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Experimental study of the gas phase chemistry of $C_3H_3^+$ with several cyclic molecules

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ABSTRACT

Rate coefficients and ion product distributions have been determined for the gas phase reactions of $C_3H_3^+$ with several homocyclic and heterocyclic molecules in a selected ion flow tube (SIFT) at 298 K. The rate coefficients for both the linear and cyclic isomers of $C_3H_3^+$ are given. l-$C_3H_3^+$ reacts by association in the majority of the reactions. c-$C_3H_3^+$ is shown to be more reactive than previously suggested by low pressure experiments. In fact, the cyclic isomer reacts at the gas kinetic rate when the reaction involves a nitrogen containing cyclic compound but is less reactive with oxygen containing cyclic compounds. It is noted this reactivity of both the cyclic and linear isomer should be included when modeling the atmosphere of Titan due to the large number of nitrogen containing molecules that are considered to be present. Currently, the models consider electron recombination to be the only loss channel for c-$C_3H_3^+$.

1. Introduction

The $C_3H_3^+$ molecule has been studied for many different reasons. In the late 1950s Breslow was the first to successfully synthesize a derivative of the cyclic form of this molecule [1] thus demonstrating an aromatic system with only 2π electrons, i.e., the first member of the 2 + 4*n* aromatic series. $C_3H_3^+$ is often seen in the mass spectrum of organic compounds [2] and there have been many experimental and theoretical studies to determine whether the linear or cyclic isomer is the structure of lower energy. It has now been determined that the cyclic isomer, cyclopropenyl cation, is the most stable form. The linear isomer, propargyl cation, is the next most stable isomer with a heat of formation approximately 26 kcal/mol greater than that of the cyclic isomer [3–5]. $C_3H_3^+$ is also relevant to combustion chemistry. It is the most abundant ion observed in many fuel rich flames and was once thought to be the starting point for soot formation. However, it is now widely believed that the neutral radical C_3H_3 and other small resonantly stabilized radicals are responsible for the buildup of carbon in soot formation [6–9]. Furthermore, $C_3H_3^+$ is thought to exist in the interstellar medium. The first cyclic molecule discovered in interstellar clouds was c-C_3H_2 [10,11]. This is believed to be formed by electron recombination of $C_3H_3^+$, following $C_3H_3^+$ formation by radiative association of C_3H^+ with the abundant H_2 [12]. In studies of the analogous laboratory collisionally stabilized association reactions, it was concluded that equal quantities of the cyclic and linear isomer are formed by this process. However, because of the greater reactivity of l-$C_3H_3^+$, models show this ion being removed rapidly from interstellar clouds through ion-molecule reactions while c-$C_3H_3^+$ is mainly removed via dissociative electron recombination.

Recently a mass to charge of 39 has been detected in the ionosphere of Titan by the ion neutral mass spectrometer (INMS) onboard the Cassini spacecraft [13]. The possible identities for this mass include both linear and cyclic $C_3H_3^+$ as well as HC_2N^+. Densities of these three species from chemical models predict that c-$C_3H_3^+$ is most abundant followed by l-$C_3H_3^+$ and then HC_2N^+[14]. The current conclusion for the Titan atmosphere is that odd masses are hydrocarbons while even masses are nitrogen containing species. So for *m*/*z* 39, HC_2N^+ is less likely to be the identity, unless a more definite identification is obtained. Of the two, the cyclic isomer has been shown to be less reactive than the linear isomer [2,15,16]. Indeed, c-$C_3H_3^+$ is known to have no discernable reaction with small linear or branched hydrocarbons while l-$C_3H_3^+$ is known to react quite rapidly [2]. Therefore, it is easy to identify the isomers in a gas phase reaction by choosing an appropriate neutral reactant. For example, l-$C_3H_3^+$ reacts with benzene at the gas kinetic rate while c-$C_3H_3^+$ does not react ($\leq 10^{-13}$ cm^3 s^{-1}) [15]. Depending on the method used to form the molecular ion, it is possible to obtain different ratios of the linear to cyclic isomers. Impact of 70 eV electrons on propyne (C_3H_4) produces 70% cyclic $C_3H_3^+$ and 30% linear $C_3H_3^+$ [17] while electron impact on ethane in a high pressure ionization source creates 40% cyclic and 60% linear

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isomers [18]. There are several ion molecule reactions that produce only the cyclic form of $C_3H_3^+$ such as the reaction of CH_3^+ with C_2H_2 to give 100% c-$C_3H_3^+$ as well as the reaction of C^+ with C_2H_4 to give 80% c-$C_3H_3^+$ and a 20% mix of linear and cyclic $C_3H_2^+$ [12].

A previous study by this laboratory investigated the reactivity of CH_3^+ with a variety of cyclic molecules. The results of this study were that CH_3^+ was able to create an association complex with aromatic molecules but not with the saturated species. In many cases the association product channel was competitive with the energetically favorable proton transfer product channel. The association product channel provides a mechanism for ring growth which is important in environments such as the interstellar medium and the atmosphere of Titan. To further investigate possible mechanisms for ring growth, reactions with $C_3H_3^+$ as the reactant ion were studied. Even though $C_3H_3^+$ is an important ion as described earlier, there is little information in the literature about its reactions with cyclic molecules. The first set of reactions in this study focused on the reaction of $C_3H_3^+$ with three aromatic molecules—benzene, toluene, and pyridine [19]. It was determined that l-$C_3H_3^+$ reacts rapidly with all three aromatic molecules via an association complex. Furthermore, c-$C_3H_3^+$ proved to be very reactive with pyridine with a rate coefficient close to the gas kinetic limit. To further investigate the reactivity of both linear and cyclic $C_3H_3^+$, these studies were extended to include several aromatic and saturated nitrogen and oxygen containing heterocyclic molecules. The results of this further investigation are discussed below.

2. Experimental

A selected ion flow tube was used to study a series of ion-neutral reactions between $C_3H_3^+$ and the neutrals pyrimidine ($C_4H_4N_2$), piperidine ($C_5H_{11}N$), 1,4-dioxane ($C_4H_8O_2$), furan (C_4H_4O), tetrahydrofuran (C_4H_8O), pyrrole (C_4H_5N), and pyrrolidine (C_4H_9N). The SIFT method has been described extensively in the literature [20–22] so only a brief overview will be given here. The ion of interest was selected from an ion source using a quadrupole mass filter and focused through a 1 mm orifice into the flow tube. Then the ions were carried downstream in a helium gas flow injected supersonically into the tube through a venturi type inlet. The pressure in the flow tube was maintained at ~0.5 Torr by the helium flow (~200 Tls^{-1}), 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 was 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 their mass to charge ratios.

Specific to this experiment, $C_3H_3^+$ was created by injecting propyne (C_3H_4) into a low pressure electron impact ionization source. Due to limitations of the mass filter and collision breakup of $C_3H_3^+$ upon entering the flow tube, it was not possible to completely isolate $C_3H_3^+$ from the other hydrocarbon ions. Hence, the following ions were present in the flow tube at average percentages relative to $C_3H_3^+$: $C_3H_4^+$ (6%), $C_3H_2^+$ (10%), C_3H^+(4%). The presence of these unwanted ions can contribute to the products formed. The product distributions are usually accurate to ±5 in the percentage. However, since the contribution of these other ion to the product distribution is not known it is difficult to quantify how the error is affected. A broad approach would be to take the average percent of additional primary ions (20%) and assume they contribute equally to each product formed. Then the additional error for each reaction could be decided as 20% divided by the number of products for the reaction.

Pyrrole, pyrrolidine, furan, tetrahydrofuran, and 1,4-dioxane were obtained from Sigma–Aldrich with purities of 98%, 99.5+%, 99+%, ≥99.9%, and 99.5%, respectively. Pyrimidine and piperidine were obtained from Alfa Aesar both with manufactured purities of 99%. Benzene was obtained from Fisher Scientific with a purity of 99.5%. To eliminate dissolved gases, the liquids were further purified before use by several cycles of freeze–pump–thaw. The neat vapors proved difficult to work with because their sticky nature allowed condensation of the liquid in the neutral reactant system and on the flow tube walls. To minimize this, a 1% mixture of the reactant neutral in helium was used. This dilution was accounted for when determining the rate coefficients. Ion product distributions for the primary products and rate coefficients were determined in the usual way [20,21,23]. The rate coefficients are accurate to ±30% due to the sticky nature of the reactant gases. All reactions were studied at 298 K. Mass discrimination in the detection quadrupole was corrected for as before [22].

3. Results

3.1. Rate coefficients

As discussed before, $C_3H_3^+$ can be produced in many ways giving different ratios of cyclic to linear isomers [2,3,15–18,24–26]. The $C_3H_3^+$ produced in this study was expected to have a cyclic to linear isomer ratio of 70:30. This ratio was confirmed by reacting $C_3H_3^+$ with benzene. This is a well known reaction in which c-$C_3H_3^+$ undergoes no reaction [2,15]. Therefore, the reactive portion of the primary ion decay is attributed to l-$C_3H_3^+$. To accurately determine both the percent of reactive isomer and the rate coefficient for each isomer it was necessary to model the data. In the experiment, the counts of the primary ion mass are obtained as a function of the number density of neutral reactant [NR]. This relationship is given by

$$[\text{c-}C_3H_3^+] = [\text{c-}C_3H_3^+]_o \exp - k_c\,[\text{NR}]t \qquad (1)$$

and

$$[\text{l-}C_3H_3^+] = [\text{l-}C_3H_3^+]_o \exp - k_l\,[\text{NR}]t \qquad (2)$$

where [c-$C_3H_3^+$] and [l-$C_3H_3^+$] are the amounts of cyclic and linear isomer present at a particular neutral reactant flow, while [c-$C_3H_3^+$]$_o$ and [l-$C_3H_3^+$]$_o$ represents the initial amounts of each isomer. k_c and k_l are the reaction rate coefficients for the cyclic and linear isomers, respectfully. Since the experiment measures the mass and thus the combined amount of cyclic and linear isomers at each neutral reactant flow or concentration, the experimental data was modeled by

$$[\text{c-}C_3H_3^+] + [\text{l-}C_3H_3^+] = [\text{c-}C_3H_3^+]_o \exp - k_c\,[\text{NR}]t + [\text{l-}C_3H_3^+]_o \exp - k_l\,[\text{NR}]t \qquad (3)$$

which is the sum of Eqs. (1) and (2). The rate coefficient for each isomer can then be determined by adjusting k_c and k_l to fit the data and the ratio of each isomer initially present can be determined by adjusting [c-$C_3H_3^+$]$_o$ and [l-$C_3H_3^+$]$_o$. An example of the application of this model can be seen in Fig. 1. The model was applied to the reactions of tetrahydrofuran, furan, and 1,4-dioxane since they clearly had differing reactivities on the primary ion decay curve. Evaluation of the furan and 1,4-dioxane reactions provided a ratio of linear to cyclic isomer of 30:70 ± 1 and 29:71 ± 2, respectively, which agrees well with the 30:70 isomer ratio expected. Therefore, inter-conversion from one isomer to the other is not likely occurring in these reactions. In the reaction with tetrahydrofuran the rate for the linear and cyclic isomers were almost equal. When both rate coefficients are equal the ratio of isomers in the equations used above can take on any value equal to 100% and still fit the data.

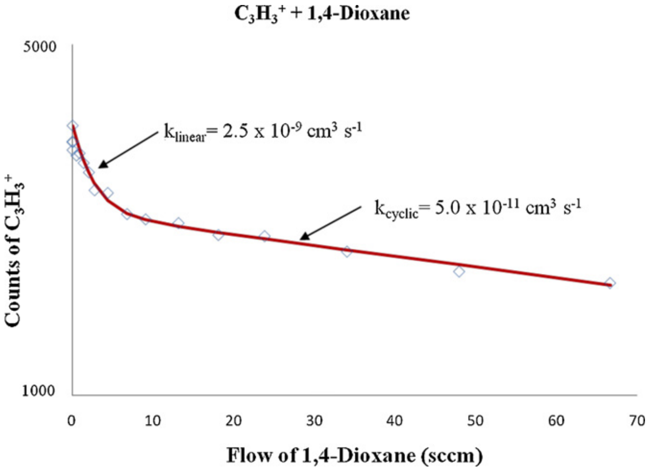

Fig. 1. Modeling of the rate coefficients for both the linear and cyclic isomers of $C_3H_3^+$ in reaction with 1,4-dioxane. The modeled line was fit by varying the initial concentrations of the two isomers and their rate coefficients.

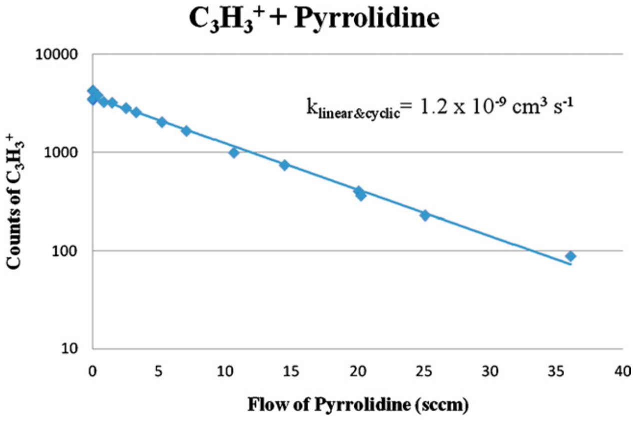

Fig. 2. The decay of the primary ion, $C_3H_3^+$, as it reacts with pyrrolidine is shown here as the log(counts of $C_3H_3^+$) versus the flow of neutral pyrrolidine ($cm^3\ min^{-1}$). This data is representative of the $C_3H_3^+$ reactions with nitrogen heterocyclic molecules. Here both linear and cyclic isomers react at the same rate but this rate is slower than those for the other nitrogen heterocyclic reactions.

Because of this, a larger range of isomer ratios can be used to fit the data in the case of tetrahydrofuran and the error associated with the ratio is much larger. Therefore, the ratio was constrained to a 30:70 linear to cyclic ratio to fit the curve. The rate coefficients for each reaction are listed in Table 1. The efficiencies listed in the table are determined for the reaction involving the linear isomer. Suffice to say, the efficiencies of the cyclic isomer reactions are often much smaller than those of the linear isomer. In the reactions involving piperidine, pyrimidine, tetrahydrofuran, furan and 1,4-dioxane, l-$C_3H_3^+$ reacts at the gas kinetic rate to within experimental error. In contrast, l-$C_3H_3^+$ reacts with the two five membered nitrogen rings, pyrrolidine and pyrrole, slower than the gas kinetic limit. There is no clear reason at this time for this diminished reactivity. However, it is also interesting to note, that in the case of the nitrogen heterocycles, the cyclic isomer appears to react at the same rate as the linear isomer so it was not possible to distinguish between them as can be seen in Fig. 2.

3.2. Ion product distributions

3.2.1. Nitrogen heterocycles

The product distributions for the reactions of pyrimidine, piperidine, pyrrole and pyrrolidine are given in Table 2. Each reaction exhibits a large amount of association. The largest association product channel occurs in the reaction with pyrimidine with an 89% abundance. The least amount of association occurs with pyrrolidine but still has a substantial abundance of 69%. Unlike the hydrocarbon rings studied previously [19], both isomers of $C_3H_3^+$ react with the nitrogen containing rings. This is not unexpected since c-$C_3H_3^+$ is known to react rapidly with nitrogen containing linear compounds like CH_3CN [16] and amines [2] through several mechanisms including hydride abstraction and association. In addition to association, the reactions of pyridine, piperidine, and pyrimidine also show a small product channel of proton transfer. The pyrrole reaction has a small charge transfer product channel along with the association product. The pyrrolidine reaction with $C_3H_3^+$ results not only in association but also in proton transfer, charge transfer and hydride abstraction.

3.2.2. Oxygen heterocycles

Three oxygen containing rings, dioxane, furan and tetrahydrofuran, were studied with the product ion distributions of these are given in Table 3. The amount of association is much less for these compounds relative to the cyclic hydrocarbons and the nitrogen heterocycles. Dioxane only has a 37% association channel and two fragmentation channels, hydride abstraction, and proton transfer. The reaction with furan, which can be seen in Fig. 3, has an

Table 1
Experimental rate coefficients, k_{exp}, for the reactions between $C_3H_3^+$ and the indicated neutrals followed by the theoretical rate coefficients, k_{theor},[a] calculated using combined variation transition state theory and classical trajectory theory [36].

Neutral molecule	l-$C_3H_3^+$ k_{exp} ($cm^3\ s^{-1}$)	c-$C_3H_3^+$ k_{exp} ($cm^3\ s^{-1}$)	k_{Theory} ($cm^3\ s^{-1}$)	Efficiency (l-$C_3H_3^+$)
Piperidine	2.1×10^{-9}	2.1×10^{-9}	1.7×10^{-9}	1.2
Pyrimidine	1.8×10^{-9}	1.8×10^{-9}	2.6×10^{-9}	0.69
Pyrrolidine	1.2×10^{-9}	1.2×10^{-9}	2.1×10^{-9}	0.57
Pyrrole	1.4×10^{-10}	1.4×10^{-10}	2.2×10^{-9}	0.06
Tetrahydrofuran	1.6×10^{-9}	1.5×10^{-10}	2.3×10^{-9}	0.70
Furan	1.8×10^{-9}	4.0×10^{-12}	1.5×10^{-9}	1.2
1,4-Dioxane	2.5×10^{-9}	5.0×10^{-11}	2.4×10^{-9}	1.0

[a] Data needed to calculate the theoretical rate coefficients were obtained from the CRC handbook and the literature [37,38]. The reaction efficiency, k_{exp}/k_{theor}, is included and calculated using the values for the linear isomer.

Table 2
Percentage ion product distributions for the reactions of $C_3H_3^+$ with the listed nitrogen heterocyclic molecules. Since c-$C_3H_3^+$ reacts with all of the nitrogen compounds, these product distributions listed are for a 70:30 ratio of cyclic to linear isomers.

Neutral reactant	Ion products	Product channel	Yield
Piperidine	$C_5H_{11}N{\cdot}C_3H_3^+$	A	76%
$C_5H_{11}N$	$C_5H_{11}NH^+$	PT	24%
954 kJ/mol			
8.03 eV			
Pyrimidine	$C_4H_4N_2{\cdot}C_3H_3^+$	A	89%
$C_4H_4N_2$	$C_4H_4N_2H^+$	PT	11%
885.8 kJ/mol			
9.33 eV			
Pyrrolidine	$C_4H_9N{\cdot}C_3H_3^+$	A	69%
C_4H_9N	$C_4H_8N^+$	HA	13%
948.3 kJ/mol	$C_4H_9NH^+$	PT	12%
8.77 eV	$C_4H_9N^+$	CT	6%
Pyrrole	$C_4H_5N{\cdot}C_3H_3^+$	A	84%
C_4H_5N	$C_4H_5N^+$	CT	16%
875.4 kJ/mol			
8.21 eV			

Ionization energies (eV) and proton affinities (kJ/mol) are given below each neutral molecular species. The recombination energy of linear $C_3H_3^+$ is 8.67 eV. The recombination energy of cyclic $C_3H_3^+$ is given as 6.6 eV, the proton affinity of c-C_3H_2 is 951.1 kJ/mol and the proton affinity of c-C_3H_2 is 885.4 kJ/mol. Product channels are indicated in the following manner: hydride ion abstraction (HA), charge transfer (CT), proton transfer (PT), association with fragmentation (AF), and association (A).

Table 3
Percentage ion product distributions for the reactions of $C_3H_3{}^+$ with the listed oxygen heterocyclic molecules.

Neutral reactant	Ion products	Product channel	Yield
Tetrahydrofuran	$C_4H_7O^+$	HA	40%
C_4H_8O	$C_4H_8O{\cdot}C_3H_3{}^+$	A	36%
822 kJ/mol	$C_4H_8OH^+$	CT	24%
9.4 eV			
Furan	$C_5H_2O^+$, $C_6H_6{}^+$	AF	42%
C_4H_4O	$C_5H_3O^+$, $C_6H_7{}^+$	AF	41%
803.4 kJ/mol	$C_4H_4OH^+$	PT	12%
8.88 eV	$C_4H_4O{\cdot}C_3H_3{}^+$	A	5%
1,4-Dioxane	$C_4H_8O_2{\cdot}C_3H_3{}^+$	A	37%
$C_4H_8O_2$	$C_4H_9O^+$, $C_3H_5O_2{}^+$	AF/F	17%
797.4 kJ/mol	$C_4H_7O_2{}^+$	HA	18%
9.19 eV	$C_5H_7O^+$, $C_4H_3O_2{}^+$, $C_6H_{11}{}^+$	AF/F	14%
	$C_4H_8O_2H^+$	PT	14%

Product channels are indicated in the following manner: hydride ion abstraction (HA), charge transfer (CT), proton transfer (PT), association with fragmentation (AF), and association (A). All other additional information is as in Table 2.

even smaller association channel at only 5%. However, the two most abundant channels are due to fragmentation of the association complex and together they account for 83% of the products. Proton transfer is present in a small abundance. In reactions involving tetrahydrofuran, the major product is hydride ion abstraction with an abundance of 40%. The association channel is the next most abundant at 36% which is very similar to the amount of association in the dioxane reaction. Proton transfer accounts for the remaining 24% of the product channel.

4. Discussion

As noted in the introduction, the $C_3H_3{}^+$ ion has undergone much scrutiny. There are several instances in the literature where the reactions of the $C_3H_3{}^+$ isomers with small linear hydrocarbon, nitrogen containing and oxygen containing molecules have been studied [16,18,24,27]. In the majority of these cases only l-$C_3H_3{}^+$ was seen to react and the dominant reaction mechanism is association. c-$C_3H_3{}^+$ is known to be unreactive with most species but was shown previously to react with NO [18], CH_3CN [16], and C_2H_5CN [28] and in all cases the only product channel was association. The present study is the first that involves the reactions of $C_3H_3{}^+$ with such a diverse and extensive number of cyclic compounds. Note that, both five membered and six membered rings are present. Heterocyclic molecules with both nitrogen and oxygen present as the heteroatom are represented. Lastly, the molecules can also be labeled as aromatic or non-aromatic and this difference in stability and availability of π electrons may affect the reactivity of the rings as was previously seen in the $CH_3{}^+$ study [29].

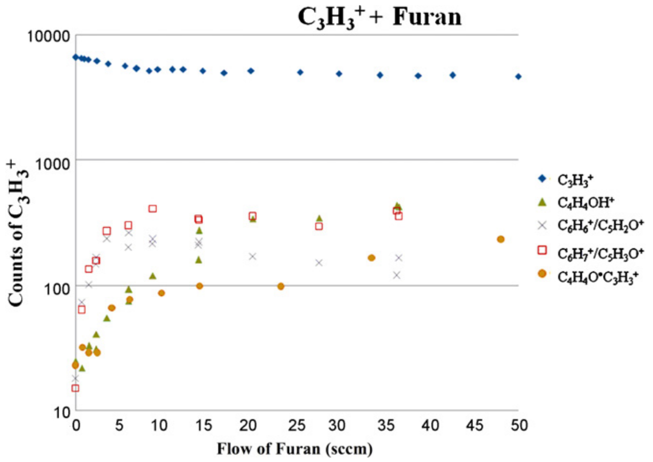

Fig. 3. Variation of the $C_3H_3{}^+$ primary ion and product ions for the reaction with furan. Notice that product ion counts are low due to the small amount of the $C_3H_3{}^+$ reacting with furan. The low product counts in conjunction with the mass discrimination in the detection quadrupole made it necessary to take data at three different resolutions. The resolution required to properly resolve the primary ion, $C_3H_3{}^+$, extremely limited the product ion signal. The resolution required to separate the product ions in the mid-mass range still limited the signal from the more massive association product channel. Thus this plot is a composite of $C_3H_3{}^+$ at a very high resolution, the $C_4H_4OH^+$, $C_6H_6{}^+/C_5H_2O^+$ and $C_6H_7{}^+/C_5H_3O^+$ at a slightly lower resolution and a much lower resolution to obtain signal for the association product channel. The mass discriminations are corrected for in determining the ion product distribution.

In the present study, the major product channel is association in 4 of the 7 reactions (piperidine (76%), pyrimidine (89%), pyrrolidine (69%), pyrrole (84%)). In two of the remaining three reactions there is a large amount of association with consecutive fragmentation. This can be determined because the product has a higher mass than either the neutral or ion separately. If the association with fragmentation and the association products channels are summed, they account for the majority of the product distribution in two of the reactions (furan (88%), and 1,4-dioxane (68%)). In only one reaction is association or fragmentation related to the association not the dominate product channel; this is tetrahydrofuran (36%). In the cases where both isomers react we were not able to isolate the individual isomers so the product distribution includes contributions from both isomers (in the 70:30 cyclic to linear ratio). Since association seems to be large in most reactions, the availability of π electrons, the presence of a heteroatom and the two different ring sizes does not seem to have much of an effect on the product distributions.

The biggest effect is seen in the rate coefficients for c-$C_3H_3{}^+$. It has been noted several times in the literature that c-$C_3H_3{}^+$ is not reactive with a variety of small organic molecules, however, Ausloos et al. surmised that c-$C_3H_3{}^+$ will react with unsaturated molecules having four or more carbon atoms (excluding linear or branched hydrocarbons) as well as aldehydes and amines by association and in some cases hydride transfer [2]. c-$C_3H_3{}^+$ was observed to react rapidly (10^{-9} $cm^3\,s^{-1}$) with the nitrogen heterocyclic molecules pyrimidine, piperidine, and pyrrolidine. In the reaction with piperidine c-$C_3H_3{}^+$ reacts very close to the collision rate. In the reactions of pyrrolidine and pyrimidine, c-$C_3H_3{}^+$ reacts at a comparatively rapid rate but not as fast as the gas kinetic limit. In the reaction with pyrrole both isomers react with the same rate coefficient (1.4×10^{-10} $cm^3\,s^{-1}$). However, unlike the other nitrogen heterocycles the rate coefficient is over an order of magnitude lower than the gas kinetic rate with a reaction efficiency of only 6%. Using the model described earlier to analyze the less reactive portion of the primary ion decay, it became apparent that c-$C_3H_3{}^+$ was also reacting with the oxygen heterocycles. The reaction with tetrahydrofuran has a comparatively fast rate coefficient on the order of 10^{-10} $cm^3\,s^{-1}$. c-$C_3H_3{}^+$ also reacts with 1,4-dioxane ($\sim 10^{-11}$ $cm^3\,s^{-1}$) and furan ($\sim 10^{-12}$ $cm^3\,s^{-1}$) though at a much slower rate. When comparing the reactions in the present study to those in the literature, it can be seen that c-$C_3H_3{}^+$ is much more reactive with the cyclic molecules. This is most likely because the majority of the previous reactions were studied using an ICR. If c-$C_3H_3{}^+$ is reacting via an association complex, the higher pressures of a SIFT would afford more stabilization making the complex less likely to dissociate to reactants. Also, with the SIFT the c-$C_3H_3{}^+$ is sure to be in its ground vibrational state before it comes in contact with the neutral gas by undergoing approximately 10^7 collisions with the carrier gas and this would increase the stabilization of the association complex.

In a previous study, we noted that association was competing with proton transfer even when proton transfer was energetically favorable [29]. In the present study, the proton transfer product channel is present in most of the reactions but in a much smaller

Table 4
A comparison of percentage ion product distributions for the reactions of CH_3^+ and $C_3H_3^+$ with the indicated neutrals.

	CH_3^+ [29]						$C_3H_3^+$					
	F	HA	CT	PT	AF	A	F	HA	CT	PT	AF	A
Cyclohexane	14%	68%	18%					100%				
Piperidine	40%	34%	22%	4%						24%		76%
Pyrrolidine	46%	32%	18%	4%				13%	6%	12%		69%
1,4-Dioxane	67%	14%	19%					18%		14%	31%	37%
Tetrahydrofuran	–	–	–	–	–	–		40%		24%		36%
Benzene	5%	31%	17%		39%	8%				16%		84%
Toluene	–	–	–	–	–	–					57%	43%
Pyridine		20%	21%	9%		50%				20%		80%
Pyrimidine	24%	19%	25%	9%		24%				11%		89%
Pyrrole	21%		64%	7%		8%			16%			84%
Furan		74%	26%							12%	83%	5%

Product channels are indicated in the following manner: fragment (F), hydride abstraction (HA), charge transfer (CT), proton transfer (PT), association with fragmentation (AF), and association (A). Product distributions for the reactions of $C_3H_3^+$ with benzene, toluene, and pyridine are from Ref. [19].

abundance compared to association. The proton affinity of the cyclic isomer of C_3H_2 is given as 951.1 kJ/mol [30]. This proton affinity is larger than the proton affinities of all of the rings except for piperidine. No experimental value for the proton affinity of the linear isomer of C_3H_2 is available in the literature so one was computed via the CBS-QB3 method of Montgomery et al. [31] using the Gaussian 03 package [32]. The proton affinity was calculated to be 885.4 kJ/mol. The proton affinities of piperidine and pyrrolidine are higher than that of l-C_3H_2 so the proton transfer product seen in both reactions is expected. The proton transfer product channel seen in the reaction with pyrimidine is thermoneutral, however, the product channel is small and is most likely driven by the fraction of interactions that are energetically allowed by the kinetic energy in a Maxwell–Boltzmann distribution and by internal energy in a Boltzmann distribution. In the reactions with furan and 1,4-dioxane proton transfer is not expected since the reactions are decidedly endothermic. However, both reactions show a small amount of proton transfer. The driving force behind this proton transfer is unknown but there are several occasions in the literature where l-$C_3H_3^+$ proton transfers to neutrals with lower proton affinities than the one calculated for l-C_3H_2. For instance, reaction of l-$C_3H_3^+$ with H_2O (PA = 691 kJ/mol) [16], NH_3 (853.6 kJ/mol) [16], CH_3OH (754.3 kJ/mol) [33], C_2H_5OH (776 kJ/mol) [34] all have a proton transfer product channel. Interestingly, a majority of these molecules contain an oxygen atom, just like furan and 1,4-dioxane.

A comparison of products from the CH_3^+ study [29] to the products obtained in our previous $C_3H_3^+$ study [19] and the products obtained in the present $C_3H_3^+$ study is given in Table 4. In the CH_3^+ reactions, only those involving an aromatic ring resulted in association of the ion and neutral. In contrast, the present study shows association as a product channel for every reaction except cyclohexane. Thus the availability of π electrons does not seem to be necessary to form an association complex with $C_3H_3^+$. Also, in the reactions of $C_3H_3^+$, the amount of fragmentation of the rings is very low. This can be explained by considering the recombination energies (RE) of each ion. CH_3^+ has an RE of 9.84 eV while l-$C_3H_3^+$ (c-$C_3H_3^+$) has an RE of only 8.67 eV (6.6 eV). In the CH_3^+ studies, charge transfer was energetically favorable and was seen as a product channel in all of the reactions studied. Excess energy left over from the charge transfer likely contributed to the fragmentation of the ring. While in reactions involving l-$C_3H_3^+$, charge transfer is energetically favorable with only two neutral species and both of these reactions are close to thermoneutral. In fact, the only reaction that has product masses possibly identified as fragmentation of the ring is the 1,4-dioxane reaction. Because this ring has two oxygen heteroatoms, one mass can often be identified by several different molecular formulas. For example, the product mass peak at 73 amu could be identified as either

$$C_3H_3^+ + C_4H_8O_2 \rightarrow C_4H_9O^+ + C_3H_2O \tag{4}$$

or

$$C_3H_3^+ + C_4H_8O_2 \rightarrow C_3H_5O_2^+ + C_4H_6\,(CH_3 + C_3H_3) \tag{5}$$

Reaction (4) requires the loss of an oxygen atom and the acquisition of a hydrogen atom to the dioxane molecule which would have to occur through association with fragmentation. Reaction (5) requires the loss of a CH_3 neutral which could be the result of either association with fragmentation or unimolecular dissociation due to a charge transfer reaction. Unimolecular dissociation is not expected to occur since charge transfer is not energetically favorable in this reaction. Neither reaction (4) or (5) is likely to occur without an intermediate association complex to assist in rearrangement and fragmentation. Therefore, it is most likely that the fragmentation is due to the breakup of the association complex. Unfortunately, it was not possible to calculate which product is more energetically favorable due to insufficient thermodynamic data in the literature. In the case of CH_3^+ versus $C_3H_3^+$ reactions resulting in fragmentation, the reactions of the latter do not have enough energy to drive fragmentation with the studied rings. Instead, the low energy of the system translates into a very stable association complex that does not require the presence of π electrons to stabilize the complex as is required for the CH_3^+ associations with the same neutrals.

5. Conclusions

The reactivity of both linear and cyclic $C_3H_3^+$ with several linear molecules has previously been studied, mostly using an ICR. The present study involves the reactivity of both isomers with several different types of cyclic molecules in the higher pressure environment of the SIFT. The major product in all but one reaction was association or association with fragmentation. Linear $C_3H_3^+$ reacts at or near the gas kinetic rate in the reactions involving piperidine, pyrimidine, tetrahydrofuran, furan and 1,4-dioxane, but reacts more than 30% slower than the theoretical upper limit for the reactions involving pyrrolidine and pyrrole. The cyclic isomer proves to be slowly reactive with the oxygen heterocyclic species but very reactive with the nitrogen heterocyclic species.

These data have implications to the much scrutinized atmosphere of Titan. A peak corresponding to the mass of $C_3H_3^+$ has been identified in the mass scans taken of Titan's ionosphere. It is one of the most abundant peaks in the scan with a density of approximately 90 cm^{-3}. A recent model calculated the cyclic and linear $C_3H_3^+$ densities to be 34 cm^{-3} and 1.8 cm^{-3}, respectively [14]. In the model, the only loss channel for c-$C_3H_3^+$ is electron recombination. However, the present study shows that in the higher pressure (0.5 Torr) environment of the SIFT, c-$C_3H_3^+$ has the possibility of reacting with ring compounds at an appreciable rate, especially those containing nitrogen. The pressure in Titan's ionosphere (at ∼1000 km) is too low [35] for collisionally stabilized association complexes to form, however, the pressure of the atmosphere increases significantly approaching the surface. Thus, models of Titan's lower atmosphere should consider association reactions of c-$C_3H_3^+$ as a loss channel where nitrogen containing ring compounds are likely to exist.

The data received from the extended Cassini Mission have transformed the old perceptions and models of Titan due to the presence of complex organic compounds, nitrogen containing species, and large negative ions indicated by the many instruments aboard the Cassini Orbiter. In spite of all of the new data, there is still a lot of uncertainty about Titan's atmosphere since the identities of most of the chemical species have not been firmly established. The models created assume chemical formulas dependant on the information known such as the neutral composition and the ionization of these neutrals. The models build up the larger masses from this starting point through various reaction pathways. However, if a reaction pathway is missed this could affect the entire model. This emphasizes how important it is to study in the laboratory every reaction which could possibly take place in Titan's atmosphere. The data collected in the present study identifies reaction pathways that have not been considered before but given the conditions of Titan's atmosphere might very well be important.

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