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Studies of reactions of a series of ions with nitrogen containing heterocyclic molecules using a selected ion flow tube

L. Dalila Fondren, Jason McLain, Douglas M. Jackson, Nigel G. Adams *, Lucia M. Babcock

Department of Chemistry, University of Georgia, Athens, GA 30602, USA

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Abstract

A series of reactions between NH_3^+, O_2^+, O^+, Kr^+, N^+, N_2^+, Ar^+, Ne^+, NH_4^+ and H_3O^+ and three heterocyclic molecules (pyridine, pyrimidine and piperidine) were studied using a selected ion flow tube (SIFT) at 298 K. The stability of each ring was investigated through reactivity and the rate coefficients and ion product distributions were determined for each reaction. Most of the reactions proceed by charge transfer or proton transfer when energetically possible, with varying degrees of fragmentation. Based on microreversibility, gas phase formation routes are suggested for the production of ionized pyridine and pyrimidine. If these reverse reactions proceed with no or small activation energy barriers, this would be of interest for formation of heterocyclic rings in the interstellar medium and in the Titan atmosphere. Dissociation mechanisms leading to the major fragment product ions in both the pyridine and pyrimidine reactions have been studied and provide information about the site of interaction between the ions and molecules.
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Keywords: Selected ion flow tube; Nitrogen heterocycle; Interstellar medium; Ion–molecule reaction; Titan ionosphere

1. Introduction

Many cyclic organic molecules have been discovered in interstellar gas clouds (ISC), with both homocyclic and heterocyclic variants being detected, and possibly also in the Titan atmosphere. This is important, because many biological molecules are heterocyclic and the presence of heterocyclics in these extraterrestrial regions could suggest this as a source of prebiotic materials, which can then be transported by comets and meteors to planets in evolving stellar systems and act as nutrients for life. For example, thymine ($C_5H_6N_2O_2$), cytosine ($C_4H_5N_3O$) and uracil ($C_4H_4N_2O_2$), three of the nucleotides of DNA and RNA are composed partially of the heterocyclic base pyrimidine. The organic rings that have been detected so far include *c*-C_3H_2 [1], *c*-C_2H_4O [2,3], *c*-C_3H [4], *c*-C_2H_3N and *c*-C_2H_5N [5] and *c*-C_3H_2O [6] along with *c*-C_6H_6 being found in ISC [7] and possibly in Titan's atmosphere [8,9]. Polycyclic aromatic hydrocarbons (PAHs) are another class of molecule that are thought to be present in the interstellar medium. It is believed that these types of molecules are responsible for some of the diffuse interstellar bands (DIBs) seen in ISC though this is yet to be verified. Also, just recently, it was suggested by Hudgins et al. that the 6.2 μm interstellar emission line seen in infrared emission spectra of interstellar clouds is due to the substitution of a nitrogen atom into the endoskeleton of these PAHs (generating PANHs) [10].

To add to the information available on this topic, this study focuses on the ion–molecule reactions of three different nitrogen containing heterocyclic compounds; pyrimidine ($C_4H_4N_2$), pyridine (C_5H_5N), and piperidine ($C_5H_{11}N$), as shown in Fig. 1. The study was undertaken to determine the stability of the heterocyclics with the deposition of varying amounts of energy as determined by the recombination energy of the various ions (ranging from 10 to 22 eV) used in reactions with the neutrals. The presence of pyrimidine and pyridine in the ISC was first investigated in the early 1970s with little success [11]. More recently, these two molecules, and other nitrogen containing molecules like these, were the focus of interstellar searches by Kuan et al. [5,12]. Of the several different regions of the interstellar medium surveyed, only one line that potentially indicates the presence of pyrimidine was detected. The interstellar feature W51 e1/e2 provided this single line that coincides perfectly

* Corresponding author.
E-mail address: adams@chem.uga.edu (N.G. Adams).

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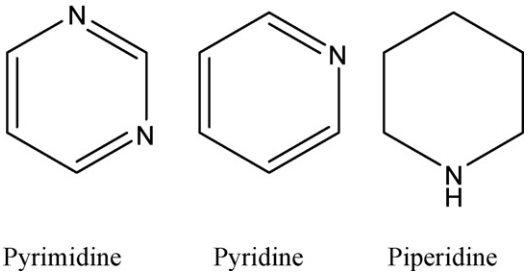

Fig. 1. Structural diagrams of several heterocyclic molecules as indicated.

with the $J \leq 55$ band head of pyrimidine. However, the detection of one line is by no means considered a positive identification, but it is possible that several conditions conspire to make the other expected lines undetectable. Since large ring molecules are predicted to be unstable in these regions, they will have low relative abundances and hence the population of rotationally excited states is anticipated to be low. Also, the presence of spectral lines from other chemical species can interfere with the observation of expected lines especially where they are close to the limit of detectability. Thus, it is important to note that the absence of spectral features may not necessarily be due to the absence of the target molecule. Pyridine has also been targeted but with no positive identification to date [5,12]. Laboratory data on the stability of both pyrimidine and pyridine against UV radiation has been collected and both molecules are expected to survive only in UV shielded environments such as hot cores [13].

Titan's atmosphere has been extensively probed with the Cassini Ion and Neutral Mass Spectrometer (INMS). An ion peak at a mass to charge ratio, *m*/*z*, of 79 was detected that could be due to protonated benzene or possibly ionized pyridine [14]. Since pyridine has a large proton affinity, efficient proton transfer reactions with ions such as the dominant $HCNH^+$ should occur yielding an abundant ion with an *m*/*z* of 80. The INMS data [14] indicate the *m*/*z* of 79 as being comparable with the *m*/*z* of 80 (indeed dominating it in the altitude region of 1400–1600 km) and thus an identification of $m/z = 79$ as ionized pyridine is highly unlikely. However, it is known that Titan's ionosphere is composed mostly of nitrogen with hydrocarbons, so the formation of nitrogen containing linear and cyclic molecules is likely to be facile. Even though the mass to charge ratios are accurately known, the identifications are not certain. Chemical modeling is a valuable means of better interpreting the mass spectral data. For modeling to be successful, it is essential for relevant laboratory kinetic data to be available. As a contribution to this effort, the stability and reactivity of various rings were probed in the present study. Rate coefficients and ion product distributions have been determined for a series of charge transfer reactions in which varying amounts of energy were deposited in the heterocyclic rings. In addition to establishing the relative stabilities, these studies suggested several gas phase formation routes to heterocyclic ion production. These new data will be valuable in understanding the chemistry of the molecules in the gas phase and will give information on the conditions that are needed for these molecules to form in ISC and the Titan atmosphere. Probing regions with these conditions will improve the likelihood of the detection and identification of these molecules.

2. Experimental

The reactions of pyridine (C_5H_5N), pyrimidine ($C_4H_4N_2$) and piperidine ($C_5H_{11}N$) with ions of various recombination energies (RE): NH_3^+, O_2^+, O^+, Kr^+, N^+, N_2^+, Ar^+, Ne^+ (10–22 eV) and NH_4^+ and H_3O^+ were studied using a selected ion flow tube (SIFT). The technique has been described in detail before [15,16] and will not be discussed in depth here. Two different types of ion sources were used to produce the ions of interest. A high-pressure electron impact source was generally used to generate polyatomic ions, while a microwave discharge cavity was used when producing atomic ions because it provided a larger number density of ions in the flow tube. The ions of interest were selected using a quadrupole mass filter and focused through a 1 mm orifice into the flow tube. There the ions were carried downstream in a helium gas flow injected into the tube at supersonic flow through a Venturi type inlet. The pressure in the flow tube was maintained at ~0.5 Torr by the helium flow, which was exhausted from the flow tube by a Roots pump. Downstream of the ion injection port, and after the thermalization of the ions, the reactant neutrals were introduced into the flow tube. A small portion of the reactant and product ions were then sampled at the end of the reaction region through a pinhole orifice in the detection nose cone, while the rest was evacuated by the Roots pump. A quadrupole mass filter and an electron multiplier counting system located after the nose cone were used to quantitatively identify the ions by the mass to charge ratio.

The three reactant species used in this study are liquids at room temperature and it proved to be difficult to work with the neat vapors. When trying to determine accurate neutral flows, problems arose due to the gases sticking to the walls of the flow tube and it was not possible to stabilize flows and thus get linear semi logarithmic decays for the primary ion. To eliminate these problems, 1% mixtures of the reactant neutral in helium were used, keeping the reactant pressure below its saturated vapor pressure to minimize condensation. No evidence for dimerization was detected, which we have observed in other experiments with liquids of similar vapor pressures [17].

Pyridine was obtained from Sigma–Aldrich with a manufactured purity of >99.9%. Both pyrimidine and piperidine were obtained from Alfa Aesar with manufactured purities of 99%. The liquids were further purified by several cycles of freeze-pump-thaw before use, in order to eliminate dissolved gases. Rate coefficients and percentage product ion distributions were determined using standard techniques [18]. The rate coefficients are accurate to ±20%, while the product distributions are accurate to ±5 in the percentage. All measurements were made at 298 K.

3. Results

Ion product distributions for the reactions of pyridine, pyrimidine and piperidine are given in Table 1. These have been corrected for mass discrimination in the detection quadrupole

Table 1
Product distributions (%) for the reactions of pyridine, pyrimidine and piperidine with the ions indicated

Reactant ion	Pyridine ion product	%	Pyrimidine ion product	%	Piperidine ion product	%
Ne^+ (21.56 eV)	$C_4H_3^+$, C_3NH^+	54	$C_2H_2^+$	46	$C_2H_4^+$, CH_2N^+	18
	$C_4H_2^+$, C_3N^+	21	$C_3H_2N^+$, $C_4H_4^+$, $C_2N_2^+$	32	$C_3H_6^+$, $C_2H_4N^+$	14
	$C_5H_5N^+$	13	C_3NH^+, $C_4H_3^+$	11	$C_3H_5^+$, $C_2H_3N^+$	13
	$C_4H_4^+$	12	$C_3H_3N^+$, $C_2N_2H^+$	7	$C_2H_5^+$, CH_3N^+	11
			$C_4H_3N_2^+$	≤4	$C_2H_6^+$, CH_4N^+	10
					$C_3H_3^+$, C_2NH^+	7
					$C_4H_6^+$, $C_3H_4N^+$	6
					$C_4H_7^+$, $C_3H_5N^+$	6
					$C_4H_8^+$, $C_3H_6N^+$	6
					$C_3H_7^+$, $C_2H_5N^+$	5
					$C_2H_3^+$, HCN^+	4
Ar^+ (15.76 eV)	$C_4H_4^+$	66	$C_3H_3N^+$, $C_2N_2H^+$	54	$C_4H_8^+$, $C_3H_6N^+$	26
	$C_5H_4N^+$	15	$C_2H_2^+$	21	$C_2H_5^+$, CH_3N^+	19
	$C_4H_5^+$, $C_3H_3N^+$	12	$C_3H_2N^+$, $C_4H_4^+$, $C_2N_2^+$	22	$C_4H_7^+$, $C_3H_5N^+$	10
	$C_3H_3^+$, C_2NH^+	7	$C_4H_4N_2^+$	≤4	$C_2H_6^+$, CH_4N^+	9
					$C_2H_4^+$, CH_2N^+	8
					$C_3H_5^+$, $C_2H_3N^+$	8
					$C_3H_6^+$, $C_2H_4N^+$	7
					$C_3H_8^+$, $C_2H_6N^+$	4
					$C_5H_{11}N^+$	4
					$C_4H_9^+$, $C_3H_7N^+$	3
					$C_3H_7^+$, $C_2H_5N^+$	2
N_2^+ (15.58 eV)	*l*-$C_4H_4^+$	43.5	$C_3H_3N^+$, $C_2N_2H^+$	71	$C_4H_8^+$, $C_3H_6N^+$	32
	c-$C_4H_4^+$	43.5	$C_2H_2^+$	17	$C_2H_5^+$, CH_3N^+	15
	$C_4H_5^+$, $C_3H_3N^+$	13	$C_3H_2N^+$, $C_4H_4^+$, $C_2N_2^+$	12	$C_2H_4N^+$, $C_3H_6^+$	12
					$C_4H_7^+$, $C_3H_5N^+$	10
					$C_4H_9^+$, $C_3H_7N^+$	8
					$C_2H_5N^+$, $C_3H_7^+$	7
					$C_3H_8^+$, $C_2H_6N^+$	7
					$C_3H_5^+$, $C_2H_3N^+$	5
					$C_5H_{11}N^+$	4
N^+ (14.53 eV)	$C_4H_4^+$	54	$C_3H_3N^+$, $C_2N_2H^+$	64	$C_4H_8^+$, $C_3H_6N^+$	30
	$C_5H_5N^+$	46	$C_4H_4N_2^+$	31	$C_3H_8^+$, $C_2H_6N^+$	19
			$C_3H_2N^+$, $C_4H_4^+$, $C_2N_2^+$	≤3	$C_2H_4N^+$, $C_3H_6^+$	13
			$C_2H_2^+$	≤2	$C_4H_7^+$, $C_3H_5N^+$	13
					$C_2H_5N^+$, $C_3H_7^+$	12
					$C_3H_5^+$, $C_2H_3N^+$	9
					$C_5H_{11}N^+$	4
Kr^+ (14 eV)	*l*-$C_4H_4^+$	70	$C_3H_3N^+$, $C_2N_2H^+$	91	$C_4H_8^+$, $C_3H_6N^+$	44
	c-$C_4H_4^+$	30	$C_3H_2N^+$, $C_4H_4^+$, $C_2N_2^+$	≤3	$C_4H_9^+$, $C_3H_7N^+$	31
			$C_3H_4N^+$	≤3	$C_2H_5^+$, CH_3N^+	15
			$C_4H_4N_2^+$	≤3	$C_2H_6^+$, CH_4N^+	7
					$C_2H_4^+$, CH_2N^+	3
O^+ (13.62 eV)	$C_4H_4^+$	100	$C_3H_3N^+$, $C_2N_2H^+$	100	–	–
O_2^+ (12.07 eV)	$C_5H_5N^+$	100	$C_4H_4N_2^+$	100	$C_5H_{10}N^+$	46
					$C_5H_{11}N^+$	17
					$C_3H_8^+$, $C_2H_6N^+$	14
					$C_3H_7^+$, $C_2H_5N^+$	10
					$C_4H_9^+$, $C_3H_7N^+$	10
					$C_5H_{10}^+$, $C_4H_8N^+$	3
NH_3^+ (10.07 eV)	$C_5H_5N^+$	100	–	–	–	–
H_3O^+ (6.4 eV)	$C_5H_5NH^+$	100	$C_4H_4N_2H^+$	100	$C_5H_{11}NH^+$	91
					$C_5H_{10}N^+$	9
NH_4^+ (4.8 eV)	$C_5H_5NH^+$	100	$C_4H_4N_2H^+$	100	$C_5H_{11}NH^+$	100

Recombination energies of the reactant ions are given beside their identification [31]. The ionization energies of the heterocyclic molecules are 9.26, 9.33 and 8.03 eV, respectively [31].

Table 2
Experimental rate coefficients, k_{exp}, for the reactions between the three neutral molecules and the indicated ions are listed followed by the theoretical rate coefficients, k_{theor}, calculated using combined variational transition state theory and classical trajectory theory [19]

Primary ion	k_{exp} (10^{-9} cm^3 s^{-1})	k_{theor} (10^{-9} cm^3 s^{-1})	Efficiency[a]
C_5H_5N			
Ne^+	3.4	3.18	1.07
Ar^+	2.3	2.47	0.93
N_2^+	2.7	2.79	0.97
N^+	3.4	3.68	0.92
Kr^+	1.92	1.99	0.97
O^+	4.4	3.48	1.26
O_2^+	3.1	2.66	1.17
NH_3^+	3.6	3.4	1.06
H_3O^+	4.4	3.25	1.35
NH_4^+	3.5	3.32	1.05
$C_4H_4N_2$			
Ne^+	2.9	3.34	0.87
Ar^+	2.7	2.59	1.04
N_2^+	2.9	2.94	0.99
N^+	4.8	3.87	1.24
Kr^+	2.1	2.09	1
O^+	3.6	3.66	0.98
O_2^+	2.6	2.8	0.93
NH_3^+	2.8	3.57	0.78
H_3O^+	4.3	3.41	1.26
NH_4^+	3.1	3.49	0.89
$C_5H_{11}N$			
Ne^+	2.29	2.07	1.11
Ar^+	1.7	1.6	1.06
N_2^+	1.7	1.82	0.93
N^+	2.30	2.41	0.95
Kr^+	1.05	1.26	0.83
O_2^+	2.23	2.75	0.81
NH_3^+	2.3	2.22	1.04
H_3O^+	1.97	3.35	0.59

Data needed to calculate the theoretical rate coefficients were obtained from the literature [32].

[a] The reaction efficiency, k_{exp}/k_{theor}, is also included. All rate coefficients are expressed in units of 10^{-9} cm^3 s^{-1}.

mass filter. Mass discrimination factors were determined by monitoring the ion counts as a function of the downstream mass filter resolution. At low resolution, the ion counts became independent of resolution and, under these conditions, it was assumed that the transmission was mass independent. This was confirmed in individual reactions by determining the total ion count rate as a function of reactant gas flow after correction for mass discrimination and this was constant implying that the discrimination had been accounted for correctly.

Reactions involving NH_4^+ and H_3O^+ proceed only by proton transfer. In these cases, charge transfer is endothermic and is not expected to be a product channel, consistent with observations. With all other reactant ions, charge transfer (both dissociative and non-dissociative) is energetically possible and was detected as the main product channel.

The rate coefficients were also measured for all of the reactions and are provided in Table 2. The dilution of the reactant neutral was taken into account with each rate coefficient being corrected accordingly. Most of the reactions proceed at the gas kinetic rate to within experimental error. Theoretical rate coefficients were calculated using combined variational transition state theory and classical trajectory theory [19]. Reaction efficiencies for all reactions were at or near unity.

3.1. Pyridine

The reactions of pyridine (ionization energy, IE 9.26 eV) with ions of low recombination energies, NH_3^+ (RE 10.07) and O_2^+ (RE 12.07), resulted only in non-dissociative charge transfer. When the more energetic ion, O^+ (RE 13.62 eV), was used, fragmentation of the ring became favored. Here the only product channel generates an ion at *m/z* 52. To determine if this was $C_4H_4^+$ or $C_3H_2N^+$, reactions with C_5D_5N were performed. Then, this product ion mass was observed to move to 56 amu ($C_4D_4^+$) proving that the product was entirely $C_4H_4^+$, a common fragment of unsaturated, cyclic hydrocarbon dissociation [20] in both ion–molecule reactions and electron impact ionization. This is important because HCN is the neutral that results from this fragmentation and it is particularly stable and abundant in ISC and in Titan's ionosphere. It is interesting to note that the major product in the reactions with Kr^+ (RE 14 eV), N^+ (14.53 eV), N_2^+ (15.58 eV) and Ar^+ (15.76 eV) is also $C_4H_4^+$. As can be seen from Table 1, other dissociative and non-dissociative product channels are observed but $C_4H_4^+$ is by far the most abundant product ion. It is only when pyridine reacts with the energetic Ne^+ (RE 21.56 eV) that the $C_4H_4^+$ product channel is less significant because of the increasing fragmentation. In the Ne^+ reaction, in addition to the expected dissociative channels, the non-dissociative charge transfer is surprisingly a significant product.

Note that in these studies, there are often two possible ion products with the same mass. In one case, we were able to distinguish the product by isotopic labeling. For other reactions involving the isotopic pyridine, conflicting product masses made it impossible to determine the absolute identity of the product. Thermodynamic considerations also were used in an attempt to settle on the identity of the product ions. In all but a few cases, each possible ion product was energetically possible and thus this method could not be used to establish the ion identity. Another concern is the possibility of several isomers. In the case of $C_4H_4^+$, it is generally accepted that two linear isomers and two cyclic isomers are stable enough to form [21]. Reactions of $C_4H_4^+$ with benzene were used to determine if this molecular ion was cyclic or linear. It had been previously determined that the linear form of $C_4H_4^+$ reacts with benzene in a charge transfer reaction while the cyclic form is unreactive [22,23]. The $C_4H_4^+$ product of the reaction of Ar^+ and pyridine studied in this manner showed that 70% of the $C_4H_4^+$ was linear and 30% was cyclic. When benzene was reacted with the $C_4H_4^+$ product of the N_2^+ reaction, it was determined that a 50:50 mix of the linear and cyclic isomer was present. This study unfortunately does not provide enough information to determine which of the two linear and which of the two cyclic isomers are formed. However, following from thermodynamic considerations and the neutralization-reionization mass spectrometry study of Zhang et al. [20], it is assumed the two isomers with the lowest energy

configuration are generated. Therefore, the linear isomer is identified as the vinyl acetylene cation and the cyclic isomer as the methylene cyclopropene cation. Because of the complexity of the study, other reactions resulting in $C_4H_4^+$ as a product were not studied further to determine the identity of the isomer(s) present. Some of the other products also have isomers, such as cyclic and linear $C_3H_3^+$ that can be determined by following the rate of reactions with CO, [23] but due to the difficulty in interpreting the data these structures were not investigated.

3.2. Pyrimidine

Pyrimidine (IE 9.33 eV) was studied not only because of its biological importance but also to see how product channels differ when an additional nitrogen was present in the ring. Here an additional lone pair of electrons is gained, but the aromaticity is still preserved. As with pyridine, the reactions with O_2^+ resulted only in non-dissociative charge transfer. In the reactions of O^+, Kr^+, N^+, N_2^+ and Ar^+, an ion, $C_3H_3N^+$, is produced with the neutral product corresponding to HCN, as occurred with pyridine. It is possible for the ion mass to correspond to $C_2N_2H^+$ but there was no information available in this case to calculate the energetics. However, following from the isotope substitution in the pyridine case, the most likely ion identity is $C_3H_3N^+$ produced with the neutral HCN. The energetic reaction with Ne^+ proceeded with much fragmentation and the major product channel was $C_2H_2^+$.

3.3. Piperidine

Piperidine is quite different from the other two molecules because it is saturated and has no delocalized π electrons. The lack of aromaticity suggested that this molecule would fragment more easily and considerably more fragmentation was observed. The products of the O_2^+ reaction resulted in both dissociative (unlike the other molecules) and non-dissociative charge transfer. As Table 1 shows, the reactions of Kr^+, N^+, N_2^+ and Ar^+ all had an ion with an *m*/*z* of 56 as the main product. This corresponds to $C_4H_8^+$ and/or $C_3H_6N^+$, both being energetically possible. Also it is interesting to note that, in this case, the reaction with the more energetic Ne^+ produced a different primary product ion from the four lower energy ions: Kr^+, N^+, N_2^+ and Ar^+ (*m*/*z* 56 product was present only as a 6% product).

4. Discussion

When comparing the stability of the three-reactant molecules, it is clear that piperidine is the least stable as indicated by the large amount of fragmentation that occurs even at lower energies. This is expected considering piperidine is not aromatic, unlike pyridine and pyrimidine. One interesting similarity among all three molecules is the consistency of the primary product channel for reactions with ions of recombination energies of about 14–16 eV. The reactions were compared to the reactions of a similar set of ions previously studied with benzene [23]. In this comparison it is important to note that even though benzene is more stable, i.e., requiring around 2 eV more energy to produce fragment ions, once sufficient energy is available, more product fragments are produced than in either of the equivalent reactions involving pyridine or pyrimidine. This could be due to the particularly stable ions and neutral combinations formed when pyridine and pyrimidine initially fragment; these are not all available to the benzene reactions.

Because of the limited number of ion–molecule reactions that have been studied involving these molecules, very few direct comparisons could be made to literature data. However, there was a study that provided electron impact (EI) fragmentation data for pyridine over a range of energies (10–200 eV) [24]. It might be thought that these data can be directly compared with our product distribution; however, in the EI study the dominant process through the entire energy range was non-dissociative charge transfer with the fragmentation producing $C_4H_4^+$ as the next most important channel. The importance of the $C_4H_4^+$ channel increased as the energy of the electrons was increased. Overall, there were more fragment ions observed in the EI experiments when compared to ion–molecule reactions with similar energies. Even though less fragmentation is observed in the ion–molecule reactions, it is worth noting that the non-dissociative charge transfer is only dominant at energies below 12 eV. The differences between these two studies show the reaction mechanisms are very different, as might be expected. Also, in the EI studies, it was possible to identify all of the isobaric masses. This information can reasonably be used to determine the identity of the masses in question in the present work.

Comparison was also possible with some much earlier studies in the literature [25,26], although these were over a range of kinetic energies (1–300 eV). Plots of the literature distributions versus kinetic energy were made and extrapolated to zero kinetic energy to give a better comparison with the present data. They are listed in Table 3 for comparison to the 298 K values obtained in this study. The literature values for the reactions of Ne^+, Ar^+ and Kr^+ with pyridine and Ar^+ and Kr^+ with pyrimidine all agree very well. The major product is always the same though the actual percentage differs to some degree. The previous studies show slightly more fragmentation though most of the additional products are only a small contribution. This difference could be partially due to the inaccuracy of extrapolated product distributions and the difference in experimental techniques. Two more recent papers detail the reactions of H_3O^+ and O_2^+ with both pyridine and piperidine [27,28] as studied using a SIFT. As shown in Table 3 the product distributions in the literature agree very well with the values obtained in this study.

The site at which the ion interacts with the neutral molecule was also considered. In electron impact ionization, the loss of the electron of lowest ionization energy is expected [29] and the same can reasonably be expected of electron transfer in ion–molecule reactions. Recognizing the expected radical site then allows the most likely product ion fragments to be identified. In turn, the observed product fragments can provide information about the actual radical site and therefore information about the interaction of the ion and molecule. In the reactions of pyridine and pyrimidine, it is reasonable to expect the ion to interact with the electrons located in the highest occupied molec-

Table 3
Comparison of product distribution results from this study with literature

Reactant ion	Pyridine				Pyrimidine				Piperidine			
	This work		Literature		This work		Literature		This work		Literature	
Ne^+	$C_4H_3^+$	54%	$C_4H_3^+$	40%[a]	–	–	–	–	–	–	–	–
	$C_4H_2^+$	21%	$C_4H_2^+$	26%	–	–	–	–	–	–	–	–
	$C_5H_5N^+$	13%	$C_4H_4^+$	11%	–	–	–	–	–	–	–	–
	$C_4H_4^+$	12%	$C_2H_2^+$	8%	–	–	–	–	–	–	–	–
			$C_3H_3^+$	5%	–	–	–	–	–	–	–	–
			$C_2H_3^+$	5%	–	–	–	–	–	–	–	–
Ar^+	$C_4H_4^+$	66%	$C_4H_4^+$	42%[a]	$C_3H_3N^+$	54%	$C_2H_2^+$	56%[b]	–	–	–	–
	$C_5H_4N^+$	15%	$C_5H_4N^+$	25%	$C_2H_2^+$	21%	$C_3H_2N^+$	24%	–	–	–	–
	$C_3H_3N^+$	12%	$C_4H_3^+$	13%	$C_3H_2N^+$	22%	$C_3H_3N^+$	20%	–	–	–	–
	$C_3H_3^+$	7%	$C_4H_2^+$	8%	$C_4H_4N_2^+$	≤4%			–	–	–	–
			$C_3H_3N^+$	7%					–	–	–	–
			$C_3H_3^+$	5%					–	–	–	–
Kr^+	*l*-$C_4H_4^+$	70%	$C_4H_4^+$	77%[a]	$C_3H_3N^+$	91%	$C_3H_3N^+$	87%[b]	–	–	–	–
	c-$C_4H_4^+$	30%	$C_5H_4N^+$	14%	$C_3H_2N^+$	≤3%	$C_4H_3N_2^+$	6%	–	–	–	–
			$C_3H_3^+$	4%	$C_3H_4N^+$	≤3%	$C_3H_2N^+$	3%	–	–	–	–
			$C_4H_5^+$	4%	$C_4H_4N_2^+$	≤3%	$C_2H_2^+$	3%	–	–	–	–
			$C_5H_5N^+$	1%			$C_4H_4N_2^+$	1%	–	–	–	–
H_3O^+	$C_5H_5NH^+$	100%	$C_5H_5NH^+$	100%[c,d]	–	–	–	–	$C_5H_{11}NH^+$	91%	$C_5H_{11}NH^+$	90%[c]
									$C_5H_{10}N^+$	9%	$C_5H_{10}N^+$	10%
O_2^+	$C_5H_5N^+$	100%	$C_5H_5N^+$	100%[c]	–	–	–	–	$C_5H_{10}N^+$	46%	$C_5H_{10}N^+$	55%[c]
									$C_5H_{11}N^+$	17%	$C_5H_{11}N^+$	15%
									$C_3H_8^+$, $C_2H_6N^+$	14%	$C_3H_8^+$, C_2H_6N	10%
									$C_3H_7^+$, $C_2H_5N^+$	10%	$C_3H_7^+$, $C_2H_5N^+$	10%
									$C_4H_9^+$, $C_3H_7N^+$	10%	$C_4H_9^+$, $C_3H_7N^+$	5%
									$C_5H_{10}^+$, $C_4H_8N^+$	3%	$C_5H_{10}^+$, $C_4H_8N^+$	5%

References for literature product distribution values: superscript a [25], b [26], c [28], d [27]. Values for a and b were extrapolated to thermal energies.

ular orbital (HOMO), which in both cases involves the lone pair on the nitrogen atom. When considering well-known fragmentation mechanisms starting from the radical site on the nitrogen, an expected major product ion would be $C_3H_3N^+$ for reactions with both pyridine and pyrimidine. However, for reactions involving pyridine, the experimental data show $C_3H_3N^+$ to be present in only two reactions and then only as a minor product. As stated before, the major product in almost all pyridine reactions exhibiting dissociative charge transfer is $C_4H_4^+$. The only way for this product to form is to have the radical site on a specific carbon atom in the ring, as seen in Fig. 2. However, for pyrimidine, the major dissociative product is $C_3H_3N^+$. This could occur from either the radical site location on the nitrogen or on one of the carbons, as shown in Fig. 3. A study in which the electronic structure of pyrimidine was investigated stated that the molecular orbital involved in producing the fragment as having some nitrogen influence [26]. However, a similar study by the same group on the electronic structure of pyridine described the orbital involved in the fragmentation as being strongly carbon–carbon bonding [25]. Apparently according to these studies, the addition

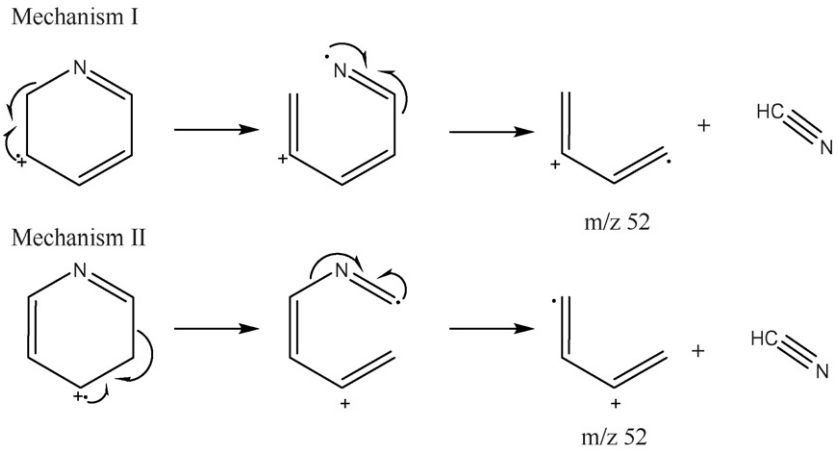

Fig. 2. Proposed pyridine dissociation mechanisms that give the experimentally observed product $C_4H_4^+$ at an *m/z* of 52.

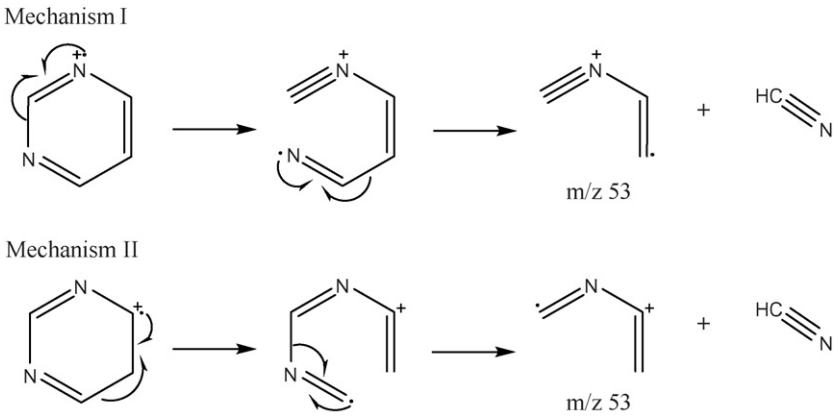

Fig. 3. Proposed pyrimidine dissociation mechanisms that give the experimentally observed product $C_3H_3N^+$ at an *m/z* of 53. In mechanism II it is also possible to generate $C_3H_3N^+$ with the radical located on either of the two carbons below the carbon radical shown.

of the second nitrogen changes the radical site. However, since both molecules have similar HOMO's, it seems strange that the radical site in the pyridine reactions would reside on a carbon atom and in the pyrimidine reactions on the nitrogen atom. It is not clear why Asbrink et al. [26] make the assumption that the orbital involved in ionization and fragmentation involves the nitrogen atom in the case of pyrimidine but not for pyridine, especially since it is possible to get the same fragmentation product if the radical is located on a carbon atom.

Apart from these data, experimentally it should be possible to determine if the nitrogen is important in the interaction of the ion and molecule. Since pyrimidine has one more nitrogen than pyridine, and hence an additional reaction site, the overall reactions involving pyrimidine should be more efficient if the reaction is taking place at the nitrogen atom. Unfortunately, all of the rate coefficients were at or near gas kinetic rate so an additional reaction site could have no effect on the rate. A study of these reactions at a higher temperature might be valuable since it would be likely to slow down the reaction and allow differences in reactivity to be distinguished. Then, it would be possible to determine if the addition of a second nitrogen increases the rate of reaction as expected.

To better understand the interaction between the ions and neutrals involved in this study, some preliminary theoretical calculations were performed. Intrinsic reaction coordinate calculations were used to determine if the ion preferred to approach the neutral from above the plane of the molecule, essentially interacting with the delocalized π electrons, or from the plane of the molecule approaching either a nitrogen lone pair or a carbon atom. Calculations were performed at the UB3LYP/6-31G* level using Gaussian 03 [30] and followed the interaction of Ne^+ with both pyridine and pyrimidine. In both cases when approaching the carbon atom in plane, the carbon is blocked by a peripheral hydrogen atom, therefore the calculations measure the interaction of the ion and hydrogen. Both calculations showed that the interaction with the π electrons was higher in energy than the interaction with the nitrogen or hydrogen. The interactions of Ne^+ with both pyridine and pyrimidine showed a slightly stronger interaction with the hydrogen than with the nitrogen. It is possible that the lower energy arises from the fact that hydrogen atom has a smaller Bohr radius than nitrogen, so at the same neutral-ion distance, there is less electron repulsion for the attack on the H-atom and thus the interaction of Ne^+ with hydrogen is lower in energy. This preliminary calculation does not support the conclusion drawn from these experiments that the ion interacts with the π electrons and therefore the radical site appears to be located on a carbon atom in the ring.

5. Conclusions

This study has addressed two very different but important observations. The first concerns the astrochemical importance of pyridine and pyrimidine, and the second regards the dissociation mechanism of the molecules. It is possible that heterocyclic molecules such as pyridine and pyrimidine are present in ISC. Several attempts have been made to identify both species there, but these species have proven to be elusive. Should these molecules exist, one possible route to their formation is identified through these experiments. Pyridine could be synthesized in the gas phase through the association reaction of $C_4H_4^+$ with HCN, while pyrimidine might be formed by the reaction of $C_3H_3N^+$ with HCN providing there are no significant barriers to inhibit the reactions. Note that such barriers could be overcome to some degree by the ion-induced dipole and ion-permanent dipole interactions. It is proposed to check this in future studies. Fragmentation patterns of all of the ringed compounds have proven them to be stable enough to exist in protected regions of ISC.

The second point of interest involves the site of ionization and mechanisms of reaction with the neutral molecules. It is expected that the lone pair of electrons on the nitrogen would be the most likely site for the initial removal of an electron. However, for pyridine, the electron impact study and this ion–molecule study have proved that the major product is not consistent with this conclusion and instead the electron most likely is taken from the π delocalized electrons. From the experimentally observed products, the radical site must be on the second or third carbon atom relative to the nitrogen. Concerning pyrimidine, even though a previous study attributes the radical site to the nitrogen atom, it is also possible for the major product to be generated

from a radical on any carbon atom in the ring except for the lone carbon atom between the two nitrogen atoms. From the information gathered on the pyridine reactions this seems a likely possibility.

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