University of Wollongong

Research Online

Faculty of Science, Medicine and Health -
Papers: part A

Faculty of Science, Medicine and Health

1-1-2017

Highly efficient gas-phase reactivity of protonated pyridine radicals with propene

Cameron Bright

University of Wollongong, ccb521@uowmail.edu.au

Matthew Prendergast

University of Wollongong, mbp163@uowmail.edu.au

Patrick Kelly

University of Wollongong

James Bezzina

University of Wollongong, jpb661@uowmail.edu.au

Stephen J. Blanksby

Queensland University of Technology, stephen.blanksby@qut.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/smhpapers>

Part of the [Medicine and Health Sciences Commons](#), and the [Social and Behavioral Sciences Commons](#)

Recommended Citation

Bright, Cameron; Prendergast, Matthew; Kelly, Patrick; Bezzina, James; Blanksby, Stephen J.; da Silva, Gabriel; and Trevitt, Adam J., "Highly efficient gas-phase reactivity of protonated pyridine radicals with propene" (2017). *Faculty of Science, Medicine and Health - Papers: part A*. 5144.
<https://ro.uow.edu.au/smhpapers/5144>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Highly efficient gas-phase reactivity of protonated pyridine radicals with propene

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-picoyl 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-picoyl 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.

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

Publication Details

Bright, C. C., Prendergast, M. B., Kelly, P. D., Bezzina, J. P., Blanksby, S. J., da Silva, G. & Trevitt, A. J. (2017). Highly efficient gas-phase reactivity of protonated pyridine radicals with propene. *Physical Chemistry Chemical Physics*, 19 (46), 31072-31084.

Authors

Cameron Bright, Matthew Prendergast, Patrick Kelly, James Bezzina, Stephen J. Blanksby, Gabriel da Silva, and Adam J. Trevitt

Highly Efficient Gas-Phase Reactivity of Protonated Pyridine Radicals with Propene

Cameron C. Bright,¹

Matthew B. Prendergast,¹

Patrick D. Kelly,¹

James P. Bezzina,¹

Stephen J. Blanksby,²

Gabriel da Silva,³

Adam J. Trevitt^{1*}

Authors' Affiliations:

1. School of Chemistry, University of Wollongong, Wollongong NSW 2522, Australia.
2. Central Analytical Research Facility, Institute for Future Environments, Queensland University of Technology, Brisbane QLD 4001, Australia.
3. Department of Chemical Engineering, The University of Melbourne, Parkville VIC 3010, Australia.

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.

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 space¹⁻⁴ and is implicated in pre-biotic chemistry and astrobiology.⁵⁻⁶ 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.⁷⁻⁸ New laboratory based studies are thus required to provide reaction rates and product pathways to ensure the development of increasingly accurate predictive models.⁹⁻¹² 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.¹³ One potential source of molecular ionisation in space is proton transfer from H_3^+ , the second most abundant interstellar molecule.¹⁴ 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.¹⁵⁻¹⁶ 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 σ -type radical that is located in the plane of the molecule and is unable to delocalise into the π 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%.¹⁷⁻¹⁸ Photodissociation of benzene at 193 and 157 nm also results in atomic hydrogen loss.¹⁹ Therefore, it is expected that pyridinium cations may undergo C-H bond homolysis via VUV photolysis to form σ -type radical cations. Positively charged ions

containing a spatially separated σ -radical are by definition *distonic* radical cations with steric and electronic separation of the charge and radical centres.²⁰ 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.²¹

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 identified²² and stratospheric propene has been positively identified.²³⁻²⁴ Laboratory investigations of Titan's atmosphere have also shown the formation of pyridinium cations from the reaction of pyridine with hydrocarbon cations.²⁵ 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.

2. Experimental

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 ²⁶ 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 μ M 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 $5 \mu\text{L min}^{-1}$, operating in positive ion mode. Radical precursor ions ($[\text{M}+\text{I}]^+$ 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 (4th harmonic, 266 nm). The laser Q-switch is then triggered internally approximately 140 μs later for optimal power density (*ca.* 30 mJ cm^{-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.

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 (Φ) were calculated from second-order rate coefficients as a percentage of Langevin model²⁷ collision rate for ion-molecule collision pairs. Ultimately, an upper limit of $\pm 50\%$ uncertainty in the second-order rate coefficient results from a high uncertainty in ion-trap gas pressure estimated at 2.5 mTorr $\pm 50\%$.

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)²⁸ level using Gaussian 09.²⁹ 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 programs³⁰⁻³² 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. Results

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^{26, 33-36}.

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 photoisociation 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 π -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 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.³⁷⁻³⁸

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 $[propene] = 2.62 \times 10^{10}$ molecule cm^{-3} for the three dehydro-*N*-pyridinium isomers are shown in Figure 1. The dominant product peak in all cases is the $[M + 42 - 15]^+$ ion at m/z 106 rationalised by C_3H_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_3H_6 adduct), m/z 120 (C_3H_6 addition with H loss), m/z 93 (C_3H_6 addition then C_2H_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 1 b and c), m/z 95 (Figure 1a) and m/z 82 (Figure 1a) 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 ($\sim 6.4 \times 10^9$ 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 + O_2 reactions with relative signal intensities that align well with those of the 4- and 3-dehydro-*N*-pyridinium + C_3H_6 reaction spectra. In contrast, 2-dehydro-*N*-pyridinium + 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 + C_3H_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 peroxy- (addition of O_2) and oxy- (addition of O_2 followed by loss of atomic oxygen) radicals³⁹⁻⁴⁰ and also indicate a potential HCO loss channel³⁹. 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 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

*et al.*⁴¹ and studied by Kislov *et al.*⁴² 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, I1_p and I2_p in Figure 2, that are connected by intermediate I3_p. The primary product at m/z 106 results from β -elimination of CH₃ from either adduct I2_p or intermediate I4_p, following a hydrogen shift from adduct I1_p. 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 1. Mass spectra from the reaction of propene (black) and O₂ (blue) with dehydro-*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 = 2.62×10^{10} molecule cm⁻³. Each mass spectrum is an average of 1000 acquisitions. O₂ reaction spectra have been scaled to fit under C₃H₆ reaction mass spectra.

Figure 2. Proposed reaction scheme for 4-dehydro-*N*-pyridinium + propene. Reactants ($R0_p$) lead primarily to the production of a C_7H_8N isomer at m/z 106 ($P3_p$) assigned as 4-vinylpyridine. H-abstraction (m/z 80) pathway is not shown. R, I, and P indicate reactants, intermediates and products respectively. Subscript p indicates *para* substitution.

3.2 Dehydro-*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 m/z 79 signal intensity and the growth of propene reaction product signals. Representative kinetic curves for m/z 79, 80, 93 and 106 for each of the three dehydropyridinium isomers are shown in Figure 3.

Figure 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 (1.28×10^{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 2σ . 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). 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 typically within $\pm 1.5\%$ of full scale at the point of largest deviation from measured data, within measurement error of ($\pm 5-10\%$, 2σ). 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 2σ 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.

$$y = A_0 \exp(-k_{(1st)}t) + C \quad \text{Eq. 1}$$

$$y = A_1 \exp(-k_{(1st)_1}t) + A_2 \exp(-k_{(1st)_2}t) + C \quad \text{Eq. 2}$$

Potential energy schemes (Figure 5, 6 and 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 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 1). Error bars represent 2σ 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 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.²⁷ 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.⁴³⁻⁴⁴ 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 gas⁴⁵ and liquid phase⁴⁶⁻⁴⁷ 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.

	<i>m/z</i>	Neutral Loss Fragment	Assigned Product	Relative signal intensity at <i>t</i> = 5 s (% of total ion signal)
2-Dehydro-<i>N</i>-pyridinium + Propene				
$k_{2nd} =$ $(7.83 \pm 0.10) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $\Phi = 70.02 \pm 0.96 \%$	80	C ₃ H ₅		4.9 ± 0.3
	93	C ₂ H ₄	P4 _o	23.2 ± 0.7
	106	CH ₃	P3 _o	57.8 ± 0.8
	120	H	P1 _o P2 _o P5 _o	5.9 ± 0.3
	121			2.3 ± 0.3
3-Dehydro-<i>N</i>-pyridinium + Propene				
$k_{2nd} =$ $(5.28 \pm 0.05) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $\Phi = 47.19 \pm 0.44\%$	80	C ₃ H ₅		2.2 ± 0.1
	93	C ₂ H ₄	P4 _m	9.0 ± 0.2
	106	CH ₃	P3 _m	73.7 ± 0.6
	120	H	P1 _m P2 _m P5 _m	4.3 ± 0.1
	121			6.6 ± 0.2
4-Dehydro-<i>N</i>-pyridinium + Propene				
$k_{2nd} =$ $(4.57 \pm 0.09) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $\Phi = 40.87 \pm 0.77\%$	80	C ₃ H ₅		1.6 ± 0.1
	93	C ₂ H ₄	P4 _p	1.6 ± 0.1
	106	CH ₃	P3 _p	86.6 ± 0.7
	120	H	P1 _p P2 _p P5 _p	1.9 ± 0.1
	121			3.5 ± 0.2

Table 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 $k_{\text{exp}}/k_{\text{langvin}} \times 100\%$. Statistical uncertainty for measured reaction efficiencies are given (2σ). Absolute accuracy is estimated at $\pm 50\%$.

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 ($I1 \rightarrow I4$) and subsequent β -scission with no reverse

barrier ($I4 \rightarrow P3$) 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 β -scission of adduct I2 ($I2 \rightarrow P3$) 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 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, R₀. Enthalpies are reported in kcal mol⁻¹.

Figure 6. Potential energy scheme for the 3-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, R0_m . Enthalpies are reported in kcal mol^{-1} .

Figure 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, R0_p. 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 β -scission (I6→P4) to yield the *N*-protonated-picoly radical and C₂H₄. 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 I5_p. H-atom transfer from the terminal propyl carbon to the ring-radical (I5→I6), followed by β -scission (I6→P4) results in formation of the *N*-protonated-picoly radical. For the 2-dehydro-*N*-pyridinium reaction, a transition state for I5_{o2} → I6_o was located with pure electronic energy 0.2 kcal mol⁻¹ higher than that of intermediate I5_{o2}. 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 (I5_{o2} → I6_o) was verified by IRC calculations and may provide a case in point for the need to improve the accuracy of ZPE calculations.⁴⁸⁻⁴⁹ 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 (I1_o→I5_{o2}→I6_o→P4_o) is energetically favourable and might be expected to result in more m/z 93 signal than is observed experimentally (Figure 3). Therefore, quantum state counting was performed on several competing transition states to quantify entropic factors contributing to the observed product branching ratios. Figure 8 summarises results for the 2-dehydro-*N*-pyridinium + propene reaction, in which transition states leading from I1_o to I4_o, I5_{o1}, I5_{o2} and I6_o 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 I1_o is given as a percentage of the total number of energetically

accessible states for the four competing TSs, given $R0_0$ – TS of vibrational energy available to the molecule. An Eckart tunnelling correction⁵⁰⁻⁵¹ is also applied. This calculated sum of states is proportional to reaction flux moving from $I1_0$, 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 2.

Figure 8. Competing transition states in the 2-dehydro-*N*-pyridinium + propene reaction m/z 106 and m/z 93 channel originating from intermediate $I1_0$. 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 $I1_0$ 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.

	Transition State	Sum of States (non-corrected)	Sum of States (tunnelling corrected)	Degeneracy	Proportion of States (%)
2-dehydro-<i>N</i>-pyridinium	$I1_o \rightarrow I4_o$ (m/z 106)	8.93×10^{18}	1.26×10^{19}	2	77.0
	$I1_o \rightarrow I5_{o1}$ (m/z 93)	1.32×10^{17}	2.08×10^{17}	1	0.6
	$I1_o \rightarrow I5_{o2}$	5.97×10^{18}	6.12×10^{18}	1	18.6
	$I1_o \rightarrow I6_o$	2.84×10^{14}	4.06×10^{14}	3	3.7
3-dehydro-<i>N</i>-pyridinium	$I1_m \rightarrow I4_m$ (m/z 106)	7.46×10^{16}	1.24×10^{17}	2	57.5
	$I1_m \rightarrow I5_{m1}$ (m/z 93)	6.66×10^{16}	1.09×10^{17}	1	25.2
	$I1_m \rightarrow I5_{m2}$	5.28×10^{16}	7.45×10^{16}	1	17.3
	$I1_m \rightarrow I6_m$	1.12×10^{12}	4.59×10^{12}	3	0.0
4-dehydro-<i>N</i>-pyridinium	$I1_p \rightarrow I4_p$ (m/z 106)	8.95×10^{18}	1.17×10^{19}	2	98.2
	$I1_p \rightarrow I5_p$ (m/z 93)	1.41×10^{16}	2.21×10^{16}	2	0.2
	$I1_p \rightarrow I6_p$	1.50×10^{11}	1.22×10^{12}	3	0.0

Table 2. Results of state counting analysis for transition states leading from intermediate I1 for each reaction.

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 $I1_o$ to $P3_o$ (m/z 106) compared to $P4_o$ (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-dehydro-*N*-pyridinium results under-predict m/z 106 by 30% compared to experimental values, indicating the $I2_m \rightarrow P3_m$ 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 $I1 \rightarrow I5$ and $I5 \rightarrow I6$, 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 $I1_o \rightarrow I5_{o2}$, further leading to preference of the m/z 106 channel.

A minor product at m/z 121 (not shown in Figure 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 C₈H₁₁N isomer or isomers. Possible candidates for this unreactive *m/z* 121 population are the resonance stabilised intermediates I4 and I7. 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.⁵² Secondary addition of propene is not observed. Formation of CH₃, C₂H₄ 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 acetylene⁵³ and hydrogen cyanide⁵⁴ 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 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,⁵⁵⁻⁵⁷ 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 system⁴² 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 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).

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 $C_8H_{11}N$ 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 ± 1 %, 47.2 ± 0.4 %, and 40.9 ± 0.9 % respectively (statistical errors at 2σ). 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 β -scission to eliminate CH_3 . Ring-mediated H-transfer along the propyl group followed by C_2H_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.

4. Acknowledgements

The authors are grateful for the financial support of the Australian Research Council through the Discovery programs (AJT and SJB: DP170101596, AJT and GdS: DP130100862 and

GdS: FT130101304). CCB, JPB and MBP were supported by Australian Government Research Training Program (RTP) Scholarships. The authors also acknowledge the generous allocation of computing resources by the NCI National Facility (Canberra, Australia) under the Merit Allocation Scheme.

References

1. Parker, D. S. N.; Kaiser, R. I.; Kostko, O.; Troy, T. P.; Ahmed, M.; Mebel, M. A.; Tielens, A. M. G. G., Gas Phase Synthesis of (Iso)quinoline and its Role in the Formation of Nucleobases in the Interstellar Medium. *The Astrophysical Journal* **2015**, *803* (2), 10.
2. Parker, D. S. N.; Yang, T.; Dangi, B. B.; Kaiser, R. I.; Bera, P. P.; Lee, T. J., Low Temperature Formation of Nitrogen-substituted Polycyclic Aromatic Hydrocarbons (PANHs)- Barrierless Routes to Dihydro(iso)quinolines. *The Astrophysical Journal* **2015**, *815* (2), 13.
3. Stoks, P. G.; Schwartz, A. W., Basic nitrogen-heterocyclic compounds in the Murchison meteorite. *Geochimica et Cosmochimica Acta* **1982**, *46* (3), 309-315.
4. Soorkia, S.; Taatjes, C. A.; Osborn, D. L.; Selby, T. M.; Trevitt, A. J.; Wilson, K. R.; Leone, S. R., Direct detection of pyridine formation by the reaction of CH (CD) with pyrrole: a ring expansion reaction. *Physical Chemistry Chemical Physics* **2010**, *12* (31), 8750-8758.
5. Parker, D. S. N.; Kaiser, R. I., On the formation of nitrogen-substituted polycyclic aromatic hydrocarbons (NPAHs) in circumstellar and interstellar environments. *Chemical Society Reviews* **2017**, *46* (2), 452-463.
6. Smith, K. E.; Callahan, M. P.; Gerakines, P. A.; Dworkin, J. P.; House, C. H., Investigation of pyridine carboxylic acids in CM2 carbonaceous chondrites: Potential precursor molecules for ancient coenzymes. *Geochimica et Cosmochimica Acta* **2014**, *136*, 1-12.
7. McElroy, D.; Walsh, C.; Markwick, A. J.; Cordiner, M. A.; Smith, K.; Millar, T. J., The UMIST database for astrochemistry 2012. *Astronomy and Astrophysics* **2013**, *550*, 36.
8. Wakelam, V.; Loison, J.-C.; Herbst, E.; Pavone, B.; Bergeat, A.; Chabot, M.; Faure, A.; Galli, D.; Geppert, W.; Gerlich, D., The 2014 KIDA network for interstellar chemistry. *The Astrophysical Journal Supplement Series* **2015**, *217* (2), 20.
9. Vuitton, V.; Yelle, R. V.; McEwan, M. J., Ion chemistry and N-containing molecules in Titan's upper atmosphere. *Icarus* **2007**, *191* (2), 722-742.
10. Öberg, K. I., Photochemistry and Astrochemistry: Photochemical Pathways to Interstellar Complex Organic Molecules. *Chemical Reviews* **2016**.
11. Fortney, J. J.; Robinson, T. D.; Domagal-Goldman, S.; Amundsen, D. S.; Brogi, M.; Claire, M.; Crisp, D.; Hebrard, E.; Imanakag, H.; de Kok, R., The Need for Laboratory Work to Aid in The Understanding of Exoplanetary Atmospheres. *arXiv:1602.06305* **2016**.
12. Ziurys, L. M., The chemistry in circumstellar envelopes of evolved stars: Following the origin of the elements to the origin of life. *Proceedings of the National Academy of Sciences* **2006**, *103* (33), 12274-12279.
13. Larsson, M.; Geppert, W. D.; Nyman, G., Ion chemistry in space. *Reports on Progress in Physics* **2012**, *75* (6), 066901.
14. Oka, T., Interstellar H(3)(+). *Proceedings of the National Academy of Sciences of the United States of America* **2006**, *103* (33), 12235-12242.
15. King, G. A.; Oliver, T. A. A.; Nix, M. G. D.; Ashfold, M. N. R., Exploring the mechanisms of H atom loss in simple azoles: Ultraviolet photolysis of pyrazole and triazole. *The Journal of Chemical Physics* **2010**, *132* (6), 064305.
16. Oliver, T. A. A.; King, G. A.; Ashfold, M. N. R., Position matters: competing O-H and N-H photodissociation pathways in hydroxy- and methoxy-substituted indoles. *Physical Chemistry Chemical Physics* **2011**, *13* (32), 14646-14662.
17. Prather, K. A.; Lee, Y. T., The Photodissociation of Pyridine at 193 nm. *Israel Journal of Chemistry* **1994**, *34* (1), 43-53.

18. Lin, M.-F.; Dyakov, Y. A.; Tseng, C.-M.; Mebel, A. M.; Hsien Lin, S.; Lee, Y. T.; Ni, C.-K., Photodissociation dynamics of pyridine. *The Journal of Chemical Physics* **2005**, *123* (5), 054309.
19. Hsu, T. C.; Shu, J.; Chen, Y.; Lin, J. J.; Lee, Y. T.; Yang, X., Dissociation rates of benzene at VUV excitation. *The Journal of Chemical Physics* **2001**, *115* (21), 9623-9626.
20. Williams, P. E.; Jankiewicz, B. J.; Yang, L.; Kenttämä, H. I., Properties and Reactivity of Gaseous Distonic Radical Ions with Aryl Radical Sites. *Chemical Reviews* **2013**, *113* (9), 6949-6985.
21. Lam, A. K. Y.; Li, C.; Khairallah, G.; Kirk, B. B.; Blanksby, S. J.; Trevitt, A. J.; Wille, U.; O'Hair, R. A. J.; da Silva, G., Gas-phase reactions of aryl radicals with 2-butyne: experimental and theoretical investigation employing the N-methyl-pyridinium-4-yl radical cation. *Physical Chemistry Chemical Physics* **2012**, *14* (7), 2417-2426.
22. Waite, J. H.; Young, D. T.; Cravens, T. E.; Coates, A. J.; Crary, F. J.; Magee, B.; Westlake, J., The Process of Tholin Formation in Titan's Upper Atmosphere. *Science* **2007**, *316* (5826), 870-875.
23. Nixon, C. A.; Jennings, D. E.; Bezard, B.; Vinatier, S.; Teanby, N. A.; Sung, K.; Ansty, T. M.; Irwin, P. G.; Gorius, N.; Cottini, V., Detection of propene in Titan's stratosphere. *The Astrophysical Journal Letters* **2013**, *776* (1), L14.
24. Li, C.; Zhang, X.; Gao, P.; Yung, Y., Vertical distribution of C₃-hydrocarbons in the stratosphere of Titan. *The Astrophysical Journal Letters* **2015**, *803* (2), L19.
25. Adams, N. G.; Mathews, L. D.; Osborne Jr, D., Laboratory chemistry relevant to understanding and modeling the ionosphere of Titan. *Faraday discussions* **2010**, *147*, 323-335.
26. Hansen, C. S.; Kirk, B. B.; Blanksby, S. J.; O'Hair, R. A. J.; Trevitt, A. J., UV Photodissociation Action Spectroscopy of Haloanilinium Ions in a Linear Quadrupole Ion Trap Mass Spectrometer. *Journal of The American Society for Mass Spectrometry* **2013**, *24* (6), 932-940.
27. Lemons, D. S.; Gythiel, A., Paul Langevin's 1908 paper "On the Theory of Brownian Motion" ["Sur la théorie du mouvement brownien," C. R. Acad. Sci. (Paris) 146, 530-533 (1908)]. *American Journal of Physics* **1997**, *65* (11), 1079-1081.
28. Zheng, J.; Zhao, Y.; Truhlar, D. G., The DBH24/08 Database and Its Use to Assess Electronic Structure Model Chemistries for Chemical Reaction Barrier Heights. *Journal of Chemical Theory and Computation* **2009**, *5* (4), 808-821.
29. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision D.01. Wallingford CT, 2009.
30. Barker, J.; Nguyen, T.; Stanton, J.; Aieta, C.; Ceotto, M.; Gabas, F.; Kumar, T.; Li, C.; Lohr, L.; Maranzana, A., MultiWell-2016 Software Suite, JR Barker, University of Michigan. **2017**.
31. Barker, J. R., Multiple-Well, multiple-path unimolecular reaction systems. I. MultiWell computer program suite. *International Journal of Chemical Kinetics* **2001**, *33* (4), 232-245.
32. Barker, J. R., Energy transfer in master equation simulations: A new approach. *International Journal of Chemical Kinetics* **2009**, *41* (12), 748-763.
33. Kadi, M.; Davidsson, J.; Tarnovsky, A. N.; Rasmusson, M.; Åkesson, E., Photodissociation of aryl halides in the gas phase studied with femtosecond pump-probe spectroscopy. *Chemical Physics Letters* **2001**, *350* (1-2), 93-98.
34. Sage, A. G.; Oliver, T. A. A.; Murdock, D.; Crow, M. B.; Ritchie, G. A. D.; Harvey, J. N.; Ashfold, M. N. R., σ^* and $\pi\sigma^*$ excited states in aryl halide photochemistry: a comprehensive

- study of the UV photodissociation dynamics of iodobenzene. *Physical Chemistry Chemical Physics* **2011**, *13* (18), 8075-8093.
35. Prendergast, M. B.; Kirk, B. B.; Savee, J. D.; Osborn, D. L.; Taatjes, C. A.; Masters, K.-S.; Blanksby, S. J.; da Silva, G.; Trevitt, A. J., Formation and stability of gas-phase o-benzoquinone from oxidation of ortho-hydroxyphenyl: a combined neutral and distonic radical study. *Physical Chemistry Chemical Physics* **2016**, *18* (6), 4320-4332.
 36. Prendergast, M. B.; Cooper, P. A.; Kirk, B. B.; da Silva, G.; Blanksby, S. J.; Trevitt, A. J., Hydroxyl radical formation in the gas phase oxidation of distonic 2-methylphenyl radical cations. *Physical Chemistry Chemical Physics* **2013**, *15* (47), 20577-20584.
 37. Lavorato, D.; Terlouw, J.; McGibbon, G.; Dargel, T.; Koch, W.; Schwarz, H., Generation of neutral and cationic hydrogen shift isomers of pyridine: a combined experimental and computational investigation. *International Journal of Mass Spectrometry* **1998**, *179-180*, 7-14.
 38. Flammang, R.; Barbieux-Flammang, M.; Gualano, E.; Gerbaux, P.; Le, H. T.; Nguyen, M. T.; Turecek, F.; Vivekananda, S., Ionized Benzonitrile and Its Distonic Isomers in the Gas Phase. *The Journal of Physical Chemistry A* **2001**, *105* (37), 8579-8587.
 39. Kirk, B. B.; Harman, D. G.; Kenttämaa, H. I.; Trevitt, A. J.; Blanksby, S. J., Isolation and characterization of charge-tagged phenylperoxyl radicals in the gas phase: direct evidence for products and pathways in low temperature benzene oxidation. *Physical Chemistry Chemical Physics* **2012**, *14* (48), 16719-16730.
 40. Maccarone, A. T.; Kirk, B. B.; Hansen, C. S.; Griffiths, T. M.; Olsen, S.; Trevitt, A. J.; Blanksby, S. J., Direct Observation of Photodissociation Products from Phenylperoxyl Radicals Isolated in the Gas Phase. *Journal of the American Chemical Society* **2013**, *135* (24), 9010-9014.
 41. Kaiser, R. I.; Parker, D. S. N.; Goswami, M.; Zhang, F.; Kislov, V. V.; Mebel, A. M.; Aguilera-Iparraguirre, J.; Green, W. H., Crossed beam reaction of phenyl and D5-phenyl radicals with propene and deuterated counterparts-competing atomic hydrogen and methyl loss pathways. *Physical Chemistry Chemical Physics* **2012**, *14* (2), 720-729.
 42. Kislov, V. V.; Mebel, A. M.; Aguilera-Iparraguirre, J.; Green, W. H., Reaction of Phenyl Radical with Propylene as a Possible Source of Indene and Other Polycyclic Aromatic Hydrocarbons: An Ab Initio/RRKM-ME Study. *The Journal of Physical Chemistry A* **2012**, *116* (16), 4176-4191.
 43. Pross, A., *Theoretical and Physical Principles of Organic Reactivity*. Wiley: 1995.
 44. Tichy, S. E.; Thoen, K. K.; Price, J. M.; Ferra, J. J.; Petucci, C. J.; Kenttämaa, H. I., Polarity of the Transition State Controls the Reactivity of Related Charged Phenyl Radicals Toward Atom and Group Donors. *The Journal of Organic Chemistry* **2001**, *66* (8), 2726-2733.
 45. Adeuya, A.; Price, J. M.; Jankiewicz, B. J.; Nash, J. J.; Kenttämaa, H. I., Gas-Phase Reactivity of Protonated 2-, 3-, and 4-Dehydropyridine Radicals Toward Organic Reagents. *The Journal of Physical Chemistry A* **2009**, *113* (49), 13663-13674.
 46. Widjaja, F.; Jin, Z.; Nash, J. J.; Kenttämaa, H. I., Direct Comparison of Solution and Gas-Phase Reactions of the Three Distonic Isomers of the Pyridine Radical Cation with Methanol. *Journal of the American Chemical Society* **2012**, *134* (4), 2085-2093.
 47. Widjaja, F.; Jin, Z.; Nash, J. J.; Kenttämaa, H. I., Comparison of the Reactivity of the Three Distonic Isomers of the Pyridine Radical Cation Toward Tetrahydrofuran in Solution and in the Gas Phase. *Journal of The American Society for Mass Spectrometry* **2013**, *24* (4), 469-480.
 48. Karton, A.; Ruscic, B.; Martin, J. M. L., Benchmark atomization energy of ethane: Importance of accurate zero-point vibrational energies and diagonal Born–Oppenheimer corrections for a ‘simple’ organic molecule. *Journal of Molecular Structure: THEOCHEM* **2007**, *811* (1), 345-353.
 49. Harding, L. B.; Georgievskii, Y.; Klippenstein, S. J., Accurate Anharmonic Zero-Point Energies for Some Combustion-Related Species from Diffusion Monte Carlo. *The Journal of Physical Chemistry A* **2017**, *121* (22), 4334-4340.
 50. Johnston, H. S.; Heicklen, J., Tunnelling Corrections for Unsymmetrical Eckart Potential Energy Barriers. *The Journal of Physical Chemistry* **1962**, *66* (3), 532-533.

51. Miller, W. H., Tunneling corrections to unimolecular rate constants, with application to formaldehyde. *Journal of the American Chemical Society* **1979**, *101* (23), 6810-6814.
52. Yu, S. J.; Holliman, C. L.; Rempel, D. L.; Gross, M. L., The beta-distonic ion from the reaction of pyridine radical cation and ethene: a demonstration of high-pressure trapping in Fourier transform mass spectrometry. *Journal of the American Chemical Society* **1993**, *115* (21), 9676-9682.
53. Soliman, A.-R.; Hamid, A. M.; Attah, I.; Momoh, P.; El-Shall, M. S., Formation of Nitrogen-Containing Polycyclic Cations by Gas-Phase and Intracuster Reactions of Acetylene with the Pyridinium and Pyrimidinium Ions. *Journal of the American Chemical Society* **2013**, *135* (1), 155-166.
54. Hamid, A. M.; El-Shall, M. S.; Hilal, R.; Elroby, S.; Aziz, S. G., Unconventional hydrogen bonding to organic ions in the gas phase: Stepwise association of hydrogen cyanide with the pyridine and pyrimidine radical cations and protonated pyridine. *The Journal of Chemical Physics* **2014**, *141* (5), 054305.
55. Chen, C.-C.; Bozzelli, J. W.; Farrell, J. T., Thermochemical Properties, Pathway, and Kinetic Analysis on the Reactions of Benzene with OH: An Elementary Reaction Mechanism. *The Journal of Physical Chemistry A* **2004**, *108* (21), 4632-4652.
56. Attah, I. K.; Soliman, A.-R.; Platt, S. P.; Meot-Ner, M.; Aziz, S. G.; Samy El-Shall, M., Observation of covalent and electrostatic bonds in nitrogen-containing polycyclic ions formed by gas phase reactions of the benzene radical cation with pyrimidine. *Physical Chemistry Chemical Physics* **2017**, *19* (9), 6422-6432.
57. So, S.; Kirk, B. B.; Trevitt, A. J.; Wille, U.; Blanksby, S. J.; da Silva, G., Unimolecular reaction chemistry of a charge-tagged beta-hydroxyperoxyl radical. *Physical Chemistry Chemical Physics* **2014**, *16* (45), 24954-24964.