Reactions of Dehydro-N-pyridinium with Small Unsaturated Hydrocarbons

Cameron C. Bright
University of Wollongong

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Reactions of Dehydro-\textit{N}-pyridinium with Small Unsaturated Hydrocarbons

Cameron C. Bright

Supervisor:
Assoc. Prof. Adam J. Trevitt

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The University of Wollongong
School of Chemistry

8\textsuperscript{th} February, 2018
Abstract

Small nitrogen containing heteroaromatics are fundamental building blocks for many biological molecules, including the DNA nucleotides. Pyridine, as a prototypical N-heteroaromatic, has been implicated in the chemical evolution of many extraterrestrial environments, including the atmosphere of Titan. This thesis describes reactions of the three dehydro-N-pyridinium radical cation isomers with a set of small, unsaturated hydrocarbons: propene, acetylene, ethene and propyne. These reactions were chosen due to their possible involvement in molecular-weight growth processes, and in the synthesis of complex organics in space. Mass spectrometric techniques are used to acquire product mass spectra, measure product branching ratios and calculate second-order rate coefficients for reactions of 2-dehydro-N-pyridinium, 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium with each neutral hydrocarbon co-reactant. Quantum chemical calculations are used to validate experimental results and elucidate possible reaction mechanisms for the propene and acetylene reaction systems. Potential energy schemes are presented, together with a quantum state counting kinetic modelling analysis for propene reactions.

Reaction efficiencies, calculated from second-order rate coefficients, increase from 4-dehydro-N-pyridinium to 3-dehydro-N-pyridinium to 2-dehydro-N-pyridinium. This trend holds for all neutral reactants and is consistent with transition state polarisation effects. Across reactions of the three dehydro-N-pyridinium isomers, propyne reactions are the most efficient, followed by propene, ethene then acetylene. Measured reaction efficiencies are correlated with submerged barrier height. This correlation may be useful in predicting reaction efficiencies when experimental data is unavailable. Common reaction products and neutral-loss pathways are identified. H-atom loss is seen in all reactions, as is the stabilisation of reaction adduct isomers. Loss of larger neutral-fragments is seen for propene and propyne reactions. Computational studies reveal propene and acetylene reactions are barrierless or de facto barrierless, suggesting these reactions may be viable in cold, extraterrestrial environments. Ethene and propyne reactions have not yet been investigated computationally. The identified barrierless and de facto barrierless pathways may be possible synthesis routes for products including quinoline and isoquinoline, viable in cold regions of space, given the presence of pyridinium and the respective neutral reactant.
Acknowledgements

There are many people that have contributed to the completion of this thesis, some directly, some indirectly, all of whom I am grateful for.

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To James, Matt, Chris, Bart. You made me feel welcome the second I joined the lab group. Congratulations to you all for graduating and the best of luck in your future careers. I wish I had more time to work with you.

To Ben, Sam, Paddy and Boris. I did enjoy those first few weeks (days?) of bossing you around the lab before you began to know your way around your projects better than I did. I know you’ve all got the skills and knowledge to be great researchers. Good luck, have fun, do your best. Thanks for the good times.

To everyone else, there are too many to name. Al Maccarone, Haibo Yu, Ben Kirk, Berwyck Poad, Jacob Byrnes, Phil Tracey, all members (past and present) of the Laser Chem Lab, all members of the CAC cluster, the entire UOW school of chemistry, and those who have helped me from outside UOW. Thank you.
Certification

I, Cameron Bright, declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree Master of Science – Research, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

_______________________________
Cameron Bright

8th February, 2018
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>CID</td>
<td>Collision induced dissociation</td>
</tr>
<tr>
<td>EA&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Electron affinity (vertical)</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray ionisation</td>
</tr>
<tr>
<td>HACA</td>
<td>Hydrogen abstraction, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt; addition</td>
</tr>
<tr>
<td>IE&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Ionisation energy (vertical)</td>
</tr>
<tr>
<td>IRC</td>
<td>Intrinsic reaction coordinate</td>
</tr>
<tr>
<td>ISM</td>
<td>Interstellar medium</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-charge ratio</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PANH</td>
<td>Polycyclic aromatic nitrogen hydrocarbon</td>
</tr>
<tr>
<td>PD</td>
<td>Photodissociation</td>
</tr>
<tr>
<td>PE</td>
<td>Potential energy</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy scheme</td>
</tr>
<tr>
<td>PRC</td>
<td>Pre-reaction complex</td>
</tr>
<tr>
<td>RRKM</td>
<td>Rice–Ramsperger–Kassel–Marcus</td>
</tr>
<tr>
<td>TS</td>
<td>Transition state</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VUV</td>
<td>Vacuum ultraviolet</td>
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<tr>
<td>ZPE</td>
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---

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---

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Figure 4.5 Kinetic curves for m/z 79 (red), 104 (blue), 105 (green) and 130 (orange) for reactions of (a) 2-dehydro-N-pyridinium, (b) 3-dehydro-N-pyridinium and (c) 4-dehydro-N-pyridinium with acetylene (6.59 × 1010 molecules × 10^-10 molecules)
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Figure 4.8a Potential energy scheme for addition of acetylene to 3-dehydro-N-pyridinium. R, PRC, I, and P denote reactants, pre-reaction complexes, intermediates and products, respectively. The two conformers of I$_{1m}$, I$_{3m}$ and I$_{5m}$, highlighted in red, green and blue, undergo secondary reactions with acetylene, shown in Figure 4.8b, c and d. Enthalpies are in kcal mol$^{-1}$, relative to R$_{0m}$.

Figure 4.9a Potential energy scheme for addition of acetylene to 4-dehydro-N-pyridinium. R, PRC, I, and P denote reactants, pre-reaction complexes, intermediates and products, respectively. I$_{1p}$ and the two conformers of I$_{3p}$, highlighted in red and green, undergo secondary reactions with acetylene, shown in Figure 4.9b and c. Enthalpies are in kcal mol$^{-1}$, relative to R$_{0p}$.

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Figure 5.2 Proposed scheme for the reaction of ethene with (top) 2-dehydro-N-pyridinium, (middle) 3-dehydro-N-pyridinium, and (bottom) 4-dehydro-N-pyridinium. R, I, and P indicate reactants, intermediates and products.
respectively. Subscript o, m, and p indicate ortho-, meta- and para-substituted reactions.

Figure 5.3 Kinetic curves for m/z 79 (red), 106 (blue), and 107 (green) from reactions of (a) 2-dehydro-N-pyridinium, (b) 3-dehydro-N-pyridinium and (c) 4-dehydro-N-pyridinium with ethene $$(6.648 \times 10^{10} \text{ molecules cm}^{-3})$$. A single-exponential function fit to the decay curve of m/z 79 is shown as a black line and fit residuals are plotted above each kinetic trace. Measurements at reaction times greater than 0.500 s are not displayed. Error bars are 2σ.

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Chapter 1 – Introduction

1 Introduction

This thesis presents results of a combined experimental and computational study into the reactions of the three dehydro-N-pyridinium radical cation isomers with a set of small, unsaturated hydrocarbons. The goal of this study is to identify trends in reactivity that can contribute to the development of a more complete understanding of N-heteroaromatic radical cation chemistry, and in doing so, lead to methods of increasingly accurate estimation of reaction efficiencies, products and product branching ratios of reactions that have not been studied experimentally. Possible implications exist in astrochemical modelling studies, where experimentally determined reaction data for many N-heteroaromatic species does not exist. New, low temperature synthetic pathways to complex organics are also identified.

First, an introduction into extraterrestrial N-heteroaromatics is given, followed by a review of neutral and cationic aromatic radical reactions of astrochemical significance and relevance to the reactions studied in this work. Distonic radical cations, which includes the three dehydro-N-pyridinium radical cation isomers, the target of this thesis, will be introduced. Finally, methods of radical generation in the laboratory and the mass spectrometric techniques used to study radical reaction systems will be discussed.

1.1 Extraterrestrial N-Heteroaromatics

The extraterrestrial environments of interstellar and circumstellar space play host to rich and diverse chemistry. Since the first identification of a polyatomic species, methyldiene (CH), in the interstellar medium (ISM) in 1937,¹ observation-based studies have grown rapidly in number and complexity. Now more than 190 molecules and ions have been identified to exist within the ISM to date. These compounds include many organic functional groups and a variety of polycyclic aromatic hydrocarbons.² Analysis of passing comets and fallen meteorites has also provided insight into the complex composition of extraterrestrial bodies, as well as circumstantial evidence for the presence of many interstellar species not yet directly detected within interstellar clouds and protoplanetary disks.³ Of interest among the growing astronomical chemical inventory are nitrogen containing aromatic heterocycles due to their possible link to the prebiotic evolution of life on Earth.
N-heterocycles are essential building blocks of many biological molecules. DNA/RNA nucleotides are derived from the base molecules pyrimidine and purine, shown in Figure 1.1, while the amino acids histidine and tryptophan contain an imidazole and indole side chain, respectively. A variety of amino acids, nucleobases and other N-heterocyclic aromatics of non-terrestrial origin have been detected in meteorites, the fallen remains of asteroids. For example, concentrations of 100-700 ppb of adenine, guanine, hypoxanthine and xanthine (purine derivatives), and up to 73 ppb uracil (pyrimidine derivative) were measured in samples of the Murchison, Murray and Orgueil meteorites. Quinoline, isoquinoline and a range of substituted pyridines were also identified in the Murchison meteorite. The cumulation of Earth based analysis of an array of meteorites over the past 60 years has led to 45 unique meteorite classifications, of which five have been reported to contain extraterrestrial amino acids and three have been determined to contain extraterrestrial nucleobases. Advances in space flight and robotics have facilitated direct compositional analysis of asteroids, comets and other celestial bodies in space itself, away from possible biological contaminants found on earth. Organic matter has been detected within the coma of comets as early as the Giotto and Vega robotic spacecraft missions on flybys of Halley’s Comet during its 1985/86 perihelion. Many of the species identified within the coma of Halley’s Comet were identified as small, unsaturated hydrocarbon and nitrile ions. The small average mass of detected molecules was attributed to photo-chemical processing and decomposition of larger “native” species during ejection from the comet nucleus and the several hundred kilometre flight to the spacecraft before detection. Nevertheless, chemical modelling of the cometary system has indicated that the pristine organic material of Halley’s Comet is likely of polymeric nature and composed of 45% hydrogen, 35% carbon, 18% oxygen and 2% nitrogen (atomic %), intriguingly, this is comparable to the elemental makeup of a human body (62% H, 12% C, 24% O, 1.1% N). More recently, in 2014, the Rosetta spacecraft mission conclusively identified the presence of the amino acid glycine in the coma of comet Churyumov-Gerasimenko with numerous other organic molecules detected on the comet nucleus surface by the Philae lander. The molecules detected in these studies are believed to be, in part, material from our solar system’s primordial days preserved within the cometary ice and are an indication of the rich chemistry of that time. Evidence is mounting that Earth as a celestial body is not unique in its ability to produce the chemical building blocks to support life. Earth may have even been “seeded” by the exogenous
delivery of essential complex molecules through impacts with comets and asteroids, subsequently making it capable of initiating the prebiotic chemistry that led to life.

![Figure 1.1 Structure of pyrimidine, purine, imidizole and indole](image)

The search continues for bio-relevant nitrogen heterocycles within carbon rich circumstellar envelopes and the molecular clouds of interstellar space, in which there have been no positive identifications of N-heterocycles to date. Charnley et al. have conducted extensive astronomical searches for pyridine, quinoline and isoquinoline towards C-rich circumstellar envelopes CRL 618, CRL 2688 and IRC +10216. The search did not identify the presence of any of these N-heteroaromatics in detectable quantities and the upper limits to column density were determined to be $7.3 \times 10^{12}$ to $2.7 \times 10^{14}$ cm$^{-2}$ across the range of N-heterocycles being investigated (instrument detection limit assuming 50 K excitation temperature). Similarly, a search for pyrimidine by Kuan et al. within the molecular clouds Srg B2(N), Orion KL and W51 e1/e2 was only able to derive pyrimidine column density upper limits of 1.7, 2.4 and $3.4 \times 10^{14}$ cm$^{-2}$, respectively. These observations suggest that even simple N-heterocyclic compounds such as pyridine, quinolone and pyrimidine, the base molecules from which many more complex biological species are derived, exist within interstellar space in abundances too low to detect with current instruments and techniques. The difficulty of detecting small concentrations of N-heterocycles is compounded by their inherently weak spectral lines, common to aromatic ring structures. This is caused by small rotational constants, hence large partition functions, leading to large distribution of energy levels and thus low state densities even at low temperatures.

The apparent low concentrations of N-heterocycles in the ISM can be explained by short lifetimes in the harsh environment of space. Specifically, N-heterocycles are susceptible to photo-destruction by UV radiation. A lab based study was conducted by Peeters et al. into the photostability of pyridine, pyrimidine and s-triazine. The study predicts a half-life of 18, 8.1 and 2.1 years within the diffuse interstellar environment for pyridine, pyrimidine and s-triazine respectively; a timescale far too short to facilitate chemical
processing into any substantial amount of more complex, biologically relevant molecule. A greater number of nitrogen aromatic ring substitutions was also observed to reduce the photostability of the molecule further reducing the likelihood of complex organics surviving within the ISM. Of the extraterrestrial environments investigated, it was determined that only dense interstellar clouds could provide sufficient protection from UV radiation through absorption by dust for pyridine and pyrimidine to survive on astronomically relevant timescales. In the case of protoplanetary disks (i.e. the disks of dense gas surrounding a newly formed star), UV radiation from the central star coupled with exposure to the interstellar UV-field present conditions that would rapidly destroy N-heterocycles.\textsuperscript{14} However, there exists an opaque inner envelope within the disk that may still allow N-heterocycles to form and survive.\textsuperscript{18-19} Spectroscopically, it is difficult to isolate the weak spectral lines of any N-heterocycle from the bright dust continuum emission to allow identification of species present within the disk. Modern facilities with unprecedented sensitivities, such as the Atacama Large Millimetre Array (ALMA), are beginning to unveil the complex chemical makeup of protoplanetary disks, raising the prospects for detection of N-heterocycles in the near future.\textsuperscript{13}

It is apparent that the survival of N-heterocycles requires an environment that provides sufficient protection from the harsh UV field of space. However, not all photochemistry acts as a force of destruction. Chemistry driven by UV radiation also has the potential to initiate formation of large, unsaturated N-heterocyclic compounds. A prime example within our own solar system is the atmosphere of Titan, the largest moon of Saturn, which contains extraterrestrial complex organics in abundance. Titan has a substantial atmosphere that extends over 1000 km above the moon’s surface with a surface pressure of 1.43 atm.\textsuperscript{20} Its primary constituents are N\textsubscript{2} (97\%) and CH\textsubscript{4} (1.5\% - 2\%) with the remainder (1\% - 1.5\%) comprising predominantly of hydrogen and small hydrocarbons.\textsuperscript{21} The upper layer of Titan’s atmosphere is constantly being showered by UV radiation from the sun, and other energetic particles from Saturn’s magnetosphere. It is predicted that the input of energy from this radiation initiates molecular weight growth reactions that polymerise small precursors (methane, nitrogen and other simple alkanes) to form the large ring-containing molecules responsible for Titan’s characteristic blue glow.\textsuperscript{21-23} In fact, current models predict that about one-third of the PAHs within Titan’s upper atmosphere contain nitrogen atoms\textsuperscript{23} leaving a high probability of pyridines, quinolines and potentially even nucleotide base molecules, purine and pyrimidine, existing on Titan.
Past research throughout the last century, traditionally grounded in combustion chemistry, has led to a large portion of simple extraterrestrial hydrocarbon chemistry incorporated into current models. However, the reactivities of many N-bearing molecules are not available in current astrochemical databases\textsuperscript{24-25} and must be estimated. The roles of charged species (protonated and radial cations) and their neutral radical counterparts are similarly underrepresented in the literature. This is in contrast to the fact that a large portion of the interstellar and circumstellar chemical inventory is composed of radicals and ions, which is due, in varying degrees, to a combination of primary (cosmic rays, high energy photons and shock waves) and secondary (secondary electrons, stellar winds, magnetospheric and auroral ions and particles) ionisation sources.\textsuperscript{26} One potential source of molecular ionisation in space is proton transfer from H$_3^+$, the second most abundant interstellar molecule.\textsuperscript{27} H$_3^+$ is ubiquitous within interstellar space as it is produced through the protonation of H$_2$ by H$_2^+$ following cosmic ray ionisation (Figure 1.2). It is a potent proton donor and thus ion-molecule reactions of H$_3^+$ with any aromatic N-heterocycle would lead to prompt protonation. Furthermore, the harsh UV photons of interstellar and circumstellar space, together with the ubiquity of cosmic rays, presents an environment facilitating C-H and N-H bond fission and radical formation from protonated and neutral N-heterocycles alike.

\begin{align*}
H_2 + \text{cosmic ray} & \rightarrow H_2^+ + e^- + \text{cosmic ray} \\
H_2^+ + H_2 & \rightarrow H_3^+ + H
\end{align*}

Figure 1.2 H$_3^+$ production in interstellar space

Many researchers are calling for laboratory experiments to measure reaction kinetics and major product pathways of N-bearing molecules and their radical and charged counterparts to improve our understanding of extraterrestrial chemical systems, and to provide direction for future searches for aromatic nitrogen heterocycles outside our solar system.\textsuperscript{22,28-31} It is the goal of this thesis to begin filling that gap by measuring gas-phase reaction kinetics, identifying major reaction products, and deducing likely reaction pathways of the dehydro-N-pyridinium radical cation family in reactions with unsaturated hydrocarbons. This will contribute to the development of a more complete understanding of N-heteroaromatic radical cation chemistry by the study of the prototypical pyridinium unit from which many larger N-heteroaromatic molecules are derived. Target reactions
include the three dehydro-N-pyridinium isomers with the common extraterrestrial hydrocarbons propene, acetylene, ethylene and propyne, with a goal to make steps towards the predictive understanding of similar reactions systems.

1.2 Molecular Weight Growth via Neutral Aromatic Radical Reactions

Radical species are atoms, molecules or ions with one (or more) unpaired electron$^{32}$ and, as such, are typically highly reactive species. Neutral aromatic radicals have been studied extensively due to their prevalence in petroleum fuels,$^{33}$ their role in combustion chemistry,$^{34-36}$ their expected contribution to the chemical evolution if interstellar$^{37}$ and circumstellar$^{38}$ space, and their effects on human health$^{39}$. Monocyclic aromatic radical reactions with short chain hydrocarbons (2 – 3 carbon atoms) are of particular interest in astrochemistry. This is due to their suspected role in the formation of polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic nitrogen hydrocarbons (PANHs), leading to molecular weight growth and increased molecular complexity of many extraterrestrial chemical systems. PAH and PANH species formed via aromatic radical chemistry have been proposed as a (partial) explanation of several longstanding astronomical mysteries, such as the origin of the diffuse interstellar bands,$^{40-41}$ the chemical mixture responsible for the blue haze of Titan,$^{21,23}$ and formation of extraterrestrial nucleobases and organics essential for life.$^{42-44}$

Much of the knowledge of aromatic radicals in combustion systems has been applied to the study of neutral radical reactions in astrochemical systems in more recent years. An established molecular weight growth mechanism involves acetylene addition, via HACA (hydrogen abstraction, $C_2H_2$ addition) pathways, originally developed in the context of soot formation in combustion systems. Various HACA routes leading to the formation of naphthalene, the simplest PAH and precursor to a plethora of larger PAHs, have been proposed by Frenklach and Wang$^{45}$ in 1991, and Bittner and Howard$^{46}$ in 1981. These pathways are shown in Figure 1.3. Several of these mechanisms have since been confirmed experimentally$^{47}$ and further investigated computationally$^{48}$ by Kaiser.

Analogous HACA mechanisms have been proposed for the formation of the simple PANHs quinoline and isoquinoline.$^{48-49}$ These mechanisms differ from naphthalene forming pathways in that the reaction begins with acetylene addition to the 3-
Chapter 1 – Introduction

dehydropyridine radical, as opposed to the phenyl radical. These mechanisms are shown in Figure 1.4.

Figure 1.3 The Frenklach, Bittner-Howard and Modified Frenklach HACA routes for gas phase synthesis of naphthalene from the phenyl radical and acetylene.

Figure 1.4 The Frenklach, Bittner-Howard and Modified Frenklach HACA routes for gas phase synthesis of isoquinoline from the 3-pyridyl radical and acetylene. Analogous routes exist leading to the formation of quinoline by radical transfer and addition of the second acetylene to the C2 position (Frenklach and Modified Frenklach), or ring closure at the C2 position (Bittner-Howard).

The HACA mechanisms presented in Figure 1.3 and Figure 1.4 proceed via the nucleophilic addition of acetylene to a phenyl radical site. This addition step requires surmounting a barrier of 3.6 kcal mol$^{-1}$ for the addition of acetylene to phenyl,$^{48}$ and 3.4 kcal mol$^{-1}$ for addition of acetylene to 3-pyridyl,$^{48}$ determined computationally using the
G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. In the context of cold interstellar clouds with temperatures on the order of 10 – 20 K, these barriers are too high for the reaction to proceed. Although the higher temperatures of circumstellar envelopes (tens to several hundred K) present an environment more supportive of HACA style reactions, up to 10% of carbon in the interstellar medium (i.e. the cold space between circumstellar envelopes) is thought to be in the form of PAHs.48-49 Several low temperature pathways facilitating PAH formation in cold interstellar environments must exist to account for this PAH population.

In 2012, Parker et al. uncovered a barrierless pathway leading to naphthalene formation in the reaction of phenyl radicals with vinylacetylene,50 presented in Figure 1.5. The reaction proceeds via formation of a van der Waals complex, along the entrance channel, with enthalpy lower than the separate reactants. The stabilisation energy of forming the van der Waals complex is greater than the energy required to surpass the addition barrier to form the covalently bound reaction adduct. Energy barriers such as this, represented in Figure 1.6, which lie in the entrance channel and are lower in energy than the separated reactants, will be termed ‘submerged’.

![Diagram](image)

**Figure 1.5** The barrierless pathway of the reaction of phenyl radicals leading to naphthalenes. The initial nucleophilic addition of vinylacetylene proceeds via formation of a van-der-Waals complex before isomerisation to the reaction adduct.
Figure 1.6 Generalised potential energy scheme of barrierless addition of reactant B to the radical species A. The reaction proceeds via a weakly bound van-der-Waals complex \([A+B]^+\).

The capacity of radical addition reactions to proceed via a van der Waals complex is partially determined by the polarizability and dipole moment of the reactants\(^{51}\). In the case of the barrierless phenyl + vinylacetylene reaction, the enhanced polarizability of vinylacetylene, \((7.70 \, \text{Å}^3)\) compared to acetylene \((3.48 \, \text{Å}^3)\), and the presence of a dipole moment, facilitates greater attractive long range dispersion forces which forms the weakly bound van der Waals complex. The internal energy released on formation of this van der Waals complex (i.e. the van der Waals complex stabilisation energy in Figure 1.6) must be greater than the energy required for isomerisation to the covalently bound reaction adduct for the reaction to be barrierless. Stronger attractive forces between reactants leads to formation of a van-der-Waals complex with greater internal energy. This suggests highly polarizable reactants or reactants with strong permanent dipoles or formal charges may play a substantial role in molecular weight growth processes in cold interstellar environments where thermal energy is not available to overcome reaction barriers. As such, the molecular weight growth reactions of positively charged aromatic radical cations will now be discussed.

1.3 Extraterrestrial Aromatic Radical Cations

Radical cations are a sub-class of free radicals that also contain a formal positive charge and often display significantly greater reactivity to their neutral counterparts. Molecular weight growth via radical cation + neutral hydrocarbon reaction pathways is predicted to contribute significantly to the chemical evolution of many extraterrestrial systems.\(^{22, 26}\)
Westlake et al. suggested the formation of tholins (tar-like particles composed of PANHs) in Titan’s upper atmosphere is initiated and mediated by radical cation reactions following ionisation of small molecules. Tholins are believed to be responsible for the characteristic blue glow of Titan’s upper atmosphere and the orange-red appearance of its surface, visible in Figure 1.7. Ionised aromatics are believed to be ubiquitous within interstellar and circumstellar environments, leading to reason that aromatic radical ion species, formed through interaction with high energy UV photons or cosmic rays, are also present in those environments. Therefore, developing a greater understanding of the chemical evolution of extraterrestrial systems requires a greater understanding of aromatic radical ion chemistry. Studies of ion-molecule reaction pathways that could initiate formation of PAHs and PANHs would be beneficial to our understanding of the first steps of molecular weight growth chemistry.

There is an underrepresentation, within the literature, of aromatic radical cation reactions, especially those involving heteroaromatic radical cations with small unsaturated hydrocarbons in the context of extraterrestrial systems. This is despite their potential importance in the chemical evolution of many extraterrestrial systems. The study of ‘distonic’ radical cation reactions is one area which may lead to new insights into PAH and PANH molecular weight growth mechanisms, and will be a target of this thesis.

Figure 1.7 Natural-colour view of Titan, backlit by the Sun to make visible both the high-altitude blue haze layer and main atmospheric orange haze. Image credit: NASA/JPL-Caltech/Space Science Institute
1.4 Distonic Radicals

Distonic radical ions are a class of molecules which possess both a radical and formal charge separated in space, as opposed to conventional radical cations which typically possess a co-located charge and radical site. Conventional radical ions are named such since historically, electron impact and chemical ionisation were the dominant methods of making cations from neutrals in mass spectrometry; both techniques resulted in colocation of radical and charge site. Figure 1.8 shows the relation between the distonic, conventional, cationic, and neutral pyridine/pyridinium family of molecules. The conventional radical cation (c) is the result of electron loss from neutral pyridine (a) or hydrogen atom loss from the nitrogen moiety of pyridinium (b). This results in the colocation of the radical and charge site on the nitrogen atom. Distonic pyridinium radicals (d) are isomers of the conventional radical cation and result from spontaneous rearrangement of hydrogen atoms from the conventional radical, or homolytic cleavage of a C-H bond and loss of atomic hydrogen from pyridinium(b). Important to note is the nature of the radical in each case. The conventional radical cation is a \( \pi \)-type radical that is partially stabilised by delocalisation throughout the aromatic \( \pi \)-system of the molecule. Conversely, distonic pyridinium radicals possess a site-specific \( \sigma \)-type radical that is in plane with the molecule and unable to delocalise into the \( \pi \)-system. Energy barriers to H-atom migration prevent movement of the radical around the aryl ring. It is this spatially separated \( \sigma \)-type radical and charge site that define aryl distonic radical cations.

Figure 1.8 Pathways between (a) neutral pyridine, (b) cationic pyridinium, (c) conventional radical N-dehydro-pyridinium, and (d) distonic 2-dehydro-N-pyridinium. The additional two distonic isomers, 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium, are not shown.
Distonic radical ions are labelled as α-distonic ions if the formal charge and radical site are on adjacent atoms while β- and γ-distonic ions are separated by one or two atoms, respectively. A large number of experimental and theoretical studies were dedicated to alkyl distonic radical ions during the 1980s and 1990s and have been reviewed by Kenttämaa. More recent studies have focused on aryl distonic radicals. Widjaja et al. and Adeuya et al. characterised the reactivity of the three dehydro-\(N\)-pyridinium isomers towards a set of saturated hydrocarbons and alcohols. Dehydro-\(N\)-pyridinium is the base structure of many \(N\)-heteroaromatic distonic radical cation species. The three isomers, 2-, 3- and 4-dehydro-\(N\)-pyridinium (shown in Table 1.1), possess sufficiently large isomerization and fragmentation energy barriers such that an isomerically pure radical population is maintained between radical generation and reaction with target neutral molecules during gas phase mass-spectrometry experiments.

The reactivity of dehydro-\(N\)-pyridinium radicals is significantly greater than their neutral radical counterparts. This is rationalised by considering polarity originating from the charge site. Protonation at the N-position increases the electrophilicity of the radical site which leads to an increased polarisation of reaction transition states; this stabilises those transition states. Protonation of the radical species effectively lowers the addition reaction barrier height (i.e. transition state energy) of many radical cation reactions. The addition of electron withdrawing groups as ring substituents can be used to draw additional electron density away from the radical site. Increasing reactivity with increasing radical electrophilicity has been observed in the gas and solution phase for dehydro-\(N\)-pyridinium radical cations.

Gas phase reactions of dehydro-\(N\)-pyridinium radical cations with simple alkanes and alcohols result in H-atom abstraction exclusively, with reaction efficiencies increasing as spatial separation between radical site and N-atom decreases. H-atom abstraction efficiencies for several reactions are given in Table 1.1. The measured efficiencies are consistent with the electrophilicity and polarisation effects described above. However, stabilisation of transitions states through polar effects of the radical species alone does not completely account for large variations in reaction efficiency across different neutral reagents. Donahue et al. developed an ionic avoided curve crossing model to rationalise reaction barrier heights of many ion-neutral radical abstraction reactions.
provides a graphical representation of this model for a radical H-atom abstraction reaction. The model is based on the interaction of reactant ground and ionic states at the transition state by argument that within many radical reactions, the state into which the electron is promoted is an ionic state. For atom-abstraction reactions, the abstraction barrier (i.e. the avoided curve crossing of these two states) is directly related to the ionic energy (ionisation energy – electron affinity, IEv – EAv) of both separated reactants.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Hydrogen Atom Abstraction Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>13</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.4</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.2</td>
</tr>
<tr>
<td>Pentanol</td>
<td>43</td>
</tr>
</tbody>
</table>

Table 1.1 Measured hydrogen abstraction reaction efficiencies reported as $k_{	ext{exp}}/k_{	ext{coll}} \times 100\%$. All reactions resulted exclusively in H abs. Extracted from Ref. 59.

Figure 1.9 Hypothetical avoided curve crossing diagram showing hydrogen atom abstraction from a H-atom donor (XH). Image reproduced from Ref 59.
By considering the ionic energy of both reactants, the trends observed in Table 1.1 can be rationalised. The model asserts that the reaction barrier, hence reaction efficiency, will be determined in part by the IE<sub>v</sub> of the neutral reactant. For example, 2-, 3-, and 4-dehydro-N-pyridinium react more rapidly with ethanol than with methanol,\textsuperscript{59} because the IE<sub>v</sub> of methanol is about 0.36 eV higher than that of ethanol. In contrast to the exclusive H-atom abstraction observed for many saturated hydrocarbon reactions, nucleophilic addition of unsaturated hydrocarbons and nitriles\textsuperscript{59} is often the dominant reaction pathway. This can be rationalised by the greater electron density in the unsaturated neutral reactants supporting nucleophilic addition to the radical site. Subsequent unimolecular isomerisation and fragmentation of the reaction adduct can lead to a range of reaction products.

1.5 Generation of Free Radicals in the Gas Phase

Several synthetic routes exist in the generation of gas-phase radicals and radical ions. One approach is to produce radicals through photolysis of a suitable radical precursor. Early photolysis experiments in the late 1940s made use of short, intense bursts of light from flash lamps\textsuperscript{63-64} until laser photolysis became more suitable with the invention of laser light sources in the 1960s. Laser photolysis, due to its monochromatic nature, has the advantage of more selective and efficient generation of gas-phase radical species from photoactive precursors. Laser photolysis has been used to generate a range of radical species from many photolabile precursors. For example, Song \textit{et al.} produced a pulsed benzyl radical beam by photolyzing argon gas doped with either ethylbenzene or benzyl chloride using 193 nm emission from an ArF excimer laser.\textsuperscript{65} Prendergast \textit{et al.} used 266 nm radiation from a Nd:YAG laser in conjunction with an ion trap mass-spectrometer to generate and isolate populations of charge tagged methyl-phenyl radical cations from bromine and iodine ring-substituted precursors.\textsuperscript{66} Many halogenated precursors have proven to produce site specific, σ-type radicals through photon-induced homolytic cleavage of the C-X bond.\textsuperscript{67-70} This is especially true for alkyl-iodide precursors that possess a strong absorption band in the range of 210 – 350 nm. This band corresponds to promotion of a non-bonding (n) electron on the iodine atom to an anti-bonding (σ*) orbital localised on the C-I bond (nσ*), which is repulsive with respect to the C-I coordinate and leads to dissociation.\textsuperscript{71-72} Aryl-iodide photodissociation is much more efficient since
strong absorption to a $\pi\pi^*$ bound state couples with the $\pi\sigma^*$ dissociative state that, again, leads to elimination of an iodine atom and formation of the radical.\textsuperscript{71-72} These aromatic absorption bands are well matched to the 4th harmonic of a Nd:YAG laser output at 266 nm which provides a practical and readily accessible means for radical synthesis within lab based photolysis experiments. A reaction scheme for the photo-dissociation synthesis of 4-dehydro-$N$-pyridinium from an iodinated precursor is shown in Figure 1.10.

\[
\text{R}^+\text{I}^- + h\nu_{266\text{ nm}} \rightarrow \text{R}^+ + \text{I}^-.
\]

Figure 1.10 266 nm photolysis of aryl C-I bonds results in bond homolysis and radical generation

Theoretical studies have determined N-H and C-H bond dissociation energies of many small aromatic N-heterocycles with results indicating preferential cleavage of N-H bonds, typically with dissociation energies around 80 to 100 kcal mol\textsuperscript{-1}, 15 to 30 kcal mol\textsuperscript{-1} less than C-H bonds of the same molecule.\textsuperscript{73-74} Photolysis of the archetypal (non-halogenated) pyridinium N-heterocycle moiety primarily generates H\textsubscript{2} via heterolytic dissociation of the N-H and adjacent C-H bond,\textsuperscript{75-76} which leads to the closed-shell 2-pyridinylium cation. However, photolysis may also lead to homolysis of a C-H bond. Unlike H\textsubscript{2} loss, homolysis and elimination of atomic hydrogen leads to a site-specific and highly reactive $\sigma$-type radical.

\section*{1.6 Mass Spectrometric Techniques}

To allow direct investigation, N-heteroaromatic radicals need to be generated \textit{in situ} during an experiment due to their reactivity. This makes mass spectrometric techniques apt to experimental study of gas-phase radical cations for several reasons. Firstly, the study of organic radicals is inherently difficulty because self-reactions and reactions with solvents or precursors occur readily. Mass spectrometers operate, typically, at low
pressures ($10^5 - 10^{-9}$ Torr) in the presence of inert buffer gases such as N$_2$, Ar or He, with trace quantities of gas-phase impurities such as O$_2$. Radical ions in such environments experience very few reactive collisions. These could include collisions with O$_2$, for example. Self-reactions and radical-precursor reactions are avoided due to coulombic repulsion of like-charged species. The perturbative effects of solvent and counter-ion interactions are also avoided.

Collision cells are common in commercial mass spectrometers and provide a method of \textit{in-situ} radical synthesis. These cells operate by colliding ions with an inert buffer gas. Energy is deposited in the ion through many repeated collisions until collision induced dissociation (CID) is achieved. The first aryl distonic radical, 4-dehydroanilinium, was synthesised by Kenttämaa and Chyall via CID of 4-iodoanilinium in a FT-ICR mass spectrometer.\textsuperscript{77} Loss of atomic iodine from 4-iodoanilinium was observed following multiple collisions with an Ar buffer gas. The resulting open-shell product ion was assigned as distonic 4-dehydroanilinium using a diagnostic dimethyl disulfide reaction, proving the viability of CID for radical synthesis in this case. Care must be taken when generating distonic radical ions by CID, since deposition of excess energy into the radical species may lead to isomerisation. Mass spectrometry is also increasingly becoming coupled with laser photodissociation\textsuperscript{78} and has been demonstrated for use in in-situ radical synthesis in mass spectrometric experiments.\textsuperscript{66-70, 79}

The utility of laser photolysis coupled mass spectrometry for \textit{in situ} radical synthesis has been used to indirectly study neutral, reactive combustion intermediates.\textsuperscript{66-67} These experiments use distonic charge-tagged radical species as analogues of their neutral radical counterparts, and have the advantage of utilising well-established, highly sensitive, and often more accessible mass spectrometry experimental setups, compared to similar neutral radical experiments. One comparative study of the reactivity of a neutral radical and its distonic charge-tagged analogue\textsuperscript{80} showed both neutral and mass spectrometric techniques provide similar, but complementary, insights into the neutral system. However, caution must be taken towards the potential perturbative effects of the charge tag when using the indirect, charged-tagged approach.\textsuperscript{81}
1.7 Summary and Thesis Overview

This thesis presents results of a combined experimental and computational study into the reactions of 2-dehydro-\(N\)-pyridinium, 3-dehydro-\(N\)-pyridinium and 4-dehydro-\(N\)-pyridinium with the common extraterrestrial hydrocarbons, ethene, acetylene, propene and propyne. It is thought that this is the first study involving the reactions of dehydro-\(N\)-pyridinium with simple unsaturated hydrocarbons, despite the potential significance of this class of reactions in the context of molecular-weight growth chemistry and synthesis of complex organics in cold extraterrestrial environments. This thesis contains five further chapters:

- Chapter 2 briefly describes the experimental techniques used throughout this thesis, including instrumental setup, \textit{in situ} radical generation, kinetic measurements, and quantum chemical calculations.

- Chapter 3 investigates reactions of the three dehydro-\(N\)-pyridinium isomers with propene. Mass spectrometry experiments are used to measure reaction kinetics and product branching ratios. Potential energy schemes for each reaction are presented and used to rationalise experimental results and assign reaction products. Work in this chapter resulted in the publication: Bright \textit{et al.}, \textit{Physical Chemistry Chemical Physics} \textbf{2017}, \textit{19} (46), 31072-31084.

- Chapter 4 investigates the reactions of the three dehydro-\(N\)-pyridinium isomers with acetylene. Mass spectrometry experiments are used to measure reaction kinetics and product branching ratios. Potential energy schemes for each reaction are presented and used to rationalise experimental results and assign reaction products.
Chapter 5 investigates the reactions of the three dehydro-N-pyridinium isomers with ethene and propyne. Reaction kinetics and product branching ratios are determined experimentally, and mechanistic schemes for each reaction are proposed. Likely reaction products are assigned and rationalised through trends observed in the previous two chapters.

Chapter 6 summarises the findings of this thesis and discusses the trends in reactivity observed across all reactions investigated. Future studies are suggested to conclude the thesis.
2 Experimental and Computational Methods

2.1 Introduction
This chapter describes the instrumentation, data acquisition, and analysis methods for gas-phase ion-molecule reaction product-detection and kinetics experiments using a modified commercial linear ion-trap mass spectrometer. Authoritative information on the construction and use of the apparatus can be found in the doctoral theses of Kirk\textsuperscript{79}, Hansen\textsuperscript{82} and Prendergast. The commercial instrument has undergone two substantial modifications in past work: (i) inclusion of a vacuum-sealed quartz widow in the backing plate to allow laser photolysis of trapped ion populations; (ii) modification of the buffer gas inlet for delivery of neutral reactant gases into the ion-trap region for investigation of ion-molecule reactions. As details of the instrument’s development and benchmarking can be found in the doctoral theses of the authors above, a brief overview of the instrumental setup will be given. Data acquisition and processing methods used in kinetics studies in this work will be described in more detail. Computational methods used to rationalise experimental results and elucidate possible reaction mechanisms will also be described.

2.2 The Modified LTQ-XL Mass Spectrometer
A modified Thermo Fisher Scientific LTQ-XL linear quadrupole ion-trap mass spectrometer was used for product detection studies and kinetic measurements of ion-molecule reactions. A schematic for the instrument is given in Figure 2.1. A brief explanation of the modifications affording optical access and the introduction of neutral reactant gases is given below.
Figure 2.1 Schematic of the modified LTQ-XL linear ion-trap mass spectrometer.

2.2.1 Optical Access

The mass spectrometer has a removable aluminium backing plate intended to allow coupling to additional mass analysers. Removal of the backing plate exposes the ion-trap assembly, which is shown in Figure 2.2. A 10 mm hole was milled in the backing plate, aligned collinearly along the z-axis of the ion trap and centred on the 2.5 mm rear lens orifice. A CF vacuum sealed 2.75 inch quartz window was mounted over the 10 mm hole to re-seal the instrument while allowing optical access to the rear lens orifice of the ion-trap at wavelengths in the range 2.0 μm – 200 nm. A Continuum Inc. Minilite II Nd:YAG pulsed laser was coupled to the LTQ-XL. A laser pulse fired axially along the ion trap through the rear lens orifice will overlap trapped ion populations that are stored within the ion-trap and eventually terminate on the rear of the skimmer cone, which is the first off-axis component encountered. Typical pulse energy of this laser system is 4 mJ at 266 nm, 8 mJ at 355 nm, 25 mJ at 532 nm, and 50 mJ at 1026 nm, operating at a maximum of 10 Hz. Pulse width is 5 ns, beam spot diameter is 3 mm. The 266 nm output is used in all photolysis and kinetics experiments described in this thesis.
2.2.2 Gas Handling and ‘Ion-Molecule’ Mode

During ‘normal’ operation of the mass spectrometer, ultra-high purity helium buffer gas is introduced into the ion trap region through the buffer gas inlet using a split flow system. This split flow system accepts input pressures of 30 – 50 psi and vents excess helium through restricted flow outlets to maintain an optimal working pressure of ~2.5 mTorr within the ion trap. A 3-way ball valve was introduced between the split flow system and buffer gas inlet and connected to an external gas handling manifold to allow introduction of neutral reactant gases directly into the ion trap for operation in ‘ion-molecule’ mode. A schematic of the external gas handling manifold and split flow system leading to the ion trap is given in Figure 2.3.

Operation in ion-molecule mode allows introduction of neutral reactant gases from one of three reactant tanks directly into the ion-trap region. Selection of a reactant tank is afforded by two 3-way ball valves, V1 and V2, and only one reactant tank can be selected at any time. The split flow system is bypassed in ion-molecule mode, therefore a mass
flow controller (MKS GE50A, 5 sccm) controlled by a multi gas controller (MKS, 647C) is used to regulate flow of reactant gas directly into the ion-trap to 1.3 sccm. This flow rate was found to maintain optimal working pressure within the ion-trap. The 2-way valve V4 is used to open or close a bypass line around the mass flow controller. The 2-way valve V5 opens and closes a connection to a vacuum pump which is used to pump down the manifold, and the 2-way valve V6 is used to isolate the external manifold from the mass spectrometer. A pressure gauge (MKS, 626B Baratron with PDR 2000 power supply and readout) measures and displays the remaining gas pressure within the selected reactant tank (V4 closed, reactant tank open) or the pressure within the manifold (V4 open, reactant tank closed).

The flow or reactant gas into the ion-trap was maintained at 1.3 sccm for a minimum of 12 h prior to kinetic measurements to ensure sufficient time for equilibration and stabilisation of reactant concentration.

Figure 2.3 Schematic of the gas handling manifold connected to the LTQ-XL mass spectrometer. The three-way valve V7 allows selection of ‘normal’ or ‘ion-molecule’ operating modes. MFC indicates a mass flow controller.
Chapter 2 – Experimental and Computational Methods

2.3 Radical Synthesis

2.3.1 Materials

2-iodopyridine (98%), 3-iodopyridine (98%) and 4-iodopyridine (97%) were purchased from Sigma-Aldrich. The neutral reactant gases propene (99.99%), ethene (99.95%) and propyne (99%) were also purchased from Sigma-Aldrich. Two acetylene specialty mixture were acquired from BOC (743 ppm ± 2% in He) and Coregas (747 ppm ± 2% in He), both of which contain < 2% acetone relative to acetylene concentration. Reactant gas tanks used in mass spectrometry experiments were diluted from these parent cylinders to concentrations of 0.01–0.05% mol/mol using ultra-high purity helium (BOC, 99.999%). Reactants were not purified further.

2.3.2 Ionisation

The 2-dehydro-N-pyridinium, 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium radical cations studied in all experiments were generated in situ from the iodinated precursors 2-iodopyridinium, 3-iodopyridinium and 4-iodopyridinium, respectively. These radical precursor ions were generated by positive electrospray ionisation of 20 μM methanolic solutions of 2-iodopyridine, 3-iodopyridine and 4-iodopyridine, respectively, introduced into the ESI source at 5 μL min⁻¹. Electrospray conditions include electrospray voltage (4 kV), capillary temperature (250 °C), sheath gas flow (8 arb. units), auxiliary gas flow (0 arb. units) and sweep gas flow (0 arb. units). These ionisation conditions remained consistent across all experiments unless otherwise stated.

2.3.3 Photolysis and CID

Iodinated precursor ions at m/z 206 were mass selected with an isolation window of 1 Th (1 mass-to-charge unit) and q-parameter of 0.250, held within the ion-trap, and subjected to either collision-induced dissociation (CID) or photodissociation (PD, 266 nm). Normalised collision energy was typically 20-25% (arbitrary units) with an activation time of 30 ms for CID experiments. Mass spectra resulting from PD and CID of the three precursor ions at m/z 206 are presented in Figure 2.4. In both cases, the appearance of a peak at m/z 79 is indicative of atomic iodine loss and formation of 2-, 3-, and 4-dehydro-N-pyridinium radical cations. An additional peak at m/z 78 is seen in the CID spectrum.
of 2-dehydro-N-pyridinium and is assigned as the pyridinylium cation (C₅H₄N⁺). This was confirmed by re-isolation and storage of m/z 78 ions in the presence of background concentrations of water within the ion trap. A product peak at m/z 96 was observed to form suggesting the addition of H₂O (18 Da) to m/z 78 ions which is in agreement with previous studies⁶⁹,⁸³ and supports the assignment of m/z 78 as pyridinylium.
Figure 2.4 Product mass spectra from 266 nm PD (blue, top) and CID (black, bottom) of (a) 2-iodopyridinium, (b) 3-iodopyridinium and (c) 4-iodopyridinium. CID spectra have been inverted for easy comparison alongside PD spectra. The m/z 79 peak corresponds to atomic iodine loss (127 Da).
PD and CID of iodinated precursor ions at m/z 206 both resulted in loss of atomic iodine and formation of dehydro-N-pyridinium radical cations at m/z 79. However, PD holds the distinct advantage of near-exclusive selectivity while maintaining high radical product yields. All product detection and kinetics experiments presented herein use PD radical synthesis unless stated otherwise.

### 2.3.4 Addressing Radical Isomerisation

Isomerisation of 2-, 3-, and 4-dehydro-N-pyridinium radical cations following PD synthesis would result in a mixed population of m/z 79 ions. Isomerisation prior to ion-molecule reactions would be detrimental to the accurate measurement of isomer-specific reaction rates and product branching ratios. Therefore, the possibility of H-atom migration to the radical site of each dehydro-N-pyridinium radical cation from adjacent ring substituents was investigated.

H-atom migration energy barriers were calculated (computational methods discussed below) and results are summarised in Figure 2.5. All barriers were found to be greater than 55 kcal mol$^{-1}$ relative to the conventional pyridinium-N-yl radical cation. Carbon-iodine bond dissociation energies for 2-, 3-, and 4-dehydro-N-pyridinium were calculated to be 70.6, 69.7 and 69.3 kcal mol$^{-1}$, respectively. Photolysis at 266 nm (photon energy of 107.5 kcal mol$^{-1}$) would deposit, at most, 38.2 kcal mol$^{-1}$ of excess energy into aromatic radical photolysis product following C-I bond dissociation. This excess energy is not sufficient to overcome H-atom migration barriers, suggesting isomerisation is not energetically accessible under experimental conditions.

![Figure 2.5 H-atom migration energy barriers in kcal mol$^{-1}$, relative to the conventional N-dehydropyridinium radical cation.](image)
Synthesis of isomerically pure populations of \( m/z \) 79 ions is supported by the results of mass spectrometry experiments presented in Chapters 3, 4, and 5. The observation of unique product peaks, differing peak distributions and separable kinetic rate coefficients is evidence that photolysis of the three iodinated precursor ions results in the three unique dehydro-N-pyridinium isomers. Previous studies also suggest energetic barriers to dehydro-N-pyridinium H-migration are sufficiently large to prevent isomerisation under similar experimental conditions.\(^{60-61}\) However, there is some evidence suggesting dehydro-N-pyridinium radical cations may isomerise during ion-molecule reactions through reactant mediated pathways. This is observed as a systematic trend in residuals of exponential functions fit to kinetic data, and disparity between first-order rate coefficients of product and reactant channels. Both observations indicate possible deviation from exponential signal decay kinetics and will be discussed throughout this thesis.

Extraction of rate coefficients and the analysis of kinetic measurements assumes that the photolysis of 2-, 3-, and 4-iodopyridinium ions results in isomerically pure populations of 2-, 3-, and 4-dehydro-N-pyridinium radical cations, respectively, prior to reaction with the neutral co-reactant.

### 2.4 Kinetic Measurements

Dehydro-N-pyridinium radical cations (\( m/z \) 79), generated by laser photolysis of the corresponding iodinated precursor, were isolated and stored in the presence of controlled concentrations of neutral reactant gas for user-defined time periods. Ion-molecule reactions between the isolated radical cations and neutral reactant gas occur for the duration of the storage cycle before reaction products and any remaining dehydro-N-pyridinium radicals are ejected from the trap and detected to acquire a single product mass spectrum. These reactions took place under pseudo first-order conditions due to a large excess of neutral reactant gas within the trap relative to the small population of dehydro-N-pyridinium radical ions. Repeat acquisitions of product mass spectra were acquired at select storage times between 0.03—10,000 ms for each reaction. Measurements across the
full range of select storage times of each dehydro-\(N\)-pyridinium isomer + neutral reaction were iterated continuously over the span of a day (6 h) and repeated for up to 6 different neutral reactant concentrations to ensure measurement-to-measurement and day-to-day consistency in measured rate coefficients.

The kinetic measurement process is represented visually in Figure 2.6. Kinetic plots were produced by integrating the area under a specified \(m/z\) region (± 0.5 Da) and normalising to the integrated signal over the entire spectrum (\(m/z\) 50-300). The normalised, integrated signal intensity was averaged over all scans for a given reaction time (mass spectrum) on a given run (single kinetic measurement). Each kinetic measurement datum was weighted based on variance then averaged and plotted against reaction time to produce a single kinetic curve which was fitted with either an exponential or biexponential function. First-order rate coefficients extracted from this fit were plotted as a function of neutral reactant concentration. Second-order rate coefficients were extracted from the slope of linear regression fits to these data. Reaction efficiencies (\(\Phi\)) were calculated from second-order rate coefficients as a percentage of the reactant collision rate calculated using the Langevin model for ion-molecule collision pairs:  

\[
\kappa_{\text{Langevin}} = 2\pi \frac{\alpha e^2}{\mu} \tag{2.1}
\]

Where:

\(\alpha\) = polarizability of neutral reactant  
\(\mu\) = reduced mass

And:

\[
\Phi = \frac{\text{Measured Second Order Rate}}{\kappa_{\text{Langevin}}} \tag{2.2}
\]

Ultimately, an upper limit of ±50% uncertainty in the second-order rate coefficient results from a high uncertainty in ion-trap gas pressure estimated at 2.5 mTorr ± 50%.
Figure 2.6 Workflow of a full kinetic measurement for a single neutral reactant/radical cation pair.
2.4.1 Neutral Reactant Concentration

The concentration of neutral reactant gas within the ion-trap was adjusted by using reactant gas tanks of differing concentration. Neutral reactant number density was calculated using Equation 3, which uses Graham’s law of effusion to account for differing effusion rates of the reactant gas and helium out of the ion-trap region:

\[
N_{\text{neutral}} = \left( \frac{p_{\text{neutral}}}{p_{\text{total}}} \right) \frac{P}{kT} \left( \frac{M_{\text{neutral}}}{M_{\text{He}}} \right)^{\frac{1}{2}}
\]

Equation 2.3

Where:

- \( N_{\text{neutral}} \) = Neutral reactant number density in the ion trap
- \( p_{\text{neutral}} \) = Gas cylinder partial pressure of neutral reactant
- \( p_{\text{total}} \) = Total pressure within the gas cylinder
- \( P \) = Pressure within the ion trap
- \( k \) = Boltzmann constant
- \( T \) = Temperature within the ion trap
- \( M_{\text{neutral}} \) = Molecular mass of the neutral reactant
- \( M_{\text{He}} \) = Molecular mass of helium (carrier gas)

2.5 Quantum Chemical Calculations

Quantum chemical calculations were performed to rationalise observed reaction products and elucidate possible reaction mechanisms. Results of these calculations are presented throughout this thesis, primarily as potential energy schemes consisting of 0 K reaction enthalpies for geometry optimised stationary points.

Optimised geometries, enthalpies and vibrational frequencies were computed at the M06-2X/6-31G(2df,p) level using Gaussian 09. Stationary points were assigned as minima, possessing no imaginary frequencies, or as transition states, possessing exactly one imaginary frequency whose normal mode projection approximates motion along the reaction coordinate. Ambiguous transition states were verified using intrinsic-reaction coordinate calculations. Calculations for molecules containing iodine (2-, 3-, and 4-iodopyridinium) were performed at the M06-2X level using the split basis set LANL2DZ + 6-31G(2df,p). All 0 K enthalpies include the zero-point vibrational energy (ZPE) correction and are reported in kcal mol\(^{-1}\).
A state counting analysis was carried out in Chapter 2 using the MultiWell 2017 suite of programs.\textsuperscript{86-88} This analysis used geometries, enthalpies and vibrational frequencies extracted from Gaussian 09 calculations, described above. The sum of states for each transition state of interest, calculated by the MultiWell 2017 software, was corrected with an Eckart tunnelling correction\textsuperscript{89-90} and multiplied by the degeneracy the transition state to give the final sum of states.
3 Propene Reactions

This chapter is reproduced from the peer-reviewed publication:


The original publication can be found in Appendix A. Experimental work, quantum chemical calculations, analysis and written publication completed by C. C. Bright.

Abstract

Small nitrogen containing heteroaromatics are fundamental building blocks for many biological molecules, including the DNA nucleotides. Pyridine, as a prototypical N-heteroaromatic, has been implicated in the chemical evolution of many extraterrestrial environments, including the atmosphere of Titan. This paper reports on the gas-phase ion-molecule reactions of the three dehydro-N-pyridinium radical cation isomers with propene. Photodissociation ion-trap mass spectrometry experiments are used to measure product branching ratios and reaction kinetics. Reaction efficiencies for 2-dehydro-N-pyridinium, 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium with propene are 70%, 47% and 41%, respectively. The m/z 106 channel is the major product channel across all cases and assigned 2-, 3-, and 4-vinylpyridinium for each reaction. The m/z 93 channel is also significant and assigned the 2-, 3-, and 4-N-protonated-picolyl radical cation for each case. H-abstraction from propene is not competitive under experimental conditions. Potential energy schemes, at the M06-2X/6-31(2df,p) level of theory and basis set, are described to assist in rationalising observed product branching ratios and elucidating possible reaction mechanisms. Reaction barriers to the production of vinylpyridinium (m/z 106) + CH₃ are the lowest identified for the 3- and 4-dehydro-N-pyridinium reactions, in support of the observed dominance of the m/z 106 ion signal. Ethylene loss via ring-mediated H-transfer along the propyl group is found to be the lowest energy pathway for the 2-dehydro-N-pyridinium reaction, suggesting a preference toward m/z 93 (N-protonated-picolyl radical cation) over the experimentally observed products. Entropic bottle-necks along the m/z 93 pathway however, associated with ring-
mediated H-atom transfer, are responsible for the dominance of m/z 106 in the 2-dehydro-
N-pyridinium + propene reaction. For all three isomers, computed barriers for all
observed reaction channels were below the entrance channel, suggesting these reactions
can contribute to molecular weight growth in extraterrestrial environments with
accelerated reaction rates in low temperature regions of space.

3.1 Introduction

Nitrogen containing heterocycles are essential building blocks of many biological
molecules. DNA/RNA nucleotides are derived from the base molecules pyrimidine and
purine while the amino acids histidine and tryptophan contain imidazole and indole side
chains, respectively. Pyridine is believed to play a part in the rich and diverse chemistry
of circumstellar and interstellar space and is implicated in pre-biotic chemistry
and astrobiology. While a large portion of simple hydrocarbon chemistry is well
described by current models, the reactivity of many similar nitrogenous molecules, and
especially their ions and radical counterparts, are not available in current astrochemical
databases. New laboratory based studies are thus required to provide reaction rates
and product pathways to ensure the development of increasingly accurate predictive
models. Reliable predictive models and improved understanding of extraterrestrial
chemical systems can then provide direction to searches for aromatic nitrogen
heterocycles outside our solar system.

A large portion of the interstellar and circumstellar chemical inventory is composed of
radicals and ions. This is due, in varying degrees, to a combination of primary (cosmic
rays, high energy photons and shock waves) and secondary (secondary electrons, stellar
winds, magnetospheric and auroral ions and particles) ionisation sources. One potential
source of molecular ionisation in space is proton transfer from H$_3^+$, the second most
abundant interstellar molecule. It acts as a potent proton donor and thus ion-molecule
reactions of H$_3^+$ with any aromatic N-heterocycle would lead to prompt protonation.
Further, the harsh UV-field of interstellar and circumstellar space together with the
ubiquity of cosmic rays presents an environment supporting C-H and N-H bond fission
and radical formation of protonated and neutral N-heterocycles alike. Previous studies
have shown that UV (266 nm) photolysis of small protonated N-heterocycles, such as the
pyridinium cation, follows the pathway of H$_2$ elimination via a dissociative $\pi\sigma^*$ state
coupled non-adiabatically to an optically-bright $\pi\pi^*$ bound state.\textsuperscript{75-76} An alternative radical formation pathway is homolysis of a C-H bond. Unlike H$_2$ loss, homolysis and elimination of atomic hydrogen leads to a site-specific and highly reactive $\sigma$-type radical that is located in the plane of the molecule and is unable to delocalise into the $\pi$ system. Although there are no studies on VUV photolysis of pyridinium, studies of the photolysis of neutral pyridine at 193 nm have reported H atom loss with yields between 9 and 10%.\textsuperscript{94-95} Photodissociation of benzene at 193 and 157 nm also results in atomic hydrogen loss.\textsuperscript{96} Therefore, it is expected that pyridinium cations may undergo C-H bond homolysis via VUV photolysis to form $\sigma$-type radical cations. Positively charged ions containing a spatially separated $\sigma$-radical are by definition distonic radical cations with steric and electronic separation of the charge and radical centres.\textsuperscript{97} The reactions of these distonic radical cations with small hydrocarbons may play a role in the chemical evolution of extraterrestrial environments, particularly molecular weight growth and synthesis of complex bio-relevant molecules, yet to this point few studies have been conducted.\textsuperscript{98}

In this work, the reaction of propene with 2-dehydro-N-pyridinium, 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium radical cations is investigated. These reactions were chosen due to their likely involvement in the chemistry of Titan’s upper atmosphere, where ionospheric pyridinium cations and propene have been tentatively identified\textsuperscript{21} and stratospheric propene has been positively identified.\textsuperscript{99-100} Laboratory investigations of Titan’s atmosphere have also shown the formation of pyridinium cations from the reaction of pyridine with hydrocarbon cations.\textsuperscript{31} Here, reaction kinetics and product branching ratios are measured at room temperature and 2.5 mTorr pressure using laser photodissociation ion-trap mass spectrometry. Quantum chemical calculations and a simplified kinetic analysis are used to support experimental observations.

### 3.2 Experimental

#### 3.2.1 Ion trap Mass spectrometry

A modified linear ion-trap mass spectrometer (Thermo Fisher Scientific LTQ XL) was used to investigate gas-phase ion-molecule reactions of 2-, 3-, and 4-dehydro-N-pyridinium radical cations with propene. The mass spectrometer was modified to include a vacuum sealed quartz window in the removable backing plate to give optical access along the internal axis of the ion trap. This allows irradiation of trapped ions by a 266 nm
Nd:YAG laser source (Continuum Minilite). The mass spectrometer was equipped with a gas handling manifold that allowed the introduction of neutral gases directly into the ion trap. The gas handling manifold is connected to a one gallon steel cylinder containing helium gas doped with neutral reagent(s). A mass flow controller (MKS GE50A, 5 sccm) regulated the flow to 1.3 sccm directly into the ion-trap which was found to maintain the optimal working pressure within the trap. See Ref\textsuperscript{68} for a more detailed description of the instrument.

The iodinated precursor cations 2-iodopyridinium, 3-iodopyridinium and 4-iodopyridinium were generated via electrospray ionisation of 20 μM methanolic solutions of 2-iodopyridine (98%, Sigma-Aldrich), 3-iodopyridine (98%, Sigma-Aldrich) and 4-iodopyridine (97%, Sigma-Aldrich), respectively, introduced into the ESI source at 5 μL min\textsuperscript{-1}, operating in positive ion mode. Radical precursor ions ([M+I]\textsuperscript{+} at m/z 206) were mass selected with an isolation window of 1 Th and q-parameter of 0.250. Other instrument parameters include: electrospray voltage (4 kV), capillary temperature (250 °C), sheath gas flow (8 arb. units), auxiliary gas flow (0 arb. units) and sweep gas flow (0 arb. units). All mass spectra presented herein are an average of at least 100 scans. Generation of dehydro-N-pyridinium radical cations is achieved by either collision-induced dissociation (CID) or photodissociation (PD) of the iodopyridinium precursor ions (m/z 206). The normalised collision energy was typically 20-25% (arbitrary units) with an activation time of 30 ms for CID experiments. Dehydro-N-pyridinium radical cation generation via photolysis was achieved with the optically coupled 266 nm laser. The precursor isolation and trapping sequence was used to trigger the flashlamp of the coupled Nd:YAG laser (4\textsuperscript{th} harmonic, 266 nm). The laser Q-switch is then triggered internally approximately 140 μs later for optimal power density (\textit{ca.} 30 mJ cm\textsuperscript{-2}). The beam enters the ion-trap through a 2.5 mm orifice in the back lens and passes axially down its internal length to overlap the trapped ion cloud.

### 3.2.2 Kinetics Measurements

Dehydro-N-pyridinium radical cations (m/z 79), generated from laser photolysis of the corresponding iodinated precursor, were mass-isolated in the presence of a controlled concentration of propene gas (Sigma Aldrich, 99.99%) and held within the ion trap for user defined time periods between 0.030–10,000 ms. Ion-molecule reactions took place
under pseudo first-order conditions due to the large excess of propene within the trap relative to the small population of dehydro-$N$-pyridinium radical ions. The flow of propene into the ion trap was maintained at 1.3 sccm for at least 12 h prior to kinetic measurements to ensure a stable propene concentration. Propene concentration within the ion trap was varied by using propene doped He gas cylinders with varying propene concentration. Pseudo first-order kinetics were measured for 2-, 3-, and 4-dehydro-$N$-pyridinium + propene reactions. Kinetic measurements of each dehydro-$N$-pyridinium isomer + propene reaction, each taking 20–30 min, were iterated continuously over the span of a day (6 h) and repeated for at least 4 different propene concentrations to ensure measurement-to-measurement and day-to-day consistency in measured rate coefficients.

Kinetic plots were produced by integrating the area under a specified $m/z$ region (± 0.5 Da) and normalising to the integrated signal over the entire spectrum ($m/z$ 50-300). The normalised, integrated signal intensity was averaged over all scans for a given reaction time (mass spectrum) on a given run (kinetic measurement). Each kinetic measurement datum was weighted based on variance then averaged and plotted against reaction time to produce a single kinetic curve which was fitted with either an exponential or biexponential function. First-order rate coefficients extracted from the fit were plotted against propene number density and second order rate coefficients were extracted from the slope of linear regression fits to these data. Reaction efficiencies ($\Phi$) were calculated from second-order rate coefficients as a percentage of Langevin model collision rate for ion-molecule collision pairs. Ultimately, an upper limit of ±50% uncertainty in the second-order rate coefficient results from a high uncertainty in ion-trap gas pressure estimated at 2.5 mTorr ± 50%.

3.2.3 Quantum Chemical Calculations and Kinetic Modelling

Quantum chemical calculations were carried out to rationalise observed reaction products and elucidate possible mechanisms. Reaction enthalpies were computed at the M06-2X/6-31G(2df,p)$^{101}$ level using Gaussian 09.$^{85}$ All stationary points were assigned as minima, possessing no imaginary frequencies, or as transition states, possessing exactly one imaginary frequency whose normal mode projection approximates motion along the reaction coordinate. Ambiguous transition states were verified using intrinsic-reaction coordinate calculations. Calculations for molecules containing iodine were performed at
the M06-2X level of theory using a LANL2DZ + 6-31G(2df,p) split basis set. All 0 K enthalpies include the zero-point vibrational energy (ZPE) correction and are reported in kcal mol$^{-1}$. For potential energy schemes and mechanisms in the following sections, stationary points are labelled R for reactants, I for intermediates or P for products. Subscript ‘o’, ‘m’, or ‘p’ indicate ortho, meta, or para substituted isomers that result from the reaction of 2-, 3-, and 4-dehydro-N-pyridinium, respectively.

The MultiWell 2017 suite of programs$^{86-88}$ was used for a state counting analysis of competing transition states. Geometries, vibrational frequencies and calculated enthalpies for transition states and intermediates investigated were taken from Gaussian 09 calculations described above.

### 3.3 Results

#### 3.3.1 Synthesis of Dehydro-N-pyridinium Radical Cations

The 2-, 3-, and 4-iodopyridinium cations ($m/z$ 206) were isolated, held within the ion-trap, and subjected to either collision-induced dissociation (CID) or photodissociation (PD, 266 nm). Mass spectra resulting from PD and CID of the three [M+I]$^+$ ions are presented in the Supporting Information (Figure S1). Both CID and PD of [M+I]$^+$ ions, in all cases, resulted in the formation of signal at $m/z$ 79 (-127 Da), indicative of I atom loss and formation of the radical cation. CID of 2-iodopyridinium ions also generated a signal at $m/z$ 78 which is assigned as the pyridinylium cation ($C_5H_4N^+$). PD resulted in essentially exclusive generation of photoproducts at $m/z$ 79. This is reminiscent of aryl-iodide photolysis studies that have shown the C-I bond to be effectively ruptured at 266 nm to produce σ-type distonic radicals$^{66, 68, 71-72, 80}$.

Activation of 2-iodopyridinium, 3-iodopyridinium and 4-iodopyridinium ions by both CID and PD resulted in the formation of dehydro-N-pyridinium ions at $m/z$ 79. However, PD holds the distinct advantage of near-exclusive product selectivity. Kinetic measurements presented herein make use of the photoisocciation synthetic route unless stated otherwise.

Isomerisation between 2-, 3-, and 4-dehydro-N-pyridinium ions would lead to mixed ion populations. Therefore, the possibility of H-atom migration to the radical site from...
adjacent ring substituents was investigated. A computational assessment of the energy barriers of isomerisation was conducted with results summarised in the Supporting Information (Figure S2). H-migration transition state barriers were found to be in excess of 55 kcal mol\(^{-1}\) for each isomer relative to the N-centred \(\pi\)-radical. C-I bond dissociation energies of 2-, 3-, and 4-iodopyridinium were calculated to be 70.6, 69.7 and 69.3 kcal mol\(^{-1}\), respectively. Photolysis at 266 nm (\(h\nu = 107.5\) kcal mol\(^{-1}\)) would deposit, at most, 38.2 kcal mol\(^{-1}\) of excess energy into the aromatic radical photolysis product following C-I bond dissociation. These barriers will prohibit H-atom migration under these experimental conditions. As will be discussed below, experimental results support this assertion. The unique distribution of product peak intensities observed in Figure 3.1 at the reaction time of 30 ms, together with distinguishable kinetic traces (see later, Figure 4) suggest that the photolysis of these three radical precursor ions result in three distinct dehydro-N-pyridinium radicals. These results will be discussed in detail in the following sections. Previous studies also suggest energetic barriers to dehydropyridinium H-migration are sufficiently large to prevent isomerisation under similar experimental conditions.\(^{60-61}\)

Radical cations at \(m/z\) 79 ([M]\(^+\)) generated through PD of 2-iodopyridinium, 3-iodopyridinium and 4-iodopyridinium cations were isolated and stored in the ion trap for varying reaction times in the presence of controlled concentrations of propene. Reaction time was varied from 0.03 to 10000 ms. Mass spectra for 30 ms reaction time and \([\text{propene}] = 2.62 \times 10^{10}\) molecule cm\(^{-3}\) for the three dehydro-N-pyridinium isomers are shown in Figure 3.1. The dominant product peak in all cases is the [M + 42 – 15]\(^+\) ion at \(m/z\) 106 rationalised by C\(_3\)H\(_6\) addition and subsequent CH\(_3\) loss to presumably yield the corresponding vinylpyridinium isomer. Minor product ions are also observed at \(m/z\) 121 (C\(_3\)H\(_6\) adduct), \(m/z\) 120 (C\(_3\)H\(_6\) addition with H loss), \(m/z\) 93 (C\(_3\)H\(_6\) addition then C\(_2\)H\(_4\) loss) and \(m/z\) 80 (direct H-atom abstraction). These product peaks grow in intensity with the decrease of \(m/z\) 79 over increasing reaction times (0.03 to 10,000 ms).

Also observed are low intensity peaks at \(m/z\) 111 (Figure 3.1 b and c), \(m/z\) 95 (Figure 3.1) and \(m/z\) 82 (Figure 3.1) that cannot be assigned from expected propene reaction channels. These peaks result from reactions with background oxygen which has entered the ion trap via the ESI source. To prove this, mass spectra were acquired for 2-, 3-, and 4-dehydro-N-pyridinium radical cation reactions with background concentrations of O\(_2\) (~6.4 \(\times\) 10\(^9\) molecules cm\(^{-3}\)) and no propene. A major product peak at \(m/z\) 111 and minor product at
\( m/z \) 95 are observed for both 4- and 3-dehydro-N-pyridinium + \( \text{O}_2 \) reactions with relative signal intensities that align well with those of the 4- and 3-dehydro-N-pyridinium + \( \text{C}_3\text{H}_6 \) reaction spectra. In contrast, 2-dehydro-N-pyridinium + \( \text{O}_2 \) reactions generated a significantly higher intensity \( m/z \) 95 signal as the major product and an additional minor peak at \( m/z \) 82. The relative intensities of these peaks align well with those observed in 2-dehydropyridinium + \( \text{C}_3\text{H}_6 \) reaction mass spectrum. These findings are in agreement with conclusions drawn from oxidation studies of phenyl-type radical cations which have observed the formation of peroxyl- (addition of \( \text{O}_2 \)) and oxyyl- (addition of \( \text{O}_2 \) followed by loss of atomic oxygen) radicals\(^{67,70}\) and also indicate a potential HCO loss channel\(^{67}\). Based on the observation of these product channels in the absence of propene and past precedent of phenyl reactivity toward oxygen, the ions at \( m/z \) 111, \( m/z \) 95 and \( m/z \) 82 are assigned oxygen reaction products.

Figure 3.2 outlines mechanistic pathways for the reaction of 4-dehydro-N-pyridinium with propene, largely based on the phenyl radical + propene reaction scheme proposed by Kaiser \textit{et al.}\(^{102}\) and studied by Kislov \textit{et al.}\(^{103}\) Nucleophilic addition of propene to the radical site dominates over H-abstraction reactions which are seen as a low intensity peak at \( m/z \) 80. Addition of propene can result in two possible adducts, \( \text{I}_1p \) and \( \text{I}_2p \) in Figure 3.2, that are connected by intermediate \( \text{I}_3p \). The primary product at \( m/z \) 106 results from \( \beta \)-elimination of \( \text{CH}_3 \) from either adduct \( \text{I}_2p \) or intermediate \( \text{I}_4p \), following a hydrogen shift from adduct \( \text{I}_1p \). 2-dehydro-N-pyridinium and 3-dehydro-N-pyridinium follow similar reaction pathways and will be discussed later. Potential energy (PE) schemes for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with propene are presented and discussed below together with kinetic measurements that are also used to further characterise this set of reactions.
Figure 3.1 Mass spectra from the reaction of propene (black) and O$_2$ (blue) with dehydro-\textit{N}-pyridinium radical cations generated by PD of (a) 2-iodopyridinium, (b) 3-iodopyridinium and (c) 4-iodopyridinium. Reaction time is 30 ms and propene concentration = 2.62 x 10$^{10}$ molecule cm$^{-3}$. Each mass spectrum is an average of 1000 acquisitions. O$_2$ reaction spectra have been scaled to fit under C$_3$H$_6$ reaction mass spectra.
3.3.2 Dehydro-\textit{N}-pyridinium + Propene Kinetics and Reaction Mechanism

Mass spectra for the reactions of 2-, 3-, and 4-dehydropyridinium with varying concentrations of propene were recorded as a function of ion trap storage time. The normalised, integrated intensity of select product peaks within a ±0.5 Th window were plotted against reaction time (0.03 to 5000 ms) to produce kinetic traces that describe the decay of \textit{m/z} 79 signal intensity and the growth of propene reaction product signals. Representative kinetic curves for \textit{m/z} 79, 80, 93 and 106 for each of the three dehydropyridinium isomers are shown in Figure 3.3. Reaction pathways responsible for observed product peaks are described below.
Figure 3.3 Kinetic curves for \( m/z \) 79 (red), 106 (blue), 93 (green) and 80 (pink) from reactions of (a) 2-dehydro-\( N \)-pyridinium, (b) 3-dehydro-\( N \)-pyridinium and (c) 4-dehydro-\( N \)-pyridinium with propene (1.28 \( \times \) 10\(^{10} \) molecules cm\(^{-3} \)). A single-exponential function fit to the decay curve of \( m/z \) 79 is shown as a black line and fit residuals are plotted above each kinetic trace. Systematic trends in the residuals are described in the text. Measurements between 0.500 and 5.000 s are not displayed. Error bars are 2\( \sigma \). Kinetic curves for minor products at \( m/z \) 120 and 121 are not shown because they would lie behind \( m/z \) 80 data points.
A single exponential, Eq. (1), was fit to the decay curve of \( m/z \) 79. Fit residuals are plotted above each kinetics plot (Figure 3.3). Although appearing to be an adequate fit at first glance, the residuals display a non-random distribution around the zero-point indicating systematic deviation from the fitted exponential function. Eq. (1) predicts measured values lie typically within \( \pm 1.5\% \) of full scale at the point of largest deviation from measured data, within measurement error of \( (\pm 5–10\%, 2\sigma) \). A biexponential function, Eq. (2), provides a closer fit and randomly distributed residuals in all cases but the additional uncertainty introduced when calculating additional fitting parameters often left the two resulting pseudo-first order rate coefficients inseparable within \( 2\sigma \) uncertainty limits. A single exponential function was used for the purpose of extracting rate coefficients. A plot of pseudo-first-order rate coefficients versus propene number density, shown in Figure 4, follows a linear trend (in accord with the pseudo first-order conditions) and second-order rate coefficients were extracted from the slope of these linear fits. y-intercepts of pseudo first-order plots in Figure 3.4 are \( 1 \pm 1 \) s\(^{-1} \), \( 1 \pm 1 \) s\(^{-1} \), and \( 5 \pm 3 \) s\(^{-1} \) for 4-, 3-, and 2-dehydropyridinium reactions, respectively (\( 2\sigma \) uncertainty).

\[
y = A_0 \exp\left( k_{(1st)} t \right) + C \quad \text{Eq. 1}
\]

\[
y = A_1 \exp\left( k_{(1st)} t \right) + A_2 \exp\left( k_{(1st)} t \right) + C \quad \text{Eq. 2}
\]

Potential energy schemes (Figure 3.5, Figure 3.6 and Figure 3.7) were produced to rationalise experiments and will be discussed throughout. Reaction enthalpies were calculated at the M06-2X/6-31G(2df,p) level of theory and are presented relative to the calculated enthalpy of each reaction’s respective entrance channel.
Figure 3.4 Pseudo first-order rate coefficients for the decay of \( m/z \) 79 plotted against the propene number density within the ion trap. The least-squares linear fit from which second-order rate coefficients were extracted are shown (results in Table 3.1). Error bars represent 2\( \sigma \) uncertainty (obscured by data point markers).

Kinetic measurements show the complete decay of signal at \( m/z \) 79 to baseline levels for all three reactions investigated indicating complete reaction of each dehydro-\( N \)-pyridinium isomer. Second-order rate coefficients extracted from the decay curve of \( m/z \) 79, presented in Table 3.1, show increasing reaction efficiencies of 41\%, 47\% and 70\% for 4-, 3-, and 2-dehydro-\( N \)-pyridinium respectively, reported as the measured rate coefficient as a percentage of collisional frequency calculated using the Langevin collision model.\(^{84}\) This trend in reaction efficiency is rationalised in part by considering the electron withdrawing nature of the nitrogen group. Protonation at the N-position draws electron density away from the radical site, which increases its electrophilicity. This leads to a stabilising effect on reaction transition states due to increased polarisation and an effective lowering of the reaction barrier.\(^{104-105}\) As radical electrophilicity increases, the effect becomes more pronounced with increasing proximity between radical and charge site. This effect has previously been observed and described in greater detail in the gas\(^{59}\) and liquid phase\(^{57-58}\) for a range of dehydro-\( N \)-pyridinium-type radical cation abstraction reactions. Further, the ionised carbene-like resonance structure of pyridinium results in a comparatively sharp increase in reaction efficiency from 3-dehydro-\( N \)-pyridinium to 2-dehydro-\( N \)-pyridinium compared to that between 4-dehydro-\( N \)-pyridinium and 3-dehydro-\( N \)-pyridinium due to partial delocalisation of positive
charge to the α and γ ring positions. This leads to enhanced radical electrophilicity and facilitates more efficient nucleophilic attack by the unsaturated double bond of propene at these positions.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Neutral Loss Fragment</th>
<th>Assigned Product</th>
<th>Relative signal intensity at t = 5 s (% of total ion signal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Dehydro-N-pyridinium + Propene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>C₂H₅</td>
<td></td>
<td>4.9 ± 0.3</td>
</tr>
<tr>
<td>93</td>
<td>C₂H₄</td>
<td>P₄ₒ</td>
<td>23.2 ± 0.7</td>
</tr>
<tr>
<td>106</td>
<td>CH₃</td>
<td>P₃ₒ</td>
<td>57.8 ± 0.8</td>
</tr>
<tr>
<td>120</td>
<td>H</td>
<td>P₁ₒ P₂ₒ P₅ₒ</td>
<td>5.9 ± 0.3</td>
</tr>
<tr>
<td>121</td>
<td></td>
<td></td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>3-Dehydro-N-pyridinium + Propene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>C₂H₅</td>
<td></td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>93</td>
<td>C₂H₄</td>
<td>P₄ₚ</td>
<td>9.0 ± 0.2</td>
</tr>
<tr>
<td>106</td>
<td>CH₃</td>
<td>P₃ₚ</td>
<td>73.7 ± 0.6</td>
</tr>
<tr>
<td>120</td>
<td>H</td>
<td>P₁ₚ P₂ₚ P₅ₚ</td>
<td>4.3 ± 0.1</td>
</tr>
<tr>
<td>121</td>
<td></td>
<td></td>
<td>6.6 ± 0.2</td>
</tr>
<tr>
<td>4-Dehydro-N-pyridinium + Propene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>C₂H₅</td>
<td></td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>93</td>
<td>C₂H₄</td>
<td>P₄ₚ</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>106</td>
<td>CH₃</td>
<td>P₃ₚ</td>
<td>86.6 ± 0.7</td>
</tr>
<tr>
<td>120</td>
<td>H</td>
<td>P₁ₚ P₂ₚ P₅ₚ</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>121</td>
<td></td>
<td></td>
<td>3.5 ± 0.2</td>
</tr>
</tbody>
</table>

Table 3.1 Measured second order rate coefficients, reaction efficiencies, and relative signal intensities for all major product channels for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with propene. Efficiencies (Φ) are reported as k_{exp}/k_{langevin} × 100%. Statistical uncertainty for measured reaction efficiencies are given (2σ). Absolute accuracy is estimated at ± 50%.

Rate coefficients for the growth of signal at m/z 106 are well matched to the decay of m/z 79 for all three isomers. The m/z 106 channel is by far the major product channel and accounts for approximately 58%, 74% and 87% of the total ion signal measured at reaction completion (t = 5 s) for 2-, 3-, and 4-dehydro-N-pyridinium, respectively. Signal at m/z 106 is assigned as vinylpyridinium (P3) possibly formed via two pathways. The first pathway begins with adduct I₁ and proceeds via a 1,2-H shift (I₁ → I₄) and
subsequent $\beta$-scission with no reverse barrier ($I_4 \rightarrow P_3$) to eliminate a methyl group. The highest barrier along this reaction pathway lies 22.1 to 25.3 kcal mol$^{-1}$ below the entrance channel and is the lowest energy pathway to any product on the potential energy scheme for 3-, and 4-dehydro-$N$-pyridinium reactions (Figures 6 and 7), supporting the observed dominance of $m/z$ 106 signal during kinetic measurements. The second pathway to vinylpyridinium proceeds via $\beta$-scission of adduct $I_2$ ($I_2 \rightarrow P_3$) with barrier heights lying 20.3, 15.8 and 16.7 kcal mol$^{-1}$ below the entrance channel for 2-, 3-, and 4-dehydro-$N$-pyridinium reactions, respectively (Figures 5, 6 and 7).
Figure 3.5 Potential energy scheme for the 2-dehydropyridinium + propene reaction showing major intermediates and expected products. Energies were calculated using the M062X/6-31G(2df,p) method and are presented relative to the entrance channel, R0ο. Enthalpies are reported in kcal mol⁻¹.
Figure 3.6 Potential energy scheme for the 3-dehydroxyridinium + propene reaction showing major intermediates and expected products. Energies were calculated using the M062X/6-31G(2df,p) method and are presented relative to the entrance channel, R0\(_m\). Enthalpies are reported in kcal mol\(^{-1}\).
Figure 3.7 Potential energy scheme for the 4-dehydropyridinium + propene reaction showing major intermediates and expected products. Energies were calculated using the M062X/6-31G(2df,p) method and are presented relative to the entrance channel, R0p. Enthalpies are reported in kcal mol⁻¹.
The \( m/z \) 106 product channel is a major pathway but is decreasingly prominent across reactions of 4-, 3-, and 2-dehydro-\( N \)-pyridinium with a corresponding increase in preference towards the \( m/z \) 93 channel and, to a lesser extent, \( m/z \) 80 and 120 channels. The \( m/z \) 93 ion signal is assigned as the \( N \)-protonated-picoly radical (P4). Three pathways are proposed for the formation of P4 for each of the three dehydro-\( N \)-pyridinium isomer reactions. The first proceeds via a 2,3-H shift along the propyl group (I1→I6) followed by \( \beta \)-scission (I6→P4) to yield the \( N \)-protonated-picoly radical and \( C_2H_4 \). The two alternative pathways involve H-atom transfer from the pyridinium ring adjacent to the propyl substituent (I1→I5). I5 comprises two potential intermediates resulting from H-atom transfer from the two ring positions ortho to the propyl group, degenerate in the case of I5p. H-atom transfer from the terminal propyl carbon to the ring-radical (I5→I6), followed by \( \beta \)-scission (I6→P4) results in formation of the \( N \)-protonated-picoly radical.

For the 2-dehydro-\( N \)-pyridinium reaction, a transition state for I5o2→I6o was located with pure electronic energy 0.2 kcal mol\(^{-1}\) higher than that of intermediate I5o2. However, applying the zero-point vibrational energy correction resulted in the transition state 0.3 kcal mol\(^{-1}\) lower in energy than the intermediate. This transition state (I5o2→I6o) was verified by IRC calculations and may provide a case in point for the need to improve the accuracy of ZPE calculations.\(^{106-107}\) The two-step mechanism of radical transfer along the propyl group via intermediate I5 is 11.6, 12.0 and 15.3 kcal mol\(^{-1}\) lower in energy than the former, single step 2,3-H shift mechanism for the 4-, 3-, and 2-dehydro-\( N \)-pyridinium reactions respectively. It is the second most energetically favourable pathway on the potential energy surface for 4-, and 3-dehydro-\( N \)-pyridinium reactions, and the most energetically favourable pathway for 2-dehydro-\( N \)-pyridinium.

Calculated transition states enthalpies indicate that the ring mediated, \( m/z \) 93 pathway identified for the 2-dehydro-\( N \)-pyridinium + propene reaction (I1o→I5o2→I6o→P4o) is energetically favourable and might be expected to result in more \( m/z \) 93 signal than is observed experimentally (Figure 3.3). Therefore, quantum state counting was performed on several competing transition states to quantify entropic factors contributing to the observed product branching ratios. Figure 3.8 summarises results for the 2-dehydro-\( N \)-pyridinium + propene reaction, in which transition states leading from I1o to I4o, I5o1, I5o2 and I6o were considered as the rate limiting step along each pathway to P3 (\( m/z \) 106) or P4 (\( m/z \) 93). Structures for each transition state are shown. The calculated sum of states through each transition state (TS) from I1o is given as a percentage of the total number of
energetically accessible states for the four competing TSs, given $R_0$ – TS of vibrational energy available to the molecule. An Eckart tunnelling correction$^{89-90}$ is also applied. This calculated sum of states is proportional to reaction flux moving from $I_1o$, through the four competing transition states in the forward direction under collision-free conditions, and is compared to experimental branching ratios below. The analysis was repeated for 3-, and 4-dehydro-$N$-pyridinium + propene reactions and results are summarised in Table 3.2.

Figure 3.8 Competing transition states in the 2-dehydro-$N$-pyridinium + propene reaction $m/z$ 106 and $m/z$ 93 channel originating from intermediate $I_1o$. The four transition states shown are the rate limiting step on each respective pathway. Dashed lines represent multiple reaction steps that have been excluded because they lie lower in energy ($m/z$ 93 channels) or are highly entropically favoured ($m/z$ 106 channel). Percentages given are the expected reaction flux from $I_1o$ through each competing transition state in forward direction only, calculated using MultiWell 2017. Only the four transition states shown and their corresponding minima are considered. Values are in kcal mol$^{-1}$. 

![Diagram of competing transition states](image)
A direct comparison of predicted reaction flux to experimentally observed branching ratios cannot be made unless all transition states and intermediates on the potential energy surface are considered. However, the simplified analysis above agrees with branching ratio trends observed experimentally. For 2-dehydro-N-pyridinium, the proportion of states leading from I1\textsubscript{o} to P3\textsubscript{o} (m/z 106) compared to P4\textsubscript{o} (m/z 93) is 77% to 23%, agreeing well with the experimental branching ratios of m/z 106 to m/z 93 channels of 71% to 29%. Results for 4-dehydro-N-pyridinium agree similarly well with experimental values. 3-dehyro-N-pyridinium results under-predict m/z 106 by 30% compared to experimental values, indicating the I2\textsubscript{m}→P3\textsubscript{m} pathway that was not considered in this analysis may contribute more significantly to the m/z 106 channel relative to the 2- and 4-dehydro-N-pyridinium reactions. The dominance of m/z 106 over m/z 93 is partially attributed to the tightness of transition states I1→I5 and I5→I6, which are 5 and 6-membered rings, respectively, as a hydrogen is transferred between the aliphatic chain and the pyridinium ring. Reaction flux in the m/z 93 channel via I5 is limited, at least partially, by the entropic bottle-neck of this required ring-formation, rather than the energetic barrier of the
transition state. These calculations also predict significant tunnelling for all transition states except for $I_{10} \rightarrow I_{502}$, further leading to preference of the $m/z$ 106 channel.

A minor product at $m/z$ 121 (not shown in Figure 3.2) is observed in kinetic experiments which grows in over increasing reaction time and then maintains a stable signal of 3.5% of total ion count for 2-dehydro-N-pyridinium, 6.6% for 3-dehydro-N-pyridinium, and 2.3% for 4-dehydro-N-pyridinium up to the reaction time limit of 10 s. This indicates the presence of an unreactive, open shell C$_8$H$_{11}$N isomer or isomers. Possible candidates for this unreactive $m/z$ 121 population are the resonance stabilised intermediates $I_4$ and $I_7$.

These intermediates lie in deep wells, 60 to 72 kcal mol$^{-1}$ below the entrance channel and thus possess significant barriers to isomerisation. The species responsible for signal at $m/z$ 121 also display minimal reactivity towards background oxygen, shown by the flat signal intensity measured over storage times up to 10 seconds, indicative of resonance stabilised radical lack of reactivity.$^{108}$ Secondary addition of propene is not observed. Formation of CH$_3$, C$_2$H$_4$ and H loss products, and rearrangement to resonance stabilised $m/z$ 121 isomers, are likely too fast for secondary addition to I1 and I2 to occur.

Although no barrier was found with enthalpy greater than the entrance channel for any of the three dehydro-N-pyridinium radicals, measured reaction efficiencies, which are less than 100% and vary between each radical isomer, indicate the rate of reactant collisions is not the rate limiting step. Therefore, the reaction entrance channel was investigated further computationally. Redundant coordinate scans indicate a barrierless lowering of energy as reactants approached from infinite distance. Transition states were then located lying 10.4, 10.0, and 7.7 kcal mol$^{-1}$ below the entrance channel for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively. A corresponding pre-reactive complex was located for the reaction of 4-dehydro-N-pyridinium and propene, lying in a very shallow well 0.02 kcal mol$^{-1}$ below the addition barrier. Previous studies have revealed the ability of pyridinium radical cations to form clusters with acetylene$^{109}$ and hydrogen cyanide$^{110}$ at room temperature, indicating ionic complexes with far greater stability than what has been calculated for the [4-dehydro-N-pyridinium + propene]$^+$ complex. In contrast, the 7.7 kcal mol$^{-1}$ of energy released on formation of the [4-dehydro-N-pyridinium + propene]$^+$ complex is expected to allow the reaction to proceed over the relatively small addition barrier of 0.02 kcal mol$^{-1}$ to preference the covalently-bound reaction adduct. Pre-reactive complexes for 2-, and 3-dehydro-N-pyridinium reactions could not be optimised using the M06-2X/6-31G(2df,p) or M06-2X/6-31+(2df,p) method, despite transition states
suggesting their existence. Optimised transition states are given in Figure 3.9. Although each reaction is energetically barrierless overall, reflection of reaction flux from [dehydro-N-pyridinium + propene]\(^+\) pre-reactive complexes back to reactants may account for the differences in measured rates between radical isomers, and the observation of reaction efficiencies lower than 100%. Involvement of pre-reactive complexes have been shown to significantly influence radical reaction kinetics in other systems,\(^{111-113}\) however further investigation is needed to quantify their effect on the dehydro-N-pyridinium + propene system. Computational kinetic modelling (RRKM-ME) studies of the phenyl radical + propene system\(^{103}\) indicates back-reaction of intermediates to reactants accounts for up to 11% of reaction flux at 7.6 Torr and 1500 K. The study reports increasing re-dissociation of intermediates to reactants with decreasing pressure, calculated from 7600 Torr to the lower limit of 7.6 Torr. Although calculated reaction flux in this re-dissociation channel drops sharply towards 0% as temperature decrease below 500 K, the relatively low pressure (~2.5 mTorr) at which dehydro-N-pyridinium + propene reactions are measured may lead to a small reduction in measured reaction efficiencies away from 100% due to contributions from a similar re-dissociation channel. Nonetheless, the addition of propene to the three radical isomers is overall barrierless and could contribute to molecular weight growth processes in low temperature, extraterrestrial environments.

![Figure 3.9 Optimised geometry of transition states for the addition of propene to each dehydro-N-pyridinium isomer. Distance between the radical site and secondary carbon is given in Angstroms. Calculations were performed using M062X/6-31G(2df,p).](image-url)
3.4 Conclusions

Ion-trap mass spectrometric product detection experiments were conducted to investigate the reaction of the three dehydro-\(N\)-pyridinium isomers with propene at room temperature and 2.5 mTorr. The \(m/z\) 106 reaction channel was measured as the dominant reaction pathway and is rationalised through the production of 2-, 3-, or 4-vinylpyridinium for the reaction of 2-, 3-, and 4-dehydro-\(N\)-pyridinium respectively. Other significant pathways include \(m/z\) 93 (\(N\)-protonated-pyridyl radical), \(m/z\) 80 (H-abstraction pathway) and \(m/z\) 120 (propenyl pyridinium). A stable signal at \(m/z\) 121 at extended reaction times is predicted to result from two possible resonance stabilised, open shell \(\text{C}_8\text{H}_{11}\text{N}\) isomers, to which no secondary addition of propene is observed. The reaction efficiency of 2-, 3-, and 4-dehydro-\(N\)-pyridinium + propene was measured at 70 \(\pm\) 1 \%, 47.2 \(\pm\) 0.4 \%, and 40.9 \(\pm\) 0.9 \% respectively (statistical errors at 2\(\sigma\)). Absolute accuracy of these measurements is estimated at \(\pm\) 50\% due to uncertainty in ion-trap pressure. H-abstraction from propene was not competitive under experimental conditions.

Potential energy schemes were produced to rationalise product branching ratios and elucidate possible mechanisms. The results reveal several possible pathways to \(m/z\) 106, 93, 80, 120 and 121 product ions. Reaction barriers to the production of vinylpyridinium (\(m/z\) 106) + CH\(_3\) were the lowest identified for the 3- and 4-dehydro-\(N\)-pyridinium reactions, supporting observed dominance of signal at \(m/z\) 106. This pathway involves a 1,2-H shift along the propyl group following nucleophilic addition and subsequent \(\beta\)-scission to eliminate CH\(_3\). Ring-mediated H-transfer along the propyl group followed by C\(_2\)H\(_4\) elimination to form \(N\)-protonated-picolyl radical cations (\(m/z\) 93) was identified as the lowest energy pathway for the 2-dehydro-\(N\)-pyridinium + propene reaction. However, quantum state counting revealed entropic bottle necks associated with ring mediated H-transfer transition states in the \(m/z\) 93 channel, further rationalising the observed dominance of \(m/z\) 106 over \(m/z\) 93 in all three reactions despite both product channels possessing reaction barriers of similar energy. No barriers were found with enthalpies higher than the entrance channel; the reaction may therefore be viable in cold, extraterrestrial environments. Differences in measured reaction rates between radical isomers may be due to formation of pre-reactive complexes prior to nucleophilic addition of propene, but further computational investigation is needed to quantify the effect on reaction kinetics. Future studies into the reaction of the three dehydro-\(N\)-pyridinium
radical cations with other small, unsaturated hydrocarbons, such as propyne, acetylene and allene, will assist in developing a predictive understanding of this class of reaction.

3.5 Acknowledgements

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3.6 Supplementary Information for Chapter 3

Sup. 1 Product mass spectra from 266 nm PD (blue, top) and CID (black, bottom) of (a) 2-iodopyridinium, (b) 3-iodopyridinium and (c) 4-iodopyridinium. CID spectra have been inverted for easy comparison alongside PD spectra. The m/z 79 peak corresponds to atomic iodine loss (127 Da).
Sup. 2 C₅H₅N⁺ H-migration calculated at the M062X/6-31G(2df,p) level. Enthalpies are given in kcal.mol⁻¹ relative to the N-centred π-radical.
4 Acetylene Reactions

4.1 Introduction

Ion-neutral reaction pathways contribute significantly to the chemical evolution of many extraterrestrial systems due to the prevalence of high energy photons, cosmic rays, and various other ionisation sources in space. The atmosphere of Saturn’s moon Titan is a case study for prebiotic Earth conditions and has therefore attracted major scientific interest. The upper layers of Titan’s atmosphere are constantly bombarded by solar radiation and energetic plasma from Saturn’s magnetosphere, resulting in a thick ionosphere above altitudes of ~800 km. The formation chemistry of Titan’s tholin haze purportedly arises in the ionosphere through ion-molecule mediated reactions, but the complete model of mechanisms and pathways has not been determined. This incomplete understanding is due to the large number of molecules and ions present along with a corresponding lack of experimentally determined reaction rates, products and product branching ratios for the reaction of those species. The HACA (hydrogen abstraction, C₂H₂ addition) processes are a plausible initiating step to grow PAH species that condense to form tholins through the formation of bi-cyclic, and larger polycyclic species. These reactions, and similar reactions involving N-containing molecules, involve the stepwise addition of small nitrile and alkyn units to aromatic molecules, radicals and ions such as benzene and pyridine, and may be followed by further co-polymerisation of larger nitrile and alkyl species at varying C:N ratios to create the massive polymeric species that make up Titan’s tholin haze.

In this work, the ion-molecule reactions of acetylene with three dehydro-N-pyridinium radical cation isomers will be investigated. Acetylene was chosen due to its prevalence in Titan’s atmosphere, and within interstellar and circumstellar space. Direct measurements of Titan’s ionosphere by the Cassini Ion-Neutral Mass Spectrometer at altitudes of 950 – 1150 km indicate an acetylene mole fraction of ~0.02% while data from the Cassini Visual and Infrared Mapping Spectrometer shows the ubiquitous presence of solid acetylene on the moon’s surface. Modelling studies fit to these measurements suggest acetylene contributes a significant component of Titan’s atmospheric hydrocarbon content throughout all layers of the upper atmosphere. Pyridinium cations were also tentatively identified in Titan’s ionosphere and have been shown to form from reactions of neutral pyridine with hydrocarbon cations in laboratory simulations of Titan’s
The ubiquity of acetylene, and the likely presence of pyridinium in regions of abundant ionising radiation and high energy particles, makes the occurrence of ion-molecule and radical ion-molecule reactions of these species very likely. In this paper we report experimentally determined reaction rates and product branching ratios at room temperature and 2.5 mTorr. Quantum chemical calculations are used to support experimental observations and elucidate possible reaction pathways.

4.2 Experimental

4.2.1 Ion-Trap Mass Spectrometry

A modified linear ion-trap mass spectrometer (Thermo Fisher Scientific LTQ XL) was used to investigate gas-phase ion-molecule reactions of 2-, 3-, and 4-dehydro-N-pyridinium radical cations with acetylene. The iodinated radical precursors 2-iodopyridinium, 3-iodopyridinium and 4-iodopyridinium were generated via electrospray ionisation of 20 μM methanolic solutions of 2-iodopyridine (98%, Sigma-Aldrich), 3-iodopyridine (98%, Sigma-Aldrich) and 4-iodopyridine (97%, Sigma-Aldrich), respectively, introduced into the ESI source at 5 μL min⁻¹, operating in positive ion mode. Iodinated precursor ions (m/z 206) were mass selected using an isolation window of 1 Th and q-parameter of 0.250. Other instrument parameters include electrospray voltage (4 kV), capillary temperature (250 °C), sheath gas flow (8 arb. units), auxiliary gas flow (0 arb. units) and sweep gas flow (0 arb. units). All mass spectra presented herein are an average of at least 100 scans.

The mass spectrometer has been modified to include a vacuum sealed quartz window in the removable backing plate to give optical access along the internal axis of the ion trap. This allows irradiation of trapped ions by a 266 nm Nd:YAG laser source (Continuum, Minilite). The mass spectrometer was equipped with a gas handling manifold that allowed the introduction of neutral gases directly into the ion trap. The gas handling manifold was connected to three one-gallon steel cylinders containing helium gas doped with varying concentrations of acetylene. A mass flow controller (MKS GE50A, 5 sccm) regulated the flow, from a single select cylinder, to 1.3 sccm directly into the ion-trap, which was found to maintain the optimal working pressure within the trap. Acetylene concentration in the ion-trap was varied by selecting a cylinder of different acetylene concentration. See Ref 68 for a more detailed description of the instrument.
Generation of dehydro-$N$-pyridinium radicals is achieved by photodissociation (PD) of iodinated precursor ions ($m/z$ 206) using the coupled 266 nm laser. The precursor cation isolation and trapping sequence was used to send a signal to a digital delay generator which subsequently triggered the flashlamp of the coupled Nd:YAG laser (4th harmonic, 266nm). The laser Q-switch is then triggered internally approximately 140 μs later for optimal power density (ca. 30 mJ cm$^{-2}$). The unfocused laser pulse enters the ion-trap through a 2.5 mm orifice in the back lens and passes axially down its internal length to overlap the trapped ion cloud.

4.2.2 Kinetic Measurements
Dehydro-$N$-pyridinium radicals ($m/z$ 79), generated from laser photolysis of the corresponding iodinated precursor, were mass-isolated in the presence of a controlled concentration of acetylene gas and held within the ion trap for selected time periods between 0.030–10,000 ms. Ion-molecule reactions took place under pseudo first-order conditions, verified below, due to the large excess of acetylene within the trap relative to the population of trapped dehydro-$N$-pyridinium radical cations. The flow of acetylene doped buffer gas into the ion trap was maintained at 1.3 sccm for at least 12 hours prior to commencing kinetic measurements to ensure a stable concentration. Acetylene concentration within the ion trap was varied by using acetylene doped He gas cylinders with varying acetylene concentration, mixed from separate dilutions of two different parent acetylene cylinders (743 ppm ± 2% in He (Coregas), and 747 ppm ± 2% in He (BOC)) with ultra-high purity helium (99.999%). No further purification was performed. Pseudo first-order kinetics were measured for 2-, 3-, and 4-dehydro-$N$-pyridinium + acetylene reactions. Kinetic measurements of each dehydro-$N$-pyridinium isomer + acetylene reaction, each taking 20–30 minutes, were iterated continuously over the span of a day (6 hours) and repeated for at least 4 different acetylene concentrations on different days to ensure measurement-to-measurement and day-to-day consistency in measured rate coefficients.

Kinetic plots were produced by integrating the area under a specified $m/z$ region (± 0.5 Da surrounding a central peak) and normalising to the integrated signal over the entire spectrum ($m/z$ 50-300). The normalised, integrated signal intensity was averaged over all scans for a given reaction time (mass spectrum) for a given kinetic measurement. Each
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kinetic measurement datum was weighted based on variance then averaged and plotted against reaction time to produce a single kinetic curve which was fitted with an exponential function, Equation 1.

\[ y = A_0 \exp(-k_{1st}t) + C \]  

Equation 1

First-order rate coefficients extracted from the fit were plotted against acetylene number density and second order rate coefficients were extracted from the slope of linear regression fits to these data. Reaction efficiencies (Φ) were calculated from second-order rate coefficients as a percentage of the collisional rate given by the Langevin rate model for ion-molecule collision pairs. Ultimately, an upper limit of ±50% uncertainty in the second-order rate coefficient results from uncertainty in ion-trap gas pressure, estimated at 2.5 mTorr ± 50%.

4.2.3 Quantum Chemical Calculations

Quantum chemical calculations were carried out to rationalise observed reaction products and elucidate possible mechanisms. Reaction enthalpies were computed at the M06-2X/6-31G(2df,p) level using Gaussian 09. All stationary points were assigned as minima, possessing no imaginary frequencies, or transition states, possessing one imaginary frequency with a normal mode projection that approximates motion along the reaction coordinate. Ambiguous transition states were verified using intrinsic-reaction coordinate calculations. All 0 K enthalpies include the zero-point vibrational energy correction and are reported in kcal mol\(^{-1}\). For potential energy schemes and mechanisms in the following sections, stationary points are labelled R for reactants, I for intermediates, P for products, or PRC for pre-reaction complexes. Subscript ‘o’, ‘m’, or ‘p’ indicate species that result from the reaction of ortho-, meta- and para-dehydro-N-pyridinium (i.e. 2-, 3-, and 4-dehydro-N-pyridinium), respectively.

4.3 Results

4.3.1 Product Detection Mass Spectrometry

2-, 3- and 4-iodopyridinium ions (m/z 206) were isolated and irradiated at 266 nm. The exclusive new product peak resulting from photodissociation (PD) of each iodopyridinium isomer is observed at m/z 79, consistent with atomic iodine loss and
formation of 2-, 3-, and 4-dehydro-N-pyridinium radical cations. Following PD, m/z 79 ions were isolated and stored in the presence of controlled concentrations of acetylene for varying reaction times. Figure 4.1 shows product mass spectra of the reaction of the three dehydro-N-pyridinium isomers with acetylene ([C₂H₂] = 5.36 × 10¹⁰ molecule cm⁻¹) at 100 ms reaction time. Two dominant peaks are observed at m/z 105 and m/z 104 for all reactions. These peaks are assigned C₂H₄ reaction adduct isomers ([M + 26]⁺) at m/z 105, and the H-atom loss channel at m/z 104. An additional minor product peak is observed at m/z 130 and assigned as the addition of a second C₂H₂ molecule to the acetylene adduct at m/z 105, followed by H-atom loss. Previous studies of the reaction of pyridinium-N-yl radical cations (the conventional radical cation) with acetylene reported addition of two acetylene molecules followed by ring closure and H-atom loss to form the quinolizinium cation.¹⁰⁹ In a reminiscent way here, the addition of two acetylene molecules to 2-, 3-, and 4-dehydro-N-pyridinium radical cations could result in formation of polycyclic N-containing heteroaromatic cations including quinolizinium, quinolinium and isoquinolinium. These pathways are unavailable to the conventional pyridinium-N-yl radical cation which reacts exclusively at the N-position.¹⁰⁹ Mechanisms for product channels discussed above are given in Figure 4.2, Figure 4.3 and Figure 4.4. The upper half of each mechanistic scheme corresponds to reaction pathways available on addition of a single acetylene molecule; the lower half corresponds to possible pathways after addition of a second acetylene molecule to each reactive intermediate of the primary reaction. Corresponding potential energy schemes for these reactions will be presented and discussed in the following section.

There are several low intensity peaks observed in mass spectra that cannot be assigned to acetylene reactions. These include m/z 95 and 120 (Figure 1a), m/z 111 and 137 (Figure 1b and c), and m/z 80, 106 and 122 (Figure 1a, b, and c). These peaks are due to reactions with background oxygen that has entered the ion-trap through the ESI source, in addition to what we assign as acetone, which is present as an impurity in the acetylene gas mixture. Mass spectra were acquired for 2-, 3-, and 4-dehydr-N-pyridinium radical cation reactions with a spiked concentration of acetone, doped into the ion-trap via the ESI (using a kimwipe soaked in acetone). These mass spectra are presented in the Supporting Information (Figure S1).

Peaks at m/z 111 and 95 are assigned as oxygen products, resulting from the addition of O₂ to each dehydro-N-pyridinium radical and subsequent oxygen atom loss, respectively.
This agrees with findings of phenyl-type radical cation oxidation studies\textsuperscript{67, 70} where formation of peroxyl- (O\textsubscript{2} addition) and oxyl- (O\textsubscript{2} addition followed by O atom loss) were observed. A peak at \(m/z\) 120 (Figure 1a) is assigned as the addition of O\textsubscript{2} to the acetylene adduct (\(m/z\) 105), and subsequent OH loss ([105 + 32 – 17]^+). This pathway has been confirmed by isolating and storing \(m/z\) 105 in the presence of oxygen which results in formation of a low intensity peak at \(m/z\) 120.
Figure 4.1 Mass spectra of the reaction of acetylene with dehydro-\textit{N}-pyridinium radicals (m/z 79) generated from PD of (a) 2-iodopyridinium, (b) 3-iodopyridinium, and (c) 4-iodopyridinium. Reaction time is 100 ms. Peaks with asterisks result from reactions with oxygen or acetone impurities. Possible structures for observed peaks are given in Figures 4.2, 4.3 and 4.4.
Figure 4.2 Mechanistic reaction scheme for 2-dehydro-N-pyridinium + acetylene. Reactants (R₀) lead to major products at m/z 105, assigned as an unreactive open-shell C₇H₇N⁺ isomer or isomers (I₁₀, I₃₀, I₅₀), and m/z 104, assigned as ethynylpyridinium (P₁₀). Addition of a second acetylene unit results in products at m/z 130 (P₂₀, P₃₀, P₄₀, P₅₀). R, I, and P denote reactants, intermediates and products, respectively. Subscript ‘₀’ indicates reactants, intermediates and products resulting from ortho-dehydro-N-pyridinium (2-dehydro-N-pyridinium).
Figure 4.3 Mechanistic reaction scheme for 3-dehydro-$N$-pyridinium + acetylene. Reactants (R0$_m$) lead to major products at m/z 105, assigned as an unreactive open-shell C$_7$H$_7$N$^+$ isomer or isomers (I1$_m$, I3$_m$, I5$_m$), and m/z 104, assigned as ethynylpyridinium (P1$_m$). Addition of a second acetylene unit results in products at m/z 130 (P2$_m$, P3$_m$, P4$_m$, P5$_m$). R, I, and P denote reactants, intermediates and products, respectively. Subscript ‘m’ indicates reactants, intermediates and products resulting from meta-dehydro-$N$-pyridinium (3-dehydro-$N$-pyridinium).
Figure 4.4 Mechanistic reaction scheme for 4-dehydro-$N$-pyridinium + acetylene. Reactants ($R_{0p}$) lead to major products at $m/z$ 105, assigned as an unreactive open-shell $C_7H_7N^+$ isomer or isomers ($I_{1p}$, $I_{3p}$), and $m/z$ 104, assigned as ethynylpyridinium ($P_{1p}$). Addition of a second acetylene unit results in products at $m/z$ 130 ($P_{2p}$, $P_{3p}$). $R$, $I$, and $P$ denote reactants, intermediates and products, respectively. Subscript ‘p’ indicates reactants, intermediates and products resulting from para-dehydro-$N$-pyridinium (4-dehydro-$N$-pyridinium).
Low intensity peaks at \( m/z \) 137 and 122 are assigned as the acetone reaction adduct ([79 + 58]+) and its methyl loss channel ([79 + 58 - 15]+), respectively. Peaks at \( m/z \) 80 and 106 are likely due to H-atom abstraction from acetone by 2-, 3-, and 4-dehydro-N-pyridinium radicals (\( m/z \) 79) and their acetylene reaction adducts (\( m/z \) 105). H-atom abstraction from acetylene to form the highly reactive ethynyl radical and pyridinium is energetically inaccessible at experimental temperatures, with calculated product enthalpies lying 14.9, 15.2, and 17.9 kcal mol\(^{-1}\) higher in energy than the entrance channel for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively. Reactions of these target radicals with acetone is the target of ongoing work in our lab.

### 4.3.2 Reaction Kinetics

Mass spectra for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with varying concentrations of acetylene were recorded at ion-trap storage times varying between 0.03 and 10,000 ms. Normalised, integrated intensity of select product peaks within a ±0.5 Th window were plotted against storage time to produce kinetic traces of the decay of \( m/z \) 79 signal intensity with corresponding growth of reaction product signals. Representative kinetic curves for \( m/z \) 79, 105, 104 and 130 at reaction times of 0 – 500 ms for each of the three dehydro-N-pyridinium isomers are shown in Figure 4.5. Kinetic curves including reaction times up to 5000 ms can be found in the Supporting Information.

The effect of acetone reactions on measured acetylene reaction kinetics is discussed in the Supporting Information. Acetone is present at \( \leq 2\% \) of the concentration of acetylene in \( \text{C}_2\text{H}_2/\text{He} \) mixed tanks. It is expected to contribute minimally to 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium reactions; acetone reactions with these two dehydro-N-pyridinium isomers have measured reaction efficiencies of 5.4\% and 6.8\%, respectively. 2-dehydro-N-pyridinium + acetone reaction efficiency was measured at an anomalously high 147\% (discussed in the Supporting Information). The highly efficient 2-dehydro-N-pyridinium + acetone impurity reaction may contribute to a slightly higher measured acetylene reaction efficiency, which is reported in Table 4.1, relative to the true reaction efficiency value, and should be interpreted with caution.

An exponential function, Equation 1, was fit to the decay curve of \( m/z \) 79 for measurements at each acetylene concentration. Fit residuals, plotted above each kinetic trace in Figure 5, display some evidence for non-random distribution around the zero-
point indicating systematic deviation from the fitted function. This was also observed in our previous studies of dehydro-N-pyridinium reactions with propene.\textsuperscript{122} However, Eq. 1 predicts measured values typically within ±1.5% of full scale at the point of largest deviation from the measured data, which is within typical measurement error of ±3% of full scale (2σ). Equation 1 was used to extract pseudo first-order rate coefficients. A plot of pseudo first-order rate coefficients vs acetylene number density, shown in Figure 6, follows a linear trend in accord with pseudo first-order conditions with respect to acetylene, and second-order rate coefficients were extracted from the slope of these linear fits. Measured reaction efficiencies, together with branching ratios for the m/z 105 and 104 channels, are given in Table 4.1.

Potential energy schemes (Figure 4.7, Figure 4.8 and Figure 4.9) were produced to rationalise experiments and will be discussed throughout. Reaction enthalpies were calculated at the M06-2X/6-31G(2df,p) level of theory and are presented relative to the enthalpy of each reaction’s respective entrance channel.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Assigned Product(s)</th>
<th>Branching Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>P1\textsubscript{o}</td>
<td>23 ± 5</td>
</tr>
<tr>
<td>105</td>
<td>I13\textsubscript{o}</td>
<td>56 ± 4</td>
</tr>
<tr>
<td>104</td>
<td>P1\textsubscript{m}</td>
<td>17 ± 3</td>
</tr>
<tr>
<td>105</td>
<td>I13\textsubscript{m}</td>
<td>70 ± 6</td>
</tr>
<tr>
<td>104</td>
<td>P1\textsubscript{p}</td>
<td>10 ± 4</td>
</tr>
<tr>
<td>105</td>
<td>I8\textsubscript{p}</td>
<td>74 ± 8</td>
</tr>
</tbody>
</table>

Table 4.1 Measured second-order rate coefficients, reaction efficiencies and branching ratios for the two primary acetylene product channels (m/z 104, 105) for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with acetylene. Efficiencies (Φ) are reported as k\textsubscript{exp}/k\textsubscript{langevin} × 100% with statistical uncertainty given at 2σ. Absolute accuracy of reaction rates and efficiencies is estimated at ±50%. Branching ratios, averaged over all acetylene concentrations, are extracted from the least squares fit of Equation 1 to kinetic curves over the initial rising portion of the m/z 105 trace to minimise the influence of secondary O\textsubscript{2} and (CH\textsubscript{3})\textsubscript{2}CO reactions. Branching ratio uncertainty is 2σ.
Figure 4.5 Kinetic curves for $m/z$ 79 (red), 104 (blue), 105 (green) and 130 (orange) for reactions of (a) 2-dehydro-$N$-pyridinium, (b) 3-dehydro-$N$-pyridinium and (c) 4-dehydro-$N$-pyridinium with acetylene ($6.59 \times 10^{10}$ molecules cm$^{-3}$). An exponential function fit to the decay curve of $m/z$ 79 is shown as a black line and fit residuals are plotted above each kinetic trace. Error bars are 2σ.
Figure 4.6 Pseudo first-order plot of measured first-order rate coefficient for the decay of signal at m/z 79 as a function of acetylene molecule number density within the ion-trap. Second-order rate coefficients were extracted from a linear least-squares fit to each data set. Error bars are 2σ (obscured by data point markers).

Kinetic measurements show the decay of signal at m/z 79 to baseline levels for reactions of all three dehydro-N-pyridinium isomers, indicating complete reaction. Reaction efficiencies were calculated to be 32%, 14% and 10% for 2-, 3- and 4-dehydro-N-pyridinium reactions, respectively, reported as a percentage of the collisional frequency of ion-molecule pairs calculated using the Langevin collision model. Reaction efficiencies appear to increase with decreasing spatial separation of charge and radical site. This trend is rationalised through increased radical electrophilicity as electron density is drawn to the N-position more strongly from the ortho position, relative to the meta and para positions. Enhanced radical electrophilicity leads to greater stabilisation of acetylene addition transition states through increased polarisation, effectively lowering the addition reaction barrier. The partial delocalisation of positive charge to the α and γ ring positions through the carbene-like resonance structure of pyridinium results in further enhancement of radical electrophilicity for 2-dehydro-N-pyridinium and 4-dehydro-N-pyridinium. This contributes to the relatively sharp increase in reaction efficiency from 3-dehydro-N-pyridinium to 2-dehydro-N-pyridinium reactions, compared to the slight increase in efficiency from 4-dehydro-N-pyridinium to 3-dehydro-N-pyridinium.
First order rate coefficients for the three major acetylene reaction channels, extracted from kinetic measurements at \([C_2H_2] = 6.59 \times 10^{10}\) molecules cm\(^{-3}\), are given in Table 4.2. Measured rate coefficients for the decay of \(m/z\) 79 ion signal are lower than those measured for the growth of ion signal in the \(m/z\) 105 and \(m/z\) 104 product channels. They are not matched within 2\(\sigma\) error. The source of this disparity has not yet been determined. Possible causes are under investigation and are discussed in the Supporting Information. These include influence from acetone reactions, which at this point seems unlikely, collisional cooling of ‘hot’ reactants and adduct isomers, which may explain the relatively high rate coefficient of the \(m/z\) 104 channel but not the disparity between the \(m/z\) 105 and 79 channels, and possible isomerisation of dehydro-N-pyridinium radicals, which can explain the relatively low rate coefficient of \(m/z\) 79 channel, but not disparity in the 4-dehydro-N-pyridinium reaction. A combination of factors may be contributing to measured first-order rate coefficients and possible causes for the disparity are currently under investigation in our lab.

<table>
<thead>
<tr>
<th>First-order rate coefficients (s(^{-1}))</th>
<th>2-dehydro-N-pyridinium</th>
<th>3-dehydro-N-pyridinium</th>
<th>4-dehydro-N-pyridinium</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m/z) 79</td>
<td>24.5 (\pm) 0.9</td>
<td>9.8 (\pm) 0.2</td>
<td>6.9 (\pm) 0.2</td>
</tr>
<tr>
<td>(m/z) 104</td>
<td>33 (\pm) 5</td>
<td>12 (\pm) 2</td>
<td>10 (\pm) 3</td>
</tr>
<tr>
<td>(m/z) 105</td>
<td>29 (\pm) 3</td>
<td>10.9 (\pm) 0.6</td>
<td>7.7 (\pm) 0.4</td>
</tr>
</tbody>
</table>

Table 4.2 First order rate coefficients extracted from kinetic measurements at an acetylene concentration of \(6.59 \times 10^{10}\) molecules cm\(^{-3}\). Errors are 2\(\sigma\).

As discussed in the previous system, pre-reaction complexes, shown in Figure 4.7a, Figure 4.8a and Figure 4.9a, were located with enthalpies 8.9, 5.4 and 4.7 kcal mol\(^{-1}\) below the entrance channel for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively. Corresponding acetylene addition barriers 6.6, 4.1 and 3.6 kcal mol\(^{-1}\) below the entrance channel for each isomer decrease with decreasing spatial separation between charge and radical site, in accord with transition state polarisation effects described above. Addition barriers such as these, which lie lower in energy than the entrance channel and are preceded by a pre-reaction complex, termed “submerged barriers”,\(^{49}\) significantly reduce reaction efficiencies when included in RRKM master equation kinetics calculations, compared to when they are omitted and the entrance channel is treated as smooth and barrierless.\(^{113}\) Reactions proceeding through submerged barriers and
containing no barriers higher in energy than the entrance channel are termed “de facto barrierless”. Potential energy schemes in Figure 4.7a, Figure 4.8a and Figure 4.9a indicate these are de facto barrierless reactions. The submerged barriers within the entrance channel present an entropic bottle neck which regulates formation of the covalently bonded addition adduct. Reflection of reaction flux from the submerged barriers, resulting in the re-dissociation of the pre-reaction complex, is a possible explanation for measured reaction efficiencies that are notably less than 100%. Barrierless reactions are expected to be 100% efficient in the absence of a re-dissociation pathway. Calculated submerged barrier heights are in agreement with measured reaction efficiencies, where the lower barrier of the 2-dehydro-N-pyridinium reaction, relative to 3- and 4-dehydro-N-pyridinium reactions, can support the greatest portion of reaction flux towards the covalently bound reaction adduct resulting in the highest observed reaction efficiency. Previous studies have observed pre-reaction complexes and van der Waals clusters containing multiple reactant units of acetylene\textsuperscript{109} and hydrogen cyanide\textsuperscript{110} with the pyridinium-N-yl radical cations.

4.3.3 Product channels and reaction mechanism

The two major product channels are assigned as formation of acetylene reaction adduct isomers (I\textsubscript{1}, I\textsubscript{3}, I\textsubscript{5\textsubscript{m}}, I\textsubscript{5\textsubscript{o}}, I\textsubscript{8\textsubscript{p}}) at m/z 105, and ethynylpyridinium (P\textsubscript{1}) at m/z 104. These two channels represent 80 ± 3%, 87 ± 3%, and 84 ± 5% of the total product ion signal for reactions of 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively, with no statistically significant trend in this contribution to total ion signal across all acetylene concentrations. The ion signal ratio between m/z 105 and 104 channels is 70:30 for 2-dehydro-N-pyridinium reactions, 81:19 for 3-dehydro-N-pyridinium reactions, and 88:12 for 4-dehydro-N-pyridinium reactions, varying less than 5% across all acetylene concentrations for all reactions, excluding at extended reaction times where secondary reactions with impurities and acetylene cause the decay of m/z 105. A small portion of the observed products are directed towards acetone reactions, seen primarily as the H-atom abstraction channels at m/z 80 and m/z 106. Preceding the complete depletion of dehydro-N-pyridinium radical cations at m/z 79 (i.e. at reaction times used to determine branching ratios), the m/z 80 channel contributes less than 2% of total ion signal in 3-, and 4-dehydro-N-pyridinium reactions, and less than 7% for 2-dehydro-N-pyridinium reactions. The m/z 106 channel contributes less than 2.5% of total ion signal for all
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reactions at these times. Direction of reaction flux into the m/z 106 acetone reaction channel may result in the m/z 105 channel appearing slightly less intense than what is expected in the absence of acetone. Contribution from the m/z 106 channel has been added to the branching ratio errors for the m/z 105 channel reported in Table 4.1.

Secondary reactions with acetone, oxygen and acetylene cause m/z 105 signal decay over extended time periods, leaving a stable population that accounts for approximately 39%, 50% and 50% of total ion signal at reaction completion (t=∞) for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively, calculated from an exponential fit to data in this region. Likely candidates for the remaining stable population of m/z 105 in each reaction are the three, resonance stabilised (1-dehydrovinyl)-pyridinium isomers, I13o, I13m and I8p (Figure 4.7a, Figure 4.8a, Figure 4.9a). These intermediates reside in deep wells 58 to 63 kcal mol\(^{-1}\) below the entrance channel and have significant barriers to isomerisation. Three pathways are proposed for their formation. The first involves a direct 1,2-H shift to the terminal carbon of the alkyl chain to form I13o, I13m or I8p from I1 (I1o→I13o, I1m→I13m, I1p→I8p). This is the most energetically favourable pathway to form (1-dehydrovinyl)-pyridinium for each reaction, with rate-limiting barriers 11.0, 7.1 and 14.2 kcal mol\(^{-1}\) below the entrance channel for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively. The 1,2-H shift transition state is preceded by rotation of the alkyl chain 90° out of plane, resulting in a bifurcation point linking the two conformers of intermediates I1, for all reactions, to I13o, I13m or I8p. The alternative two pathways to (1-dehydrovinyl)-pyridinium involve ring-mediated H-atom transfer to the terminal carbon via intermediates I3, for all reactions, and I5o and I5m, for 2-, and 3-dehydro-N-pyridinium reactions. The highest barrier along these pathways for all reactions is prohibitive, lying 2 – 4 kcal mol\(^{-1}\) above the entrance channel, with the exception of the 2-dehydro-N-pyridinium reaction proceeding through intermediate I5o (I11,o→I51,o→I52,o→I13o). This pathway contains no prohibitive barriers by virtue of H-atom transfer to and from the N-position, as opposed to C-ring positions, and has a rate limiting barrier 8.5 kcal mol\(^{-1}\) below the entrance channel.

The m/z 104 channel, in all cases assigned as ethynlypyridinium (P1), forms through β-elimination of atomic hydrogen from the two conformers of intermediate I1 (I1→P1). Reaction barriers for I11 and I12, respectively, lie 8.5 and 9.5 kcal mol\(^{-1}\) below the entrance channel for the 2-dehydro-N-pyridinium reaction, 6.4 and 6.6 kcal mol\(^{-1}\) below the entrance channel for the 3-dehydro-N-pyridinium reaction, and 5.5 kcal mol\(^{-1}\) below
the entrance channel for the 4-dehydro-N-pyridinium reaction. The two conformers of \(I_{1p}\) and their corresponding transition states in the 4-dehydro-N-pyridinium reaction are degenerate.

Figure 4.7a Potential energy scheme for addition of acetylene to 2-dehydro-N-pyridinium. R, PRC, I, and P denote reactants, pre-reaction complexes, intermediates and products, respectively. The two conformers of \(I_{1o}\), \(I_{3o}\) and \(I_{5o}\), highlighted in red, green and blue, undergo secondary reactions with acetylene, shown in Figure 4.7b, c and d. Enthalpies are in kcal mol\(^{-1}\), relative to \(R_{0o}\).

Figure 4.7b Potential energy scheme for addition of a second acetylene unit to the two conformers of \(I_{1o}\), leading to \(P_{3o}\) and \(P_{2o}(m/z\ 130)\). Enthalpies are in kcal mol\(^{-1}\), relative to \(R_{0o}\).
Figure 4.7c Potential energy scheme for addition of a second acetylene unit to the two conformers of I$_3$$_o$, leading to P$_2$$_o$ and P$_4$$_o$ (m/z 130). Enthalpies are in kcal mol$^{-1}$, relative to R$_0$$_o$.

Figure 4.7d Potential energy scheme for addition of a second acetylene unit to the two conformers of I$_5$$_o$, leading to P$_3$$_o$ and P$_5$$_o$ (m/z 130). Enthalpies are in kcal mol$^{-1}$, relative to R$_0$$_o$. 

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Figure 4.8a Potential energy scheme for addition of acetylene to 3-dehydro-N-pyridinium. R, PRC, I, and P denote reactants, pre-reaction complexes, intermediates and products, respectively. The two conformers of I$_{1m}$, I$_{3m}$ and I$_{5m}$, highlighted in red, green and blue, undergo secondary reactions with acetylene, shown in Figure 4.8b, c and d. Enthalpies are in kcal mol$^{-1}$, relative to R$_{0m}$.

Figure 4.8b Potential energy scheme for addition of a second acetylene unit to the two conformers of I$_{1m}$, leading to P$_{3m}$ and P$_{2m}$ (m/z 130). Enthalpies are in kcal mol$^{-1}$, relative to R$_{0m}$. 
Figure 4.8c Potential energy scheme for addition of a second acetylene unit to the two conformers of $I_{3m}$, leading to $P_{2m}$ and $P_{4m}$ ($m/z$ 130).

Figure 4.8d Potential energy scheme for addition of a second acetylene unit to the two conformers of $I_{5m}$, leading to $P_{3m}$ and $P_{5m}$ ($m/z$ 130).
Figure 4.9a Potential energy scheme for addition of acetylene to 4-dehydro-N-pyridinium. R, PRC, I, and P denote reactants, pre-reaction complexes, intermediates and products, respectively. I1p and the two conformers of I3p, highlighted in red and green, undergo secondary reactions with acetylene, shown in Figure 4.9b and c. Enthalpies are in kcal mol⁻¹, relative to R0p.

Figure 4.9b Potential energy scheme for addition of a second acetylene unit to I1p, leading to P2p (m/z 130).
Figure 4.9c Potential energy scheme for addition of a second acetylene unit to the two conformers of I₃ρ, leading to P₂ρ (m/z 130).

The m/z 130 channel is consistent with addition of a subsequent acetylene molecule to m/z 105 ions in the form of C₂H₂ addition followed by H-atom loss. Figure 4.7b-d, Figure 4.8b-d and Figure 4.9b-c show potential energy schemes for secondary acetylene reactions with intermediates I₁ (red), I₃ (green), and I₅ φ and I₅ m (blue) to support this assertion.

For 2-dehydro-N-pyridinium, secondary acetylene reactions system can result in formation of quinolizinium (P₃ o) or quinolinium (P₂ o) via intermediates I₁,₁ o and I₁,₂ o, respectively (Figure 4.7b). These reactions follow the pathway of nucleophilic addition of acetylene to intermediates I₁ o via a pre-reaction complex (PRC₂ o) to form a four-carbon linear alkyl chain at the ortho position of the pyridinium ring (I₂ o). This is followed by ring closure at either the N-position (I₉ o) or meta-position (I₁₀ o), and subsequent β-scission to eliminate atomic hydrogen to form quinolizinium or quinolinium. Formation of quinolizinium (I₁,₁ o→PRC₂₁,₁ o→I₂₁,₁ o→I₉ o→P₃ o) is de facto barrierless, relative to its secondary reaction entrance channel (I₁,₁ o + C₂H₂), proceeding
through a submerged acetylene addition barrier. In contrast, formation of quinolinium (I12,0→PRC22,0→I22,0→I10,0→P2,0) has an addition barrier 1.5 kcal mol\(^{-1}\) above its corresponding entrance channel (I12,0+C2H2). This is consistent with the barrier-lowering effect of increased radical electrophilicity, caused by the through-space proximity of the radical site to the N-position. Nonetheless, formation of quinolinium through secondary reaction of I12,0 is expected to occur under experimental conditions due to internal vibrational excitation of m/z 105 ions from the primary acetylene reaction, and limited collisional cooling of reaction products at 2.5 mTorr.

Secondary reactions of acetylene with intermediates I31,0, I32,0, I51,0 and I52,0 form quinolinium (P2,0), 7-methylene-7H-cyclopenta[b]pyridinium (P4,0), quinolizinium (P3,0) and 1-methylene-1H-indolizinium (P5,0), respectively. Similar pathways are proposed for each of these reactions. First, nucleophilic addition of acetylene to the radical site occurs at the meta-position (I3,0) or N-position (I5,0). This is followed by either ring-closure between terminal alkyl-chain carbons (I11,0, I8,0), or ring-closure at the β-carbon of the ortho-alkyl substituent (I12,0, I7,0). β-scission to eliminate atomic hydrogen yields the corresponding product of each pathway. Reactions of intermediates I31,0 and I32,0 to form quinolinium (P2,0) and 7-methylene-7H-cyclopenta[b]pyridinium (P4,0) are de facto barrierless, proceeding through submerged acetylene addition barriers. No addition barrier or pre-reaction complex could be located for the addition of acetylene to I5,0, which appears to be smooth and barrierless.

Similar pathways are proposed for secondary acetylene reactions in the 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium systems, shown in Figure 4.8 and Figure 4.9. Together with secondary acetylene reactions of the 2-dehydro-N-pyridinium system, described above, barrierless or de facto barrierless pathways for the formation of quinozilium (P3,0), quinolinium (P2,0, P3m), isoquinolinium (P2m, P2p), and five unique methylenecyclopentene-pyridinium fused ring species have been found. Several additional pathways to quinozilium, quinolinium and isoquinolinium with barriers 1.5 – 2.3 kcal mol\(^{-1}\) above their respective secondary reaction entrance channels were also found.

### 4.4 Discussion

Although the m/z 130 channel accounts for less than 2% of total product ion signal for all measured reactions, the lack of a formal entrance barrier is expected to result in a negative
Chapter 4 – Acetylene Reactions

(non-Arrhenius) temperature dependence between second-order rate coefficient and reactant temperature. Higher pressure, low temperature reaction conditions, supporting more rapid collisional cooling of vibrationally excited primary reaction products, are therefore expected to result in an enhanced rate of formation of these bicyclic species via the proposed de facto barrierless pathways above. Reactions at higher acetylene concentrations were also seen to slightly increase the proportion of signal in the m/z 130 channel for each dehydro-N-pyridinium reaction isomer over the range of concentrations measured (Figure S4). These factors suggest the rate of reactions studied here, and possibly similar radical cation + acetylene reactions, may be enhanced in some regions of the atmosphere of Titan, where collisional cooling is supported by pressures ranging from 0–1.43 atm, and temperatures in the region of 100–200 K.

The barrierless and de facto barrierless secondary acetylene reaction pathways identified here may also contribute to molecular weight growth in the cold environment of interstellar space. Collisional cooling of primary acetylene reaction products at pressures found in the interstellar medium is effectively non-existent and expected to result in a preference, or potential exclusive formation, of ethynylpyridinium (m/z 104 channel). However, the harsh UV-field of interstellar and circumstellar space, together with the ubiquity of cosmic rays, presents an environment supporting C-H and N-H bond fission and further radical formation from these closed-shell reaction products through HACA-style reactions. Previous studies of the reaction of propene with 2-, 3-, and 4-dehydro-N-pyridinium show the formation of 2-, 3-, and 4-vinylpyridinium as major products, which, when photolysed at VUV wavelengths, are likely to undergo H-atom loss to produce a range of radical cations, including the intermediates I1, I3, I5o and I5m, with subsequent internal energies unable to overcome the H-atom loss barriers to form ethynylpyridinium. This is a possible synthetic route for production of radical cations capable of forming a range of bycyclic N-heteroaromatics in low-temperature reaction with acetylene via the pathways identified in this work.

4.5 Conclusions

Ion-trap mass spectrometry was used to detect reaction products, measure reaction kinetics, and determine product branching ratios for the gas-phase, ion-molecule reactions of 2-dehydro-N-pyridinium, 3-dehydro-N-pyridinium, and 4-dehydro-N-pyridinium...
radical cations with acetylene at room temperature and 2.5 mTorr. Reaction efficiencies were determined to be 32 ± 3\%, 14 ± 1\%, and 10 ± 1\% for the reactions of 2-, 3-, and 4-dehydro-N-pyridinium, respectively, where statistical errors are given at 2\%. Absolute accuracy is estimated at ± 50\% due to uncertainty in gas pressure within the ion-trap. Reactions with acetone, present as an impurity in the acetylene gas mixture, may influence measure reaction kinetics, but the effect could not be quantified. The m/z 105 channel is the dominant reaction channel, and is assigned 2-, 3-, and 4-(1-dehydrovinyl)-pyridinium for each reaction. The m/z 104 channel is also prominent and is assigned 2-, 3- and 4-ethynyl-pyridinium. The m/z 105 and m/z 104 channels account for 80\%, 87\%, and 84\% ion signal in the ratio of 70:30 for 2-dehydro-N-pyridinium reactions, 81:19 for 3-dehydro-N-pyridinium reactions, and 88:12 for 4-dehydro-N-pyridinium reactions, respectively, at the point of depletion of the primary reactant (dehydro-N-pyridinium, m/z 79). A small population of m/z 105 ions underwent secondary reaction with both acetylene and acetone, preventing determination of exact branching ratios at extended reaction times for the pure dehydro-N-pyridinium + acetylene system. Secondary acetylene reaction products at m/z 130 were tentatively assigned as a mixed population of bicyclic N-heteroaromatic species.

Quantum chemical calculations were deployed to rationalise observed product branching ratios and elucidate possible mechanisms for the formation of assigned reaction products. Formation of the covalently bound primary acetylene reaction adduct is de facto barrierless for all three reactions, proceeding through a van der Waals complex and submerged transition state. All reaction barriers for the formation of (1-dehydrovinyl)-pyridinium (m/z 105) and ethynyl-pyridinium (m/z 104) lie below the entrance channel and agree with the observed branching ratios. Several barrierless or de facto barrierless pathways for the formation of quinozilium, quinolinium, isoquinolinium, and 5 unique methylenecyclopentene-pyridinium fused ring species have been identified. These pathways follow addition of a second acetylene unit to any of several primary reaction intermediates across the three reactions studied. The barrierless and de facto barrierless primary and secondary acetylene reactions identified in this work may be viable in cold, extraterrestrial environments due to the lack of reaction barriers with energies higher than the entrance channel. Similar ion-molecule reactions involving small alkynes with radical cation species should be considered for further investigation in the context of
extraterrestrial molecular weight growth chemistry due to the possibility of those reaction being barrierless or de facto barrierless.
4.6 Supporting Information for Chapter 4

4.6.1 Oxygen and Acetone reaction products

Figure S1 Mass spectra from the reaction of acetylene (black) and $\text{O}_2 + \text{acetone}$ (blue) with dehydro-$N$-pyridinium radicals ($m/z$ 79) generated by PD of (a) 2-iodopyridinium, (b) 3-iodopyridinium, and (c) 4-iodopyridinium. Reaction time is 100 ms.
Mass spectra were acquired for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with acetone and oxygen in the absence of acetylene. From the mass spectra presented in blue in Figure S1, primary reactions with acetone and oxygen are assigned. The $m/z$ 80 and 137 channels are assigned as H-atom abstraction from acetone and the acetone addition adduct, respectively. The $m/z$ 122 channel is assigned as acetone addition and subsequent methyl loss. The $m/z$ 111 channel is assigned the dioxygen addition adduct and the $m/z$ 95 channel, appearing only in the 2-dehydro-N-pyridinium reaction, is assigned as dioxygen addition with subsequent O-atom loss.

Measurements of acetylene reaction kinetics show decay of signal at $m/z$ 105 over extended time periods. This signal decay is due to secondary reactions which appear as growth of a product peaks at $m/z$ 106 (H-atom abstraction from acetone), $m/z$ 130 (secondary acetylene reactions), and $m/z$ 108. The identity of $m/z$ 108 ions is unknown; however, the $m/z$ 108 channel is assigned as a $C_7H_{10}N^+$ isomer or isomers resulting from reactions of a population of $m/z$ 105 ions with acetone. The assignment of $m/z$ 108 as an acetone reaction products is justified by considering the degree of saturation of $C_7H_{10}N^+$ isomers which cannot be rationalised through secondary oxygen or acetylene reactions pathways. Rate coefficients for the appearance of signal at $m/z$ 108 are well matched to the decay of $m/z$ 105 for all reactions, supporting the assertion that the $m/z$ 108 channel results from secondary reactions with a population of $m/z$ 105 ions.
4.6.2 Acetylene reaction kinetics data up to 5000 ms

Figure S2 Kinetic curves for m/z 79 (red), 104 (blue), 105(green) and 130 (orange) for reactions of (a) 2-dehydro-N-pyridinium, (b) 3-dehydro-N-pyridinium and (c) 4-dehydro-N-pyridinium with acetylene (6.59 × 10^{10} molecules cm^{-3}). An exponential function fit to the decay curve of m/z 79 is shown as a black line and fit residuals are plotted above each kinetic trace. Error bars are 2σ.
4.6.3 Acetone reaction kinetics

Figure S3 Kinetic curves for m/z 79 (red), 80 (blue), 122 (green), 137 (purple) and 180 (orange) for reactions of (a) 2-dehydro-N-pyridinium, (b) 3-dehydro-N-pyridinium and (c) 4-dehydro-N-pyridinium with acetone ($5.32 \times 10^{10}$ molecules cm$^{-3}$). An exponential function fit to the decay curve of m/z 79 at reaction times (a) < 200 ms, (b) < 2000 ms, (c) < 2000 ms, is shown as a black line on each plot. Deviation of these fits from data points at extended reaction time is due to non-exponential decay of signal at m/z 79. Error bars are 2σ.
Reaction kinetics were measured for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with acetone to infer the effect acetone reactions have on measured acetylene reaction rates. Measured first order reaction rate coefficients at \([\text{[(CH}_3)_2\text{CO}]] = 5.32 \times 10^{10}\) molecules cm\(^{-3}\), together with second order rate coefficients and reaction efficiencies calculated assuming pseudo first-order behaviour, are summarised in Table ST1.

<table>
<thead>
<tr>
<th>Acetone reactions</th>
<th>Measured first-order rate ((s^{-1}))</th>
<th>Calculated second-order rate ((cm^3\text{molecule}^{-1} s^{-1}))</th>
<th>Efficiency (\Phi) ((%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-dehydro-N-pyridinium</td>
<td>79 ± 23</td>
<td>((1.49 \pm 0.43) \times 10^{-9})</td>
<td>147 ± 42</td>
</tr>
<tr>
<td>3-dehydro-N-pyridinium</td>
<td>2.9 ± 0.2</td>
<td>((5.52 \pm 0.38) \times 10^{-11})</td>
<td>5.4 ± 0.4</td>
</tr>
<tr>
<td>4-dehydro-N-pyridinium</td>
<td>3.69 ± 0.06</td>
<td>((6.94 \pm 0.12) \times 10^{-11})</td>
<td>6.8 ± 0.1</td>
</tr>
</tbody>
</table>

Table ST1 First order-order rate coefficients, second-order rate coefficients, and reaction efficiencies for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with acetone. Second-order rate coefficients and efficiencies were calculated assuming pseudo first-order behaviour.

Reaction efficiencies of 147%, 5% and 7% were calculated for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium, respectively, and agree with the observed total ion signal contribution of the \(m/z\) 80 channel in acetylene reaction mass spectra and kinetic measurements which is thought to arise from reactions with acetone impurities present in the acetylene gas mixture. The observed effects of acetone reactions on acetylene reaction mass spectra and measured branching ratios are:

- The very high reaction efficiency and near exclusive production of \(m/z\) 80 ions in the 2-dehydro-N-pyridinium + acetone reaction results in up to 7% of total ion signal being diverted into the \(m/z\) 80 channel during acetylene reactions.
- In comparison, the 3-, and 4-dehydro-N-pyridinium + acetone reaction have far lower reaction efficiencies and a broader spread of reaction products. This results in contributions of < 2% of total ion signal in this \(m/z\) 80 acetone-impurity reaction channel.

Regarding kinetic measurements, acetone reactions may have a non-negligible impact on 2-dehydro-N-pyridinium + acetylene reaction kinetics, but minimal impact on 3-, and 4-dehydro-N-pyridinium + acetylene reaction kinetics. 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium + acetone reaction efficiencies are 30-60% lower than their corresponding acetylene reaction efficiencies. Considering these relatively low reaction
efficiencies, together with an acetone concentration of < 2% of the concentration of acetylene, specified by the gas supplier (corgas), acetone reactions are expected to contribute minimally to 3-, and 4-dehydro-N-pyridinium reactions. Conversely, the calculated 2-dehydro-N-pyridinium + acetone reaction efficiency is approximately 4.5 times greater than 2-dehydro-N-pyridinium + acetylene reaction efficiency. The very high efficiency of 2-dehydro-N-pyridinium + acetone reactions may result in a significant impact on measured acetylene reaction kinetics despite a relatively low concentration of acetone impurity in the gas mixture. This assertion is echoed by the relatively high contribution of the m/z 80 channel in acetylene reactions, discussed above.

A reaction efficiency of 147% for the 2-dehydro-N-pyridinium + acetone reaction, which is well over the theoretical 100% limit, may be caused by several factors, alone or in combination: Firstly, uncertainty in the first-order rate coefficient is high due to collection of fewer data points at very early reaction times. This is due to the very fast speed of reaction in combination with an instrument dead-time of approximately 18 ms following the ‘true’ start of the reaction. Uncertainty in measured first-order rate coefficients propagate to an error in the calculated reaction efficiency of 147 ± 42% (2σ), and therefore the true reaction efficiency may lie much closer to 100%. Secondly, the measurement was not repeated on multiple days and at multiple acetone concentrations, leaving accuracy of the measurement in more doubt than a repeated experiment. However, all past kinetic measurements using this instrument and method have been repeatable and suffer from the same, if any, systematic measurement errors. This measurement should therefore be internally consistent with the results of the 3-, and 4-dehydro-N-pyridinium + acetone measurements and acetylene experiments, but possibly shifted from the true efficiency value. Finally, the very high reaction efficiency could be a result of chemical effects. Interaction of the dipole moment of acetone with the positively charged nitrogen site may orient the acetone molecule preferably for H-atom abstraction from a CH$_3$ group. Further, H-atom abstraction is expected to be energetically favourable due to resonance stabilisation of the resulting acetone radical. Long range coulombic forces between reactant dipoles may also contribute to an enhanced collision rate not modelled by the Langevin collision rate model used to calculate reaction efficiencies, resulting in an artificially high calculated reaction efficiency.

These kinetic measurements must be repeated and used in combination with quantum chemical calculations to identify the mechanism behind the highly efficient 2-dehydro-
Chapter 4 – Acetylene Reactions

$N$-pyridinium + acetone reaction. Calculations of acetone + dehydro-$N$-pyridinium ion clustering and reaction dynamics will assist in identifying any possible catalytic effects of acetone on dehydro-$N$-pyridinium + acetylene reactions. Until the effect of acetone on 2-dehydro-$N$-pyridinium + acetylene reactions has been quantified, the results of kinetics experiments for this reaction, presented in the main body of this chapter, must be interpreted cautiously.

### 4.6.4 Disparity in first-order rate coefficients for Acetylene Reactions

Several possible causes for disparity in first-order rate coefficients, presented in Table 4.2, were considered. Ultimately, no single factor discussed here can explain the observed disparity. Multiple factors may be working simultaneously, or alternative factors that have not been considered may be the cause.

Acetone reactions are unlikely to be the cause of disparity between extracted rate coefficients. Reactions with acetone impurities would result in bi-exponential $m/z$ 79 signal decay behaviour which, when fit with a single exponential function, would have the effect of increasing the value of extracted rate coefficients relative to reactions free of acetone impurities. Fit residuals, presented in Figure 4.5, display some evidence for non-exponential behaviour, but this is seen in the acetone-free reactions of propene, ethene and propyne, presented in their respective chapters. First-order rate coefficients in Table 4.2 also show a relative reduction in $m/z$ 79 decay rate compared to the two product channels, supporting the assertion that acetone is not responsible.

Collisional cooling of reactants and reaction adduct isomers was also considered, but evidence suggests it is not the cause of the disparity in reaction rates. Collisional cooling would result in the quenching of the re-dissociation channel over time, as the highest energy pathway of the reaction, and a more gradual quenching of the H-atom loss channel, as the second highest energy pathway of the reaction. A relatively sharp decrease in formation of H-atom loss products ($m/z$ 104) is expected as that pathway becomes accessible to a diminishing population of ‘hot’ $m/z$ 105 ions, corresponding to a relatively high rate coefficient. Similarly, re-dissociation of $m/z$ 105 ions to reactants ($m/z$ 79) will reduce as they are collisionally cooled, resulting in a slowing of the growth of $m/z$ 105 ion-signal and an expected rate coefficient lower than that of the $m/z$ 79 channel.
Collisional cooling may describe the observation of a higher \( m/z \) 104 channel rate coefficient, but the relatively low \( m/z \) 79 rate coefficients can’t be explained.

The 4-dehydro-\( N \)-pyridinium isomer was found to be the most energetically preferable of the three dehydro-\( N \)-pyridinium isomers. Conversion of a small population of 2-, or 3-dehydro-\( N \)-pyridinium radical cations to 4-dehydro-\( N \)-pyridinium, which reacts at a slower rate, would result in extraction of a lower first-order rate coefficient when the data is fit with a single exponential function. Any partial isomerisation of the \( m/z \) 79 ion population could also create the systematic trend in fit residuals observed for all reactions. Disparity between product channel rate coefficients may be a result of the differing branching ratios of each dehydro-\( N \)-pyridinium isomer. These factors suggest isomerisation of dehydro-\( N \)-pyridinium ions could be the cause; however, no energetically accessible isomerisation pathway has been identified, and isomerisation does not explain the disparity in rate coefficients extracted for the 4-dehydro-\( N \)-pyridinium reaction. Calculations of acetylene-mediated isomerisation should be a target of future computational studies, as these reactions could provide a viable pathway for isomerisation.

<table>
<thead>
<tr>
<th>First-order rate coefficients (s(^{-1}))</th>
<th>2-dehydro-( N )-pyridinium</th>
<th>3-dehydro-( N )-pyridinium</th>
<th>4-dehydro-( N )-pyridinium</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m/z \ 79 )</td>
<td>24.5 ± 0.9</td>
<td>9.8 ± 0.2</td>
<td>6.9 ± 0.2</td>
</tr>
<tr>
<td>( m/z \ 104 )</td>
<td>33 ± 5</td>
<td>12 ± 2</td>
<td>10 ± 3</td>
</tr>
<tr>
<td>( m/z \ 105 )</td>
<td>29 ± 3</td>
<td>10.9 ± 0.6</td>
<td>7.7 ± 0.4</td>
</tr>
</tbody>
</table>

Table 4.3 First order rate coefficients extracted from kinetic measurements at an acetylene concentration of \( 6.59 \times 10^{10} \) molecules cm\(^{-3}\). Errors are 2\( \sigma \).
4.6.5 Variation in secondary acetylene reaction product branching ratio with acetylene concentration

Figure S4 Branching ratio of the m/z 130 channel as a function of acetylene concentration. Error bars are 2σ.
5 Ethene and Propyne Reactions

5.1 Introduction

In this chapter, the reactions of ethene and propyne with 2-, 3-, and 4-dehydro-N-pyridinium are investigated. Product mass spectra are presented, and mechanistic schemes of several possible pathways to reaction products are proposed for each reaction. Measured reaction kinetics and product branching ratios, calculated second order rate coefficients and efficiencies are also presented for each reaction. Trends in observed product branching ratios are rationalised through trends in calculated intermediate and transition state enthalpies observed in previous chapters, in the absence of a computational investigation.

5.2 Ethene Reactions

2-, 3- and 4-iodopyridinium cations (m/z 206) were isolated, held within the ion-trap, and subjected to photodissociation at 266 nm which resulted in the formation of signal at m/z 79, indicative of atomic iodine loss and formation of the corresponding dehydro-N-pyridinium radical cation. The radical cation population at m/z 79 was isolated, stored in the ion-trap, and allowed to react in the presence of a controlled concentration of ethene. Mass spectra were collected at select reaction times between 0.03 – 5000 ms. Representative mass spectra for the reaction of each dehydro-N-pyridinium isomer with ethene are given in Figure 5.1, where [C$_2$H$_4$] = 1.075 × 10$^{11}$ molecule cm$^{-3}$ and reaction time = 30 ms.

Two dominant product peaks are observed at m/z 106 and m/z 107 for the reaction of ethene with all three dehydro-N-pyridinium isomer reactions. In each case, the m/z 107 peak is assigned the ethene addition adduct and isomers thereof ([79 + 26]$^+$), and the m/z 106 channel is assigned as H-atom loss ([79 + 26 - 1]$^+$). A small population of ions at m/z 80 is also observed and is assigned the H-atom abstraction channel. Proposed mechanistic pathways for the m/z 106 and 107 channels of each ethene reaction is presented in Figure 5.2.

2-, 3-, and 4-vinylpyridinium (P1 in Figure 5.2) are proposed as the most likely reaction products in the m/z 106 channel for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively, and form in either a two or three-step process. The two-step process
proceeds via nucleophilic addition of ethene to form a primary ethyl-radical substituted pyridinium species (I1), followed by β-scission and elimination of atomic hydrogen to form vinylpridinium (P1). The three-step process involves ethene addition to form the primary ethyl-radical (I1), followed by 1,2-H atom shift along the alkyl group to give the secondary ethyl-radical (I2). Subsequent β-scission and H-atom elimination from the primary carbon of the alkyl group results in formation of vinylpridinium (P1). Cis- and trans- stereoisomerisation pathways exist for all intermediates in the proposed 2-, and 3-dehydro-N-pyridinium reaction mechanisms. Stereoisomers do not exist for the 4-dehydro-N-pyridinium reaction due to rotational symmetry.

Signal in the m/z 107 channel in each reaction is proposed to result primarily from the resonance stabilised intermediates I2. These intermediates likely lie in deep energetic wells with significant barriers to isomerisation due to resonance stabilisation of the radical. Collisional cooling of the m/z 107 ion population within the ion-trap may prevent further isomerisation or H-atom loss. There was no observation of secondary reactions of ethene with isolated m/z 107 or 106 ion populations.
Figure 5.1 Mass spectra from the reaction of ethene with 2-dehydro-N-pyridinium (top), 3-
dehydro-N-pyridinium (middle), and 4-dehydro-N-pyridinium (bottom). Reaction time is 30 ms and ethene concentration = $1.075 \times 10^{11}$ molecule cm$^{-3}$. Each mass spectrum is an average of 300 acquisitions.
Figure 5.2 Proposed scheme for the reaction of ethene with (top) 2-dehydro-N-pyridinium, (middle) 3-dehydro-N-pyridinium, and (bottom) 4-dehydro-N-pyridinium. R, I, and P indicate reactants, intermediates and products respectively. Subscript o, m, and p indicate ortho-, meta- and para- substituted reactions.

Kinetic traces were collected for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with ethene at two ethene concentrations ($6.648 \times 10^{10}$ molecules cm$^{-3}$, and $4.678 \times 10^{10}$ molecules cm$^{-3}$) at reaction times between 0.03 – 5000 ms. A ±0.5 Th window surrounding a central m/z peak was used to extract normalised, integrated intensity of each major m/z channel as a function of reaction time. Representative kinetic traces at $[\text{C}_2\text{H}_4] = 6.648 \times 10^{10}$ molecules cm$^{-3}$ are given in Figure 5.3. Second order rate coefficients, reaction efficiencies and product branching ratios were extracted and averaged over measurements at the two ethene concentrations; the results are given in Table 5.1.
Figure 5.3 Kinetic curves for m/z 79 (red), 106 (blue), and 107 (green) from reactions of (a) 2-dehydro-N-pyridinium, (b) 3-dehydro-N-pyridinium and (c) 4-dehydro-N-pyridinium with ethene ($6.648 \times 10^{10}$ molecules cm$^{-3}$). A single-exponential function fit to the decay curve of m/z 79 is shown as a black line and fit residuals are plotted above each kinetic trace. Measurements at reaction times greater than 0.500 s are not displayed. Error bars are 2σ.
Chapter 5 – Ethene and Propyne Reactions

| Ion signal at m/z 79 decays to baseline levels over time, indicating complete reaction of each dehydro-N-pyridinium radical cation. Reaction efficiencies calculated from the extracted decay rate of m/z 79 signal show increasing efficiencies of 14%, 19%, and 39% for 4-, 3-, and 2-dehydro-N-pyridinium reactions, respectively. This increase in reaction efficiency with increasing proximity of radical and charge site is in accord with transition state polarisation effects described in previous chapters. First order rate coefficients for each major m/z channel, extracted from kinetic measurements at [C$_2$H$_4$] = 6.648 × 10$^{10}$ molecules cm$^{-3}$, are given in Table 5.2. Rate coefficients for the growth of ion signal in the m/z 107 channel are equal to the decay of m/z 79 within measurement error for all three reactions. However, extracted rate coefficients for signal growth in the m/z 106 channel are ~20% greater than those for the decay of m/z 79 signal. These rates are not matched within measurement error for the 2-, and 3-dehydro-N-pyridinium reactions. The disparity in measured first-order rate coefficients may be due to collisional cooling of reactants and reaction adduct isomers, or a result of isomerisation of dehydro-N-pyridinium radical cations. Both isomerisation and collisional cooling were discussed in the previous chapter and are expected to have similar effects on kinetic measurements of ethene reactions. In the case of 4-dehydro-N-pyridinium reactions here, the rate of decay of m/z 79 ion signal in matched to both product channels at m/z 106 and m/z 107, while

<table>
<thead>
<tr>
<th>2-Dehydro-N-pyridinium + Ethene</th>
<th>m/z</th>
<th>Neutral Loss Fragment</th>
<th>Assigned Product</th>
<th>Relative signal intensity at t = 5 s (% of total ion signal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{2nd} = (4.17 \pm 0.37) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>80</td>
<td>C$_2$H$_3$</td>
<td></td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>$\Phi = 39.3 \pm 6.9 %$</td>
<td>106</td>
<td>H</td>
<td>P$_1$</td>
<td>56.7 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>107</td>
<td>I$_2$$_v$</td>
<td></td>
<td>39.8 ± 0.6</td>
</tr>
<tr>
<td>3-Dehydro-N-pyridinium + Ethene</td>
<td>m/z</td>
<td>Neutral Loss Fragment</td>
<td>Assigned Product</td>
<td>Relative signal intensity at t = 5 s (% of total ion signal)</td>
</tr>
<tr>
<td>$k_{2nd} = (2.02 \pm 0.25) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>80</td>
<td>C$_2$H$_3$</td>
<td></td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>$\Phi = 19.0 \pm 2.3 %$</td>
<td>106</td>
<td>H</td>
<td>P$_1$$_m$</td>
<td>29.7 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>107</td>
<td>I$_2$$_m$</td>
<td></td>
<td>66.4 ± 1.1</td>
</tr>
<tr>
<td>4-Dehydro-N-pyridinium + Ethene</td>
<td>m/z</td>
<td>Neutral Loss Fragment</td>
<td>Assigned Product</td>
<td>Relative signal intensity at t = 5 s (% of total ion signal)</td>
</tr>
<tr>
<td>$k_{2nd} = (1.52 \pm 0.22) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>80</td>
<td>C$_2$H$_3$</td>
<td></td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>$\Phi = 14.3 \pm 2.1 %$</td>
<td>106</td>
<td>H</td>
<td>P$_1$$_p$</td>
<td>23.7 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>107</td>
<td>I$_2$$_p$</td>
<td></td>
<td>71.1 ± 0.9</td>
</tr>
</tbody>
</table>

Table 5.1 Second-order rate coefficients, reaction efficiencies and product branching ratios for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium radical cations with ethene.
Chapter 5 – Ethene and Propyne Reactions

rate coefficients for 2-, and 3-dehydro-\textit{N}-pyridinium reactions are not. This agrees with the assertion that isomerisation may be the cause of disparity between measured rate coefficients. 4-dehydro-\textit{N}-pyridinium is the lowest energy dehydro-\textit{N}-pyridinium isomer, inclusive of the conventional \textit{N}-dehydropyridinium radical cation. As the lowest point on this energy gradient, 4-dehydro-\textit{N}-pyridinium ions are the least likely to isomerise during experiments, compared to 2-, and 3-dehydro-\textit{N}-pyridinium ions. This is reflected in the parity of measured product and reactant rate coefficients for the 4-dehydro-\textit{N}-pyridinium reaction, and the greatest disparity of measured rate coefficients for the 2-dehydro-\textit{N}-pyridinium reaction.

<table>
<thead>
<tr>
<th>First-order rate coefficients (s(^{-1}))</th>
<th>2-Dehydro-\textit{N}-pyridinium</th>
<th>3-Dehydro-\textit{N}-pyridinium</th>
<th>4-Dehydro-\textit{N}-pyridinium</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{m/z} 79</td>
<td>26.2 ± 0.6</td>
<td>12.9 ± 0.2</td>
<td>9.6 ± 0.3</td>
</tr>
<tr>
<td>\textit{m/z} 106</td>
<td>31.1 ± 3.2</td>
<td>16.1 ± 2.6</td>
<td>11.4 ± 2.0</td>
</tr>
<tr>
<td>\textit{m/z} 107</td>
<td>25.6 ± 1.6</td>
<td>13.3 ± 0.7</td>
<td>9.8 ± 0.4</td>
</tr>
</tbody>
</table>

Table 5.2 First order rate coefficients extracted from kinetic measurements at an ethene concentration of \(6.648 \times 10^{10}\) molecules cm\(^{-3}\).

Product branching ratios were extracted from kinetic measurements. The \textit{m/z} 106 channel is the dominant product channel for 2-dehydro-\textit{N}-pyridinium reactions, contributing 57% of total ion signal at reaction completion, while the \textit{m/z} 107 channel contributes 40%. The ratio of \textit{m/z} 106 to 107 signal decreases to 30%:66% for 3-dehydro-\textit{N}-pyridinium reactions, and 24%:71% for 4-dehydro-\textit{N}-pyridinium reactions, showing a decreasing preference towards the \textit{m/z} 106 channel and increasing preference towards the \textit{m/z} 107 channel. This branching ratio trend is possibly due to a decreasing amount of internal energy available to the addition adduct, from \textit{ortho} to \textit{meta} to \textit{para} reactions, which is needed to overcome H-atom loss barriers. Potential energy schemes presented in previous chapters show 2-dehydro-\textit{N}-pyridinium as the highest energy of the three isomers, followed by 3-dehydro-\textit{N}-pyridinium then 4-dehydro-\textit{N}-pyridinium. Calculations of 2-dehydro-\textit{N}-pyridinium reactions with propene and acetylene show the greatest enthalpy difference between reaction adduct and separated reactants, compared to the 3-, and 4-cases. Product branching ratios presented here suggest this trend in reaction enthalpy is also true for ethene reactions, where ethene addition to 2-dehydro-\textit{N}-pyridinium radicals results in the greatest amount of internal energy released on ethene addition, which is then
available to overcome H-atom loss barriers and results in an increased preference towards the H-loss channel (m/z 106).

5.3 Propyne Reactions

2-, 3- and 4-iodopyridinium cations (m/z 206) were isolated, held within the ion-trap, and subjected to photodissociation at 266 nm which resulted in appearance of ion signal at m/z 79, consistent with atomic iodine loss and formation of the corresponding dehydro-N-pyridinium radical cation. The radical cation population at m/z 79 was isolated, stored in the ion-trap, and allowed to react in the presence of a controlled concentration of propyne. Mass spectra were collected at select reaction times between 0.03 – 5000 ms. Representative mass spectra for the reaction of each dehydro-N-pyridinium isomer with propyne are given in Figure 5.4, where [C₃H₄] = 7.48 × 10¹⁰ molecule cm⁻³ and reaction time = 30 ms.

Product peaks at m/z 104, m/z 118 and m/z 119 are observed for each of the three dehydro-N-pyridinium reactions. These channels are assigned as the propyne reaction adduct and its isomers at m/z 119, the H-atom loss channel at m/z 118, and the methyl loss channel at m/z 104. Low intensity product peaks at m/z 93, assigned as the acetylene loss channel, and m/z 80, assigned as the H-atom abstraction channel, are also observed for each reaction. A non-exhaustive mechanistic scheme for the reaction of 2-dehydro-N-pyridinium with propyne is given in Figure 5.5. Reactions of propyne with 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium are expected to follow similar pathways.

2-, 3-, and 4-Ethynylpyridinium (P1 in Figure 5.5) is proposed as the most likely product in the m/z 104 channel and may be formed following β-scission and elimination of a methyl group from reaction adduct I₂. Reaction adduct I₁ may also form ethynylpyridinium by first isomerising to I₂, through intermediate I₃, before elimination of the methyl group.

Many H-atom loss pathways exist, making it impossible to assign specific products to the m/z 118 channel without a computational assessment of reaction barriers and product enthalpies. Some possible products include prop-1-yn-1-yl-pyridinium (P2), propadienyl-pyridinium (P3), cyclopentene-fused pyridinium (P4 and P7), 3H-indolizininium (P5₀), prop-2-yn-1-yl-pyridinium (P6), and several others not included in Figure 5.5.
The \( m/z \) 119 channel is assigned as \( \text{C}_8\text{H}_9\text{N}^+ \) open shell isomers that are likely collisionally cooled in the ion-trap and are unable to overcome neutral loss barriers. Possible structures for these isomers are I5 and I14, which are stabilised through delocalisation of the radical into the \( \pi \)-system of the pyridinium ring and alkyl chain.

2-, 3-, and 4-\( \text{N} \)-protonated-picolyl radicals (P8) are proposed as the most likely product in the low intensity \( m/z \) 93 channel for each reaction. At least seven steps are required to eliminate neutral acetylene from the propyne addition adduct and form the \( \text{N} \)-protonated-picolyl radical; this includes a 2,3-H atom shift over a double bond (I11 \( \rightarrow \) I13) which is likely to be unfavourable compared to ring-mediated H-atom transfer via I12. The most likely pathway to production of protonated picolyl radicals incorporates ring-mediated H-atom transfer, and follows the steps R0 \( \rightarrow \) I2 \( \rightarrow \) I8 \( \rightarrow \) I9 \( \rightarrow \) I10 \( \rightarrow \) I11 \( \rightarrow \) I12 \( \rightarrow \) I13 \( \rightarrow \) P8.
Figure 5.4 Mass spectra from the reaction of propyne with 2-dehydro-N-pyridinium (top), 3-dehydro-N-pyridinium (middle), and 4-dehydro-N-pyridinium (bottom). Reaction time is 30 ms and propyne concentration = $7.48 \times 10^{10}$ molecule cm$^{-3}$. Each mass spectrum is an average of 300 acquisitions.
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Figure 5.5 Proposed scheme for several possible product pathways of the reaction of 2-dehydro-N-pyridinium and propyne. This reaction scheme is not exhaustive and does not show cis/trans isomerisation. R, I, and P indicate reactants, intermediates and products respectively. Subscript o indicates ortho-substituted reactions. Similar pathways are expected for 3- and 4-dehydro-N-pyridinium + propyne reactions.

Kinetic traces were collected for the reaction of 2-, 3-, and 4-dehydro-N-pyridinium with propyne at a concentration of $7.48 \times 10^{10}$ molecules cm$^{-3}$ at reaction times between 0.03 – 5000 ms. A ±0.5 Th window surrounding the central $m/z$ peak was used to extract normalised, integrated intensity of each major $m/z$ channel as a function of reaction time. Representative kinetic traces are given in Figure 5.6. Second order rate coefficients, reaction efficiencies and product branching ratios extracted from kinetic traces are given in Table 5.1. Calculations of second-order rate coefficients and reaction efficiencies assume pseudo first-order behaviour.
Figure 5.6 Kinetic curves for m/z 79 (red), 104 (blue), 118 (green), and 119 (orange) from reactions of (a) 2-dehydro-N-pyridinium, (b) 3-dehydro-N-pyridinium and (c) 4-dehydro-N-pyridinium with propyne (7.476 × 10^{10} molecules cm^{-3}). A single-exponential function fit to the decay curve of m/z 79 is shown as a black line and fit residuals are plotted above each kinetic trace. Measurements at reaction times greater than 0.500 s are not displayed. Error bars are 2σ.
Ion signal at m/z 79 decays to baseline levels over time, indicating complete reaction of each dehydro-N-pyridinium radical cation. Reaction efficiencies calculated from the extracted decay rate of m/z 79 signal show increasing efficiencies of 52%, 60%, and 85% for 4-, 3-, and 2-dehydro-N-pyridinium reactions, respectively. First order rate coefficients for each major m/z channel, extracted from kinetic measurements at [C_3H_4] = 7.476 × 10^{10} molecules cm^{-3}, are given in Table 5.4.

<table>
<thead>
<tr>
<th>First-order rate coefficients (s^{-1})</th>
<th>2-Dehydro-N-pyridinium</th>
<th>3-Dehydro-N-pyridinium</th>
<th>4-Dehydro-N-pyridinium</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z 79</td>
<td>71 ± 3</td>
<td>51 ± 1</td>
<td>44 ± 1</td>
</tr>
<tr>
<td>m/z 118</td>
<td>78 ± 9</td>
<td>62 ± 18</td>
<td>52 ± 6</td>
</tr>
<tr>
<td>m/z 119</td>
<td>51 ± 26</td>
<td>49 ± 5</td>
<td>41 ± 2</td>
</tr>
</tbody>
</table>

Table 5.4 First-order rate coefficients extracted from kinetic measurements at a propyne concentration of 7.476 × 10^{10} molecules cm^{-3}.

Combined ion signal in the m/z 104, 118 and 119 channels contribute over 90% of the total ion signal for all three reactions at completion; however, the ratio of ion signal of these three channels varies significantly across the three dehydro-N-pyridinium isomer reactions. The H-atom loss channel at m/z 118 dominates the reaction of 2-dehydro-N-
pyridinium + propyne, contributing 89% of the total ion signal, while the m/z 104 and 119 channels are relatively non-competitive. The m/z 118 and 119 channels contribute 48% and 32% of total ion signal, respectively, for 3-dehydro-N-pyridinium reactions, while the m/z 104 channel is non-competitive. All three channels contribute an approximately equal portion of ~32% of total ion signal for 4-dehydro-N-pyridinium reactions.

The exclusive dominance of the m/z 118 channel in 2-dehydro-N-pyridinium + propyne, not seen in reactions of the 3- and 4-dehydro-N-pyridinium isomers, suggests involvement of the adjacent N-position, most likely in ring-mediated H-atom transfer pathways. Energetic barriers for H-atom transfer to and from the N-position are typically lower than that for the equivalent C-position, which is seen in calculations of H-atom transfer pathway barriers for propene reactions presented in Chapter 3. Ring-mediated H-atom transfer via the N-position, relative to a C-position, would increase reaction flux through intermediates I4, I8 and I12, increasing reaction flux directed towards the H-loss products P4, P5, P6 and P7.

The 3-dehydro-N-pyridinium reaction does not have access to the N-mediated H-atom transfer pathways available in the ortho- case. As such, reaction flux passing through intermediates I4 and I8 is limited relative to the 2-dehydro-N-pyridinium reaction and a reduction in ion-signal contribution by the m/z 118 channel is observed. A corresponding rise in ion-signal contribution by the m/z 119 channel suggests available H-loss pathways are partially energetically restricted, which allows a significant population of m/z 119 ions to stabilise by collisional cooling over time. The methyl loss channel remains non-competitive for 3-dehydro-N-pyridinium + propyne reactions, indicating the I2 → P1 transition state energy is high relative to available H-atom loss and isomerisation pathways.

Equal ion-signal contribution from the m/z 104, 118 and 119 channels is observed for 4-dehydro-N-pyridinium + propyne reactions. Like 3-dehydro-N-pyridinium reactions, N-mediated H-atom transfer pathways are not available in the para- case which prevents dominance of the H-atom loss channel at m/z 118. A significant population of m/z 119 ions is stabilised through collisional deactivation, similar to 3-dehydro-N-pyridinium reactions. Unlike 2-, and 3-dehydro-N-pyridinium reactions, the methyl loss pathway is competitive, indicating a lowering of the I2 → P1 transition state energy. This may occur
due to transition state polarisation effects caused by partial delocalisation of positive charge from the N-position to the para and ortho ring positions through a carbene-like resonance structure. A computational assessment of intermediate, product and transition state energies is needed to support these predictions.

5.4 Conclusions

Product mass spectra and reaction kinetics for the reactions of ethene and propyne with 2-, 3-, and 4-dehydro-N-pyridinium were measured. Vinyl-pyridinium, at \( m/z \) 106, and collisionally stabilised open-shell \( \text{C}_7\text{H}_9\text{N}^+ \) isomers, at \( m/z \) 107, are identified as the two major product channels for each ethene reaction. Product branching ratios between these two channels slightly preference the \( m/z \) 106 channel for the 2-dehydro-N-pyridinium reaction, and change systematically to preference the \( m/z \) 107 channel for the 4-dehydro-N-pyridinium reaction. Ethene reaction efficiencies, calculated from measured first-order rate coefficients, are 39%, 19% and 14% for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively.

Three major product channels were identified for each propyne reaction: methyl loss at \( m/z \) 104, H-atom loss at \( m/z \) 118, and collisional stabilisation of open-shell \( \text{C}_8\text{H}_9\text{N}^+ \) isomers at \( m/z \) 119. Product branching ratios of these three channels vary greatly across each dehydro-N-pyridinium isomer which is attributed to involvement of N-mediated H-atom transfer pathways in ortho substituted reactions, or lack thereof in meta and para substituted reactions. Transition state polarisation effects may also contribute to observed product branching ratios. Propyne reaction efficiencies, assuming pseudo-first order behaviour, are 85%, 60%, and 52% for 2-, 3-, and 4-dehydro-N-pyridinium reactions, respectively.
6 Summary and Conclusion

Ion-molecule reactions of 2-dehydro-\(N\)-pyridinium, 3-dehydro-\(N\)-pyridinium and 4-dehydro-\(N\)-pyridinium radical cations with four small, unsaturated hydrocarbons have been studied at room temperature and 2.5 mTorr. Product branching ratios and reaction kinetics were measured, and possible reaction pathways have been identified. The key findings of each studied reaction are consolidated and summarised in this chapter with a focus on identifying trends in reactivity displayed across all reactions.

6.1 Reaction Efficiency

Reaction efficiencies, summarised in Table 6.1, follow a consistent trend across reactions of the three dehydro-\(N\)-pyridinium isomers with each neutral reactant: 2-dehydro-\(N\)-pyridinium is consistently the most efficient of the three isomers, 4-dehydro-\(N\)-pyridinium is consistently the least efficient. This result agrees with the expected rise in reactivity of an increasingly electronegative radical site as its distance from the positively charged N-position is reduced.\(^{57-59}\) A relatively sharp increase in reaction efficiency is observed from reactions of 3-dehydro-\(N\)-pyridinium to 2-dehydro-\(N\)-pyridinium, compared to 4-dehydro-\(N\)-pyridinium to 3-dehydro-\(N\)-pyridinium, and is rationalised through partial delocalisation of positive charge to the \(para\) and \(ortho\)-ring positions. These two effects have been described in greater detail in Chapter 3.3.2 and 4.3.2.

Across the four neutral reactants, propyne reactions have the highest reaction efficiency, followed by propene, ethene, then acetylene. This ordering of reaction efficiency is maintained for each of the three dehydro-\(N\)-pyridinium isomers and is moderately correlated with neutral reactant dipole moment strength, despite a small sample size of only four neutral reactants. Propyne has a dipole moment of 0.784 D, the strongest dipole moment of all four reactants, while propene has a dipole moment of 0.366 D. Both ethene and acetylene have no net dipole. Propyne and propene reaction efficiencies are comparable, lying within 10 – 15% efficiency of each other for each dehydro-\(N\)-pyridinium isomer, and are much greater than ethene and acetylene efficiencies, which are also clustered within 10% of each other but 30% lower than that of propyne and propene. This creates two groupings; acetylene and ethene with no net dipole moment and lower reaction efficiency, and propene and propyne which have significant dipole
moments and higher reaction efficiency. Of course, any effects caused solely by molecular dipole moments fail to explain the observed difference of reaction efficiency between acetylene and ethene reactions, and the observed trend may be coincidental. There must be additional or alternate neutral reactant properties that influence reaction efficiency; for example, the quadrupole moment of ethene and acetylene. Alkyl chain length shows a similar correlation to reaction efficiency and should be investigated in future work. Degree of saturation has no clear correlation with efficiency for this set of reactions.

<table>
<thead>
<tr>
<th>Reaction Efficiencies (%)</th>
<th>2-dehydro-(N)-pyridinium</th>
<th>3-dehydro-(N)-pyridinium</th>
<th>4-dehydro-(N)-pyridinium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>32.4 ± 2.5</td>
<td>14.2 ± 0.4</td>
<td>10.0 ± 0.1</td>
</tr>
<tr>
<td>Ethene</td>
<td>39.3 ± 6.9</td>
<td>19.0 ± 2.3</td>
<td>14.3 ± 2.1</td>
</tr>
<tr>
<td>Propene</td>
<td>70.0 ± 1.0</td>
<td>47.2 ± 0.4</td>
<td>40.9 ± 0.8</td>
</tr>
<tr>
<td>Propyne</td>
<td>84.7 ± 4.0</td>
<td>59.9 ± 1.5</td>
<td>52.2 ± 0.7</td>
</tr>
</tbody>
</table>

Table 6.1 Reaction efficiencies of 2-, 3-, and 4-dehydro-\(N\)-pyridinium with each neutral reactant.

Previous experimental and computational studies suggest that reaction rate of radical ion-molecule reactions, similar to those studied here, are significantly impacted by submerged addition barriers in the entrance channel.\textsuperscript{111-113} This is supported by reaction efficiencies and quantum chemical calculations presented in this thesis. Figure 6.1 shows a negative, linear relationship between calculated submerged barrier height, relative to the entrance channel of each reaction, and measured reaction efficiency. Three data points are plotted for both acetylene and propene, corresponding to each of the three dehydro-\(N\)-pyridinium isomer reactions with the respective neutral. Submerged barrier enthalpies were not calculated for ethene and propyne reactions and should be considered as a target of future work to expand and validate this apparent trend. The observed correlation can be explained as an effect of the entropic restriction presented by the submerged barrier. The number of available quantum states able to pass reaction flux to the covalently bound reaction adduct is dictated, at least partially, by the submerged barrier height. Lowering the submerged barrier opens more energetically accessible vibrational states at the submerged barrier transition state, which is the point of greatest entropic restriction, allowing a greater portion of reaction flux to proceed towards reaction products. The converse is also true. Raising the submerged barrier height decreases the number of
energetically available vibrational states and increases reaction flux in the re-dissociation channel. The energy of stabilisation when forming a pre-reaction complex between neutral and radical cation may be important in predicting reaction efficiency, as it determines the base energy from which any submerged addition barrier rises from. Neutrals likely to experience stronger attractive forces with their radical ion counterpart, such those with strong dipole moments, may be more likely to undergo highly efficient reactions. This assertion agrees with the observed correlation between reaction efficiency and neutral dipole moment, described above.

Figure 6.1 Linear trend between submerged barrier height and measured reaction efficiency. Error bars (obscured by data markers) are $2\sigma$.

### 6.2 Neutral Loss Channels

Product branching ratios were extracted from kinetic traces of each $m/z$ channel for each reaction. The branching ratio of each $m/z$ channel was taken as the asymptotic limit of the exponential function fit to that channel’s kinetic trace. Stated errors, given at $2\sigma$, are statistical errors extracted from the exponential fit. Table 6.2 reports product branching ratios of each neutral loss channel for each reaction, in which several common neutral loss channels are identified.

Stabilisation of addition adduct isomers (i.e. no neutral loss fragment) was observed for all reactions in varying degrees. It is a major product channel for all acetylene and ethene reactions, and for 3-dehydro-$N$-pyridinium and 4-dehydro-$N$-pyridinium + propyne
H-atom loss was seen for all reactions studied. It is a major neutral loss channel for all ethene and propyne reactions, and for 2-dehydro-N-pyridinium + acetylene reactions. It was observed as a minor channel for all propene reactions, and for 3-dehydro-N-pyridinium and 4-dehydro-N-pyridinium + acetylene reactions. In all cases, H-atom loss occurs through a β-scission mechanism, and is available as a single-step pathway for each reaction following addition of the neutral, or as a multi-step pathway that can proceed through a range of reaction intermediates. H-atom loss barriers, where calculated, are typically higher in energy than isomerisation pathways, and are less energetically favourable than loss of larger neutral fragments such as CH₃ or C₂H₄. The relatively large number of H-atom loss pathways, especially for propene and propyne reactions, and the
energetic preference towards adduct isomerisation, suggests the H-atom loss channel will consist of a range of reaction products. Identification of H-atom loss products is difficult for that reason. Computational kinetic modelling may be required to provide an accurate estimation of specific product branching ratios in the H-atom loss channel.

Larger neutral loss fragments were observed for propene and propyne reactions, compared to ethene and acetylene, afforded by the addition of the larger alkyl groups. These include methyl loss, which is the major channel for all propene reactions, $\text{C}_2\text{H}_4$ loss, seen as a minor product channel for propene reactions, and $\text{C}_2\text{H}_2$ loss, observed as a trace product channel for propyne reactions. Of all neutral reactants, propene reactions were unique in their preference towards these higher molecular weight neutral-loss pathways, which is attributed to the three-carbon chain length of propene and the double bond reaction site, rather than a triple bond. Radical attack of the double bond of propene creates an alkyl substituent, and isomers thereof, that contain no double bonds and are rotationally hindered only by delocalisation of the lone electron into the $\pi$-system of the pyridinium ring. The flexibility of the alkyl substituent supports more efficient ring-mediated H-atom transfer which can place the radical in position for $\beta$-scission of a C-C bond. A direct H-atom shift along the chain is also possible following propene addition, but energetically less preferable than ring-mediated H-atom transfer. In contrast, attack over the triple bond of propyne creates a more rigid alkyl substituent which is rotationally hindered by a double bond, together with delocalisation of the radical into the $\pi$-system of the molecule. Ring mediated H-atom transfer along the alkyl chain is less efficient due to greater rotational hindrance, and a direct H-atom shift to the radical site over the double bond is expected to have higher transition state barriers compared to the single bond case of propene reactions. The presence of the double bond in the case of propyne reaction adducts also introduces a need for multiple-step isomerisation to access intermediates capable of $\beta$-scission and elimination of $\text{C}_2\text{H}_2$.

The H-abstraction channel was not competitive for any reaction studied. Larger neutral reactants with a greater proportion of saturated carbon atoms are expected to show greater preference towards H-abstraction pathways than what is seen in this work.\textsuperscript{59}

No unique $m/z$ channel was identified for reactions of each neutral with the three dehydro-$N$-pyridinium isomers. However, 2-dehydro-$N$-pyridinium reactions with acetylene, ethene and propene displayed the greatest distribution of ion-signal across all product
channels. This may be due a relative lowering of isomerisation barriers through involvement of the N-ring position in ring-mediated H-atom transfer, as discussed above. Conversely, ion-signal in the 2-dehydro-N-pyridinium + propyne reaction was directed into the least number of product channels, showing a near exclusive preference towards H-atom loss. Calculations of propyne reaction intermediate and transition state enthalpies are needed to identify why this is the case.

### 6.3 Reaction Products

Table 6.3 summarises the major, minor and trace products that have been assigned for reactions of the four neutral reactants with each dehydro-N-pyridinium isomer. Several assigned reaction products, or groupings of similar reaction products, are common across multiple neutral reactants. Barrierless or de facto barrierless pathways have been identified for all assigned propene and acetylene reaction products, suggesting formation of these products may be viable in cold, extraterrestrial environments. Barrierless or de facto barrierless pathways may exist for ethene and propyne reactions and should be a target for future computational studies.
Table 6.3 Major, minor, and trace products identified for each reaction studied. Ortho-, meta-, or para- substitution results from reactions of 2-, 3-, and 4-dehydro-N-pyridinium, respectively.

<table>
<thead>
<tr>
<th>Reaction Products</th>
<th>Bicyclic Products</th>
<th>Ethynylpyridinium</th>
<th>Vinyl-Pyridinium</th>
<th>Other ally-substituted pyridinium</th>
<th>Protonated-pirol radical</th>
<th>Other open-shell molecules</th>
<th>Pyridinium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-dehydro-N-pyridinium</td>
<td>**</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-dehydro-N-pyridinium</td>
<td>**</td>
<td>✓</td>
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<td></td>
</tr>
<tr>
<td>4-dehydro-N-pyridinium</td>
<td>**</td>
<td>✓</td>
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<td></td>
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<tr>
<td>Ethene</td>
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<tr>
<td>2-dehydro-N-pyridinium</td>
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<td></td>
<td>✓</td>
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<td></td>
<td></td>
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<tr>
<td>3-dehydro-N-pyridinium</td>
<td>✓</td>
<td></td>
<td>✓</td>
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<td></td>
<td></td>
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<tr>
<td>4-dehydro-N-pyridinium</td>
<td>✓</td>
<td></td>
<td>✓</td>
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<tr>
<td>Propene</td>
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<tr>
<td>2-dehydro-N-pyridinium</td>
<td>✓</td>
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<tr>
<td>3-dehydro-N-pyridinium</td>
<td>✓</td>
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<tr>
<td>4-dehydro-N-pyridinium</td>
<td>✓</td>
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<tr>
<td>Propyne</td>
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<td></td>
</tr>
<tr>
<td>2-dehydro-N-pyridinium</td>
<td>**</td>
<td></td>
<td>✓</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3-dehydro-N-pyridinium</td>
<td>**</td>
<td></td>
<td>✓</td>
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</tr>
<tr>
<td>4-dehydro-N-pyridinium</td>
<td>**</td>
<td></td>
<td>✓</td>
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</tr>
</tbody>
</table>

Vinyl-pyridinium is a major product of reactions involving the two, singularly-saturated neutral reactants, propene and ethene. It was not detected as a product of propyne or acetylene reactions. Vinyl-pyridinium will likely appear as a major product of addition reactions between other terminal alkenes and dehydro-N-pyridinium radical cations, due to an immediately accessible β-scission pathway to vinyl-pyridinium from the secondary-carbon addition adduct, shown in Figure 6.2.

![Figure 6.2](image-url)  
Figure 6.2 Single-step pathway to vinyl-pyridinium following nucleophilic addition of a terminal alkene at the secondary carbon position.
Similarly, addition at the primary carbon of a terminal alkene (excluding ethene) will likely result in propenyl- or allyl-substituted pyridinium due to two immediately accessible β-scission pathways, shown in Figure 6.3. Preference towards the allyl pathway is expected for reactions of longer alkyl chains, where $R = \text{methyl, ethyl, etc.}$, due to greater radical stabilisation by the neutral loss fragment.

![Figure 6.3 Single-step pathways to allyl- and propenyl-substituted pyridinium.](image)

Ethynyl-pyridinium is assigned as a product in reactions of acetylene and propyne. It is produced in a single-step β-scission mechanism and is a likely product of other terminal alkyn e reactions with the dehydro-$N$-pyridinium isomers. Important to note is that H-abstraction reactions will likely dominate over addition reactions as the unsaturated tail of any terminal alkyn e or alkene target reactant becomes larger. The observed reaction channels here may be useful for elucidating reaction pathways for future experiments involving larger neutrals with multiple sites of unsaturation, such as vinyl-acetylene.

Ring-mediated H-atom transfer was found to be a significant isomerisation pathway in the protonated-picolyl radical reaction product channel for propene reactions, and the same is expected for reactions of propyne. Transition state enthalpy calculations show ring-mediated H-transfer is energetically preferable compared to a direct H-atom shift; however, in propene reactions, transient ring formation at ring-mediated transition states present an entropic restriction which was found to limit reaction flux through these pathways, despite their enthalpic preference over competing neutral loss channels. Ultimately, ring-mediated H-atom transfer must be considered as a likely isomerisation pathway in ortho substituted reactions due to a significant energetic preference for H-atom transfer to and from the N-ring position, compared to a C-ring position. The N-ring position is not accessible in meta and para substituted reactions so ring-mediated H-atom transfer pathways are not expected to be as competitive for these reactions.
Bi-cyclic reaction products have been tentatively assigned for the reactions of acetylene and propyne. These products occur in low abundances. In the case of acetylene, addition of a second acetylene molecule to a reactive intermediate is required. Barrierless or de facto barrierless acetylene reaction pathways have been identified for the formation of quinozilium, quinolinium, isoquinolinium, and 5 unique methylenecyclopentene-pyridinium fused ring species. Several cyclopentene-pyridinium fused ring species are predicted for propyne reactions, but quantum chemical calculations have not been conducted to investigate their likelihood of forming under experimental conditions. The barrierless pathways identified in this thesis are interesting in the context of cold, extraterrestrial environments. The lack of any reaction barrier above the entrance channel suggests synthesis of molecules such as quinoline, isoquinoline, quinozilium, and other species identified throughout this thesis, may be viable in the interstellar medium, given the presence of pyridinium. Unfortunately, neither pyridinium nor pyridine, as a pyridinium precursor, have been identified in interstellar or circumstellar space to date. Modern astronomical observatories, such as the Atacama Large Millimetre Array (ALMA), and future facilities, such as the Square Kilometre Array (SKA), are raising the prospects of detection of N-heterocycles in the near future, especially within dense interstellar clouds and protoplanetary disks.

6.4 Unanswered Questions

Several unanswered questions remain in this study, towards which future work should be directed. Namely, there is some evidence for non-exponential kinetic behaviour visible in the systematic trend of fit residuals for all kinetic measurements. The origin for this has not been determined. There is also disparity between extracted first-order rate coefficients of reactant and product channels for some reactions, which is possibly a symptom of the same, unidentified cause. Two potential contributing factors were investigated:

- Isomerisation of dehydro-N-pyridinium radical cations is possible cause of non-exponential kinetic behaviour and disparity between first-order rate coefficients. The 4-dehydro-N-pyridinium isomer was found to be the most energetically preferable of the three dehydro-N-pyridinium isomers, followed by 3-dehydro-N-pyridinium then 2-dehydro-N-pyridinium. Isomerisation of the 2-, and 3-dehydro-N-pyridinium isomers along this energy gradient, towards 4-dehydro-N-pyridinium, could account
for the observation of low rate coefficients for the \textit{m/z} 79 channel, relative to product channels of each reaction. Differing product branching ratios of the three dehydro-\textit{N}-pyridinium isomers may be the cause of disparity between rate coefficients of the different product channels. Non-exponential signal decay kinetics can also be explained by a mixed population of \textit{m/z} 79 ions, caused by isomerisation. However, some disparity between reaction rates, and evidence for non-exponential kinetics, is seen in 4-dehydro-\textit{N}-pyridinium reactions, which is not explained by radical isomerisation; 4-dehydro-\textit{N}-pyridinium is the lowest energy isomer and unlikely to isomerise to the higher energy 3-, or 2-dehydro-\textit{N}-pyridinium isomers. Energetically accessible isomerisation pathways have not been identified. Low-energy reactant-mediated isomerisation pathways are currently being investigated.

- Collisional cooling of ‘hot’ reactants and reaction adduct isomers was considered as a possible source of disparity between first-order rate coefficients. Collisional cooling would result in quenching of the re-dissociation and neutral loss pathways for all reactions, and is expected to result in higher rate coefficients for the neutral-loss and reactant channels, relative to the reaction adduct stabilisation channel. This is only partially true for measured first-order rate coefficients. Neutral-loss pathways typically have the highest rate coefficient, which agrees with the collisional cooling assertion, but the reactant channel (\textit{m/z} 79) has a lower rate coefficient than all product channels in acetylene reactions, which does not agree. Plots of pseudo-first order rate coefficient of product channels against reactant concentration are described well by a linear fit which indicates no deviation from pseudo-first order behaviour and suggests collisional cooling does not occur on the same time scale as measured reactions.

Ultimately, no single factor considered can fully explain the observed disparity between some first-order rate coefficients. There are likely multiple factors acting simultaneously, or alternate causes that have not been considered here.
6.5 Future work and suggestions

In addition to answering the above questions, there are several potential future studies that would benefit the continued development of a more comprehensive understanding of dehydro-N-pyridinium reactions towards unsaturated hydrocarbons:

- The observed trend between reaction efficiency and submerged barrier height should be verified by completing a computational study of the ethene and propyne reaction systems. This trend may be useful for more accurate estimation of second-order reaction rate coefficients for reactions with no experimental data.
- Kinetic modelling studies would be useful for estimating product branching ratios for neutral loss channels in which many possible isomers exist, such as the H-atom loss channel. Common products may exist for different neutral reactants.
- Unequivocal identification of bi-cyclic reaction products, possibly using action spectroscopy of reaction products, would support the calculated barrierless and *de facto* barrierless pathways and confirm these reactions as possible synthesis pathways for complex organic synthesis, and as possible molecular-weight growth mechanisms in cold environments.
- Many molecules identified in the ISM contain multiple sites of unsaturation. Therefore, neutral reactants such as vinyl-acetylene, diacetylene, and larger polyynes may be interesting targets for future studies. Bi-cyclic ring formation is a possible product pathway due to the high degree of unsaturation and longer carbon chain length of these neutral reactants.

6.6 Conclusion

This study has explored the reactivity of the three dehydro-N-pyridinium isomers towards a set of small, unsaturated hydrocarbons: propene, acetylene, ethene and propyne. These reactions were chosen due to their potential significance to molecular-weight growth processes in extraterrestrial environments, and as possible synthetic routes to complex organics in space. No previous study has investigated the reactions of the three dehydro-N-pyridinium isomers towards unsaturated hydrocarbons in this context.

Mass spectrometric techniques were used to synthesis dehydro-N-pyridinium radicals *in situ*, acquire product mass spectra, and measure reaction kinetics and product branching
ratios. These data reveal several trends in dehydro-\(N\)-pyridinium reactivity towards the neutral species studied in this thesis: Measured reaction efficiencies are correlated with submerged barrier height. This correlation may be useful in predicting reaction efficiencies when experimental data is unavailable once the trend is verified with additional data. Common reaction products were also identified, including vinyl-pyridinium in alkene reactions, and ethynyl-pyridinium in alkyne reactions. Computational studies revealed propene and acetylene reactions are barrierless or de facto barrierless, suggesting these reactions may be viable in cold, extraterrestrial environments. Assigned acetylene and propene reaction products, including quinoline and isoquinoline, could be synthesised in the ISM in the presence of pyridinium and the respective neutral reactant. This could be occurring readily, undetected, within dense interstellar clouds and protoplanetary disks.
7 References


