

SELECTED ION FLOW TUBE STUDIES OF ION-MOLECULE REACTIONS RELEVANT
TO THE INTERSTELLAR MEDIUM AND TITAN'S ATMOSPHERE

by

LEAH STAVISH

(Under the Direction of Nigel G. Adams)

ABSTRACT

A Selected Ion Flow Tube has been used to investigate a series of ion-molecule reactions relevant to modeling the interstellar medium and Titan's atmosphere. N^+ and N_2^+ reactions with the cyclic molecules benzene, cyclohexane, pyrrole and pyrrolidine were studied and result primarily in dissociative charge transfer. Charge transfer reactions of these neutrals, as well as the N-containing rings piperidine, pyridine, pyrimidine, 2-methylpyridine, and N-methylpyrrole and the linear hydrocarbon chain hexane, with the rare gas ions Xe^+ , Kr^+ , and Ar^+ examined the neutral's stability. Generally, 6-membered aromatic rings were the most stable. N_2 is the main component of Titan's atmosphere, so reactions of N^+ and N_2^+ are of particular importance there. Ring compounds are of interest due to their biological implications and are detected in both the interstellar medium and Titan's atmosphere. Rate coefficients and product distributions are reported for these reactions, adding to the kinetic data available for the models.

INDEX WORDS: Selected Ion Flow Tube, Positive Ion-Molecule Reaction, Interstellar Medium, Titan Ionosphere, Cyclic Molecule

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Interstellar space and planetary atmospheres are vast and intriguing environments, much of which are not well understood by scientists. Molecules were not predicted to exist in the interstellar medium (ISM) because it was thought to be too diffuse [1]. Perceptions of this medium changed when the first molecule, CH, was detected in the ISM in 1937 [2] followed soon by the detections of CN [3] and CH⁺ [4]. Technological advances in spectroscopic techniques allowed observations of increasingly complex gas-phase molecules [5]. This has given a greater understanding of the processes occurring there, as well as raising many questions. Currently, ~160 molecules have been detected [6] and ~77 are organic species. Positive [4,7-22] and negative [23-29] ions, as well as various classes of organic compounds, including hydrocarbons, aldehydes, ketones, acids, ethers, alcohols, and amines, have been detected. The detection of the ring compounds c-SiC₂ [30], c-C₃H [31], c-C₃H₂ [32], c-CH₂OCH₂ [33], c-C₃H₂O [34], c-C₂H₃N, c-C₂H₅N [35], and benzene [36] suggest the possibility of biologically important ring molecules being discovered here [1]. Glycoaldehyde [37], the simplest sugar, and acetamide [38], the most basic molecule with a peptide bond, have been detected. The detection of glycine, the simplest amino acid, was proposed [39], but was later disputed [40]. However, it is believed that planetesimals and interplanetary dust particles delivered prebiotic materials to early Earth [41]; thus understanding of processes in the ISM could lead to knowledge of processes which may have occurred at that time. Sophisticated models are necessary to account for the great complexity in the ISM and these rely on laboratory

measurements many of rate coefficients and product distributions for ion-molecule reactions. Modelers use these kinetic data to interpret measurements of chemical compositions, determine chemical pathways, and predict the conditions favorable for detection [5].

Investigations of the atmospheres of planets and planetary satellites reveal information that aids in the understanding of the evolution of our Solar System. Organic chemistry processes in Titan's atmosphere are of particular importance due to its similarities with the early Earth's atmosphere [42]. Titan is the only planetary satellite in our Solar System that has a significant atmosphere [43], and this was first recognized in 1944 [44]. The Voyager missions, which encountered Saturn in 1980 and 1981, revealed that the Titan atmosphere was denser than the Earth's atmosphere and was mainly composed of N_2 . Hydrocarbon and nitrile chemistry was occurring [45], but still much was left unknown. The desire to learn more about this satellite, and for *in situ* measurements under the thick haze, led to the Cassini-Huygens mission [46] launched on October 15, 1997 [47]. The spacecraft reached orbital insertion around Saturn on July 1, 2004 [47] and consists of two principle components: The Huygens Probe and the Cassini Orbiter [45]. The Huygens Probe descended down to the surface of Titan on January 14, 2005, making measurements of the atmosphere and surface as it went. The Cassini Orbiter contains twelve instruments for measurements of various properties of Titan and Saturn's other satellites [48], Saturn, and Saturn's magnetosphere [47]. The Ion and Neutral Mass Spectrometer (INMS) is the only *in situ* instrument [49] onboard the orbiter which is designed to study Titan's atmosphere [47]. The primary focus of the INMS instrument is investigating the structure and composition of Titan's upper atmosphere, above 900 km from its surface, and its interaction with Saturn's magnetosphere [50]. INMS measurements have confirmed that complex chemistry is occurring [43] and suggested that many more N-containing molecules are present than were

predicted [51]. Most of the even masses seen by the INMS are missing from the pre-Cassini models [43]. The great success of the mission has caused NASA to extend the original four year mission, completed in June 2008, until September 2010 [52]. Many of the species identified in Titan's atmosphere have also been seen in the ISM [43], including the key prebiotic molecules [53] HCN [54,55] and HC₃N [56,57]. The chemistry occurring in this ionosphere is important and influences the chemistry of the entire atmosphere and surface because molecules formed here can diffuse to lower altitudes [51] and may eventually precipitate down onto the surface [50]. However, since the INMS obtains only mass spectra, laboratory data is essential to the interpretation of the measured spectra and the formation of models of atmospheric composition [46].

Ion-molecule reactions are important in both the ISM [5] and Titan's atmosphere [43] and usually they have no activation barriers [58]. Larger, more complex molecules can be formed in ion-molecule reactions by carbon insertion, nitrogen insertion, condensation, and radiative and collisional association reactions [58]. Charge transfer in ion-molecule reactions assist in ionization of abundant ions [5]. These processes were investigated using the Selected Ion Flow Tube technique to study some of the ion-molecule reactions which are relevant in the ISM and Titan's atmosphere.

The neutrals studied in this thesis include the N-containing rings pyrimidine (C₄H₄N₂), pyridine (C₅H₅N), pyrrole (C₄H₅N), pyrrolidine (C₄H₉N), piperidine (C₅H₁₁N), 2-methylpyridine (C₆H₇N), and N-methylpyrrole (C₅H₇N), the hydrocarbons rings benzene (C₆H₆) and cyclohexane (C₆H₁₂), and the linear hydrocarbon chain hexane (n-C₆H₁₄). Most of these neutrals (pyrimidine, pyridine, pyrrole, 2-methylpyridine, N-methylpyrrole, and benzene) are aromatic species which have greater stability than their saturated counterparts. Some characteristics that

contribute to this stabilization are that their electrons are delocalized in a π system and they have full bonding molecular orbitals and empty nonbonding and antibonding molecular orbitals. Adding or removing an electron from these molecules results in destabilization [59]. Organic ring compounds, especially those containing nitrogen, are of particular interest due to their biological implications [60,61]. Pyrimidine is the nucleobase of cytosine in DNA and RNA, thymine in DNA, and uracil in RNA [1]. Some substituted pyridines occur naturally [62] and are known to bind metals important for biological activity [63] and as catalyst for chemical reactions [64]. Pyrrole is a component of heme in hemoglobin and chlorophyll in chloroplast [1]. Pyrrolidine is the ring of the amino acid proline [65]. Searches have been conducted for pyrimidine [35,60,66,67], pyridine [60,67], and pyrrole [68,69] in the ISM with no success. Analysis of meteoritic organic matter has revealed pyrimidine [70] and substituted pyridines [71], so the possibility of finding these species in the gas phase is hopeful since molecules in the gas phase can condense to form meteors. Ionized pyridine has been detected [72] by the INMS, as well as benzene [73] and protonated benzene [72]. Data from the INMS T5 flyby suggests the presence of neutrals and ions at masses that correspond with the masses of pyridine and 2-methylpyridine. These also give an upper limit to the mole fraction of a neutral at the mass of pyrrole [43]. Indications of aromatic molecules, polycyclic aromatic hydrocarbons (PAH), and polycyclic aromatics containing one or more nitrogen atoms (PANH) are seen throughout the ISM [1]. The haze surrounding Titan may contain prebiotic molecules [74] and is thought to be composed of large organic molecules and PAH's [73,74]. Models show that PAH polymers are the largest contributors to the haze and are believed to be formed from benzene by a sequence of acetylene additions and H atom removals [74]. As mentioned before, benzene has been detected in both the ISM [36] and Titan's atmosphere [73]. Aromatic hydrocarbons have been identified

by the strong infrared emission bands known as aromatic infrared bands (AIB). Unidentified infrared emission (UIE) features include the AIB, as well as aliphatic features, broad emission plateaus, and many broad, weaker features. These UIEs are thought to arise partially from aromatic units with a variety of functional groups. The diffuse interstellar absorption bands (DIB) are ubiquitous in the ISM [1] and are attributed to PAH's [75,76] and PANH's [77], although the carriers have not been positively identified. No specific PAH molecule has been detected anywhere in interstellar space [1]. The identification process becomes more difficult as the size of the molecule increases. Detection of complex molecules requires measurement of many transitions because of the greater number of energy levels that can be excited and line confusion from smaller species. Consequently, molecules may be present even though they have not been detected [1]. In Titan's atmosphere, neutral species, even as minor as those with mole fractions of ~1 ppm, play a large role in the ion composition and chemistry of the ionosphere [43,51].

N_2 is the major component of Titan's atmosphere and is ionized to N^+ and N_2^+ by solar radiation and energetic plasma from Saturn's magnetosphere [72] in approximately equal abundance [45]. Reactions with these ions were chosen because they provide the starting point to Titan's ion chemistry [78]. The charge transfer reactions with the ions Xe^+ , Kr^+ , and Ar^+ have been studied to investigate the stability of the neutrals following excitation by charge transfer. These ions have been detected as neutrals in the ISM [79], with implications of the ionized forms Kr^+ and Ar^+ as well [80]. The ionization potential of Xe is smaller than those of Ar and Kr [81], so it is thought that ionization processes can apply to the ionization of Xe. In Titan's atmosphere, only Ar has been detected which is surprising since rare gases have existed

throughout the solar nebula and hence should have been incorporated into the formation of the satellite [82].

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CHAPTER 2

EXPERIMENTAL

A Selected Ion Flow Tube (SIFT) was used to study ion-molecule reactions at room temperature (~ 298 K). The general technique has been reviewed in the literature [1] previously. The ions were produced in a remote ion source, either a low pressure ionization source (LPIS) or a microwave source. The LPIS was employed to generate the N^+ and N_2^+ ions as well as rare gas ions Xe^+ , Kr^+ , and Ar^+ in some cases. This ion source minimizes secondary reactions in the source and so was well suited for these ions. The microwave source produces larger ion currents and was used for producing most of the rare gas ions. Electrostatic lenses accelerated and focused the ion beam into a quadrupole mass filter where the ion of interest was mass selected and focused by another set of electrostatic lenses through an orifice (1 mm dia.) in the SIFT disk and into the flow tube. The upstream ion current was monitored via a picoammeter attached to the SIFT disk. The pressure of the source gas in the ion source was varied, along with the potentials of the lenses, until the maximum ion current was attained. Ultra high purity Helium (Airgas, Inc.) carrier gas was passed through a molecular sieve trap chilled by liquid nitrogen for further purification before injection into the flow tube through a Venturi inlet. The ions were thermalized by collisions in the flow tube ($\sim 10^7$) with the carrier gas which was maintained at a pressure of ~ 0.5 Torr and exhausted downstream by a Roots pump. The neutral reactants were introduced into the flow tube through ring type injectors at one of three reaction lengths which is related to the reaction time. The product ions were sampled downstream through an orifice in a nose cone and focused by electrostatic lenses through a second

quadrupole into a channel multiplier for detection. A downstream picoammeter attached to the nose cone monitored ion current. Diffusion pumps maintained the pressures in the SIFT chamber and detection system ($\sim 10^{-5}$ Torr) which were measured by ion gauges upstream and downstream. Extrel electronics were used for supplying voltages to the two quadrupoles. The primary and product ions were counted for ten seconds at a series of neutral reactant flows and plots were made of these ion counts versus the neutral flow. An example of this type of plot is seen in Figure 2.1. The information gathered was used to determine both the rate coefficients and the product distributions.

The decay of the primary ion allows the calculation of the reaction rate coefficient. The general equation for the reaction is $A^+ + B \rightarrow C^+ + D$, giving the rate equation below.

$$\frac{d[A^+]}{dt} = -k[A^+][B] \quad (2.1)$$

In Equation 2.1, $[A^+]$ is a signal proportional to the concentration of the primary ion, $[B]$ is the concentration of the reactant neutral, k is the rate coefficient, and t is the reaction time. In these experiments, the concentration of the reactant neutral is much larger than the concentration of the primary ion; thus the reactant neutral concentration is considered constant and the rate equation can be integrated as followed, with C as a constant of integration.

$$\ln[A^+] = -k[B]t + C \quad (2.2)$$

The rate coefficient is determined from the slope of the line divided by the reaction time. The reaction time is found by dividing the length of the reaction zone by the average velocity of the ions. All of the reactant neutrals are liquids with vapor at room temperature. To minimize condensation of these neutrals and make accurate determination of neutral flows, mixtures in He were made using less than the neutral's vapor pressure. Dissolved gases in the liquids were eliminated by several freeze-pump-thaw cycles before making the mixtures. The rate

coefficients reported have taken account of this dilution. For these sticky vapors, rate coefficients are accurate to $\pm 25\%$

The product distributions were determined by plotting the fractional distribution for each primary product ion versus the neutral reactant flow as seen in Figure 2.2. Details of ion product determination can be found in the literature [2]. Points at very low neutral flows are often not accurate due to the error associated with determining low concentrations. These points were removed and the curves were extrapolated to zero to find the percentage of each ion product produced in the primary reaction. Mass discrimination effects of the quadrupole were taken into account when reporting these percentages. The product distributions are accurate to ± 5 in the percentage.

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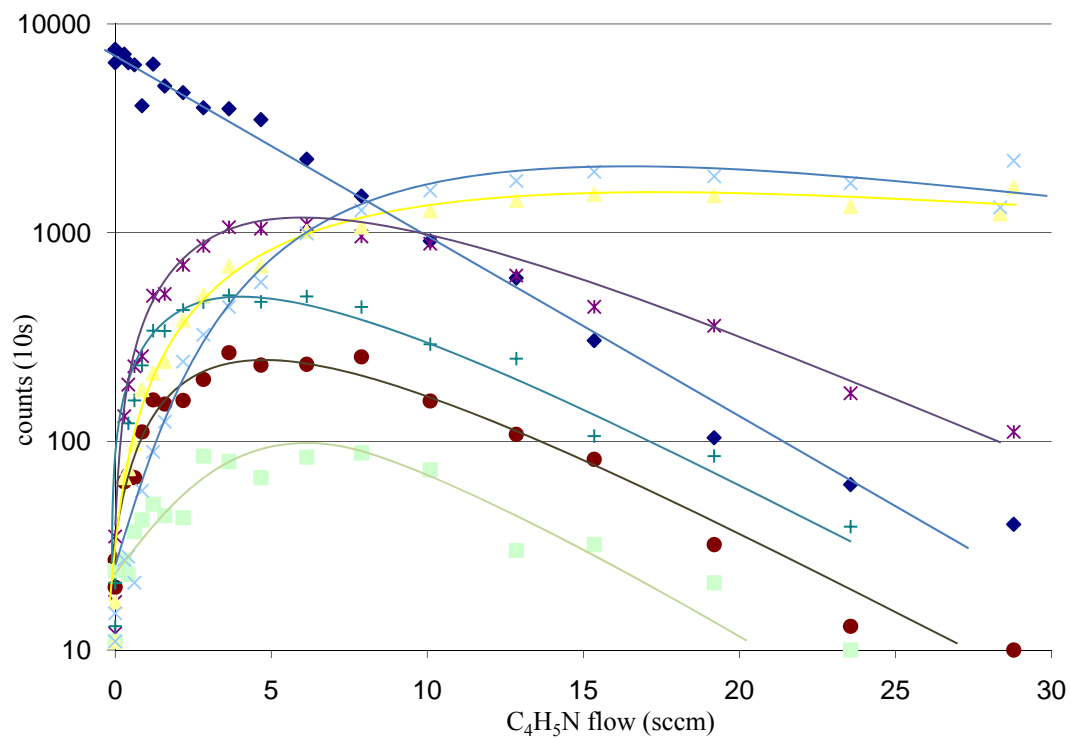


Figure 2.1. Semi-logarithmic plot of the decay of the primary ion N_2^+ and the variations of the product ions in reaction with pyrrole. Note that the linearity of the primary ion decay over two orders of magnitude lowers the errors associated with the rate measurement.

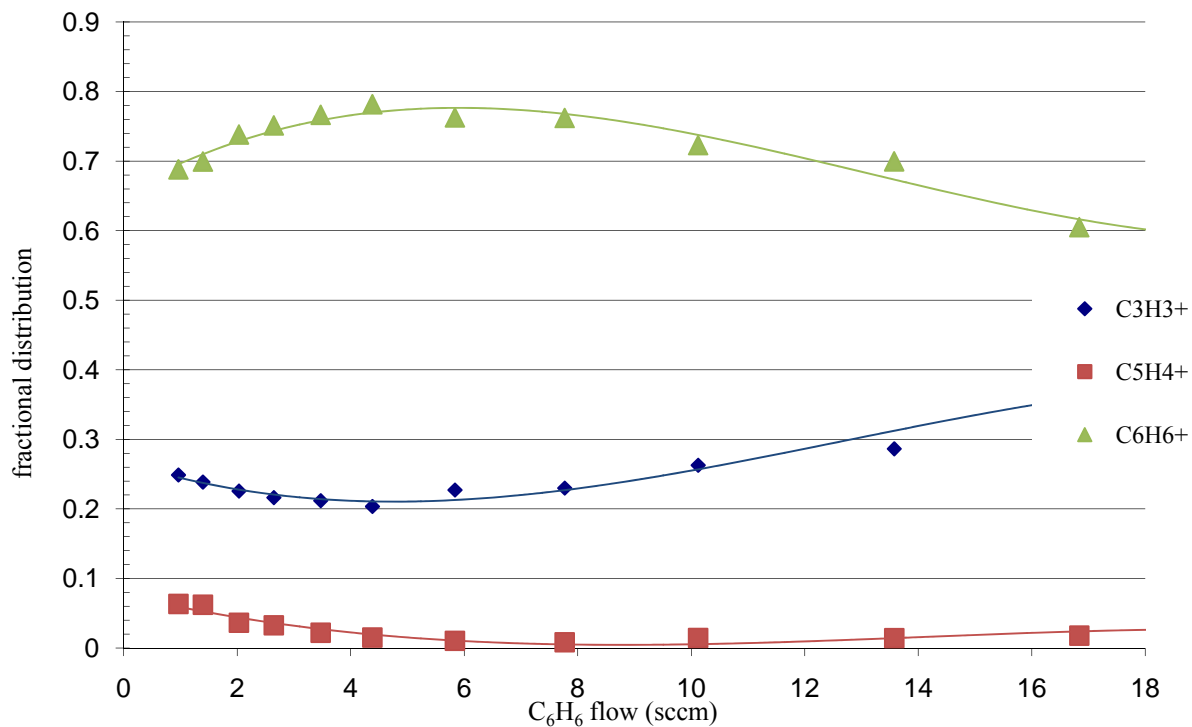
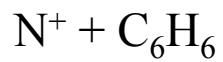


Figure 2.2. Fractional distribution of the ion products of the reaction of N^+ and benzene plotted versus the neutral flow of benzene.

CHAPTER 3

REACTIONS OF N^+ AND N_2^+ WITH SEVERAL CYCLIC MOLECULES STUDIED USING A SELECTED ION FLOW TUBE¹

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3.1 ABSTRACT

A selected ion flow tube, SIFT, has been used to investigate the reactions of N^+ and N_2^+ with four cyclic molecules (pyrrole, pyrrolidine, benzene, and cyclohexane) at 298K. These species are of particular interest to the chemistry of both Titan's ionosphere and of interstellar molecular clouds. Rate coefficients and product distributions have been determined to provide kinetic data needed for accurate models of these media and establish chemical routes. The majority of reactions proceed at the gas kinetic rate; only pyrrolidine reacts slower. The reactions result mainly in dissociative charge transfer, except the reaction of benzene with N^+ , in which the major product is non-dissociative charge transfer. Comparisons are made between each neutral with the two reactant ions (N^+ and N_2^+) of differing recombination energies and also between each reactant ion with neutrals differing in ionization energy and aromaticity. Fragmentation channels are discussed and compared with electron impact ionization.

3.2 INTRODUCTION

Reactions of cyclic molecules are of interest because many are abundant in interstellar molecular clouds, ISC, and some have also been detected in Titan's atmosphere. Detected ring molecules in ISC include *c*- C_3H , *c*- C_3H_2 , *c*- CH_2OCH_2 [1], *c*- C_2H_3N , *c*- C_2H_5N [2], *c*- C_3H_2O [3], as well as C_6H_6 [4] (benzene). Ring compounds identified in Titan's atmosphere are *c*- $C_3H_3^+$ [5], C_6H_6 [6], and *c*- $C_5H_5N^+$ and/or *c*- $C_6H_7^+$ [7]. Also, polycyclic aromatic hydrocarbons [8], PAHs, and those containing one or more nitrogen atoms, PANHs, are thought to be responsible for unidentified IR emissions [9].

N_2 is the major neutral component of Titan's atmosphere (95% N_2 and 5% CH_4) [10]. It forms N_2^+ and N^+ when subjected to solar extreme ultra-violet radiation and the energetic

electrons of Saturn's magnetosphere, initiating complex chemical reaction sequences [7]. N_2^+ and N^+ provide the starting point for ionospheric models of Titan's major ion chemistry [5,11,12] including reactions with cyclic molecules, and therefore these are of interest in the present study.

Chemical models are vital for predicting the existence of observed species. Species in ISC are mainly detected by microwave emissions, hence their identity is conclusive. Models of ISC seek to predict abundances of the different species, for comparison with abundances observed, in order to establish chemical routes [13]. In its probing of Titan's atmosphere, the Cassini INMS (Ion Neutral Mass Spectrometer) obtains only mass spectra of ions and neutrals. Models are used to interpret mass spectrometric abundances in terms of molecular identity by comparing those masses detected by Cassini with those predicted by the models [7]. This establishes the chemical routes, but requires a large amount of chemical kinetic data, including both rate coefficients and product distributions.

The present study consists of the reactions of N_2^+ and N^+ with the neutrals pyrrole ($\text{C}_4\text{H}_5\text{N}$), pyrrolidine ($\text{C}_4\text{H}_9\text{N}$), benzene (C_6H_6), and cyclohexane (C_6H_{12}). N_2^+ and N^+ have large recombination energies (15.58 eV and 14.53 eV) leaving ample energy for fragmentation. Rate coefficients and product distributions are reported, providing some of the data needed for the models.

3.3 EXPERIMENTAL

The reactions were studied using a Selected Ion Flow Tube (SIFT) at 298K. Details of the technique can be found in the literature [14,15] and this will not be described in depth here. A low pressure ionization source was employed with nitrogen as the source gas to create the primary ions, N_2^+ and N^+ , by electron impact. These ions were then mass selected by a

quadrupole mass filter and injected into the flow tube. Here helium carrier gas transported them downstream to the detection quadrupole/ion counting system. The total pressure in the flow tube was maintained at ~ 0.5 Torr by the He flow, which was evacuated by a Roots pump after sampling the ions. Ring type injectors introduced the reactant neutral into the flow tube downstream of the ion injection port and after the ions had thermalized by collisions ($\sim 10^7$) with the He.

All of the reactant neutrals, used in this study, are liquids at room temperature.

Pyrrolidine and pyrrole have low vapor pressures and their vapors tend to stick to the flow tube wall, making accurate determination of flows difficult. To eliminate this obstacle, mixtures were made of these and of the two higher vapor pressure liquids, benzene and cyclohexane [16].

Samples were prepared by evaporating the neat vapors into an evacuated vessel and diluting with helium. Cyclohexane was diluted in a 9.98% mixture while the other three samples were diluted to $\sim 1\%$ mixtures, keeping the reactant pressure less than its saturated vapor pressure to minimize condensation on the vessel walls. Pyrrole apparently readily dimerizes [17], but no evidence for this was seen and the energies associated are unknown. Dimerization would be noticeable in that the experimental rate coefficient is likely to be greater than predicted by the calculated theoretical collisional rates. This would occur since the concentration in the mixture of the neutral would be incorrect due to the dimer monomerization after injection.

Sigma-Aldrich provided three of the liquid reactants with quoted purities of 98% for pyrrole, 99.5+% for pyrrolidine, and $\geq 99\%$ for cyclohexane. Benzene was obtained from Fisher Scientific with a purity of 99.5%. Additional purification of these liquids was achieved by freeze-pump-thaw cycles, removing dissolved gases before use. The high purity helium used for both dilution and as the carrier gas (National Welders Specialty Gases) was passed through a

molecular sieve cooled with liquid nitrogen for additional purification before use. Rate coefficients and product distributions were determined in the usual way [14,15,18,19] taking into account the dilution of the reactant neutrals. Rate coefficients are accurate to $\pm 25\%$ and product distributions to ± 5 in the percentage. Mass discrimination effects in the detection quadrupole mass filter have been taken into account.

3.4 RESULTS AND DISCUSSION

The experimental reaction rate coefficients, k_{exp} , are given in Table 3.1 as well as the theoretical collisional rate coefficients, k_{theor} , which were determined using parameterized trajectory calculations [20]. Experimental values are quoted from the literature, k_{lit} , where available [21,22]. Our values are within reasonable error of the experimental literature values. The reactions of N_2^+ and N^+ with benzene and N^+ with cyclohexane are the only reactions in this study for which rate coefficients have been previously reported. Most reactions proceed within experimental error of the gas kinetic values except those with pyrrolidine as the reactant neutral. It is unknown why these pyrrolidine reactions are less efficient than the other reactions studied, but reactions with this neutral in another study [23], as well as another in the literature [24], show the same effect. Note that reaction efficiencies and rate coefficients, both experimental and theoretical, are larger for reactant neutrals with π electrons in the ring due to the attractive forces they create with the positive ions.

Ion product distributions for the reactions studied are given in Table 3.2. The literature product distributions for the benzene reactions with N_2^+ and N^+ and cyclohexane with N_2^+ are included in parentheses and agree reasonably well with our product distributions. None of the other reactions in this study have prior ion product distributions for comparison. Electron

impact, EI, ionization abundances are shown for discussion and comparison of the fragmentation channels. Photoionization efficiency, PIE, curves are also useful in predicting expected fragment ions, but the estimated ion abundances do not correlate with those from ion-molecule reactions, consistent with previous observations [21].

The products of the reactions of each neutral with the two reactant ions of differing recombination energy are compared. Reactant neutrals differing in aromaticity (i.e. aromatic benzene versus cyclohexane and aromatic pyrrole versus pyrrolidine) are included in this study. These comparisons are readily seen in Table 3.3, which gives ΔE , the energy difference between the recombination energy of the reactant ion and the ionization energy of the reactant neutral, and indicates which species are aromatic. The ΔE values quoted denote the amount of energy left over after the neutral has been ionized by charge transfer which is available to break bonds and fragment the neutral. It is expected that fragmentation products arising from charge transfer will be the same as the products seen following EI ionization of the neutral. However, charge transfer fragmentation abundances will differ due to the narrow distribution of internal energy transferred to the neutral in ion-molecule reactions [25]. If products are seen in ion-molecule reactions which are not seen in the EI spectrum, other channels such as hydride ion abstraction or association are expected to be the precursors prior to fragmentation to yield products.

The reactions result mainly in dissociative charge transfer, except the reaction of benzene with N^+ , in which the major product is non-dissociative charge transfer. This result can be explained by the aromatic stability of benzene and the smaller ΔE value of the reaction. N_2^+ has larger recombination energy than N^+ , thus giving a larger ΔE value for each neutral, and produces more fragment ions than N^+ in all cases except with pyrrole. Unfortunately, in most cases, the heat of formation of one or more of the possible products is unknown, making

definitive assignment of the ion products impossible. However, in a few cases it is possible to calculate the enthalpy of reaction. Production of N_2 in the N^+ reactions with pyrrole and pyrrolidine is exothermic for the possible product channels. This may be a partial explanation of why N^+ reactions with pyrrole produce more fragments than the corresponding N_2^+ reactions, although this effect is not seen in the pyrrolidine reactions. In addition, energetics associated with insertion of reactant ions into the neutral products to form C-N bonds have been examined. Again, unfortunately, just a few of the heats of formation are present in the literature, but where available, only some reactions are exothermic. The major product (m/z 43) for both of the pyrrolidine reactions can be identified as $C_2H_5N^+$ based on known EI fragmentation mechanisms since this m/z appears as the most abundant peak in the EI spectrum.

3.4.1 PYRROLE AND PYRROLIDINE

The pyrrole reactions are unique in this study because the reactant ion with greater recombination energy gives less fragmentation. The products of the reaction with N_2^+ are all in the EI spectrum of pyrrole [26] and can be explained by fragmentation after charge transfer. However, some of the products of the reaction with N^+ cannot. The ion at m/z 52 ($C_4H_4^+$ and/or $C_3H_2N^+$) occurs on pyrrole's EI spectrum with <1% actual abundance compared with the 15% product of the ion-molecule reaction. The difference in the distribution of internal energies can influence abundances for EI versus ion-molecule reactions [25], but also, this product could occur through other channels. Products at m/z values of 53 ($C_4H_5^+$ and/or $C_3H_3N^+$) and 54 ($C_3H_4N^+$) are not found on the EI spectrum and thus probably arise from channels other than charge transfer. Both ion-molecule reactions with pyrrole give products at m/z 40 which could be identified as either $C_3H_4^+$ and/or $C_2H_2N^+$. If this product was $C_3H_4^+$, it could give HCN as the

neutral product, which is energetically possible. This is worth noting since HCN is abundant in both ISC and Titan's atmosphere [5,27], and this reaction could provide a small part of the source. Although benzene is the only neutral in this study which has been identified in ISC [4] and Titan's atmosphere [6], the possibility of other homo- and also heterocyclic compounds is likely [9].

All products of the pyrrolidine reactions occur also on the EI spectrum [26]. Therefore, it is reasonable to conclude that all products were formed after charge transfer to the neutral and can be produced by known EI fragmentation mechanisms [25]. Both reactions with pyrrolidine give the major product at m/z 43, which could be $C_3H_7^+$ and/or $C_2H_5N^+$. When pyrrolidine loses an electron by EI ionization, it will most likely be taken from the nitrogen's lone pair since those electrons are in the highest occupied molecular orbital (HOMO) [28]. The same is expected after charge transfer in ion-molecule reactions, placing the radical site on the nitrogen. Starting here with known EI fragmentation mechanisms, the ion $C_2H_5N^+$ can be assigned to m/z 43 after two consecutive radical-site initiated α cleavage reactions [28].

3.4.2 BENZENE AND CYCLOHEXANE

The benzene reactions in the current study have product distributions that agree reasonably well with the literature. The reaction of benzene with N^+ yields products shown on its EI spectrum [26], except for $C_5H_4^+$, which is only a small product (7%) in this reaction. Thus, it should be formed after ionization by a channel other than charge transfer. All observed products of the reaction with N_2^+ , as well as the remaining N^+ products, are considered to result after charge transfer since they are visible on benzene's EI spectrum. It is possible that the products $C_5H_3^+$ and $C_6H_4^+$ are formed via another fragmentation channel because their EI peak

abundances are small, although their product abundances in this reaction with N_2^+ are also low. The major product in the reaction of benzene with N_2^+ is $C_4H_4^+$ and this is not seen when reacting this neutral with N^+ . (Note though that small percentages of both cyclic and linear isomers of $C_4H_4^+$ have been reported in the literature [21].) This could result from the smaller ΔE value and benzene's aromatic stability. The $C_5H_4^+$ product ion of the reaction of benzene with N^+ again gives the neutral product HCN and is energetically feasible. As noted before, the reaction between benzene and N^+ is the only reaction in this series which gives non-dissociative charge transfer as the major product channel. This is consistent with benzene's aromatic stability and the small ΔE value.

Reactions of N_2^+ and N^+ with neutral cyclohexane give similar product ions and distributions. The literature product distribution for the reaction of cyclohexane with N_2^+ has been previously reported [25] and matches well with the current study. Products of both reactions are seen in the EI spectrum for cyclohexane [26]. $C_5H_7^+$ and $C_6H_{11}^+$ have small EI abundances, in agreement with the fact that they are not seen in the reaction with N^+ and may be negligible in the reaction with N_2^+ . Additionally, these ions are not reported in the literature product distribution.

3.4.3 AROMATICITY

Aromatic species are more stable than their saturated counterparts. Part of their stability comes from having full bonding molecular orbitals and empty nonbonding and antibonding molecular orbitals. Taking away or adding an electron will destabilize the compound. Another stabilizing characteristic is the delocalization of electrons in the π system. This effect can be seen by examining the compound's resonance contributors.

Pyrrole and pyrrolidine have the same ring structure but differ in aromaticity. Pyrrole has six π electrons which are delocalized in a conjugated ring. The structure of pyrrole is not simple; instead it is described by five contributing resonance structures. The lone pair on the nitrogen is included in this aromatic system and nitrogen is given a partial positive charge as a result of this delocalization. One measure of aromaticity is a compound's resonance energy. Large resonance energies indicate stability and that the resonance contributors are more equivalent [29].

Resonance energy can be determined by comparing the experimental heat of hydrogenation of the molecule with a calculated heat of hydrogenation of a molecule which has isolated double bonds [30]. For pyrrole, the resonance energy is approximately 88 kJ/mol [29]. This can account for some of the difference in reactivity of pyrrole and pyrrolidine. In comparing the pyrrolidine reactions to the pyrrole reactions, one would expect the pyrrole reactions to produce less fragment ions since pyrrole is aromatic, but the opposite occurs when N^+ is the reactant ion, which may be due to the smaller ΔE value of the reaction of N^+ with pyrrolidine. The pyrrole reactions have slightly larger non-dissociative charge transfer product percentages than the corresponding pyrrolidine reactions, which is expected based on aromaticity arguments.

Benzene and cyclohexane also have the same ring structure, differing in aromaticity. Benzene's six π electrons are delocalized through two equivalent resonance contributors, giving 151 kJ/mol of resonance energy [29]. Benzene fragments less upon reaction, which is expected by its aromaticity, and gives much larger non-dissociative charge transfer product percentages than the same reactions with cyclohexane.

3.4.4 ISOMERS

When looking at the data from the reaction of benzene with N_2^+ , product ions $C_4H_4^+$ and $C_6H_5^+$ showed indications of being composed of two isomers, one reactive and one unreactive with neutral benzene. The counts of each product increased and then began decreasing until a constant signal remained. To determine the product percentages of each isomer, a kinetic model was fitted to the data according to the integrated rate laws given by the following equations:

$$[N_2^+] = [N_2^+]_0 \exp(-k_1 [C_6H_6] t) \quad (1)$$

$$[c - C_6H_5^+] = f_s [N_2^+]_0 (1 - \exp(-k_1 [C_6H_6] t)) \quad (2)$$

$$[l - C_6H_5^+] = \frac{k_1 f_l [N_2^+]_0}{k_2 - k_1} (\exp(-k_1 [C_6H_6] t) - \exp(-k_2 [C_6H_6] t)) \quad (3)$$

In these equations, $[\]$ denotes the concentration. The rate coefficient of the initial reaction of N_2^+ with benzene is given as k_1 , which includes f_l and f_s as the product fractions of reactive and unreactive isomers produced. The rate coefficient k_2 is for the further reaction of one of the isomers with benzene. The variables k_1 , k_2 , f_l , and f_s were changed until the modeled curve fit the experimental data. An example of this situation is given in Figure 3.1. Although this effect was not seen in the literature for $C_6H_5^+$ [21], we observed differing reactivities with benzene and were able to determine the percentages of the reactive versus unreactive isomers of $C_6H_5^+$. Despite the fact that we were unable to determine these structures experimentally, we assume the reactive isomer is the lower energy phenylium ion based on its reactivity with other hydrocarbons [31,32].

Similar equations were used to find product percentages of the $C_4H_4^+$ isomers. For the linear $C_4H_4^+$ isomer, vinyl acetylene ion, it has been established that there is a reaction whereas for the cyclic isomer, methylene cyclopropene ion, there is none [33].

3.5 CONCLUSIONS

The current study includes reactions with primary ions N_2^+ and N^+ , which are produced from the major neutral component of Titan's atmosphere, N_2 , and gives kinetic data useful for modelers. In Titan's atmosphere, the H_2 present [5] rapidly reacts with N_2^+ [14,19,34-36]. However, N^+ does not react with H_2 due to the large reaction barrier [37,38], so its chemistry is important in modeling Titan's ionosphere. Most of the reactions give many assorted fragmentation products, but there are some common ion products with sizable abundances. The ion product at m/z 41 ($C_3H_5^+$ and/or $C_2H_3N^+$) is observed in all studied reactions except for those with benzene. This m/z has been detected in Titan's atmosphere and is presumed to be $C_3H_5^+$ [7]. The assignment is logical since $C_3H_5^+$ does not react with H_2 or CH_4 [39,40] and $C_2H_3N^+$ will accept a proton from both species [41]. Common ions in the reactions of pyrrole and benzene are those at m/z 39 ($C_3H_3^+$ and/or C_2HN^+). This m/z has also been noted in Titan's ionosphere and is believed to be $C_3H_3^+$ [7]. The possibility of C_2HN^+ contributing to the ion density is not established because its reactions with H_2 and CH_4 have so far not been studied. The neutral HCN produced in reactions of N_2^+ with pyrrole and N^+ with both pyrrole and benzene is significant since this neutral is an important part of the chemistry of Titan and ISC and these reactions could provide partial sources. Benzene has been identified in both ISC [4] and Titan's atmosphere [6]. Pyrrole has yet to be detected, but PANHs are thought to be responsible for unidentified IR emissions [9] so the possibility of finding pyrrole is promising.

3.6 ACKNOWLEDGEMENTS

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Table 3.1. Experimental rate coefficients, k_{exp} , for the reactions of N^+ and N_2^+ with the neutrals listed, along with the theoretical gas kinetic rate coefficients, k_{theor} , established by parameterized trajectory calculations [20], rate coefficients from the literature [21,22], k_{lit} , included in parentheses when available. Values for polarizability [16,42,43] and dipole moment [24,44] of the neutrals were used to calculate the theoretical gas kinetic rate coefficients.

Primary Ion	$k_{exp} (10^{-9} \text{ cm}^3 \text{ s}^{-1})$	$k_{theor} (10^{-9} \text{ cm}^3 \text{ s}^{-1})$	Efficiency ^a
Pyrrole (C ₄ H ₅ N)			
N ⁺	3.47	3.31	1.05
N ₂ ⁺	3.03	2.53	1.20
Pyrrolidine (C ₄ H ₉ N)			
N ⁺	1.88	3.06	0.61
N ₂ ⁺	1.21	2.33	0.52
Benzene (C ₆ H ₆)			
N ⁺	2.56	2.19 (2.00)	1.17
N ₂ ⁺	1.85	1.66 (1.60)	1.11
Cyclohexane (C ₆ H ₁₂)			
N ⁺	2.04	2.34 (2.40)	0.87
N ₂ ⁺	1.56	1.69	0.92

^a Reaction efficiency, k_{exp}/k_{theor}

Table 3.2. Ion product distributions (%) for reactions between N^+ and N_2^+ and the neutrals listed along with literature ion product percentages in parentheses [21,25] when available. Actual abundances from electron impact ionization are included for discussion. Ionization energies are given under the neutrals and the recombination energies under the ions [26].

Neutral Reactant	Ion Product	N^+ 14.53 eV %	N_2^+ 15.53 eV %	EI 70 eV %
Pyrrole (C₄H₅N) 8.21 eV	C ₃ H ₃ ⁺ , C ₂ HN ⁺	14	38	16
	C ₃ H ₄ ⁺ , C ₂ H ₂ N ⁺	12	13	13
	C ₃ H ₅ ⁺ , C ₂ H ₃ N ⁺	8	27	15
	C ₄ H ₄ ⁺ , C ₃ H ₂ N ⁺	15	0	<1
	C ₄ H ₅ ⁺ , C ₃ H ₃ N ⁺	15	0	0
	C ₃ H ₄ N ⁺	16	0	0
	C ₄ H ₄ N ⁺	8	≤5	2
	C ₄ H ₅ N ⁺	12	17	24
	Pyrrolidine (C₄H₉N) 8.77 eV	C ₂ H ₆ ⁺ , CH ₄ N ⁺	0	10
C ₃ H ₅ ⁺ , C ₂ H ₃ N ⁺		7	13	6
C ₃ H ₆ ⁺ , C ₂ H ₄ N ⁺		0	23	9
C ₃ H ₇ ⁺ , C ₂ H ₅ N ⁺		63	45	36
C ₄ H ₈ N ⁺		24	≤2	10
C ₄ H ₉ N ⁺		6	7	7
Benzene (C₆H₆) 9.24 eV	^a C ₃ H ₃ ⁺	22(12)	12(17)	4
	l-C ₄ H ₄ ⁺	0(2)	30(36)	7
	c-C ₄ H ₄ ⁺	0(3)	7(5)	
	C ₅ H ₃ ⁺	0	≤3(2)	2
	C ₅ H ₄ ⁺	7(7)	0	0
	C ₆ H ₄ ⁺	0(1)	6(4)	2
	c-C ₆ H ₅ ⁺	0	19	
		(7)	(24)	11
	l-C ₆ H ₅ ⁺	0	≤2	
C ₆ H ₆ ⁺	71(68)	21(12)	39	
Cyclohexane (C₆H₁₂) 9.80 eV	C ₃ H ₅ ⁺	23	51(49)	14
	C ₃ H ₆ ⁺	8	6(7)	7
	C ₃ H ₇ ⁺	9	≤4	3
	C ₄ H ₇ ⁺	19	23(27)	7
	C ₄ H ₈ ⁺	28	6(12)	21
	C ₅ H ₇ ⁺	0	≤2	<1
	C ₅ H ₉ ⁺	≤3	0(1)	5
	C ₆ H ₁₁ ⁺	0	≤5	<1
	C ₆ H ₁₂ ⁺	10	≤3(6)	15

^aIdentified in literature as c-C₃H₃⁺.

Table 3.3. Energy differences, number of product channels, and aromaticity of neutrals (as given by Y for yes and N for no) for reactions listed.

Reactants	Energy Difference, ΔE	Number of Product Channels	Neutral Aromaticity
Pyrrole (C₄H₅N) 8.21 eV			Y
	N ⁺ 6.32 eV	8	
	N ₂ ⁺ 7.37 eV	5	
Pyrrolidine (C₄H₉N) 8.77 eV			N
	N ⁺ 5.76 eV	4	
	N ₂ ⁺ 6.81 eV	6	
Benzene (C₆H₆) 9.24 eV			Y
	N ⁺ 5.29 eV	3	
	N ₂ ⁺ 6.34 eV	8	
Cyclohexane (C₆H₁₂) 9.80 eV			N
	N ⁺ 4.73 eV	7	
	N ₂ ⁺ 5.78 eV	8	

^aCalculated by subtraction of ionization energy of neutral (listed under each species) from recombination energy of ion (14.53 eV for N⁺ and 15.58 eV for N₂⁺) [26].

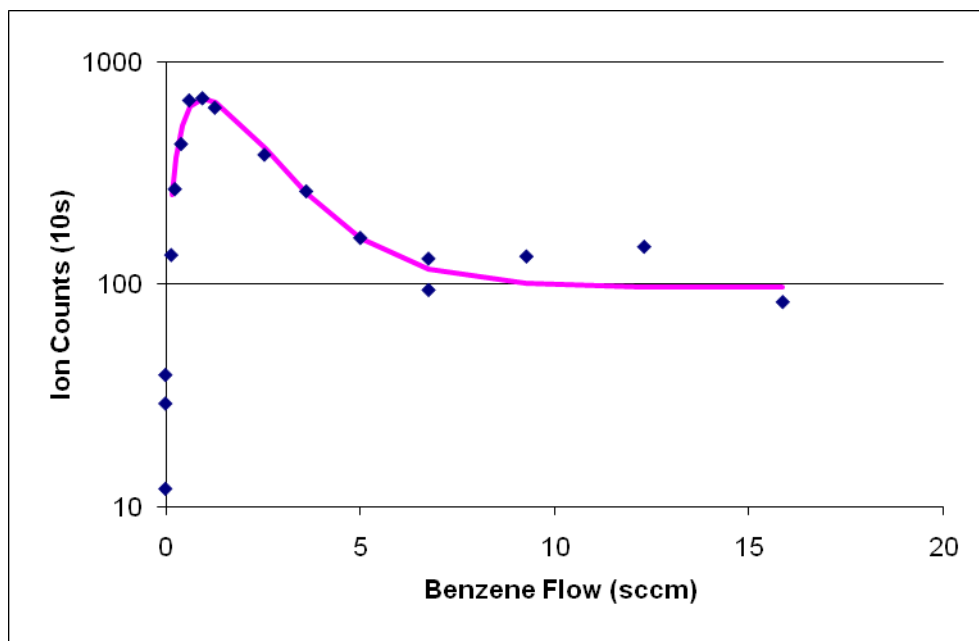


Figure 3.1. Behavior of the $C_6H_5^+$ ion product from the reaction of N_2^+ with benzene illustrating two isomeric forms and the modeled curve.

CHAPTER 4

CHARGE TRANSFER STUDIES OF GAS PHASE ION-MOLECULE REACTIONS¹

¹ Stavish, Leah, Fondren, L. Dalila, Adams, Nigel G. Int. J. Mass Spectrom., 2009, to be submitted.

4.1 ABSTRACT

The charge transfer reactions of a series of neutral compounds were studied with Xe^+ , Kr^+ , and Ar^+ using a selected ion flow tube (SIFT) at 298 K. The neutrals included aromatic homocyclic (benzene, C_6H_6) and heterocyclic (pyrimidine, $\text{C}_4\text{H}_4\text{N}_2$; pyridine, $\text{C}_5\text{H}_5\text{N}$; pyrrole, $\text{C}_4\text{H}_5\text{N}$) species and saturated homocyclic (cyclohexane, C_6H_{12}) and heterocyclic (pyrrolidine, $\text{C}_4\text{H}_9\text{N}$; piperidine, $\text{C}_5\text{H}_{11}\text{N}$) species. Also included were aromatics with a methyl group attached to the ring (2-methylpyridine, $\text{C}_6\text{H}_7\text{N}$; N-methylpyrrole, $\text{C}_5\text{H}_7\text{N}$) and a linear hydrocarbon chain (hexane, C_6H_{14}). Some reactions have been studied previously and most of those were not repeated here, but were included in the discussion. The stability of the neutrals was investigated based on reactivity and fragmentation patterns in these reactions. Charge transfer is energetically favorable in all of the reactions, but non-dissociative charge transfer typically occurs only with aromatic neutrals. Dissociative charge transfer is common, with varying amounts of fragmentation, and was compared with other ionization methods; laser, photo-, and electron impact ionization. Six-membered aromatic neutrals were found to be more stable than five-membered aromatic species, regardless of differing numbers of nitrogen atoms in the ring and additional methyl groups attached. The process of charge transfer in ion-molecule reactions is influential in controlling the degree of production of abundant ions in both the interstellar medium and the Titan atmosphere. Product distributions and rate coefficients were determined to provide kinetic data necessary to assist in modeling these media. Common ion and neutral products thought to be important in Titan's atmosphere are emphasized.

4.2 INTRODUCTION

Detection of molecules in the interstellar medium (ISM) began in 1937 with the detection of CH [1]. Detections of CN [2] and CH⁺ [3] soon followed, and currently approximately 160 molecules are known to exist there [4]. Of these, ~77% are organic, including many hydrocarbon and nitrile species. Several organic cyclic molecules have also been discovered including the aromatic ring benzene [5]. Diffuse interstellar absorption bands (DIBs) have been observed and have been attributed to polycyclic aromatic hydrocarbons (PAH's) [6,7] and PAH's with one or more nitrogen atoms substituted into the carbon skeleton of the ring (PANH's) [8]. To establish chemical routes to these species, models of the reactions thought to occur have been characterized [9] using kinetic reaction data, including product distributions and rate coefficients, determined in the laboratory [10]. Abundances of species detected in the interstellar medium are compared with abundances predicted by modelers to establish and confirm chemical routes.

Similar molecules have been observed in the ionosphere of Titan, a planetary satellite of Saturn. Detection of a dense planet-like atmosphere, composed of primarily nitrogen, led to exploration by the Voyager missions in the 1970's and 1980's [11]. Recently, the Ion and Neutral Mass Spectrometer (INMS) on the Cassini spacecraft has made *in situ* observations revealing a complex hydrocarbon and nitrile chemistry [12], including the identification of benzene [13] and other ring compounds [12]. The haze layers of Titan's atmosphere are believed to be comprised of heavy organic molecules and ions, and some of these are thought to be aromatic compounds [14]. Note that the Cassini INMS obtains only mass spectra of ions and neutrals and not the molecular composition. To deduce this requires modeling of the total atmospheric chemistry and comparison between the observed and predicted mass spectra.

Charge transfer in ion-molecule reactions occurs both in the ISM and in Titan's atmosphere. This reaction process plays a meaningful role in managing the degree of ionization of the abundant ions [15]. Stability of the molecules can be determined from the fragmentation patterns due to the excess energy following charge transfer. This is determined from the difference between the ionization energy (IE) of the neutrals and recombination energy (RE) of the ions. The neutral noble gases used as ions in this study, xenon, krypton, and argon, are present in the ISM [16], with ionized Ar and Kr implied as well [17]. The ionization potential of Xe is smaller than that of Ar and Kr, and thus ionization processes are thought to apply for the ionization of Xe. In Titan's atmosphere, only Ar has been detected. This is surprising given the reasoning that these gases have existed throughout the solar nebula, and consequently should have been included in the formation of both Saturn and Titan [18]. The neutrals in this study included aromatic and saturated rings, both homo- and heterocyclic, as well as a linear hydrocarbon chain. Reactions of Kr^+ and Ar^+ with the neutrals pyrimidine ($\text{C}_4\text{H}_4\text{N}_2$), pyridine ($\text{C}_5\text{H}_5\text{N}$), benzene (C_6H_6), and piperidine ($\text{C}_5\text{H}_{11}\text{N}$) have been studied previously and these studies were not repeated; the data are included to draw correlations with the reactions currently under study. The reaction of Ar^+ with benzene is the only reaction studied which has been investigated previously and is repeated here for comparison. Reactions of Xe^+ , Kr^+ , and Ar^+ and the neutrals cyclohexane (C_6H_{12}), pyrrolidine ($\text{C}_4\text{H}_9\text{N}$), and pyrrole ($\text{C}_4\text{H}_5\text{N}$) have not been reported before. Additionally, studies were made of the reactions of hexane (C_6H_{14}), 2-methylpyridine ($\text{C}_6\text{H}_7\text{N}$), and N-methylpyrrole ($\text{C}_5\text{H}_7\text{N}$) with the ions Xe^+ and Ar^+ . In addition, some of the reaction rate coefficients and ion product distributions add to the chemical kinetic data available to modelers, establishing chemical routes in the ISM and aiding interpretation of mass spectral data from Titan's atmosphere.

4.3 EXPERIMENTAL

A selected ion flow tube (SIFT) was used to study the ion-molecule reactions of Xe^+ , Kr^+ , and Ar^+ with the series of neutrals at room temperature (298 K). Ne^+ reactions were not studied due to the complex formed with the Helium carrier gas, NeHe^+ . No evidence for such ions was obtained for the other rare gases studied. The SIFT technique will not be discussed in detail here, since there is a considerable amount of literature on the subject [19,20]. The ions were produced in two different ionization sources from the gases xenon, argon and krypton. Both a low pressure ionization source and a microwave discharge source are suitable for this study because the ions involved are monatomic ions, which are readily produced. However, the microwave discharge source gave larger ion signals. A quadrupole mass filter selected the ions to be injected into the flow tube, where helium gas carried the ions downstream to a detection quadrupole/ion counting system. The He flow maintained the total pressure in the flow tube at ~ 0.5 Torr and was exhausted by a Roots pump after the ions were sampled. Reactant neutrals were introduced into the flow tube via ring type injectors downstream of the ion injection port so that the ions had time to thermalize by collisions ($\sim 10^7$) with the He.

Sigma-Aldrich provided the neutrals N-methylpyrrole (99%), pyrrole (98%), pyrrolidine (99.5%), pyridine (>99.9%), 2-methylpyridine (98%), cyclohexane ($\geq 99\%$), and hexane (95%). Piperidine and pyrimidine were obtained from Alfa Aesar, both with quoted purities of 99%, and benzene from Fisher Scientific with a purity of 99.5%. All of these neutrals are liquid at room temperature and their neat vapors condense on walls, making the stabilization and determination of flows difficult. To avoid this condensation, 1% mixtures were made of the neutrals, using less than the saturated vapor pressure in He. Before making the mixes, the vials of liquids were purified to remove dissolved gases by several freeze-pump-thaw cycles. Airgas, Inc. supplied

the ultra high purity He used for both mixture dilution and as the carrier gas. Additional purification of the He was performed by passing it through a molecular sieve trap cooled with liquid nitrogen. Rate coefficients and ion product distributions were determined in the standard way [19-22], and the dilution of reactant neutrals with He and mass discrimination in the detection quadrupole mass filter were accounted for. Rate coefficients for reactions with these sticky vapors are accurate to $\pm 25\%$ and product distributions to ± 5 in the percentage.

4.4 RESULTS AND DISCUSSION

The experimental rate coefficients, k_{exp} , measured in this study are given in Table 4.1. These are compared with the theoretical collision rate coefficients computed using parameterized trajectory calculations [23] to determine the efficiency of the reactions. The literature value of the rate coefficient for the reaction of Ar^+ with benzene is included in parentheses [24] and agrees well with our measurement. Most reactions proceed at the gas kinetic values within experimental error, but four are less efficient. It is unknown why these, the reactions of Xe^+ with N-methylpyrrole, pyrrolidine, and pyridine, and Kr^+ with pyrrolidine, are not as efficient as the other reactions studied. Although the reaction of Ar^+ with pyrrolidine is within experimental error, reactions with pyrrolidine are generally lower in efficiency [25-27].

Table 4.2 gives the ion product distributions for the reactions studied with the three ions, Xe^+ , Kr^+ , and Ar^+ , as well as some studied by Arnold et al. [24] and by Fondren et al [28]. Most of the determinations of ion product distributions previously reported were not repeated, but are included here to draw comparisons. Reactions of Xe^+ and Ar^+ with hexane, 2-methylpyridine, and N-methylpyrrole were studied to compare the relative stabilities of a straight chain hydrocarbon and the effects of methyl groups on the stability of pyridine and pyrrole rings. The

ion product distributions for these reactions are given in Table 4.3. Some of the ion products given in both Tables 4.2 and 4.3 can have more than one composition. It was generally not possible to distinguish the specific ion products on thermodynamics grounds because the lack of energetic information in the literature. Because of this, for each ion mass all possible products are given. However, in some cases, ion products were identified based on photoionization (PI) and femtosecond laser ionization dissociation patterns from the literature. Isotopic labeling can also provide structural information but is beyond the scope of this study.

Energetic considerations are generally useful in determining if a given reaction product channel is exothermic. Comparison of the IEs of the neutrals with the REs of the ions indicates if non-dissociative charge transfer is a favorable product channel. In all of these reactions, the IEs of the neutrals are less than the REs of the ions so that charge transfer is exothermic and this is observed. Note if a reaction channel is exothermic, the reaction does not necessarily occur. Although charge transfer in all of the reactions is exothermic, the non-dissociative charge transfer product is not always seen since the excess energy in the reaction can be used to produce fragmentation products. Fragmentation products in ion-molecule reactions can often be predicted by examining the electron impact (EI) ionization spectra of the neutral. The products seen there are the same products assumed following charge transfer in ion-molecule reactions, but note that abundances will differ due to differences in internal energy distributions of the two ionization processes [29]. PI and other dissociative ionization methods can suggest product fragments as well, but again the abundances differ from those in ion-molecule reactions [24,30]. The value of these comparisons is that fragmentation products seen in ion-molecule reactions, which are also seen in the EI spectrum of the neutral, can be assumed to proceed following charge transfer. If products are observed which are absent from the EI spectrum, another

reactive channel such as hydride abstraction or association could occur prior to fragmentation [29]. Discussion of the channels suspected to be precursors of fragmentation are included, based on this argument. Comparison of proton affinities (PAs) is a well known measure in determining whether proton transfer can occur in ion-molecule reactions. Hydride ion affinities (HIAs) provide the same utility for predicting if hydride abstraction can manifest, but these are not widely used. The hydride abstraction product channel is exothermic when the HIA value of the reactant ion is greater than the HIA value of the ion created from hydride abstraction of the neutral reactant. HIAs can be calculated relatively easily provided that the associated energetics are known [29]. For the reactions in this study, needed energetics for rare gas monohydrates are not in the literature due to the fact that they are Rydberg molecules and have unstable van der Waals ground states [31]. The HIAs for the neutrals in Table 4.2 were calculated and found to be piperidine (838.3 kJ/mol) < cyclohexane (1048.3 kJ/mol) < pyridine (1144.8 kJ/mol) < pyrrolidine (1164.2 kJ/mol) < pyrimidine (1177.4 kJ/mol) < benzene (1223.5 kJ/mol) < pyrrole (1268.1 kJ/mol). It can be reasonably assumed that when hydride abstraction is seen the HIA of the reactant ion is greater than the HIA of the hydride abstraction product ion.

Reactions with the ion of lowest recombination energy, Xe^+ (RE: 12.13 eV), give the non-dissociative charge transfer as the main product channel for the aromatic reactant neutrals pyrimidine ($\text{C}_4\text{H}_4\text{N}_2$), pyridine ($\text{C}_5\text{H}_5\text{N}$), benzene (C_6H_6), pyrrole ($\text{C}_4\text{H}_5\text{N}$), 2-methylpyridine ($\text{C}_6\text{H}_7\text{N}$), and N-methylpyrrole ($\text{C}_5\text{H}_7\text{N}$). In these reactions, the saturated neutrals cyclohexane (C_6H_{12}), pyrrolidine ($\text{C}_4\text{H}_9\text{N}$), piperidine ($\text{C}_5\text{H}_{11}\text{N}$), and hexane (C_6H_{14}) yield fragmentation as the main product channel, showing no non-dissociative charge transfer product and only small hydride abstraction products. N-methylpyrrole is the only aromatic neutral studied which exhibits a hydride abstraction product when reacted with Xe^+ .

Kr^+ has a higher recombination energy (RE: 14.00 eV) than Xe^+ and generally produces more fragmentation products, as expected. Non-dissociative charge transfer ion products are observed for Kr^+ reactions with all aromatic neutrals except pyridine, and is the main product channel in the reaction with benzene. This product channel is seen with the saturated cyclic molecule cyclohexane as well. Hydride abstraction products are observed for reactions with cyclohexane, benzene, pyrrolidine, and pyrrole. The main product channel for Kr^+ reactions with all reactant neutrals, other than benzene, results from fragmentation.

The ion with the greatest recombination energy in this study is Ar^+ (RE: 15.76 eV); thus more energy is available for fragmentation of the neutrals. Reactions with the aromatic neutrals pyrimidine, benzene, and 2-methylpyridine and the saturated cyclic molecule piperidine all give non-dissociative charge transfer ion products though the percentages of these products are small. All Ar^+ reactions with aromatic neutrals, besides pyrimidine, show hydride abstraction products, and these product channels are not observed with any of the saturated neutrals. The main product channel for all Ar^+ reactions studied is fragmentation.

4.4.1 CYCLIC HYDROCARBONS: CYCLOHEXANE AND BENZENE

The main product in all reactions studied with cyclohexane results from fragmentation, however the main ion product is C_4H_8^+ for the reactions with the lower recombination energy ions Xe^+ and Kr^+ while for the Ar^+ reaction, the main product is C_3H_5^+ . Non-dissociative charge transfer surprisingly only occurs in the reaction with Kr^+ . Hydride abstraction is not seen for the reaction with Ar^+ but exists in small percentages for the other ions. All of the product ions from reactions of cyclohexane are found on its EI spectrum and can be thought of resulting after charge transfer. The hydride abstraction product has an abundance of only 1% on the EI

spectrum and is not seen in the PI spectrum of cyclohexane [32]. This could indicate that the hydride abstraction product is formed directly by hydride abstraction rather than following the charge transfer product channel.

The reaction of Kr^+ with cyclohexane produces $\text{C}_6\text{H}_{11}^+$ and $\text{C}_6\text{H}_{12}^+$ which are at the same mass-to-charge ratio (m/z) as the Krypton isotopes $^{83}\text{Kr}^+$ and $^{84}\text{Kr}^+$. Elimination of all but one injected isotope was not possible. To determine the amount of counts attributed to product ions, a kinetic model was fitted to the data. Integrated rate laws gave the following equations:

$$[{}^{84}\text{Kr}^+] = [{}^{84}\text{Kr}^+]_0 \exp[-\text{C}_6\text{H}_{12}]kt \quad (4.1)$$

$$[\text{C}_6\text{H}_{12}^+] = f_s [{}^{84}\text{Kr}^+]_0 (1 - (\exp[-\text{C}_6\text{H}_{12}]kt)) \quad (4.2)$$

In these equations, $[\]$ indicates the concentration and the rate coefficient is given as k , which includes f_s as the product fraction of the ion product under study. Adding $[{}^{84}\text{Kr}^+]$ and $[\text{C}_6\text{H}_{12}^+]$ counts together gave the modeled counts of m/z 84. The values of k and f_s in the model were varied until the modeled curve fit the experimental data, as seen in Figure 4.1.

The ion product distributions for the benzene reactions are as expected due to the aromatic stability of this neutral. Non-dissociative charge transfer is the main product channel for reactions with Xe^+ and Kr^+ and is observed in a small percentage with Ar^+ . This is the only product channel observed in the Xe^+ reaction and the literature reaction with $\text{Kr}^+(^2\text{P}_{3/2})$. The literature reaction with $\text{Kr}^+(^2\text{P}_{1/2})$ contains a second product which is formed by hydride abstraction, and this product is seen in the reaction with Ar^+ as well. Although Arnold et al. [24] reported different product distributions for the two spin states of Kr^+ , separating spin states is beyond the scope of the current study. Note that Xe^+ , Kr^+ , and Ar^+ showed no evidence of differing reaction rates due to the two spin states. This implies only the lower spin state ($^2\text{P}_{3/2}$) was present. The main product in benzene's reaction with Ar^+ , $l\text{-C}_4\text{H}_4^+$, is formed from

fragmentation. The only product seen in the benzene reactions, but absent in the EI and PI [24] spectra, is the fragment $C_4H_5^+$ and could occur via fragmentation after hydride abstraction or association.

Cyclohexane and benzene are six membered cyclic hydrocarbons, but cyclohexane is saturated while benzene is aromatic. This effect is evident when comparing the reactivities of the two neutrals. Cyclohexane fragments more than benzene in all reactions, except with Ar^+ . Non-dissociative charge transfer proceeds in all benzene reactions and is the main product in the benzene reactions with Xe^+ and Kr^+ . This type of product channel is observed in only one cyclohexane reaction; Kr^+ gives a 12% product. There are no common ion products in the cyclohexane and benzene reactions.

4.4.2 CYCLIC 5-MEMBERED N-CONTAINING: PYRROLIDINE AND PYRROLE

Non-dissociative charge transfer does not occur in any of the pyrrolidine reactions. Hydride abstraction products are seen with Xe^+ and Kr^+ . The main product in all of the reactions is the fragmentation product $C_2H_5N^+$. Kr^+ and Ar^+ reactions have almost the same fragmentation products. No PI spectra were available in the literature for comparison, but all of the pyrrolidine ion products are seen in its EI spectrum and observed when pyrrolidine is ionized via femtosecond laser ionization in an intense 800 nm laser field [30]. The ion product $C_2H_5N^+$ was assigned based on known unimolecular dissociation mechanisms [33]. Assignments of other ions given in the product distributions were determined from dissociation schemes in the literature [30]. Note that all fragments formed incorporate nitrogen into the ion product and leave hydrocarbon neutrals.

The main product in the reaction of Xe^+ with pyrrole is non-dissociative charge transfer. This product channel is seen in a small percentage in the reaction with Kr^+ and is absent in the Ar^+ reaction. The hydride abstraction product is present in the pyrrole reactions with Kr^+ and Ar^+ , and in similar percentages. The major product in the Kr^+ and Ar^+ reactions results from fragmentation and is $\text{C}_2\text{H}_3\text{N}^+$ for the Kr^+ reaction and $\text{C}_3\text{H}_3^+/\text{C}_2\text{HN}^+$ for the Ar^+ reaction. m/z 53 ($\text{C}_4\text{H}_5^+/\text{C}_3\text{H}_3\text{N}^+$) is the only ion product which is absent from pyrrole's EI and PI [34] spectra and would have to be formed following a reactive channel other than charge transfer. Ion assignments given for fragmentation products are from the literature when available [34].

In comparing the stability of the five-membered nitrogen-containing ring compounds, saturated pyrrolidine and aromatic pyrrole, both neutrals produce a comparable amount of fragmentation products with each ion. However, non-dissociative charge transfer is not seen with pyrrolidine, whereas this is the main product in the reaction of pyrrole with Xe^+ and a small product in the reaction of pyrrole with Kr^+ . Also, the hydride abstraction product is seen in reactions of pyrrolidine with Xe^+ and Kr^+ in greater percentages than the Kr^+ and Ar^+ reactions with pyrrole which give this product. Pyrrole's stability is understood to be due to the delocalization of π electrons in this aromatic system [35,36].

4.4.3 CYCLIC 6-MEMBERED N-CONTAINING: PIPERIDINE, PYRIDINE, AND PYRIMIDINE

The piperidine reaction with Xe^+ and the reactions with Kr^+ and Ar^+ [28] produce many fragmentation products. Interestingly, non-dissociative charge transfer is only observed for the reaction with Ar^+ , which is the ion with the greatest recombination energy, but gives only a 4% product. Hydride abstraction is seen only in the reaction with Xe^+ in a small percentage.

$C_5H_9N^+$ is the main product in the Xe^+ reaction, while the main product for both the Kr^+ and Ar^+ reactions is $C_4H_8^+/C_3H_6N^+$. This ion is also present in the product distribution for the reaction with Xe^+ and is a sizable product (20%). m/z 69 ($C_5H_9^+/C_4H_7N^+$) and 79 ($C_5H_5N^+$) are absent in piperidine's EI spectrum, but are seen in its reaction with Xe^+ . It is interesting that the main product in the Xe^+ reaction has an abundance of $\leq 1\%$ on the EI spectrum and the product may be formed via a product channel other than charge transfer because this is the only case that the main product is not formed following charge transfer. Ion product assignments based on dissociation patterns given in the literature is not possible here since no PI or other ionization methods are available and the EI spectrum reports only m/z values.

The pyridine reaction with Xe^+ and the reactions with Kr^+ and Ar^+ in the literature [28] give few fragmentation products. Non-dissociative charge transfer is seen only in the Xe^+ reaction, in which it is the major product. The main product in the reactions with Kr^+ and Ar^+ is $C_4H_4^+$ which is seen as the only fragmentation product in the reaction with Xe^+ . The pyridine reaction with Ar^+ reaction gives the hydride abstraction product, which is not seen in the other two reactions. When comparing the ion products to the EI fragments, all products occur in the EI spectrum and are thought to result from dissociative charge transfer. Literature PI fragmentation allowed the assignment of the m/z 52 product as $C_4H_4^+$ [37].

The pyrimidine reaction with Xe^+ and data on the reactions with Kr^+ and Ar^+ from the literature [28] all show non-dissociative charge transfer products. This is the main product channel in the Xe^+ reaction, accounting for 84%. Non-dissociative charge transfer products are present at small percentages in the Kr^+ and Ar^+ reactions as well, with 3% and 4% respectively. $C_3H_3N^+$ is the major product of the Kr^+ and Ar^+ reactions and is also seen in the Xe^+ reaction. Pyrimidine's EI spectrum contains the majority of fragments seen in the product distribution of

the Xe^+ , Kr^+ , and Ar^+ reactions, only $\text{C}_4\text{H}_2\text{N}_2^+$ is absent. However, the literature PI reports this ion [37], so the mechanism by which it was formed is cannot be deduced. The ion product $\text{C}_3\text{H}_4\text{N}^+$, which is reported in the literature as a 3% product for the reaction with Kr^+ , is not seen in the PI spectrum [37] and has $\leq 1\%$ abundance in the EI spectrum. The product percentage for this ion is negligible and could be included in the associated error in the product distribution. Ion assignments reported were taken from the literature [37].

Piperidine, pyridine, and pyrimidine are six-membered rings that contain nitrogen. Piperidine and pyridine both contain one nitrogen atom in their rings, but piperidine is saturated whereas pyridine is aromatic. Pyrimidine is aromatic also, but two nitrogen atoms are present in this ring compound. More fragmentation is expected and seen in reactions with piperidine since it is saturated. Pyrimidine reactions generally produce more fragments than the same reactions with pyridine, but non-dissociative charge transfer products occur for all pyrimidine reactions studied while only the Xe^+ reaction with pyridine gives this product channel.

4.4.4 ADDITIONAL STUDIES: HEXANE, 2-METHYLPYRIDINE, AND N-METHYLPYRROLE

These additional studies were made only with the ions of lowest and highest recombination energy, Xe^+ and Ar^+ , to study the reactivities of the three neutrals.

Hexane is a straight chain hydrocarbon studied for comparison with reactions of cyclohexane. Non-dissociative charge transfer is not seen in any hexane reaction. The major product in the Xe^+ reaction is C_4H_9^+ and this product distribution also contains a 5% hydride abstraction product; neither of these products are seen in the Ar^+ reaction with hexane. The major product in the Ar^+ reaction is C_3H_5^+ , which is absent in the Xe^+ reaction. The $\text{C}_5\text{H}_{10}^+$

fragmentation product from the reaction with Xe^+ is absent in both the EI and PI [32] spectra, so its formation is considered to result from a reactive channel other than charge transfer. Other ions not present in the PI spectra are C_2H_3^+ , C_2H_4^+ , and C_4H_7^+ which are all products in the reaction with Ar^+ . C_2H_3^+ has an abundance of 9% in the EI spectrum and is believed to form in charge transfer, but the two ions C_2H_4^+ and C_4H_7^+ have negligible EI abundances so may result from another product mechanism. C_2H_4^+ is a minor product in this reaction and might be attributed to the error of ± 5 in the percentage of the product distribution.

In comparing hexane reactions with cyclohexane reactions, hexane reactions produce only dissociative charge transfer fragmentation products and cyclohexane gives the non-dissociative charge transfer product with Kr^+ and hydride abstraction products with both Xe^+ and Kr^+ . The Xe^+ reactions with hexane and cyclohexane contain similar amounts of fragmentation products. However, the hexane reaction with Ar^+ produces more fragments than its reaction with cyclohexane, indicating the comparable stability of the saturated ring and linear compounds.

2-methylpyridine is an aromatic compound with its methyl group on the carbon next to the nitrogen in the ring. Both reactions with this neutral give non-dissociative charge transfer products, and this the major product of the Xe^+ reaction. The Xe^+ reaction with 2-methylpyridine only has one other product which is a fragmentation product at m/z 66 ($\text{C}_5\text{H}_6^+/\text{C}_4\text{H}_4\text{N}^+$). The Ar^+ reaction gives the hydride abstraction product in addition to many fragmentation products. The EI spectrum does not indicate the negligible $\text{C}_5\text{H}_6\text{N}^+$ product formed in the Ar^+ reaction so it may be included in the error of the product distribution. Unfortunately, the literature lacks PI or other dissociative ionization studies for comparison with our data.

In comparing this neutral to its non-methylated counterpart, the results are very similar for the reactions with Xe^+ . Both neutrals give 94% non-dissociative charge transfer as the main product channel and contain only one other product which is a different fragment ion for each reaction. However, there is a 5% non-dissociative charge transfer product in the reaction of Ar^+ with 2-methylpyridine whereas none with pyridine, although this product could be attributed to the error associated with the product distribution. Ar^+ reactions with both pyridine and 2-methylpyridine give hydride abstraction products in nearly the same percentages, but the 2-methylpyridine reaction produces many more fragmentation products. The methyl group on the ring does not seem to provide much, if any, stabilization.

N-methylpyrrole has its methyl group on the nitrogen in the pyrrole ring, maintaining aromaticity. In its reaction with Xe^+ , it gives non-dissociative charge transfer as the main product channel as well as a 30% hydride abstraction product. Products seen in the reaction of N-methylpyrrole with Xe^+ are observed in the reaction with Ar^+ , excluding the non-dissociative charge transfer product. All of the products from these reactions are also observed in the EI spectrum of N-methylpyrrole and are expected to form via dissociative charge transfer. PI and other dissociative ionization methods were not available in the literature for this neutral.

Compared to the pyrrole reactions, the N-methylpyrrole product distributions are similar in that the main product in the Xe^+ reactions is non-dissociative charge transfer. However, the Xe^+ reaction with pyrrole has no hydride abstraction and the same reaction with N-methylpyrrole has a significant hydride abstraction product. Both Ar^+ reactions have comparable hydride abstraction products and the Ar^+ reaction with N-methylpyrrole produces more fragmentation. This indicates that the methyl group is not stabilizing in this case.

4.5 CONCLUSIONS

Significant non-dissociative charge transfer typically occurs only when aromatic species are reactant neutrals. When the ion with the lowest RE studied, Xe^+ , is the primary ion, the aromatic neutrals give this as the major product channel and product percentages decrease, and in some cases vanish, as the RE of the ion increases. Even when non-dissociative charge transfer is the main product, other fragmentation products exist with the exception of the benzene reaction with Xe^+ . This indicates that benzene is the most stable compound in this study. For reactions with benzene, pyrimidine, and 2-methylpyridine, the non-dissociative charge transfer product is seen for all reactant ions. Although this product channel is only seen in the pyridine reaction with Xe^+ , few fragmentation products exist in pyridine reactions with all three ions. This result demonstrates that the six-membered aromatic neutrals studied are more stable than the five-membered aromatic species, even with differing numbers on nitrogen atoms in the ring and with methyl groups added. When hydride abstraction products are seen for aromatic species, they are produced with higher RE ions, while they are generated with lower RE ions for saturated neutrals. This observation follows the trend of the known HIAs for the neutrals in Table 2, except that the aromatic pyridine has a HIA value smaller than that of the saturated pyrrolidine. The aromatic N-methylpyrrole reactions produce hydride abstraction products with both the lower RE ion Xe^+ and the higher RE ion Ar^+ . The main products in reactions with saturated compounds are fragmentation products and main products differ for aromatics depending on the excess energy in the reaction.

A variety of fragmentation products exist in the reactions studied. Some common ion products which are also identified as abundant ions in Titan's atmosphere include m/z 39 (C_3H_3^+), 41 (C_3H_5^+) [12], 42 (CH_3CNH^+) [38], and 52 ($\text{C}_3\text{H}_2\text{N}^+$) [12]. The stable ion C_3H_3^+ is

seen as a product ion in the Ar^+ reaction with benzene. Its m/z is seen as a product ion in Ar^+ reactions with pyrrole, pyridine, and N-methylpyrrole and the reaction of Kr^+ with pyrrole, although ion compositions could not be defined in this study. For ions with m/z 41, the reactions of cyclohexane with Ar^+ and Kr^+ and hexane with Ar^+ produce C_3H_5^+ as a product ion. However the product ion at this m/z could not be assigned when seen in the piperidine reactions with Xe^+ and Ar^+ . This m/z was assigned based on literature dissociation patterns as $\text{C}_2\text{H}_3\text{N}^+$ in all pyrrole reactions studied and pyrrolidine reactions with Kr^+ and Ar^+ . CH_3CNH^+ is a possible ion product in the Ar^+ reactions with pyrrolidine, piperidine, and N-methylpyrrole, the reaction of pyrrolidine with Kr^+ , and also the reaction of piperidine with Xe^+ . The same m/z value is seen in all reactions studied with both cyclohexane and hexane, but with these hydrocarbons as reactant neutrals, it must be assigned as C_3H_6^+ .

The ion product distributions in Tables 4.2 and 4.3 do not list the probable neutral products because in many cases it is difficult to assign even the ion products due to lack of energetic information in the literature. Still many reactions can produce several neutrals which are abundant in Titan's atmosphere. C_2H_2 [38] may be created in the reactions of Ar^+ with benzene (with C_4H_4^+), pyridine (with $\text{C}_3\text{H}_3\text{N}^+$), 2-methylpyridine (with $\text{C}_4\text{H}_5\text{N}^+$), and N-methylpyrrole (with $\text{C}_3\text{H}_5\text{N}^+$), and the Kr^+ reaction with pyrimidine (with $\text{C}_3\text{H}_4\text{N}^+$) as well as all the pyrrole reactions studied (with $\text{C}_2\text{H}_3\text{N}^+$). HCN is an important neutral in both Titan's atmosphere [38] and the ISM [39]. This neutral is a possible product in all reactions studied with the neutrals pyridine (with C_4H_4^+), pyrimidine (with $\text{C}_3\text{H}_3\text{N}^+$), 2-methylpyridine (with C_5H_6^+), and N-methylpyrrole (with C_4H_6^+). Additionally, the reactions of Xe^+ and Kr^+ with pyrrole can also produce HCN (with C_3H_4^+). The neutral C_2H_4 [38] is common in Ar^+ reactions with 2-methylpyridine (with $\text{C}_4\text{H}_3\text{N}^+$), and N-methylpyridine (with $\text{C}_3\text{H}_3\text{N}^+$), and the reactions of both

Kr⁺ and Ar⁺ with piperidine (with C₃H₇N⁺), pyrrole (with C₂HN⁺), and pyrimidine (with C₂N₂⁺). All reactions of cyclohexane and pyrrolidine studied can give neutral C₂H₄ as a neutral product, with ion products C₄H₈⁺ and C₂H₅N⁺ respectively, in large abundance.

Kinetic laboratory data is vital for modeling the ISM and especially the Titan atmosphere. Although benzene is the only neutral in this study which has been detected in Titan's atmosphere, protonated benzene and ionized pyridine are present [12] and other ring compounds are likely to be found given that Titan's haze layers are thought to be comprised of heavy organic compounds [14]. The dominate chemistry occurring here consists of hydrocarbon and nitrile species [12], and charge transfer reactions regulate the degree of ionization in these systems [15].

4.6 ACKNOWLEDGEMENTS

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Table 4.1. Experimental rate coefficients, k_{exp} , for the neutrals molecules indicated studied with Xe^+ , Kr^+ , and Ar^+ . These are followed by the theoretical gas kinetic rate coefficients, k_{theor} ,^a established using parameterized trajectory calculations. A literature rate coefficient value for $Ar^+ + C_6H_6$ [24] is included in parentheses.

Primary Ion	k_{exp} ($\times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	k_{theor} ($\times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	Efficiency ^b
Hexane (C_6H_{14})			
Xe^+	1.15	1.11	1.04
Ar^+	1.54	1.54	1.00
Cyclohexane (C_6H_{12})			
Xe^+	1.00	1.09	0.92
Kr^+	1.18	1.20	0.98
Ar^+	1.66	1.50	1.11
2-methylpyridine (C_6H_7N)			
Xe^+	1.88	1.66	1.13
Ar^+	2.51	2.31	1.09
Pyrimidine ($C_4H_4N_2$)			
Xe^+	2.02	1.90	1.06
Pyridine (C_5H_5N)			
Xe^+	1.35	1.86	0.73
Benzene (C_6H_6)			
Xe^+	1.16	1.08	1.07
Ar^+	1.37 (1.30)	1.47	0.93
Pyrrolidine (C_4H_9N)			
Xe^+	0.952	1.55	0.61
Kr^+	1.10	1.69	0.65
Ar^+	1.78	2.07	0.86
Pyrrole (C_4H_5N)			
Xe^+	1.44	1.69	0.85
Kr^+	1.76	1.85	0.95
Ar^+	2.73	2.26	1.21
Piperidine ($C_5H_{11}N$)			
Xe^+	1.09	1.14	0.96
N-methylpyrrole (C_5H_7N)			
Xe^+	1.28	1.85	0.69
Ar^+	1.98	2.54	0.78

^aNeutral polarizabilities and dipole moments used to calculate the theoretical rate coefficients were obtained from the literature [40-45].

^bReaction efficiency, k_{exp}/k_{theor} .

Table 4.2. Ion product distributions (%) for the reactions of Xe⁺, Kr⁺, and Ar⁺ with the neutral molecules listed, with literature values [24,28] indicated by parentheses and electron impact (EI) abundances [46] provided for discussion. Recombination energies of the ions, ionization energies of the neutrals, and electron energy in the electron impact fragmentation are included [46].

Neutral Reactant	Ion Product	Xe ⁺	Kr ⁺	Ar ⁺	EI
		12.13 eV %	14.00 eV %	15.76 eV %	70.00 eV %
Cyclohexane (C₆H₁₂) 9.88 eV	C ₃ H ₅ ⁺		16	67	14
	C ₃ H ₆ ⁺	12	9	12	7
	C ₃ H ₇ ⁺	7	6		3
	C ₄ H ₇ ⁺	10	19	17	7
	C ₄ H ₈ ⁺	46	31	4	21
	C ₅ H ₉ ⁺	16	4		5
	C ₆ H ₁₁ ⁺	9	3		≤1
	C ₆ H ₁₂ ⁺		12		15
Pyrimidine (C₄H₄N₂) 9.33 eV	C ₂ H ₂ ⁺			(21)	13
	C ₃ H ₂ N ⁺ , C ₄ H ₄ ⁺ , C ₂ N ₂ ⁺		(3)	(22)	7
	^a C ₃ H ₃ N ⁺ , C ₂ HN ₂ ⁺	12	(91)	(54)	18
	C ₃ H ₄ N ⁺		(3)		≤1
	C ₄ H ₂ N ₂ ⁺	4			
C ₄ H ₄ N ₂ ⁺	84	(3)	(4)	47	
Pyridine (C₅H₅N) 9.26 eV	C ₃ H ₃ ⁺ , C ₂ NH ⁺			(7)	3
	C ₄ H ₄ ⁺	6	(c-30; l-70)	(66)	24
	C ₄ H ₅ ⁺ , C ₃ H ₃ N ⁺			(12)	3
	C ₃ H ₄ N ⁺			(15)	5
C ₅ H ₅ N ⁺	94			42	
Benzene (C₆H₆) 9.24 eV	C ₃ H ₃ ⁺			12 (c-13)	4
	C ₄ H ₄ ⁺			c-10 (7); l-33 (48)	7
	C ₄ H ₅ ⁺			3	
	C ₅ H ₅ ⁺			3 (3)	2
	C ₆ H ₄ ⁺			5 (3)	2
	C ₆ H ₅ ⁺		^b (² P _{1/2} : 18)	27 (18)	11
C ₆ H ₆ ⁺	100	^b (² P _{1/2} : 82; ² P _{3/2} : 100)	7 (8)	39	
Pyrrolidine (C₄H₇N) 8.77 eV	CH ₂ N ⁺		9	21	8
	CH ₄ N ⁺		4	4	3
	C ₂ H ₃ N ⁺		5	21	6
	C ₂ H ₄ N ⁺		12	20	9
	C ₂ H ₅ N ⁺	72	56	34	36
	C ₄ H ₈ N ⁺	28	14		10
Pyrrole (C₄H₅N) 8.21 eV	CH ₂ N ⁺		14		12
	C ₃ H ₃ ⁺ , C ₂ HN ⁺		12	80	16
	C ₃ H ₄ ⁺ , C ₂ H ₂ N ⁺	13	28		13
	C ₂ H ₃ N ⁺	16	30	5	15
	C ₃ H ₂ N ⁺			4	≤1
	C ₄ H ₅ ⁺ , C ₃ H ₃ N ⁺			5	5
	C ₄ H ₄ N ⁺		8	6	2
	C ₄ H ₅ N ⁺	71	8		24
Piperidine (C₅H₁₁N) 8.03 eV	C ₂ H ₄ ⁺ , CH ₂ N ⁺		(3)	(8)	6
	C ₂ H ₅ ⁺ , CH ₃ N ⁺		(15)	(19)	6
	C ₂ H ₆ ⁺ , CH ₄ N ⁺		(7)	(9)	6
	C ₃ H ₅ ⁺ , C ₂ H ₃ N ⁺	2		(8)	2
	C ₃ H ₆ ⁺ , C ₂ H ₄ N ⁺	9		(7)	5
	C ₃ H ₇ ⁺ , C ₂ H ₅ N ⁺	13		(2)	5
	C ₃ H ₈ ⁺ , C ₂ H ₆ N ⁺			(4)	7
	C ₄ H ₇ ⁺ , C ₃ H ₅ N ⁺	12		(10)	2
	C ₄ H ₈ ⁺ , C ₃ H ₆ N ⁺	20	(44)	(26)	9
	C ₄ H ₉ ⁺ , C ₃ H ₇ N ⁺		(31)	(3)	9
	C ₅ H ₉ ⁺ , C ₄ H ₇ N ⁺	4			
	C ₅ H ₅ N ⁺	7			
	C ₅ H ₉ N ⁺	30			≤1
	C ₅ H ₁₀ N ⁺	3			20
C ₅ H ₁₁ N ⁺			(4)	11	

^aIon assigned here as C₃H₃N⁺[37], but reported in the literature as either of the two ions.

^bSeparate reactions of the Kr⁺ spin states [24].

Table 4.3. Ion product distributions (%) for the reactions of Xe⁺ and Ar⁺ with the neutral molecules listed along with electron impact (EI) abundances [46] provided for discussion. Recombination energies of the ions, ionization energies of the neutrals, and electron energy used for ionization are included [46].

		Xe ⁺	Ar ⁺	EI
		12.13 eV	15.76 eV	70.00 eV
Neutral Reactant	Ion Product	%	%	%
Hexane (C₆H₁₄) 10.13 eV	C ₂ H ₃ ⁺		≤3	9
	C ₂ H ₄ ⁺		≤2	2
	C ₂ H ₅ ⁺		22	12
	C ₃ H ₅ ⁺		47	13
	C ₃ H ₆ ⁺	10	5≤	8
	C ₃ H ₇ ⁺	14	15	12
	C ₄ H ₇ ⁺		6	≤1
	C ₄ H ₈ ⁺	17		9
	C ₄ H ₉ ⁺	52		19
	C ₅ H ₁₀ ⁺	≤2		
C ₅ H ₁₁ ⁺	≤5		≤1	
2-methylpyridine (C₆H₇N) 9.37 eV	C ₄ H ₄ ⁺ , C ₃ H ₂ N ⁺		6	3
	C ₄ H ₅ ⁺ , C ₃ H ₃ N ⁺		7	≤1
	C ₄ H ₆ ⁺ , C ₃ H ₄ N ⁺		≤4	≤1
	C ₅ H ₅ ⁺ , C ₄ H ₃ N ⁺		10	6
	C ₅ H ₆ ⁺ , C ₄ H ₄ N ⁺	6	18	14
	C ₅ H ₇ ⁺ , C ₄ H ₅ N ⁺		7	4
	C ₅ H ₄ N ⁺		21	6
	C ₅ H ₅ N ⁺		≤4	≤1
	C ₅ H ₆ N ⁺		≤2	
	C ₆ H ₆ N ⁺		16	8
C ₆ H ₇ N ⁺	94	≤5	27	
N-methylpyrrole (C₅H₇N) 7.99 eV	C ₃ H ₃ ⁺ , C ₂ HN ⁺		7	7
	C ₃ H ₆ ⁺ , C ₂ H ₄ N ⁺		12	7
	C ₄ H ₄ ⁺ , C ₃ H ₂ N ⁺		≤2	≤1
	C ₄ H ₅ ⁺ , C ₃ H ₃ N ⁺		39	8
	C ₄ H ₆ ⁺ , C ₃ H ₄ N ⁺	≤4	≤4	4
	C ₄ H ₇ ⁺ , C ₃ H ₅ N ⁺	≤3	13	4
	C ₅ H ₆ ⁺ , C ₄ H ₄ N ⁺		≤5	≤1
	C ₅ H ₄ N ⁺		9	2
	C ₅ H ₆ N ⁺	30	9	22
C ₅ H ₇ N ⁺	63		30	

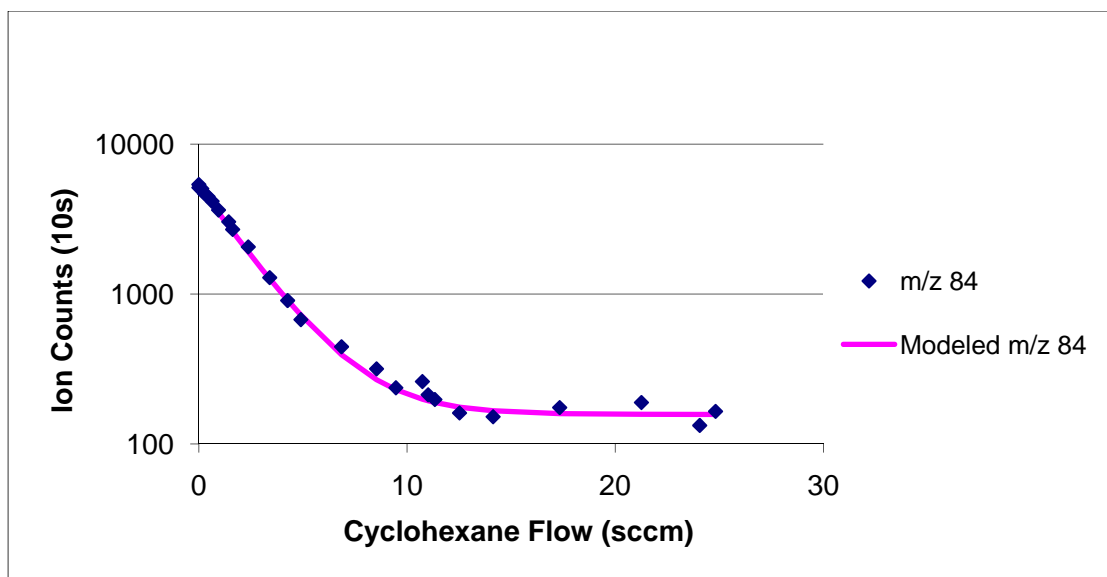


Figure 4.1. Ion and product counts of m/z 84 ($^{84}\text{Kr}^+$ and $\text{C}_6\text{H}_{12}^+$) for the reaction of Kr^+ with cyclohexane. The dots represent experimental data and the curve was created from the integrated rate laws of the model. See equations 4.1 and 4.2.

CHAPTER 5

CONCLUSIONS AND FUTURE DIRECTIONS

Ion-molecule reactions have been studied to provide kinetic data for models of the ISM and Titan's atmosphere and to investigate the stabilities of neutral molecules which are of possible importance in these media. Non-dissociative charge transfer typically only occurred with aromatic neutrals. Even in reactions where this product channel was seen in large abundance, dissociative charge transfer products were also observed, except in the reaction of benzene with Xe^+ which has the smallest RE of the ions studied. Six-membered aromatic neutrals were shown to be more stable than five-membered aromatic neutrals regardless of the number of nitrogen atoms in the ring or methyl groups attached. Saturated neutrals produced many fragmentation products, as expected by aromaticity considerations.

In most cases, there were multiple product structures possible at each m/z . Product ions could not be assigned based on energetics due to the lack of information in the literature. Some ion assignments were made here based on dissociative ionization studies [1-5]. Isotopically labeled experiments would provide accurate determination of product structures [6,7]. This would be important for characterizing the Titan atmosphere since the INMS only obtains mass spectra. Reaction mechanisms could also be investigated by isotopically labeled studies [6,8].

The reaction conditions used are not directly relevant to the characteristics of Titan's atmosphere. The pressure of the flow tube in the reactions was maintained at ~0.5 Torr which corresponds to an altitude of 230 km in the Titan atmosphere [9]. Reactions should be studied at a variety of pressures to account for the changes in pressure with altitude [10-12]. Note that measurements were made at room temperature; thus low temperature studies are needed in order to accurately measure the reaction rates and product distributions and explain the discrepancies between observations and photochemical models [10-13].

The importance of large organic molecules in both the ISM [14,15] and Titan's atmosphere [16] results in the need for studies of reactions involving these complex species. The mass spectrometer of the INMS measures ions and neutrals only up to 99 amu [17], but larger molecules have been detected by the Cassini Plasma Spectrometer (CAPS). The Ion Beam Spectrometer (IBS) of the CAPS onboard the Cassini Orbiter has been able to detect masses between 100-350 amu of positive ions and the CAPS Electron Spectrometer (ELS) has identified negative ions with masses between 20-8000 amu. These observations came as a surprise because these instruments were not designed for this purpose. The IBS resolution is only adequate enough to separate families of peaks, but some prominent peaks were detected and identified as naphthalene, anthracene derivatives, and an anthracene dimer. Kinetic data from ion-molecule reactions of these species and reactions that could lead to their formation would be beneficial to investigate. The ELS acquired spectra containing a broad peak with a range of masses for negative ions between 100 and ~8000 amu [18]. Negative ions have also been detected in the ISM [19-25]. This evidence motivates studies of negative ion-molecule reactions to provide kinetic data for inclusion in models. In addition, the routes to formation of these large negative

ions can be investigated through reactions of known small negative ions with large neutral ring compounds.

The increasing number of detected molecules in the ISM and the great success of the Cassini orbiter observations are providing new insights in astrochemistry. These advancements of current knowledge also inspire more questions. In this regard, now is an important and intriguing time for the future of astrochemistry.

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