the dissociation energy ($E_o$). Typically, experiments will only determine the microcanonical rate constants because this is the only portion that the rate theories can be tested.\textsuperscript{21}

$$k(T) = \int_{E_o}^{\infty} P(E,T)k(E)dE$$  \hspace{1cm} (3.13)

For the RRKM theory, the microcanonical dissociation rates are defined in terms of the probability of a set of oscillators to dissociate once an energy in excess of the dissociation energy is absorbed by the molecule.\textsuperscript{21} This leads to the derivation of the equation 3.14 below, where $\sigma$ is the number of pathways that a process can occur (reaction degeneracy), $N^\dagger(E-E_o)$ the sum of vibrational states in the transition state at an energy from 0 to $E-E_o$, $h$ the Planck’s constant, and $\rho(E)$ the density of vibrational states at an energy $E$.\textsuperscript{21}

$$k(E) = \frac{\sigma N^\dagger(E-E_o)}{h \rho(E)}$$  \hspace{1cm} (3.14)

The important assumption for the applications of this theory is that energy can flow between the vibrational modes and will do so in a strictly statistical process.\textsuperscript{21} This allows the thermal distribution of the ground state of the molecule to be directly transposed to the cationic state upon the absorption of a photon (Figure 3-3).

3.7 Data Collection and Analysis

Once a particular molecule or a set of related molecules are chosen, data is collected from either the Advanced Light Source (ALS) or the Swiss Light Source (SLS) depending on the nature of the studies. This section will describe the process of collecting and analyzing data from both facilities.
Figure 3-3. The potential energy curves of a neutral species (AB) and cation (AB\(^+\)) where the thermal distribution is shifted directly upward to the cationic state with the same populations.\(^{23}\)

### 3.7.1 Advanced Light Source (ALS)

The apparatus at the ALS described in chapter 2.1 is used to study gas phase combustion and atmospheric reactions.\(^5,10\) The data is collected over a range of photon energies that is decided beforehand based on the ionization energies of the starting material and suspected products. Products can be predicted through many known combustion mechanisms as described by Zádor et al.\(^{24}\) Once the energy range is selected, it is scanned from the lowest to highest energy in 0.025 eV steps. At each photon energy, the photolysis laser is fired 240 times at a frequency of 4 Hz while the ions effuse out of the pinhole into the synchrotron radiation from the ALS. The resulting data, because of the multiplex capability of the apparatus, is represented by a 3-dimensional block, where the signal is a function of the photon energy (eV), mass-to-charge ratio (m/z), and reaction time (ms) as shown in Figure 3-4. Then, the data is sliced into 2-dimensional plots for visualization.
Figure 3-4. An example of the 3-dimensional data block obtained using the time resolved multiplex photoionization mass spectrometer at the ALS. The three axes are reaction time, mass-to-charge ratio (m/z), and photon energy (eV). In order to visualize the data on a computer, 2-dimensional slices are taken as shown.5

The two main 2-dimensional plots are the photon energy vs. m/z (energy resolved mass spectrum) and reaction time vs. m/z (time resolved mass spectrum; Figure 3-5). From photon energy vs. m/z, 1-dimensional slices at a selected mass yield photoionization efficiency curves (Figure 3-6). These spectra are used for identification of species, including isomers. The same process of taking 1-dimensional slices at a selected m/z from the time vs. m/z image is then used to study the kinetic traces of each relevant species. 0 ms represents the t₀ of the reaction, i.e., when the photolysis laser is fired. Three possibilities are shown in Figure 3-7 for the temporal behavior of a selected species, i.e., stable products, radicals, or starting material. Once all species have been identified, the kinetic traces of stable products are used to determine primary against secondary products. Products that appear at the same rate as the depletion of starting material are the most likely primary products sometimes. Depending on the specific experimental condition secondary reactions, especially those involving radicals, can be as fast as primary ones. The signal intensity and cross sections of these products and starting material are then used to quantify the product formations (see section 3.4). In addition, any observed radicals can be used to verify or propose possible reaction mechanisms.
Figure 3-5. Sample 2-dimensional slices of the data obtained from the time resolved multiplex photoionization mass spectrometer at the ALS. The top plot is photon energy vs. m/z and the bottom one is time vs. m/z.

Figure 3-6. Sample PIE curve of m/z = 114 showing the identification of different isomers based on the good agreement of the superimposition of experimental and/or simulated PIE curves onto the experimental data.
Figure 3-7. Sample kinetic traces showing a stable product formation (top), radical (center), and depletion (bottom).
3.7.2 Swiss Light Source (SLS)

The apparatus described in section 2.2 at the Swiss Light Source is used to study the photoionization behavior and dissociation rates of energy selected ions for various thermodynamic calculations. Like at the ALS, data is collected over a range of photon energies above the ionization energy of the species in question. After ionization the electrons are accelerated towards the detector and will arrive at its center if they have no excess kinetic energy. On the other hand, if they have excess kinetic energy, they will reach the outer ring of the detector or blocked by the mask. This procedure will provide an image like the one shown in Figure 3-8 below.

![Figure 3-8](image.png)

**Figure 3-8.** A typical image of the detection of electrons from the PEPICO instrument. White corresponds to the highest count and blue is the lowest.

Using the i²PEPICO program v1.5.2, an area defined as “circle” is used to count all of the coincidences that are within the center of the mask and correspond to the zero kinetic energy electrons. Next, an area is defined as “ring” will average the number of counts around the center to determine the average number of hot electrons that reach the detector. The subtraction of the ring counts from the center counts will provide the TPES as described in section 3.3. Figure 3-9 shows this process pictorially. With the use of delay lines (see section 2.2.4.2), it is possible to relate each electron count to the complementary fragmentation incident. This will supply a time-of-flight mass spectrum (TOF-MS) as shown in Figure 3-10.
Figure 3-9. Images showing the process of subtracting hot electrons from the zero kinetic energy electrons to provide the TPES.

Figure 3-10. A time-of-flight mass spectrum obtained after subtracting the hot electrons from the zero kinetic energy electrons. The x-axis is the time-of-flight (μs) and the y-axis is counts (a.u.)

Once a TOF-MS is obtained and the time-of-flights of all ions and fragments are known, the TOF-MS can be integrated at each photon energy to obtain the counts for all ions and fragments. Then, the fractional abundance of each ion or fragment can be plotted against the photon energy. This is known as a breakdown diagram (Figure 3-11).
A set of vibrational frequencies for the cationic and neutral parent, and transition states to products should be obtained through \textit{ab initio} or density functional methods. In addition, the rotational constants of the neutral parent must also be found to calculate the internal energy distribution using the Boltzmann formula below\textsuperscript{26}. In this equation $\rho(E)$ is the classical density of states function for rotational motions at an energy $E$, $k_B$ is the Boltzmann constant, and $T$ is the temperature.

$$P(E) = \frac{\rho(E) e^{-E/k_B T}}{\int_0^\infty \rho(E) e^{-E/k_B T}}$$

\textbf{Figure 3-11}. An experimentally obtained breakdown diagram showing the change in relative abundance of the parent ion (red circles) with respect to the first daughter ion (green circles).

This information can then be used in the MiniPEPICO program v189\textsuperscript{f26} to fit the experimental data using the RRKM theory describe in section 3.6.

In the cases with a “slow” first dissociation (rates between $10^3$–$10^7$ s\textsuperscript{-1}) an asymmetric peak will be observed in the TOF-MS. This is caused by only a limited percentage of the ions having enough excess energy to dissociate immediately. When this happens, the asymmetric peak must also be modeled as it contains rate information. This process is also performed in the MiniPEPICO program and a successful fit
is shown in Figure 3-12. The rest of the dissociations will happen at a slower rate due to the loss of translational momentum and the broadening of the daughter ions internal energy distribution (Figure 3-13) so the TOF peaks do not need to be fit.

**Figure 3-12.** A successful modeling of a TOF distribution of a daughter ion to obtain the dissociation rate information.

**Figure 3-13.** Experimentally determined internal energy distributions of a parent ion (P(C$_2$H$_5$)$_3^+$ compared to the broadening of the daughter cation (HP(C$_3$H$_5$)$_2^+$) and the neutral daughter ion (C$_2$H$_4$ + translational motion).
Once all dissociations have been successfully modeled, the curve should appear similar to Figure 3-14. With this information it is possible to extrapolate the 0 K appearance energies of the ions. The 0 K appearance energy (AE) of the first dissociation can easily be found as the photon energy where all of the parent ions dissociate. The first example is a fast dissociation (rates above $10^7$ s$^{-1}$), as shown in Figure 3-11. In this case, the 0 K AE is found when the ratio of parent ions to daughter ions reaches zero. The ratio can be found through equation 3.16. Here, $P_i$ is the normalized internal energy at a specific photon energy and $E_0 - IE$ is the difference between the photon energy that the parent ion signal vanishes ($E_0$) and the ionization energy of the neutral parent molecule ($IE$).

$$BD(hv) = \int_{0}^{E_0 - IE} P_i(e, hv) dE$$ (3.16)

In Figure 3-11, this occurs at 10.37 eV, which will be shown in chapter 6. Appearance energies for ions that form through a slow dissociation (rates between $10^3$ and $10^7$ s$^{-1}$) can be found through a similar method, but with an additional term to account for ions that do not dissociate within the timescale of the experiment and have an internal energy exceeding the dissociation barrier (i.e. the ions are detected before they dissociate). This additional term is shown in equation 3.17 where $\tau_{max}$ is the probability that the ion does not dissociate before detection and $k(E)$ is the internal energy-dependent rate constant.

$$BD(hv) = \int_{0}^{E_0 - IE} P_i(e, hv) dE + \int_{E_0 - IE}^{+\infty} P_i(e, hv) \cdot \exp(-k(E) \cdot \tau_{max}) dE$$ (3.17)

For competing (parallel) dissociations of species $i$ compared to all other species $j$, the 0 K appearance energy of $i$ can be calculated using equation 3.18. The term $k_i(E)/\sum_j k_j(E)$ is the branching ratio at a specific ion internal energy.

$$BD_i(hv) = \int_{E_0 - IE}^{+\infty} P_i(e, hv) \cdot \frac{k_i(E)}{\sum_j k_j(E)} \left(1 - \exp\left(-\sum_j k_j(E) \cdot \tau_{max}\right)\right) dE$$ (3.18)

The MiniPEPICO program contains a downhill simplex algorithm to fit these values, or they can be manually adjusted to obtain the best fit. Using these appearance energies and ionization energies it is possible to obtain very precise measurements of bond dissociation energies. Also, with the breakdown diagrams it is possible to obtain the dissociation rates of the parent ions if the rates are between $10^3$ and $10^7$
s$^{-1}$. Rates faster than this could not be observed in our experiments and slower rates cannot be discerned from competing processes, such as radiative decay. Therefore, they will not be discussed.

**Figure 3-14.** A modeled breakdown diagram that is used to extrapolate 0 K appearance energies, bond dissociation energies, and dissociation rates.$^{26}$
3.8 References


Chapter 4

Absolute Photoionization Cross-Sections of Selected Furanic and Lactonic Potential Biofuels

4.1 Abstract

Absolute photoionization cross sections of the molecules $\gamma$-butyrolactone (GBL), $\gamma$-valerolactone (GVL), $\alpha$-angelicalactone (AAL), and $\gamma$-methylene-$\gamma$-butyrolactone (GMGB), including partial ionization cross sections for dissociative ionization, are measured. The experiments are carried out using photoionization mass spectrometry (PIMS) at the Advanced Light Source, and an orthogonal extraction time-of-flight spectrometer is used for mass analysis. Photoionization of furan, 2-methyl furan (2-MF), and 2,5-dimethyl furan (2,5-DMF) is also investigated to confirm the accuracy of our measurements, which show a good agreement of the absolute partial photoionization cross sections with literature values. CBS-QB3 calculations of adiabatic ionization energies (AIE) and appearance energies (AE) agree well with the experimental results.

4.2 Introduction

Increasing demands for energy and a diminishing supply of fossil fuels are pushing the development of next generation biofuels. Commercial firms are already producing various biofuel alternatives or additives on an industrial scale for public use. Some of the alternatives being produced include esters, ethers, alcohols, furans, and lactones. Extensive combustion studies have been performed on saturated hydrocarbons, but the combustion of lactonic biofuels have not been studied as extensively.

Several techniques have been developed to determine photoionization cross sections of various molecules. Haddad et al. used a double ion beam in a dual ionization chamber to measure the cross sections of water, while West and Kjeldsen used a merged beam method to measure the cross sections of atomic ions. Cool et al. developed the technique of using PIMS to determine the cross sections of various molecules via the comparison to a known standard such as propene. A number of photoionization mass spectrometry (PIMS) studies have already been performed on biofuels, but lactones have not been
thoroughly studied. One technical issue is their low vapor pressure, which makes it difficult to quantify the amount in the gas phase.

In this paper the PIMS technique is used to determine the cross section of 3 furans and 4 lactones, namely furan, 2-methyl furan (2-MF), 2,5-dimethyl furan (2,5-DMF), γ-butyrolactone (GBL), γ-valerolactone (GVL), α-angelicalactone (AAL), and γ-methylene-γ-butyrolactone (GMGB), depicted in Figure 4-1. The furans are included in this study to establish the accuracy of the determination of cross sections for the dissociative photoionization fragments, by comparison with literature measurements. To the best of our knowledge, no studies on the photoionization cross sections of the four lactones have been reported. The fundamental importance of these measurements resides in providing crucial quantities that allow fuel quantification via photoionization mass spectrometry and development of quantitative kinetic models for the complex combustion of fuels.

GVL has been chosen for this study because of its promise as a next generation biofuel; it has been produced efficiently by various methods. One method of production developed by Heeres et al. includes a dehydration/hydrogenation of C_6-sugars using an acid catalyst. They report yields as high as 62% for the conversion to GVL from D-fructose using molecular hydrogen and a water soluble homogenous Ru-catalyst. Also, Deng et al. have developed a catalytic conversion process from biomass using a ruthenium catalyst and without an external H_2 supply. They reported yields as high as 95% starting with levulinic acid at temperatures of 200 °C. GVL also has potential applications as a starting material for developing new solvents and new methods of producing alkenes. The other three lactones studied are potential products of the initial oxidation of GVL based on established mechanisms for analogous molecules.

4.3 Experimental

4.3.1 Apparatus

Experiments were performed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory in Berkeley, CA. The apparatus will be briefly described here; a more in depth description has been provided elsewhere. Helium was flowed through the liquid samples, kept at 20 °C in a thermostatically controlled glycol bath. The resulting gas mixture (He carrying the equilibrium 20 °C vapor
a calibration gas containing 1% each of ethene, propene, and butene in argon, and additional He diluent are introduced into the reactor tube via calibrated mass flow controllers. The reaction tube is a 62 cm quartz slow flow reactor that is held at a pressure of 4 Torr. The gases effuse through a 650 μm pinhole into a source chamber that is evacuated by a 3200 L s⁻¹ oil-free turbomolecular pump and are directed into the ionizing beam.

Figure 4-1. Structures of the compounds investigated. A) furan, B) 2-methyl furan (2-MF), C) 2,5-dimethyl furan (2,5-DMF), D) γ-butyrolactone, (GBL) E) γ-valerolactone, (GVL) F) α-angelicalactone, (AAL) G) γ-methylene-γ-butyrolactone (GMGB). The numbering of the carbons on AAL and GMGB is the same as GVL.

The synchrotron radiation is generated by an undulator and filtered through a windowless gas filter filled with 30 Torr of Ar or Kr to remove higher undulator harmonic frequencies. The desired wavelengths are then selected by a 3m off-plane eagle monochromator with an energy resolution of 25 meV. After ionization, the ions are extracted, collimated and directed into a pulsed-extraction orthogonal acceleration mass spectrometer. The mass resolution \( M/ΔM \) is approximately 1600. After detection the signals are normalized at each photon energy for the photon current of the ALS using a calibrated VUV sensitive photodiode.

4.3.2 Measurement Procedures

All compounds had a stated purity of 99%, except for α-angelicalactone, which had a purity of 98%. Samples were degassed by freeze-pump thaw cycles and stored under vacuum until use. The vapor pressure of the sample at 20 °C was measured using a low pressure transducer with a 0.5% accuracy of
reading. This value is then divided by the total pressure in the bubbler during operation to calculate the mole fraction of the sample flowing from the bubbler to the reactor.

Adiabatic ionization energies (AIE) are determined with a linear extrapolation of the initial onsets of the photoionization efficiency curves as outlined and discussed elsewhere. Appearance energies (AE) are determined in this work using a procedure developed by Ruscic and Berkowitz. They accurately simulated photoion yield curves via a thermal distribution function outlined by Haarhoff, which was then convolved with many different functions until the best fit is obtained. They reported that the exponential functions give the most accurate simulations and AEs at 0 K can then be extrapolated by adding $2kT$ to the threshold energy used in the function.

Photoionization cross sections are determined using the relative ion signal ($S$) of a molecule $i$ at a specific photon energy ($E$) according to the expression

$$S_i(E) = \Lambda \sigma_i(E) c_i \alpha_i$$

that is a function of a mass- and photon energy-independent instrument factor ($\Lambda$), the energy dependent photoionization cross section ($\sigma_i(E)$), the concentration ($c_i$), and mass discrimination factor ($\alpha_i$). The mass discrimination factor, which accounts for mass-dependent detection efficiencies of parent ions, was derived experimentally for all masses ($m_i$) as

$$\alpha_i = m_i^{\beta}$$

where $\beta$ has been determined to be equal to $0.643 \pm 0.086$ using a gas mixture of known composition and photoionization cross sections. Using equation 4.1, the photoionization cross section of the target molecule ($\sigma_T$) can be found as a ratio of the signal intensity of the target ($S_T$), signal intensity of the standard ($S_S$), the concentrations of the target and standard ($C_T$ and $C_S$), the mass discrimination factors of the target and standard ($\alpha_T$ and $\alpha_S$), and the photoionization cross section of the standard ($\sigma_S$).

$$\sigma_T = \frac{S_T(E) \sigma_S(E) \alpha_S \alpha_T}{S_S(E) \alpha_T \alpha_S}$$

Mass discrimination factors are dependent on sampling efficiencies and the nature of the orthogonal time-of-flight design. For parent ions the composite mass discrimination factor is determined experimentally
by fitting to equation (4.2). The mass discrimination factor for daughter ions arising from dissociative ionization should depend on the kinetic energy release between the daughter ion and the neutral co-fragment, which complicates determining the mass discrimination factor for daughter ions. In this work we assume, for simplicity, that the mass discrimination factor for a given m/z ratio is independent of whether the ion is a parent or daughter ion. This assumption is supported by good agreement between our measured daughter ion intensities and literature values (Figures 4-2 to 4-4) for the furanic compounds. Previous experiments using known gas mixtures have shown that the uncertainties in measured cross sections on this mass spectrometer are at most ±15%.46

4.4 Computational

Structural parameters, including bond lengths, angles, and harmonic vibrational frequencies of reaction species are calculated using the CBS-QB3 (Complete Basis Set) composite model of Petersson and colleagues.48-50 This electronic structure method is chosen because it provides accurate energy calculations at relatively low computational cost. All molecular calculations were performed using the Gaussian 09 program suite51 and visualized in Gaussview 5.052 or Mask 1.3.0.053 (molecular modeling and simulation kit version 1.3.0.0). All molecules have real frequencies, so they represent a minimum of the potential energy surface, and the spin contamination is negligible.

Adiabatic ionization energies are determined by taking the difference between the CBS-QB3 calculated lowest electronic energy of the singlet neutral state and doublet cation state. The appearance energies at 0 K of dissociative fragment ions are determined from the CBS-QB3 0 K energies of the products (A+, dissociative ionization fragment or daughter ion, and B, neutral fragment) subtracted from the CBS-QB3 0 K energy of the neutral parent (AB) as shown in the reaction below.

\[ AB \rightarrow A^+ + e^- + B \]  (4.4)

All the electronic energies are zero-point corrected. The parent molecule is always in its lowest energy singlet neutral state, the fragment ion in its lowest energy doublet cation state, and the neutral fragment in its lowest energy singlet neutral state unless otherwise noted. The uncertainties associated with the
computed values are estimated to be within 0.05 eV, based on the computational accuracy of 4-5 kJ mol\(^{-1}\) given by Montgomery et al.\textsuperscript{54}

### 4.5 Results

#### 4.5.1 Furan, 2-methyl furan (2-MF), and 2,5-dimethyl furan (2,5-DMF)

The photoionization cross sections of the furanic compounds and dissociative fragments have been previously studied.\textsuperscript{31-32} Figures 4-2 to 4-4 show the derived photoionization cross sections compared to the literature values for furan, 2-MF, and 2,5-DMF. Our experiment shows a threshold for furan ionization at 8.86 ± 0.05 eV, which agrees well with the literature values of 8.88 ± 0.04 eV\textsuperscript{31} and 8.86 ± 0.03 eV\textsuperscript{32} and the CBS-QB3 calculated value of 8.92 eV.

![Figure 4-2. Molecular photoionization cross section for furan (full circles), compared with the reported literature results (open triangles and squares).\textsuperscript{31-32}](image)

In the investigated photon energy range furan does not have any dissociative ionization fragments. The second threshold at 10.2 ± 0.1 eV is caused by a second spectral band, due to an excited electronic state of the cation. The absolute average deviation in the energy range 8.5 – 11.15 eV is 9% with respect to the absolute photoionization cross section reported by Xie et al.\textsuperscript{32} and 7% from the ones measured by Yang et al.\textsuperscript{31} These values are well below the largest estimated average uncertainty of 15% stated earlier.\textsuperscript{46} The ionization threshold of 2-MF is 8.38 ± 0.05 eV, which agrees well with the literature value of 8.38 ± 0.03 eV\textsuperscript{32} and with the CBS-QB3 calculated value of 8.43 eV.
The dissociative fragment at $m/z = 81$ corresponds to the loss of a hydrogen atom from the methyl group as previously reported. The AE at 0 K is determined to be $10.8 \pm 0.1$ eV and matches very well with the CBS-QB3 calculated value of 10.81 eV. As shown in Figure 4-3, the partial photoionization cross sections of 2-MF and the dissociative fragment match very well with the reported literature values with an absolute average deviation of 8% for the parent molecule from 8.35 to 11.2 eV and an absolute average deviation of 6% for the dissociative fragment from the AE to 11.2 eV. Similar to furan, 2-MF has a second threshold at 9.9 ± 0.1 eV due to another transition. Lastly, 2,5-DMF was determined to have an adiabatic ionization energy of $7.95 \pm 0.05$ eV, which agrees well with the literature value of $7.95 \pm 0.03$ eV and the CBS-QB3 calculated value of 8.01 eV. There are two observed dissociative fragments at $m/z = 95$ (loss of H atom) and $m/z = 81$ (loss of CH$_3$). The hydrogen atom is removed from one of the methyl groups with a mechanism similar to the 2-MF dissociative ionization due to the weaker Csp$^3$-H bond compared to Csp$^2$-H bonds. The calculated 0 K AE of 10.39 eV for $m/z = 95$ agrees very well with the experimental value of $10.4 \pm 0.1$ eV and literature value of $10.45 \pm 0.05$ eV. The dissociative fragment at $m/z = 81$ has a 0 K AE of $10.6 \pm 0.1$ eV that is much lower than the literature value of $10.76 \pm 0.05$ eV but in good agreement with the CBS-QB3 calculated value of 10.53 eV.
Figure 4-4. Molecular and dissociative fragment photoionization cross section for 2,5-dimethyl furan (full circles, squares, and triangles), compared to the reported literature results (open squares and triangles). The inset shows the 0 K extrapolation of the \( m/z = 81 \) AE based on the procedure by Ruscic and Berkowitz outlined in the text. The 0 K AE for \( m/z = 81 \) has been obtained using the procedure by Ruscic and Berkowitz. The optimized structure of the \( m/z = 81 \) fragment is analogous to the daughter ion resulting from H loss in 2-MF. Figure 4-4 shows that the partial photoionization cross section of 2,5-DMF is in good agreement with the literature results presented by Xie et al., with an absolute average deviation of 13% from 7.93 to 11 eV. The cross sections of the dissociative fragments have an absolute average deviation of 10% and 14% for \( m/z = 95 \) and \( m/z = 81 \), respectively, in the photon energy range 9.5 to 11 eV. Table 4-1 reports the partial photoionization cross sections of furan, 2-methylfuran, 2,5-dimethylfuran, and their dissociative fragments.

4.5.2 γ-Butyrolactone (GBL) and γ-Valerolactone (GVL)

The adiabatic ionization energy of GBL was measured by Jinno et al. to be 10.06 ± 0.03 eV. The vertical ionization of the first and second bands were also determined to be 10.26 ± 0.02 eV by Jinno et al., Bain et al., and Gerson et al., and 10.93 ± 0.03 eV by Jinno et al., respectively. Through INDO (Intermediate Neglect of Differential Overlap) calculations, Jinno et al. determined that the first band is caused by the removal of an electron from the lone pair on the oxygen of the carbonyl group and the second band is caused by a removal of the electron in the non-bonding \( \pi_{\text{OCO}} \) molecular orbital.
Table 4-1. The partial photoionization cross sections (σ) of furan, 2-methyl furan (2-MF), 2,5-dimethyl furan (25-DMF), and the dissociative fragments reported in megabarns (Mb) at selected energies. (N/D means no data was taken at that energy)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Furan</th>
<th>2MF</th>
<th>m/z = 81</th>
<th>25-DMF</th>
<th>m/z = 95</th>
<th>m/z = 81</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.988</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>2.17</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>8.188</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>8.77</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>8.388</td>
<td>0.00</td>
<td>1.34</td>
<td>0.00</td>
<td>12.06</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>8.588</td>
<td>0.00</td>
<td>4.92</td>
<td>0.00</td>
<td>12.07</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>8.788</td>
<td>0.02</td>
<td>7.70</td>
<td>0.00</td>
<td>12.29</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>8.988</td>
<td>2.19</td>
<td>9.10</td>
<td>0.00</td>
<td>12.27</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.188</td>
<td>5.22</td>
<td>12.01</td>
<td>0.02</td>
<td>13.94</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>9.388</td>
<td>7.95</td>
<td>12.41</td>
<td>0.00</td>
<td>15.00</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>9.588</td>
<td>8.58</td>
<td>13.14</td>
<td>0.01</td>
<td>16.81</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>9.788</td>
<td>9.46</td>
<td>14.84</td>
<td>0.01</td>
<td>16.54</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>9.988</td>
<td>10.61</td>
<td>15.37</td>
<td>0.01</td>
<td>19.98</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>10.188</td>
<td>11.73</td>
<td>19.62</td>
<td>0.03</td>
<td>23.42</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>10.388</td>
<td>13.82</td>
<td>22.93</td>
<td>0.06</td>
<td>27.80</td>
<td>0.18</td>
<td>0.01</td>
</tr>
<tr>
<td>10.588</td>
<td>17.38</td>
<td>26.76</td>
<td>0.37</td>
<td>30.96</td>
<td>0.70</td>
<td>0.11</td>
</tr>
<tr>
<td>10.788</td>
<td>18.23</td>
<td>27.27</td>
<td>1.80</td>
<td>31.10</td>
<td>2.22</td>
<td>0.36</td>
</tr>
<tr>
<td>10.988</td>
<td>18.94</td>
<td>27.29</td>
<td>3.35</td>
<td>29.05</td>
<td>4.41</td>
<td>0.73</td>
</tr>
<tr>
<td>11.188</td>
<td>18.82</td>
<td>26.31</td>
<td>4.95</td>
<td>N/D</td>
<td>N/D</td>
<td>N/D</td>
</tr>
</tbody>
</table>

This assignment is consistent with the photoionization behavior of saturated ester molecules. As expected, a similar trend is observed with GVL except the extra methyl group causes more electron delocalization. The Jinno et al. orbital calculations show a large amount of electron delocalization, which is common for saturated ring compounds. Our Hartree-Fock (HF) calculations with the 6-31+G(d’) basis set of the orbital energies are substantially lower than the INDO calculations performed by Jinno et al. (HOMO: -12.27 eV, HOMO-1: -13.45 eV) due to the semi-empirical inner atomic orbital approximations used in the INDO method compared to the iterations to the lowest energy wave functions of the HF method (Figure 4-5). The HF molecular orbital energy calculations can assist in assigning spectral components; the differences in the HOMO and HOMO-1 orbitals can be used to estimate the energy difference of the two components according to Koopmans’ theorem.

Our experiments show an ionization threshold for GBL at 10.10 ± 0.05 eV, which is in good agreement with the adiabatic ionization energy reported by Jinno et al. This result agrees with the CBS-QB3 calculated value of 10.13 eV. GBL dissociatively ionizes above 10.2 ± 0.1 eV to produce neutral CO₂.
and a \( \text{C}_3\text{H}_6^+ \) ion. The calculated lowest energy structure of \( \text{C}_3\text{H}_6^+ \), which yields a calculated appearance energy closer to the experimental value, is similar to cyclopropane with the interatomic distances between carbons 2 and 3 and carbons 3 and 4 at 1.49 Å and carbons 2 and 4 at 2.05 Å (see Figure 4-1 for the numbering scheme of GBL).

<table>
<thead>
<tr>
<th>Difference of Orbital Energies</th>
<th>GBL</th>
<th>GVL</th>
<th>Difference of Orbital Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_0 ) (HOMO-1)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>( n_0 ) (HOMO-1)</td>
</tr>
<tr>
<td>( \pi_{\text{CO}} ) (HOMO)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>( \pi_{\text{CO}} ) (HOMO)</td>
</tr>
</tbody>
</table>

**Figure 4-5.** The difference between the HOMO and HOMO-1 orbital energies and electron distribution of \( \gamma \)-butyrolactone (GBL) and \( \gamma \)-valerolactone (GVL) obtained from the HF/6-31+G(d’) orbital calculations.

Other isomers were tried but they all yielded AEs much different from the experimental finding. The CBS-QB3 calculated AE at 0 K is 10.22 eV. The experimental determination of the dissociative photoionization cross section includes a correction for the contribution of propene that was used in the standard calibration gas mixture. The photoionization cross section to GBL\(^+\) and the \( \text{C}_3\text{H}_6^+ \) fragment after correction are presented in Figure 4-6 and in Table 4-2. The total cross section for the molecule and the fragment increases with photon energy in a quasi-linear fashion above the appearance energy. This is common for compounds with ester functional groups due to the closely spaced overlapping bands that arise from the small difference between the molecular orbital energies.\(^{35,64-66}\)

GVL has a slightly lower ionization threshold than GBL, at 9.98 ± 0.05 eV (Figure 4-7), due to greater electron delocalization in the cation caused by the interaction of the methyl group with the \( \pi \) orbitals.\(^{67}\)
Table 4-2. The partial photoionization cross sections for γ-butyrolactone (GBL), γ-valerolactone (GVL), and their dissociative fragment reported in megabarns (Mb) at selected energies.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>GBL $m/z = 42$</th>
<th>GVL $m/z = 85$</th>
<th>GVL $m/z = 56$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.613</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9.813</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>10.013</td>
<td>0.02</td>
<td>0.02</td>
<td>0.34</td>
</tr>
<tr>
<td>10.213</td>
<td>0.59</td>
<td>0.16</td>
<td>1.36</td>
</tr>
<tr>
<td>10.413</td>
<td>1.66</td>
<td>0.32</td>
<td>1.70</td>
</tr>
<tr>
<td>10.613</td>
<td>2.42</td>
<td>0.80</td>
<td>2.00</td>
</tr>
<tr>
<td>10.813</td>
<td>2.81</td>
<td>1.50</td>
<td>2.21</td>
</tr>
<tr>
<td>11.013</td>
<td>3.20</td>
<td>2.27</td>
<td>2.51</td>
</tr>
</tbody>
</table>

Figure 4-6. Molecular and dissociative fragment photoionization cross section for γ-butyrolactone.

The experimental threshold agrees well with the CBS-QB3 calculated adiabatic ionization energy of 9.98 eV. GVL dissociates into two fragments with appearance energies below 11 eV. The first dissociative fragment at $m/z = 56$ is determined to be $\text{C}_4\text{H}_8^+$ with a structure resembling the bonding of methyl cyclopropane but with a more pronounced carbon 2-3-4 angle of 104°, where the interatomic distance between carbon 2 and carbon 4 decrease from 2.39 Å in GVL to 2.35 Å.
Other $m/z = 56$ isomers were tried, such as cis- and trans-butene cations that yield an AE of 9.23 and 9.18 eV, respectively, and methyl-cyclopropane cation yielding an appearance energy of 9.72 eV. Therefore, these isomers were eliminated based on their calculated appearance energies much lower than the experimental value. The experimental 0 K AE, $10.3 \pm 0.1$ eV, is in good agreement with the calculated value of 10.23 eV. This fragment forms in a similar fashion to $m/z = 42$ in GBL where the neutral fragment is CO$_2$. Like $m/z = 42$ in GBL, the $m/z = 56$ signal was corrected for the contribution of the 1-butene signal from the standard calibration gas mixture before the photoionization cross section was calculated. The second dissociative fragment at $m/z = 85$, (C$_4$H$_5$O$_2^+$, singlet cation state) has a 0 K AE of $10.8 \pm 0.1$ eV from the loss of a CH$_3$ in a doublet neutral state. This value is in good agreement with the CBS-QB3 calculated value of 10.78 eV. The optimized structure of the cation has a structure similar to GBL except carbon 4 has only one hydrogen and the bond between carbon 4 and the esteric oxygen decreases from 1.44 Å to 1.23 Å due to the formation of a resonance structure. Using the experimentally derived appearance energy at 0 K in the equation below, employing the procedure by Ruscic and Berkowitz$^{44}$ outlined in the Measurement Procedures section, it is possible to estimate the bond dissociation energy of the C-C bond at 0 K, $D_0^\circ$(R-CH$_3$), where R-CH$_3$ stands for GVL and AIE(85) is the adiabatic ionization energy of the fragment.
\[ D_0^0(R - CH_3) = AE(85^+, R - CH_3) - AIE(85) \] (4.5)

Using the CBS-QB3 calculated ionization energy of 6.91 eV for the fragment, which is optimized as described above, the derived \( D_0^0(R - CH_3) \) is 375 ± 5 kJ mol\(^{-1}\). Then, employing the heat content functions, \( H_{298}^0 - H_0^0 \), for the species involved in the dissociation reaction the bond dissociation energy at 298 K, \( D_{298}^0(R - CH_3) \), is obtained as 382 ± 5 kJ mol\(^{-1}\), which is in good agreement with the literature value for the \( D_{298}^0(CH_3-CH_2OC(O)CH_2CH_2CH_3) \) of 375 ± 4 kJ mol\(^{-1}\). This molecule is chosen for comparison due its similarity to GVL-CH\(_3\) bond arrangement. The bond dissociation energy of the C-CH\(_3\) bond in GVL at 298 K can also be calculated only using the CBS-QB3 energies. In this case \( D_{298}^0(R - CH_3) \) is derived as 380 ± 5 kJ mol\(^{-1}\).

The partial photoionization cross sections of GBL and GVL are fairly similar and the addition of the methyl group causes GVL’s partial photoionization cross section to decrease by an average of 20% above 10.51 eV. However, the total photoionization cross section of GVL increases by an average of 30% above 10.61 eV due to the methyl group on the C\(_6\)H\(_5\)\(^+\) fragment compared to the C\(_3\)H\(_6\)\(^+\) fragment. In this energy range, \( m/z = 85 \) contributes very little to the total photoionization cross section of GVL. As stated earlier, the error of the partial photoionization cross section measurements are at most ±15% on our mass spectrometer.

4.5.3 \( \alpha \)-Angelicalactone (AAL) and \( \gamma \)-Methylene-\( \gamma \)-Butyrolactone (GMGB)

Thorstad et al.\(^{68}\) reported AAL having an ionization energy of 9.62 ± 0.05 eV using electron ionization techniques. Thorstad et al.\(^{68}\) also reported that AAL does not create any dissociative fragments at low ionization energies, unlike other lactones, because there are no hydrogen atoms on adjacent carbon atoms to the esteric oxygen to form a more stable resonance structure. To the best of our knowledge, there are no previously published results on GMGB ionization.

Figure 4-8 shows the cross sections of AAL, which is much larger than the saturated lactones because ionization occurs from the \( \pi \) orbitals of the C=C double bond.
Our experiments show that AAL has an adiabatic ionization energy of 8.97 ± 0.05 eV, which is much lower than the previously reported electron ionization value, but agrees well with the CBS-QB3 calculated AIE of 8.94 eV. As in the previous reports, there are no dissociative fragments observed in the investigated energy range. AAL presents a much more prominent shoulder at 10.2 ± 0.1 eV compared to GBL and GVL photoionization spectra. The first band is caused by a removal of an electron from the bonding π molecular orbital localized on the C=C bond as shown in Figure 4-9.

**Figure 4-9.** Orbital energy and electron distribution of α-angelicalactone (AAL) and γ-methylene-γ-butyrolactone (GMGB) obtained from the HF/6-31+G(d’) orbital calculations.
Using Koopmans’ theorem, it can be estimated that the second spectral feature appears at about $10.0 \pm 0.1$ eV from the removal of an electron from the carbonyl group ($n_o$). This is in fairly good agreement with the experimentally observed threshold of $10.2 \pm 0.1$ eV. The positions of the two bands are consistent with photoionization behavior of unsaturated esters that have been studied previously.\textsuperscript{35,70}

Figure 4-10 shows the photoionization spectrum for GMGB. The shape and photoionization cross section is nearly identical to AAL, with the ionization threshold at $9.05 \pm 0.05$ eV, in good agreement with the CBS-QB3 calculated AIE value of 8.98 eV. With the HF orbital energies in Figure 4-9 and Koopmans’ theorem, it can be estimated that the second band should appear around $9.9 \pm 0.1$ eV, in agreement with the experimental feature at $10.1 \pm 0.1$ eV.

![Figure 4-10](image)

**Figure 4-10.** Molecular and dissociative fragment cross sections of $\gamma$-methylene-$\gamma$-butyrolactone showing the partial cross section of GMGB. The inset shows the experimental AIE of GMGB obtained using a linear extrapolation of the initial onset as described in Ref.\textsuperscript{43}

GMGB dissociatively ionizes into one fragment below 11 eV. The AE at 0 K of the cyclic-$\text{H}_2\text{COC(CH}_2\text{)CH}_2^+$ ion is determined to be $10.6 \pm 0.1$ eV, which is in agreement with the CBS-QB3 calculated AE of 10.64 eV. This fragmentation is favored by the increased stability of the ion when the esteric oxygen decreases the interatomic distance from 2.36 Å to 1.80 Å and breaks the bond to carbon 1, allowing the formation of neutral CO. These fragmentation patterns are not observed in AAL because the
The double bond within the ring does not allow any stable resonance structures to form between the esteric oxygen and the adjacent carbons, and also increases steric strain, preventing resonance across the ring.

Table 4-3 shows the photoionization cross sections of GBL and GVL together with their dissociative fragments. The addition of the C=C double bond increases the partial photoionization cross sections of AAL and GMGB by an average of 20 and 30 times, respectively, compared to GVL above 10.62 eV. GMGB with respect to AAL has an average increase of 1.4 times above 10.62 eV that shows the methylene group increases the partial photoionization cross section. The smaller photoionization cross sections of GBL and GVL are not uncommon. In fact, several saturated esters, such as methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propanoate, ethyl propanoate, methyl isobutanoate, and methyl butanoate, have photoionization cross sections ranging from 3 to 16 MB.35

Table 4-3. Partial photoionization cross section of α-angelicalactone (AAL), γ-methylene-γ-butyrolactone (GMGB) and its dissociative fragment reported in megabarns (Mb) at selected energies.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>GMGB m/z = 70</th>
<th>AAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.841</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>9.041</td>
<td>0.34</td>
<td>0.92</td>
</tr>
<tr>
<td>9.241</td>
<td>2.33</td>
<td>3.50</td>
</tr>
<tr>
<td>9.441</td>
<td>6.88</td>
<td>8.69</td>
</tr>
<tr>
<td>9.641</td>
<td>12.82</td>
<td>12.20</td>
</tr>
<tr>
<td>9.841</td>
<td>19.39</td>
<td>15.50</td>
</tr>
<tr>
<td>10.041</td>
<td>24.73</td>
<td>17.94</td>
</tr>
<tr>
<td>10.241</td>
<td>34.19</td>
<td>20.98</td>
</tr>
<tr>
<td>10.441</td>
<td>49.52</td>
<td>30.68</td>
</tr>
<tr>
<td>10.641</td>
<td>64.17</td>
<td>43.79</td>
</tr>
<tr>
<td>10.841</td>
<td>69.59</td>
<td>50.24</td>
</tr>
<tr>
<td>11.041</td>
<td>73.87</td>
<td>54.03</td>
</tr>
</tbody>
</table>

4.6 Conclusion

Adiabatic ionization energies and appearance energies were presented for three furans and four lactones, along with the photoionization cross sections of the parent and dissociative fragments of the lactones. The presented method to derive photoionization cross sections of daughter ions has been tested and confirmed with furanic compounds, for which literature values are available. The CBS-QB3 calculations agreed very well with the experimental AIE and AE values. The use of Koopmans’ theorem
with the calculated orbital energies allows the depiction of the observed shoulders in the photoionization spectra fairly accurately. The photoionization fragmentation patterns are also explained and described.

4.7 Acknowledgments

We acknowledge the American Chemical Society – Petroleum Research Fund Grant # 51170 UNI6, the University of San Francisco Faculty Development Fund for financial support, the usage of the chemistry computer cluster at the University of San Francisco supported by professors Claire Castro and William Karney, and the Advanced Light Source (ALS) division at the Lawrence Berkeley National Laboratory for beamtime allocation. We also thank Dr. John Savee from Sandia National labs for sharing his insight throughout the writing of this paper. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The Sandia authors and the development of the experimental apparatus are supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, of the U.S. Department of Energy. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.
4.8 References


76


Chapter 5

Study of Low Temperature Chlorine Atom Initiated Oxidation of Methyl and Ethyl Butyrate Using Synchrotron Photoionization TOF-Mass Spectrometry

5.1 Abstract

The initial oxidation products of methyl butyrate (MB) and ethyl butyrate (EB) are studied using a time- and energy-resolved photoionization mass spectrometer. Reactions are initiated with Cl• radicals in an excess of oxygen at a temperature of 550 K and a pressure of 6 Torr. Ethyl crotonate is observed as the sole isomeric product of concerted HO₂-elimination from initial alkylperoxy radicals formed in the oxidation of EB. Analysis of the potential energy surface of each possible alkylperoxy radical shows that the RγO₂ radical is the isomer that undergoes this concerted HO₂-elimination. Two lower-mass products (formaldehyde and acetaldehyde) are observed in both methyl and ethyl butyrate reactions. Quantum chemical (CBS-QB3) calculations show that beta-scission of the R₃O₂ alkylperoxy radicals of MB or EB can produce formaldehyde or acetaldehyde, respectively, from the methyl or ethyl group. However, secondary reactions of alkylperoxy radicals with HO₂ radicals can form weakly bound complexes that subsequently decompose into the aforementioned products and smaller radicals. These pathways are more energetically favorable and are a more likely explanation for the formation of formaldehyde and acetaldehyde. The time traces for formaldehyde and acetaldehyde product formation from MB confirm that they are products of secondary reactions.

5.2 Introduction

In recent years, the production of new biofuels has started to grow due to increased environmental awareness, cost effectiveness, and a drive for energy independence. For example, ethanol is used today as a fuel additive to boost combustion and decrease pollutants, but has the disadvantage of corrosive properties,¹² which limit the amount that can be added. Therefore, other alternatives such as esters, ethers, and furans³⁵ have been sought in the last few years.

Esters, such as methyl butyrate (MB) and ethyl butyrate (EB), shown in Scheme 5-1, have been proposed as additives and even replacements to conventional gasoline.⁶⁷ Both compounds have the
advantages of relatively low freezing points and high boiling points. Methyl butyrate has a melting point of \(-85.8 \pm 0.1 \degree C\) and a boiling point of \(101.9 \pm 0.1 \degree C\), while ethyl butyrate has a melting point of \(-97 \pm 6 \degree C\) and a boiling point of \(121.1 \pm 0.4 \degree C\). This allows the fuels to be handled under normal and extreme conditions without special precautions. The vapor pressures are relatively low (40.0 Torr at 30 \degree C for MB and 15.5 Torr at 25 \degree C for EB), which makes their use in a homogeneous-charge compression-ignition (HCCI) engine difficult, but possible. MB and EB have very low toxicity and indeed are already employed in the food industry as flavor agents.

These esters have gained considerable interest because they can be produced through both first and second generation biofuel production methods. The “first-generation” method used is primarily transesterification of vegetable oils and also some lipids from animal fats. Second-generation biofuels must use biomass from a non-food crop. In this regard, there is an extensive amount of research on producing biodiesel from non-food sources such as rapeseed, jatropha, hemp, and microalgae.

In order to accurately assess the overall impact of new fuels, their oxidation mechanisms must be considered. Oxidation reactions of ethyl butyrate and ethyl propanoate have been studied through ab initio methods and methyl butyrate combustion has been the subject of many experiments that include exhaust analysis, shock tubes, rapid compression machine, opposed flow diffusion flame, and a jet stirred reactor. There have also been detailed kinetic modeling studies of methyl butyrate with various methods. More recently, the reaction of MB + Cl\(^+\) + O\(_2\) has been studied using photoionization mass spectrometry to analyze the HO\(_2\)-elimination and cyclic ether formation pathways from the alkyl peroxy radicals formed in initial reactions of fuel radicals with O\(_2\). Ethyl butyrate combustion has been studied
in the high temperature kinetic and modeling investigation by Hakka et al.\textsuperscript{30} and the ignition delay time measurements of Dayma et al.\textsuperscript{31} In this work chlorine initiated reactions of MB and EB are studied at 550 K in the presence of oxygen at a pressure of 6 Torr. The HO\textsubscript{2}-elimination pathways for the reaction of EB-derived radicals with O\textsubscript{2} are analyzed and compared to similar pathways in MB oxidation. CBS-QB3 calculations are performed for the HO\textsubscript{2}-elimination pathways and for bimolecular reactions between organic peroxy radicals (RO\textsubscript{2}) and HO\textsubscript{2} radicals. The aim is to understand the role of the esteric alkyl group in the low-temperature oxidation reactions of esters, chemistry that can occur during the compression heating in HCCI and other advanced engine designs.

5.2.1 Fundamental Low Temperature Oxidation Chemistry of Oxygenates and Bimolecular Reactions

At low temperature and in the presence of oxygen, the reaction between an organic radical (R) and O\textsubscript{2} yields an RO\textsubscript{2} radical.\textsuperscript{32} Several well-known reaction pathways are possible for the decomposition of RO\textsubscript{2} species. Among them, the most common at low temperatures is the concerted HO\textsubscript{2}-elimination that forms an unsaturated coproduct. However, the RO\textsubscript{2} radical could also undergo internal H-abstraction to form a hydroperoxyalkyl radical (QOOH). These QOOH species could then decompose or undergo bimolecular reactions with a second O\textsubscript{2} to initiate a chain branching reaction. More details about the decomposition of RO\textsubscript{2} radicals can be found elsewhere.\textsuperscript{32}

The HO\textsubscript{2} radical produced from RO\textsubscript{2} decomposition is unreactive with closed-shell organic molecules at low temperatures, which is why it is generally considered chain-inhibiting. However, it has been observed that HO\textsubscript{2} radicals can react with RO\textsubscript{2} to create stable hydroperoxide species (ROOH) along with O\textsubscript{2}.\textsuperscript{33-40} It was previously thought that the ROOH species were formed through a hydrotetraoxide intermediate (ROOOOH) but recent theoretical work suggests this reaction occurs by forming a weakly bound RO\textsubscript{2}···HO\textsubscript{2} complex in the triplet state, which then forms triplet O\textsubscript{2} and a singlet ROOH.\textsuperscript{41-46} At elevated temperatures the ROOH species can decompose into oxy (RO) and hydroxyl (OH) radical. The RO radicals are then able to decompose further into stable products and smaller radicals. It should be noted that other radical-radical reactions could occur, i.e., RO\textsubscript{2} + RO\textsubscript{2}, which could produce many smaller species.
We did not consider these reactions in this study, which is designed to focus in the initial reaction steps of low-temperature ignition, namely the formation and decomposition of RO₂ radicals.

5.3 Experimental

Experiments were performed using a multiplexed time- and energy-resolved photoionization mass spectrometer at the Advanced Light Source of the Lawrence Berkeley National Laboratory. The apparatus has been described in detail elsewhere⁴⁷-⁴⁹ and will be only briefly discussed here. It consists of four main parts: the chemical reactor tube, photoionization region, orthogonal acceleration mass spectrometer, and the detector. Vacuum ultraviolet (VUV) synchrotron radiation is directed into a rare gas filter to remove radiation at undulator harmonics, and the desired wavelength is selected using a 3 m Eagle off-plane monochromator before entering the photoionization chamber.

The reaction tube is a 60 cm quartz slow flow reactor through which radical precursors, reactants, and excess helium flow. Gas in the reaction tube is held at temperatures between 298 and 800 K and pressures of 1 to 10 Torr during these experiments. Reactants (stated purity of 99%) are purified using freeze-pump-thaw technique then diluted in gas cylinders with He (approximately 1% in He). Cl radicals are produced from a 1% mixture of Cl₂ in He, which is photolyzed with a 351-nm excimer laser firing at a rate of 4 Hz. A portion of the reaction mixture effuses through a 650 μm pinhole in the side of the reaction tube, and is skimmed before entering the ionizing region, where neutrals are ionized by VUV radiation. The ions are accelerated, collimated, and orthogonally extracted into a field-free drift region, after which they are detected by a microchannel plate detector. The current apparatus has a mass resolution \((M/\Delta M)\) of approximately 1600.

This apparatus measures the ion intensity as a function of the mass-to-charge ratio \((m/z)\), reaction time, and ionizing photon energy for each neutral species. The photoionization spectra and time traces are used to identify reaction species at each \(m/z\). Pre-photolysis signal is subtracted from the time trace at each \(m/z\). The experimental photoionization (PI) spectrum is extracted by integrating over the time range of interest at each photon energy, normalized by the ALS photon flux at that energy. These PI spectra are compared to reference experimental spectra or simulated spectra to identify the spectral carriers. Typical
experiments have number densities of $\sim 4 \times 10^{13}$ molecules/cm$^3$ of MB or EB, $\sim 2 \times 10^{16}$ molecules/cm$^3$ O$_2$, and $\sim 4 \times 10^{12}$ atoms/cm$^3$ of Cl$^\bullet$ radicals (post-photolysis).

5.4 Computational Methods

Calculations of molecular parameters, including harmonic vibrational frequencies, bond distances, and ionization energies, are performed using the CBS-QB3 composite model$^{50}$ developed by Petersson and colleagues.$^{51}$ This method is chosen because it provides reliable energies and geometries at relatively low computational cost. These calculations are performed using Gaussian 09 software.$^{52}$

Adiabatic ionization energies (AIE) are calculated by taking the difference of the CBS-QB3 zero-point corrected energies at the optimized structures of the ground electronic states of the neutral and cation. The CBS-QB3 method has a mean absolute deviation of 4.6 kJ/mol compared to the experimental data of the G2/97 test set.$^{53-55}$

The B3LYP method and CBSB7 basis set was used to scan the potential energy surface (PES) to find an approximate geometry for the saddle point. Once an approximate saddle point is located, it is optimized as a transition state and the zero-point corrected energy is calculated using the CBS-QB3 method. The optimized saddle point is then confirmed using intrinsic reaction coordinate (IRC) calculations, again with the B3LYP/CBSB7 method. The optimized structures for the minima on the potential energy surface have no imaginary frequencies, while each of the saddle points have only one imaginary frequency.

5.5 Results and Discussion

5.5.1 Photoionization Behavior of Ethyl Butyrate

During reactions, daughter ions of the reactants or products could be produced by the synchrotron radiation if the photon energy is above the dissociation threshold. Therefore, it is imperative to understand the photoionization and photodissociation patterns of each reactant and product to distinguish them from daughter ions. The photoionization of methyl butyrate has been well studied$^{56-59}$ and will not be reported here. However, the photoionization behavior of ethyl butyrate has not been investigated. We determine the ionization onset with a linear fit to be 9.83 ± 0.05 eV, which is in good agreement with the CBS-QB3 calculated AIE of 9.89 eV. The PI spectrum of EB and dissociative fragments are shown in Figure 5-1. EB
presents dissociation patterns that are very similar to the results reported by Wang et al.\textsuperscript{56} for ethyl propanoate. EB dissociatively ionizes at 10.15 ± 0.1 eV yielding a fragment at \( m/z = 88 \), which is suspected to be the ethyl acetate enol ion (\( \text{CH}_2\text{CH}_2\text{C(\text{OH})OCH}_2\text{CH}_3^+ \)).

**Figure 5-1.** Absolute photoionization spectra of ethyl butyrate with main dissociative fragments (top) and minor dissociative fragments (bottom). The insert shows the linear fit that was used to determine the ionization onset of EB as 9.83 ± 0.05 eV.

The loss of \( \text{C}_2\text{H}_4 \) proceeds via a direct bond scission of carbon 2 and 3 from the formation of the low-energy distonic intermediate of the \( \text{CH}_2\text{CH}_2\text{CH}_2\text{C(\text{OH})OCH}_2\text{CH}_3^+ \) ion similar to MB.\textsuperscript{57,58} This dissociation pattern has also been reported by Wang et al.\textsuperscript{56} in various esters. The formulas of the dissociative fragments presented in Table 5-1 are determined from the absolute mass in the PI mass spectrum.
Table 5-1. Dissociative fragments and appearance energies of ethyl butyrate.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragments</th>
<th>0 K Appearance Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>C₆H₉O₂⁺ + CH₃</td>
<td>10.25 ± 0.1</td>
</tr>
<tr>
<td>88</td>
<td>C₄H₈O₂⁺ + C₂H₄</td>
<td>10.15 ± 0.1</td>
</tr>
<tr>
<td>71</td>
<td>C₄H₇O⁺ + C₂H₅O</td>
<td>10.65 ± 0.1</td>
</tr>
<tr>
<td>70</td>
<td>C₄H₆O⁺ + C₂H₆O</td>
<td>10.50 ± 0.1</td>
</tr>
</tbody>
</table>

5.5.2 Experimental results - Product Identification.

In a previous study, the main products of the reaction of MB + Cl• + O₂ was determined to be methyl crotonate (CH₃CH=CHC(O)OCH₃).²⁹ Methyl crotonate is two a.m.u. smaller than MB. In a similar manner, the main product of the EB + Cl• + O₂ reaction was also two a.m.u. smaller than EB, giving rise to possible products with the formula C₆H₁₀O₂ (m/z = 114). The experimental PI spectrum for m/z = 114 is presented in Figure 5-2.

![Figure 5-2. PI spectrum of m/z = 114 from the EB + Cl• + O₂ reaction. The solid black line is the measured PI spectrum of ethyl crotonate.](image)

We measured the PI spectrum of two potential products that were commercially available, ethyl crotonate (CH₂CH=CHC(O)OCH₂CH₃) and vinyl butyrate (CH₃CH₂CH₂C(O)OCH=CH₂). The PI spectrum for ethyl crotonate matches the m/z = 114 spectrum nearly exactly, with an ionization onset of 9.66 ± 0.05 eV.

In order to ensure there are no other products in the spectrum in Figure 5-2, we calculated the ionization energies of all possible products as shown in Scheme 5-2. Only ethyl but-3-enoate (CH₂=CHCH₂C(O)OCH₂CH₃) has an ionization energy similar to the onset in Figure 5-2. We can compare
this to the previous study on MB + Cl• + O₂ that found no methyl but-3-enoate (CH₂=CHCH₂C(O)OCH₃) was produced in the reaction based on the reaction energetics. Therefore, we suspect that the only product in the m/z = 114 spectrum is ethyl crotonate. We will further explore the sole assignment of ethyl crotonate with the help of quantum chemical calculations in section 5.5.3.

Scheme 5-2. List of possible products from the HO₂-elimination from EB and their calculated ionization energies in eV.

Two smaller products are observed in both the MB and EB reactions. The PI spectra are shown in Figure 5-3. The first, m/z = 30, is readily identified as formaldehyde compared to the spectrum recorded by Copper et al.⁵⁰ The second product (m/z = 44) can easily be assigned as acetaldehyde using the previously measured spectrum.⁶¹ Based on the structure of MB and EB, plus the excess of oxygen, there are numerous pathways that could explain the observations formaldehyde and acetaldehyde. We will examine many of these pathways computationally in section 5.5.4 and discuss the feasibility of each one.
Figure 5-3. PI spectra from $m/z = 30$ (left) and $m/z = 44$ for MB + Cl• + O$_2$ (a) and EB + Cl• + O$_2$ (b). The solid black lines are the reported PI spectra of formaldehyde or acetaldehyde.

5.5.3 Comparison between Theory and Experiment – HO$_2$-Elimination Reactions from EB Radicals.

The HO$_2$-elimination reactions from MB radicals have been studied previously, so we will only discuss reactions with EB radicals in comparison with MB radicals. We computed reaction energetics for hydrogen abstraction from MB and EB by Cl• radicals to determine the likely RO$_2$ radicals. The results are summarized in Scheme 5-3. As expected, the radical formed by abstracting a hydrogen atom from C$_\beta$ is most favorable, by nearly 20 kJ/mol or more, due to vinoxylic resonance stabilization. However, it is energetically possible to form an alkyl radical on all of the carbons (except for C$_\alpha$ where there are no hydrogen atoms available). We then scanned the PES for the addition of O$_2$ to each of the radical sites and found all to be barrierless.

Using the optimized structures of the RO$_2$ radicals, we began to study the PES of the HO$_2$-elimination pathways for each EB radical. Figure 5-4 shows the results of these calculations for the reactions that are limited to 5-membered rings for the transition states. Larger rings are entropically unfavorable due to the large interatomic distance between the peroxy radical and the H atom. The HO$_2$ can be removed directly through a single transition state (concerted HO$_2$-elimination) or step-wise by forming a QOOH
radical followed by dissociation of \( \text{HO}_2 \). Examples of these competing pathways are shown in Scheme 5-4 for \( \text{R}_\beta \text{O}_2 \). Possible \( \text{HO}_2 \)-elimination products are shown in Scheme 5-5 that are again limited to transition states with 5-membered rings. In all cases, the concerted \( \text{HO}_2 \)-elimination channels have a lower barrier than does isomerization to a \( \text{QOOH} \) radical (Figure 5-4).

Scheme 5-3. Possible hydrogen abstraction reactions for MB and EB. The numbers are the relative 0 K CBS-QB3 energies compared to the reactants in kJ/mol. Labels (\( \text{R}_\beta, \gamma, \delta, \text{m, e} \)) are used to denote the radical sites.
Scheme 5-4. The two possible reactions for HO$_2$-elimination from adjacent carbons in the oxidation of EB radical (R$_\beta$). The top pathway is the concerted HO$_2$-elimination and the bottom involves isomerization to a QOOH intermediate.

Figure 5-4. Potential energy surfaces for the reaction of the initial EB radicals. Relative energies are at 0 K calculated with the CBS-QB3 method for a) R$_\beta$ with C$_\gamma$, b) R$_\gamma$ with C$_\beta$, c) R$_\gamma$ with C$_\delta$, d) R$_\delta$ with C$_\gamma$, e) R$_m$ with C$_e$, and f) R$_e$ with C$_m$. 
As in MB oxidation, the well for O\(_2\) addition to the \(R_\beta\) radical from EB is shallower than for the other radical sites due to the resonance stabilization of the alkyl radical. In addition, the barrier for direct HO\(_2\)-elimination is nearly as high or above the energy of the reactants so it is expected that \(R_\beta\)O\(_2\) will principally dissociate back to \(R_\beta\) + O\(_2\). The deepest well for the O\(_2\) addition in EB oxidation was for \(R_m\) at -149.6 kJ/mol, but very close in energy to \(R_\gamma\) at -148.8 kJ/mol. The lowest barrier for concerted HO\(_2\)-elimination of EB radicals is for \(R_\gamma\)O\(_2\) taking the H atom from C\(_\beta\), at -38.6 kJ/mol; elimination from \(R_m\)O\(_2\) with the H atom from C\(_e\) was found to be significantly higher at -17.3 kJ/mol. The concerted HO\(_2\)-elimination pathways from \(R_\gamma\)O\(_2\) with C\(_\delta\) and from \(R_m\)O\(_2\) with C\(_\gamma\) are very similar energetically while the reaction between \(R_c\)O\(_2\) and C\(_m\) has a slightly higher barrier (but still lower than the reactants). The combination of a deep well for O\(_2\) addition and low reaction barrier for HO\(_2\)-elimination of \(R_\gamma\)O\(_2\) to ethyl crotonate support the assignment of a single isomer in the \(m/z = 114\) spectrum.

Scheme 5-5. All possible products from the HO\(_2\)-elimination reactions of EB radicals with the condition that all transition states have 5-membered rings.
The time traces for the formation of $m/z = 114$ is shown in the right column of Figure 5-5 compared to the depletion of EB. We also included the time traces for MB + Cl• + O₂ reaction in the left column. For the MB + Cl• + O₂ reaction, it is clear to see that the formation of $m/z = 100$ (methyl crotonate) rises at the same rate as the MB depletion. This signifies that methyl crotonate is a primary product from direct oxidation of the MB RγO₂ radical. The rise of $m/z = 114$ in the EB reaction is much slower by comparison. This could be due to the reaction conditions in the present study so more experiments will be needed to confirm the formation of ethyl crotonate as a primary product.

**Figure 5-5.** Time traces for the identified products for the MB + Cl• + O₂ (left column) and EB + Cl• + O₂ (right column) reactions compared to the depletion of the reactants ($m/z = 102$ and 116 for MB and EB, respectively). The excimer laser is fired at 0 ms.
5.5.4 Comparison between Theory and Experiment – Observation of Formaldehyde and Acetaldehyde

The PI spectra for $m/z = 30$ and $44$ in both MB and EB oxidation reactions are shown in Figure 5-3, and the time traces are presented in Figure 5-5. The experimental PI spectra are in excellent agreement with the previously measured spectra for formaldehyde$^{60}$ and acetaldehyde.$^{61}$ Surprisingly, oxidation of each ester produces both of these aldehydes. Based on the energetics shown in Figure 5-6, the $R_m$ radicals likely do not directly decompose into smaller products and radicals.

![Figure 5-6. PES of the dissociation of $R_m$. Relative energies are at 0 K calculated with the CBS-QB3 method.](image)

The reaction pathways shown in Figure 5-7 show a rearrangement for the $R_m$ alkylperoxy radicals to form formaldehyde from MB and acetaldehyde from EB. Both reaction paths are energetically plausible within the computational errors. It is interesting that changing the methyl group to an ester group can decrease the barrier of this pathway by 18.1 kJ/mol. The time traces for the MB reaction show that the formation of formaldehyde and acetaldehyde are slower than the formation of methyl crotonate. Therefore, it appears that the formation of formaldehyde and acetaldehyde from MB is due to secondary reactions. The signal-to-noise ratio is too low to accurately determine if the rate of formation of formaldehyde and acetaldehyde is slower than the formation of ethyl crotonate from EB. However, the reactions in Figure 5-7 can explain only the formation of formaldehyde from MB and acetaldehyde from EB. The observations of acetaldehyde from MB and formaldehyde from EB will be explained below.
Figure 5-7. PES of the reaction of O$_2$ with R$_m$ and subsequent rearrangement to form CH$_3$CH$_2$CH$_3$(O)OO• along with formaldehyde or acetaldehyde. Relative energies are at 0 K calculated with the CBS-QB3 method. The transition state for MB is included for clarity.

Figure 5-8 presents similar pathways as in Figure 5-7, except for peroxo radicals located on R$_\beta$, R$_\delta$, or R$_\gamma$. In all cases the bond formation between the oxygen and C$_\alpha$ and subsequent CH$_3$O• or C$_3$H$_5$O• elimination is at least 49.4 kJ/mol higher in energy than the initial reactants.

Figure 5-8. PES of the reaction of R$_\beta$, R$_\gamma$, or R$_\delta$ with O$_2$, where the peroxo radical forms a bond with C$_\alpha$ to elimination the CH$_3$O• or C$_3$H$_5$O•. The radicals further dissociate to produce formaldehyde or acetaldehyde respectively. The left side is methyl butyrate and the right side is ethyl butyrate. Relative energies are at 0 K calculated with the CBS-QB3 method.
Because these reactions are energetically unfavorable, they are unlikely to contribute to the product formation. In each reaction, the saddle points and final products are higher in energy than the starting radicals and O₂, although as noted above, if they were formed, the alkoxy radicals could react with O₂ to form the aldehydes and HO₂ radicals to lower the final product energy.

Finally, we analyzed the PESs of the reactions of the peroxy radicals with HO₂ radicals. The source of HO₂ radicals are the reactions shown in Figure 5-4. Scheme 5-6 shows two sample reactions of R₃O₂ and R₄O₂ to produce acetaldehyde and formaldehyde, respectively.

Figure 5-9 shows the energies of the weakly bound triplet state RO₂···HO₂ complexes for R₅O₂, R₆O₂, and R₇O₂ compared to the starting reactants. The saddle point for the transfer of the hydrogen atom to the closed-shell hydroperoxide species and ¹⁴O₂ is lower in energy than the initial reactants. Naturally, the formation of two closed-shell species is much lower in energy than the starting alkyl radicals and reactants.
by at least 291.3 kJ/mol. The loss of an OH from the hydroperoxide species is barrierless and lower in energy than its initial reactants (R_x (x = β, γ, δ) + O_2 + HO_2) to give a RO radical. A small barrier of roughly 50 kJ/mol exists for each decomposition of the RO radicals, which could produce formaldehyde and acetaldehyde from both MB and EB.

Figure 5-9. PES of the reactions of R_γO_2, R_δO_2, and R_εO_2 with HO_2. The top shows R_γO_2 and R_δO_2 for MB, middle shows R_γO_2 and R_δO_2 for EB, and the bottom shows R_εO_2 for EB. Relative energies are at 0 K calculated with the CBS-QB3 method.

Figure 5-10 displays stationary point energies for the reactions between R_mO_2 and HO_2. The reaction path for MB is identical to the aforementioned pathways up to the formation of the RO radical.
Figure 5-10. PES of the reactions of R\textsubscript{m}O\textsubscript{2} with HO\textsubscript{2}. The top shows R\textsubscript{m}O\textsubscript{2} for MB and the bottom shows R\textsubscript{m}O\textsubscript{2} for EB. Relative energies are at 0 K calculated with the CBS-QB3 method.

We found it was energetically competitive for one hydrogen from the dissociating CH\textsubscript{2}O to transfer to the carbonyl group to form butanoic acid and formyl radical. We could not locate a barrier for the dissociation of the CH\textsubscript{2}O group without a hydrogen atom transfer, but the final products are nearly equal to the transition state of the competing reaction. Therefore, these two reaction could occur simultaneously if the direct dissociation is barrierless. This same reaction can occur for EB, except the radical formed is acetyl radical. However, the ethyl group can also rotate to a different stereoisomer and act as a protecting group as shown
by the PES of the dotted-dashed blue line in the bottom panel of Figure 5-8. The second isomer is only 8.1 kJ/mol higher in energy but the dissociation barrier is 41.8 kJ/mol higher in energy than the barrier to form butanoic acid. However, the barrier for the formation of acetaldehyde is below the energy of the reactants so it is possible in our experiment. For MB, all of the stable minima have the hydrogen atoms on C8 located near the carbonyl group so it is likely that the hydrogen atom transfers to the carbonyl oxygen during dissociation.

The time traces for the formation of formaldehyde and acetaldehyde from MB and EB, compared to the reactant depletion, are shown in Figure 5-5. The rises of the products at m/z = 30 and 44 in the MB + Cl• + O2 reaction are much slower than the reactant depletion, suggesting that both formaldehyde and acetaldehyde are secondary products from the reactions of alkylperoxy radicals with HO2. The signal-to-noise ratio for the m/z = 30 and 44 time traces in the EB reaction is too low to definitively assign these as primary or secondary products. There have been a few experimental and theoretical studies on the reaction rates of RO2 radicals with HO2.34-36, 40-42, 45, 62-68 Most studies estimate the reaction rate coefficients for the RO2 + HO2 → products to be on the order of 10^{-13} to 10^{-11} cm^3 molecules^{-1} s^{-1} for temperatures between 298 and 600 K, which is comparable to the reaction rate coefficients of the HO2-elimination reactions. A particularly interesting observation from Boyd et al. was that larger molecules seem to have higher rate coefficients for the RO2 + O2 → products reactions.64 In addition, at temperatures above 500 K, the singlet PES for the RO2 + HO2 reactions have been predicted to have comparable reaction rates despite the higher energy reaction paths.45 These observations support our assignment of formaldehyde and acetaldehyde as secondary products from the radical-radical reactions of RO2 with HO2 for MB.

5.6 Conclusions

We report the Cl• initiated reactions of MB and EB in the presence of excess O2, studied using time- and energy-resolved photoionization mass spectrometry. One product, ethyl crotonate, results from the elimination of HO2 radical from RO2 formed by O2 addition to radicals formed from EB, similar to the case for MB oxidation. The potential energy surfaces for all HO2-elimination reactions from EB have been analyzed through quantum chemical computations and show the concerted HO2-elimination from RγO2 to
be the lowest energy pathway. Two other products, formaldehyde and acetaldehyde, were also observed in
the reactions with MB and EB. The time traces for MB oxidation show that both products are formed
through secondary reactions. PESs of the reactions of alkylperoxy radicals with HO$_2$ were analyzed and
show that these reactions are energetically possible and can explain the formation both formaldehyde and
acetaldehyde.

5.7 Acknowledgments

We acknowledge the American Chemical Society – Petroleum Research Fund Grant # 51170 UNI6, the University of San Francisco Faculty Development Fund for financial support, the usage of the chemistry computer cluster at the University of San Francisco supported by professors Claire Castro and William Karney. Additional computational support was provided by Kenneth Smith and Brown University Center for Computation and Visualization. We would also like to acknowledge the Advanced Light Source (ALS) division at the Lawrence Berkeley National Laboratory for beamtime allocation. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The Sandia authors and the development of the experimental apparatus are supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, of the U.S. Department of Energy. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.
5.8 References


Chapter 6

Photoelectron-Photoion Coincidence Spectroscopy (PEPICO) Study of Potential Biofuel Additives

6.1 Abstract

In this investigation, the dissociative photoionization of two biofuel additives, 1,3,5-trimethyl benzene (mesitylene) and γ-valerolactone (GVL) were studied, using the imaging photoelectron-photoion coincidence apparatus (iPEPICO) at the Vacuum Ultraviolet (VUV) beamline of the Swiss Light Source (SLS). For energy selected mesitylene ions, only one dissociation reaction is observed below 13 eV, which corresponds to a triply degenerate CH$_3$ loss. For GVL ions, the loss of neutral CO$_2$ is detected, with an appearance energy of 10.37 ± 0.04 eV. Reaction rates as a function of ion internal energy are determined from statistical modeling.

6.2 Introduction

Dwindling fossil fuel supplies and pollution have been a major driving force for finding cheap, clean, and renewable energy sources.$^1$ Biofuels derived from renewable materials are potentially attractive to replace fossil fuels.$^{2-3}$ These biofuels include many oxygenated species such as alcohols,$^{4-6}$ ethers,$^{7-8}$ esters,$^{2, 9-11}$ and lactones.$^{12-14}$ Accurate thermodynamic data is vital for kinetic modeling studies of combustion processes.$^{15}$ In this study we focus on three proposed fuel additives. They are 1,3,5-trimethyl benzene (mesitylene) and γ-valerolactone (GVL).

Mesitylene has been suggested as a lead-free additive for aviation fuel to increase the octane number.$^{16}$ The kinetic properties of its combustion have been studied by Diévart et al.$^{17}$ using shock ignition delay, laminar burning velocity, and variable pressure flow reactor experiments. Data obtained were compared to theoretical models of toluene combustion. Shock tube experiments and kinetic modeling have also been reported on a fuel blend containing n-dodecane, iso-octane, and n-propylbenzene, along with mesitylene.$^{16}$ Furthermore, Downs et al.$^{18}$ measured a pre-ignition rating of 100, which means mesitylene is unlikely to ignite in the engine prior to the desired ignition time. Ionization of mesitylene has been characterized with many techniques including photoelectron spectroscopy,$^{19-24}$ photoionization mass
spectrometry (PIMS), and electron impact. However, there are no published results on its dissociation dynamics or bond energy of the methyl groups.

γ-valerolactone (GVL) has been proposed as a replacement to fuels and fuel blends because of its chemical properties and energy equivalency to petroleum based fuels. GVL is not prone to volatile emissions because of its high boiling point (207 °C) and low vapor pressure. In regards to safety, GVL does not produce a measurable amount of peroxides, even after exposure to ambient conditions, which means it does not tend to lead to violent explosions. Furthermore, GVL also has a distinct smell, which makes it easy to detect spills or leaks. Recently, GVL has been studied with PIMS, yielding an adiabatic ionization energy of 9.98 ± 0.05 eV, along with 0 K appearance energies (AEs) and possible structures of two fragments.

In this work, the dissociation dynamics of internal energy selected ions of mesitylene and GVL are studied using the imaging photoelectron-photoion coincidence (iPEPICO) spectroscopy apparatus at the Vacuum Ultraviolet (VUV) beamline of the Swiss Light Source (SLS). Mesitylene and GVL are examined in the 8.3 – 13.0 eV and 9.74 – 10.50 eV photon energy range, respectively. A single dissociation pathway is observed for each mesitylene and GVL. The structure of the dissociative fragment of GVL is compared to the previous report.

6.3 Experimental

The iPEPICO apparatus located at the Paul Scherrer Institute (PSI) has been described in detail previously and only a summary will be provided here. Synchrotron radiation for the VUV beamline at the SLS is generated using the X04DB bending magnet. The VUV radiation is collimated with a platinum coated copper mirror into a turntable style grazing incidence monochromator. Only one of the three available silicon gratings (600 mm⁻¹) was used in these experiments, which has the ability to select wavelengths between 5 and 15 eV. The light is then directed into the differentially pumped gas filter that is filled with 10 mbar of pure Ne when above 11 eV or 10 mbar of a of 60% Ne, 30% Ar, and 10% Kr mixture when below 11 eV. These gases are used to suppress higher resonance frequencies. The photon
energies are calibrated using the 1\textsuperscript{st} and 2\textsuperscript{nd} order autoionization lines of argon and neon, confirming a photon energy resolution around 3 meV.

Mesitylene (98\%) and γ-valerolactone (98\%) were purchased from Sigma-Aldrich. Samples were degased, flushed with argon, and effused into the instrument through a 30 cm long, 6 mm outer diameter Teflon tube. A needle valve controlled the flow of sample vapor into the apparatus that was held at a temperature of 298 K and a pressure between 3.5 x 10^{-6} mbar. Ions and electrons produced with the synchrotron radiation were accelerated using an extraction field ranging between 20-160 V cm\(^{-1}\).\(^{32}\) Photoelectrons were detected using Roentdek DLD40 position sensitive delay line detectors.\(^{32}\) The photoelectrons are velocity map imaged, based on their off axis momentum. This allows the zero kinetic energy electrons to be focused in a small center spot (with 1 meV resolution at the threshold) while electrons with excess kinetic energy (hot electrons) are directed on rings outside of the center circle. Hot electrons were subtracted according to the method described by Sztáray and Baer\(^{34}\) using the \textit{i2PEPICO} v1.5.2 program to yield threshold photoelectron spectra (TPES).\(^{32}\) Photoions were detected on a non-imaging Chevron-stack of MCPs after their mass was analyzed through a Wiley-McLaren-type time-of-flight (TOF) ion optics.

If the dissociation rate (k) of the parent ion is slow compared to the time scale of the experiment, (k between 10^{4} – 10^{7} s\(^{-1}\)) that is, the parent ion is metastable, the dissociation rates can be measured experimentally, as the daughter-ion TOF peaks have asymmetric shapes. The rate information can be obtained by modeling the exponentially decaying tail of these peaks.\(^{35}\) Using the TOF spectra at various energies, the fractional abundance of daughter ions from the parent ion can also be determined. Plotting this fractional abundance against the photon energy is known as the breakdown diagram. Breakdown diagrams and TOF spectra were modeled using the MiniPEPICO v189f program\(^{36}\) to obtain dissociation rates using the Simplified Statistical Adiabatic Channel Model (SSACM)\(^{35}\) for mesitylene and Rice-Ramsperger-Kassel-Marcus (RRKM)\(^{35}\) theory for GVL.
6.4 Computational Techniques

6.4.1 Ab Initio Calculations

In order to successfully model breakdown diagrams, quantum chemical calculations are performed. Harmonic vibrational frequencies and rotational constants of the neutral parent molecule are determined through *ab initio* methods to calculate the thermal energy distribution. Vibrational frequencies of the parent molecular ions and the transition state structures for the unimolecular decompositions pathways are also computed. In addition, adiabatic ionization energies (AIE) and 0 K appearance energies (AE) are also calculated. The G3MP2B3\textsuperscript{37} composite method was used for all of the calculation stated above. This method has a reported average absolute deviation of 5.23 kJ mol\textsuperscript{-1} (0.054 eV) from 299 experimentally determined enthalpies of formation, ionization energies, electron affinities, and proton affinities\textsuperscript{37} and it was chosen because of the accurate results for geometry optimizations and energetics, combined with the relatively low computational cost. All calculations were carried out in the Gaussian 09 program suite\textsuperscript{38} and visualized using Gaussview 5.0.9.\textsuperscript{39} Reactants and daughter ions were checked for spin contamination after the geometry optimization, frequency calculation, and final single point energy calculation. The optimized geometries of the parent molecules and fragments contained no imaginary (negative) frequencies, ensuring that they represent a minimum on the potential energy surface. When a model transition state structure had no imaginary frequency, the vibrational frequency corresponding to the stretching motion of the bond that breaks is removed and the remaining vibrational frequencies are used in the statistical modeling of the PEPICO experiment. The vibrational frequencies used for modeling are provided in the supplemental material.

6.4.2 Statistical Modeling

Breakdown diagrams show the fractional ion abundance as a function of photon energy. Modeling the breakdown diagram requires the thermal energy distribution of the neutral molecules. It is then assumed that this thermal energy distribution can be transposed directly onto the ion potential energy surface upon ionization and dissociate once the internal energy surpasses the any of the dissociation energies.\textsuperscript{35} This assumption is valid when the width of the thermal energy distribution is smaller than the depth of the
potential energy well. The internal energy of the ion, $E_{int}^{ion}$, created from the absorption of radiation can be described by the equation below, where $h \nu$ is the photon energy, $E_{int}^{neutral}$ is the internal energy of the parent molecule, and AIE is the adiabatic ionization energy.

$$E_{int}^{ion} = h \nu + E_{int}^{neutral} - \text{AIE} \quad (6.1)$$

Both rate theories used in this report use the following expression to calculate dissociation rates, which is shown in equation 6.2.

$$k(E) = \frac{\sigma N_t(E-E_o)}{h \rho(E)} \quad (6.2)$$

Here, $\sigma$ is the reaction degeneracy, $N_t(E-E_o)$ is the sum of states in the transition state, $h$ is Planck’s constant, and $\rho(E)$ is the density of states for the fragmenting ion. The difference between the two rate theories is in the treatment of the sum of states in the transition state. We used rigid activated complex RRKM theory (RAC-RRKM) for GVL, which has been proven accurate in most cases of metastable ionic dissociation, even without a well-defined transition state structure such as in the case of a reverse barrier. When dissociations take place on a potential energy surface without a barrier, the effective transition states (that are used to model experimental data) could vary in tightness and may be energy dependent. Depending on the tightness of the TS, the activation entropy ($\Delta S^{\ddagger}$) will change, which will consequently change the slope in the breakdown diagram. A tight transition state will have a near zero or negative $\Delta S^{\ddagger}$ while a loose transition state will have a positive $\Delta S^{\ddagger}$. The $\Delta S^{\ddagger}$ determined for this report are calculated at 600 K by convention. The calculated vibrational frequencies used to fit the breakdown diagrams are presented in the supplemental material.

The slow and barrierless dissociation of mesitylene ($10^3 \text{ s}^{-1} < k < 10^7 \text{ s}^{-1}$) and the need to calculate rates over several orders of magnitude required the use of the Simplified Statistical Adiabatic Channel Model (SSACM). As stated above, SSACM uses equation 6.2 to determine the dissociation rates, but the sum of states is includes the vibrational frequencies and moments of inertia. In addition, an adjustable parameter is used when determining the sum of states to keep the dissociation rates from rising too quickly.
This parameter is called the rigidity factor \( f_{rigid}(E) \) and it accounts for the anisotropy of the potential energy surface. Equation 6.3 shows the functional form that was used, which was derived for dissociating systems where short range interactions are dominated by valance forces. Here, \( E - E_o \) is the excess energy distributed between the neutral and cationic fragments and \( c \) is a fitting parameter to describe the transition from the anisotropic to the isotropic region of the potential.\(^{35}\)

\[
f_{rigid}(E) = \exp\left(-\frac{E - E_o}{c}\right)
\]  

(6.3)

Another useful piece of information obtained from modeling breakdown diagrams are the AEs of daughter ions. The AE of the daughter ion can be used to determine the bond dissociation energy (BDE) of the neutral parent molecule if only a single bond breaks according to equation 6.4, where \( \text{AIE}_{\text{fragment}} \) is the adiabatic ionization energy of the neutral daughter fragment.

\[
\text{BDE} = \text{AE} - \text{AIE}_{\text{fragment}}
\]  

(6.4)

In cases where the heat of formation of the neutral parent molecule, \( \Delta_f H^0_0(P) \), and neutral fragment, \( \Delta_f H^0_0(\text{N.F.}) \), are known, it is possible to determine the heat of formation through the experimental AE.

\[
\Delta_f H^0_0(\text{fragment}) = \text{AE} - \Delta_f H^0_0(\text{N.F.}) + \Delta_f H^0_0(P)
\]  

(6.5)

6.5 Results and Discussion

6.5.1 Mesitylene

6.5.1.1 Threshold Photoelectron Spectrum and TOF Spectra

The TPES of mesitylene (Figure 6-1) is reported from 8.3 to 12.1 eV. The adiabatic ionization energy of mesitylene was found to be 8.41 ± 0.01 eV. This is in good agreement with the reported values\(^{19-26}\) and the G3MP2B3 calculated value of 8.46 eV. Neutral mesitylene was optimized with \( C_{3v} \) symmetry while the cation was found to have \( C_1 \) symmetry due to rotations of the methyl groups. Hartree-Fock molecular orbital calculations with the 6-311++(d,p) basis set showed that the HOMO and HOMO-1 of the neutral molecule are degenerate orbitals with \( E \) symmetry (Figure 6-2). The HOMO-2 has \( A_1 \) symmetry and lies 2.4 ± 0.1 eV above the AIE as it can be seen from the appearance of a peak in the threshold photoelectron spectrum in Figure 6-1. This spectrum is very similar to benzene, which has two degenerate
E_{1g} orbitals as the HOMO and HOMO-1 and an A_{2u} orbital as the HOMO-2. In fact, the photoelectron spectrum of benzene shows a nearly identical pattern with a separation between the HOMO/HOMO-1 and HOMO-2 of $2.26 \pm 0.04 \text{ eV}$.\textsuperscript{43} In the TOF spectra shown in Figure 6-3, mesitylene ($m/z = 120, C_9H_{12}^+$) as a single peak between 14.25 and 14.35 $\mu$s.

![Photoelectron Spectrum](image)

**Figure 6-1.** The recorded photoelectron spectrum for mesitylene in the 8.39 to 12.1 eV photon energy range. The AIE is shown at 8.41 eV and a second excitation from the HOMO-2 $^1A$ orbital is shown at 10.8 eV.

![optimized HOMO](image)

**Figure 6-2.** The optimized HOMO (a), HOMO-1 (b), and HOMO-2 (c) for mesitylene using the HF/6-311++(d,p) level of theory.

Only one dissociative fragment was observed in the energy range of this study, the loss of a neutral CH$_3$ group. Starting around 11.7 eV, the peak corresponding to the methyl loss ($m/z = 105, C_8H_7^+$) is observed in the 13.3 – 14.5 $\mu$s TOF range. The peak is highly asymmetric, representing a slow dissociation and a
metastable parent ion. Above 12.3 eV the \( m/z = 105 \) peak becomes symmetric, meaning the parent ion is no longer metastable.

![Figure 6-3](image)

**Figure 6-3.** Selected time-of-flight distributions for mesitylene in the 11.75-12.75 eV photon range showing the slow dissociation of the \( \text{C}_9\text{H}_{10}^+ \) \( (m/z = 105) \) daughter ion.

### 6.5.1.2 Breakdown Diagram, Modeling, and Thermochemistry

An asymmetric peak was observed with the lower energy dissociations, which corresponds to a “slow” dissociation. As stated above, these asymmetric peaks contain rate information and must be modeled to obtain the dissociation rates. Figure 6-3 shows experimental TOF spectra and fits where the daughter ion peak gradually becomes symmetric at increasing photon energies. To obtain dissociative photoionization appearance energies, both the breakdown curve and these asymmetric daughter ion time-of-flight distributions need to be modeled, using statistical rate theory. Figure 6-4 shows the modeled breakdown diagram compared to the experimental data from 11.0 to 12.5 eV. The optimized breakdown diagram was obtained using the calculated frequencies from the optimized geometries of neutral mesitylene (with \( \text{C}_3v \) symmetry), neutral methyl radical, and \( m/z = 105 \) daughter ion, along with an SSACM rigidity factor of 200 meV. Mesitylene has three identical methyl groups so the reaction symmetry was set to 3. In modeling the dissociation rates to fit the experimental data, the vibrational frequencies of the parent ion and the product fragments were not adjusted or scaled and the only fitting parameter was the SSACM rigidity factor.
Figure 6-4. Modeled breakdown diagram of the mesitylene cation (red line) and the C₈H₉⁺ daughter ion (blue line) from 11.00 to 12.50 eV superimposed on the experimental breakdown diagram.

When a proper fit to both the breakdown curve and the time-of-flight distributions was achieved, the AE for the m/z = 105 daughter ion was found to be 12.00 ± 0.06 eV. This is in very good agreement with the CBS-QB3 calculated value of 11.95 eV. The log₁₀ of k(E) at the photon energy of 12.00 eV are shown in Figure 6-5 plotted against the internal energy. The sharp onset is observed on similar molecules, such as halogenated benzenes. This steep onset is indicative of a direct dissociation to the daughter ion as expected. In addition, the dissociation rates for mesitylene cation are comparable to the dissociation rates to the aforementioned halobenzenes.

Figure 6-5. Plot of log₁₀ of the microcanonical rate constant against the ion internal energy for the loss of CH₃ from the mesitylene cation at the photon energy of 12.0 eV.
The formation of the \( m/z = 105 \) daughter ion involves only a single bond fission, so the bond energy can be determined simply from the daughter ion appearance energy, as stated above. The AIE of the \( m/z = 105 \) daughter ion was calculated using the CBS-QB3\(^{45-46}\) composite method. This method was used because one imaginary frequency was consistently found when calculating the total electronic energy of the neutral \( \text{C}_8\text{H}_9 \) fragment. In addition, significant spin contamination (\( <S^2> = 1.099 \)) was observed after the geometry optimization, which required the use of the restricted open shell (RO) form of the CBS-QB3\(^{37}\) method. The ionization energies calculated with ROCBS-QB3 have a reported mean absolute deviation of 0.042 ± 0.01 eV.\(^{47}\) This method produced an AIE of 7.92 eV for the \( m/z = 105 \) daughter ion. Using the calculated AIE of the daughter ion and the experimental AE in equation 6.4, we derived a BDE of 394 ± 6 kJ mol\(^{-1}\). This is similar to the reported value for the methyl loss of toluene.\(^{48}\) The enthalpy of formation of mesitylene in the gas phase is \(-15.9 ± 1.3 \) kJ mol\(^{-1}\).\(^{49}\) Along with the AE and heat of formation of \( \text{CH}_3 \) radical (149.0 ± 0.8 kJ mol\(^{-1}\)),\(^{50}\) equation 6.5 gives a heat of formation for the \( \text{C}_8\text{H}_9^+ \) ion as 993 ± 6 kJ mol\(^{-1}\).

6.5.2 \( \gamma \)-Valerolactone

6.5.2.1 Threshold Photoelectron Spectrum and TOF Spectra

Figure 6-6 shows the recorded TPES for GVL from 9.74 to 10.50 eV. The peak at 9.91 ± 0.02 eV is identified as the AIE. It is in good agreement with the calculated value of 9.93 eV and reported value of 9.98 ± 0.05 eV.\(^{30}\) The vertical ionization energy (VIE) is also assigned at 10.10 ± 0.02 eV. Figure 6-7 shows the TOF distributions for the parent ion (GVL) centered at 12.06 μs and a slightly asymmetric peak for a daughter ion centered at 9.03 μs. Only a single dissociation was observed below 10.5 eV, which was determined to be the 1-butene ion (vide infra). This dissociation was found to have a barrier and the BD and TOF spectra were fit using RRKM theory.
**Figure 6-6.** The experimental photoelectron spectrum of GVL from 9.74 – 10.5 eV showing the AIE at 9.91 eV and VIE at 10.10 eV

**Figure 6-7.** Selected time-of-flight distributions for GVL in the 9.90-10.50 eV photon range showing the slow dissociation of the C₄H₈⁺ (m/z = 56) daughter ion.

### 6.5.2.2 Breakdown Diagram, Modeling, and Thermochemistry

The BD of GVL to m/z = 56 is presented in Figure 6-8. The parent ion signal starts to decrease around 10.0 eV and becomes zero just below 10.4 eV. We calculated several possible structures for the m/z = 56 cation. They include 1-butene, cis- and trans-2-butene, methyl cyclopropane cation, and C₃H₅O⁺. The reaction energies for all C₄H₈⁺ ions relative to neutral GVL are presented in Table 6-1.
Figure 6-8. Breakdown diagram of GVL in the 9.74 – 10.50 eV photon energy range showing the AE of the C₄H₈⁺ daughter ion. Red circles and blue squares are experimental points for m/z = 100 and 56, respectively, and solid lines represent the simulated breakdown diagram.

Table 6-1: List of possible products for the C₄H₈⁺ isomers from GVL and relative energies using the CBS-QB3 method.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Relative Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GVL → 1-butene⁺ + CO₂ + e⁻</td>
<td>9.75</td>
</tr>
<tr>
<td>GVL → Trans-2-butene⁺ + CO₂ + e⁻</td>
<td>9.15</td>
</tr>
<tr>
<td>GVL → Cis-2-butene⁺ + CO₂ + e⁻</td>
<td>9.20</td>
</tr>
<tr>
<td>GVL → Methyl cyclopropane⁺ + CO₂ + e⁻</td>
<td>9.72</td>
</tr>
</tbody>
</table>

All of the relative energies are below the observed dissociation barrier in Figure 6-8. The CBS-QB3 thermochemical limit of the C₃H₄O⁺ ion [5] is much higher than the experimental AE at 11.20 eV as shown in Figure 6-9, which means we can exclude this ion. Therefore, we scanned the potential energy surface to search for a transition state to the C₄H₈⁺ ions. We scanned the surface along the bonds between carbons (a) and (b) and carbon (d) and O using the B3LYP method with the CBSB7 basis set. A saddle point was found with a bond length of 2.32 Å between carbon (a) and (b) and 1.73 Å between carbon (d) and O (Figure 6-10).
Figure 6-9. Possible reaction pathways for the decomposition of GVL to $m/z = 56$. The calculated energies of the GVL cation ([2]), transition state ([3‡]), and products ([4] and [5]) are relative to neutral GVL [1]. The black line represents the neutral potential energy surface and red lines are the cationic potential energy surface. The carbons are labeled a-e.

Figure 6-10. Potential energy surface of GVL+ over the elongation of the bonds between carbons (a) and (b) and carbon (d) and O using the B3LYP method and CBSB7 basis set. The values presented on the color scale are the energies in Hartrees and the black dot denotes the location of the transition state.
The B3LYP/CBSB7 vibrational frequencies of this transition state was used to model the TOF distributions and BD diagram in Figures 6-7 and 6-8, respectively. They were not scaled during the fitting so the only adjustable parameter was the dissociation barrier. The $\Delta S^\ddagger_{600 \text{K}}$ was found to be $-4.70 \text{ J mol}^{-1} \text{K}^{-1}$ and the dissociation was found to be $3700 \text{ cm}^{-1}$ (0.46 eV). Adding this barrier to the AIE lead to an appearance energy of $10.37 \pm 0.04 \text{ eV}$. This value was in very good agreement with our CBS-QB3 AE of 10.34 eV (Figure 6-9). Therefore, the $m/z = 56$ ion comes from this transition state.

During the relaxed scans of the potential energy surface, shown in Figure 6-10, a hydrogen atom would spontaneously transfer between carbons (c) and (d). Thus leading us to the assignment of $m/z = 56$ as the 1-butene cation. However, cis-2-butene, trans-2-butene, and methyl cyclopropane are also possible because the internal energy of the parent ion is high enough to overcome any of the barriers for H atom transfer or rotations. Further studies will be needed to identify which isomers are produced.

We used the TOF fits to determine the dissociation rates using RAC-RRKM theory. The $\log_{10}$ of the microcanonical rates as a function of ion internal energy are plotted in Figure 6-11. The fast reaction rates and shallow onset justify the use of RAC-RRKM theory. Therefore, using our experimentally determined data, and the known known enthalpy of formations of GVL ($-406.5 \pm 1.1 \text{ kJ mol}^{-1})^{51}$ and CO$_2$ ($-393.151 \pm 0.13 \text{ kJ mol}^{-1})^{50}$ it is possible to derive the heat of formation for the 1-butene cation of $987 \pm 4 \text{ kJ mol}^{-1}$.

![Figure 6-11. Plot of $\log_{10}$ of the microcanonical rate constant against the ion internal energy for the loss of CO$_2$ from GVL cation at the photon energy of 10.37 eV.](image)

122
6.6 Conclusions

The imaging photoelectron-photon coincidence apparatus at the Swiss Light Source was used to measure dissociation rates, bond energies, and the heat of formation of various ions. Mesitylene parent ion dissociates to form \( \text{C}_9\text{H}_9^+ \) ion and neutral methyl radical. The C-C bond of the methyl group of mesitylene was found to have a dissociation energy of \( 386 \pm 6 \text{ kJ mol}^{-1} \). GVL dissociates to neutral \( \text{CO}_2 \) and \( \text{C}_4\text{H}_8^+ \) ion with a structure similar to methyl cyclopropane but with an elongated bond between the tertiary carbon and one of the carbons within the ring. The AE matches the calculated and previously reported value and a heat of formation was determined to be \( 985.3 \pm 4 \text{ kJ mol}^{-1} \).

6.7 Acknowledgments

The authors would like to acknowledge the American Chemical Society – Petroleum Research Fund Grant # 51170 UNI6. We would also like to thank professors William Karney and Claire Castro, along with the University of San Francisco Faculty Development Fund for usage and maintenance of the computational facilities used in this report. Additional computational support was provided by the Brown University Center for Computation and Visualization. In addition, we would like to thank Dr. Zachary Piazza for providing scripts that aided in the data analysis and other helpful discussions. Lastly, we gratefully acknowledge the Swiss Light Source for beamtime allocation.
6.8 References


