A SIFT Ion-Molecule Study of Some Reactions in Titan's Atmosphere. Reactions of N^+ , N_2^+ , and HCN^+ with CH_4 , C_2H_2 , and C_2H_4

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The results of a study of the ion-molecule reactions of N^+ , N_2^+ , and HCN^+ with methane, acetylene, and ethylene are reported. These studies were performed using the FA-SIFT at the University of Canterbury. The reactions studied here are important to understanding the ion chemistry in Titan's atmosphere. N^+ and N_2^+ are the primary ions formed by photo-ionization and electron impact in Titan's ionosphere and drive Titan's ion chemistry. It is therefore very important to know how these ions react with the principal trace neutral species in Titan's atmosphere: Methane, acetylene, and ethylene. While these reactions have been studied before the product channels have been difficult to define as several potential isobaric products make a definitive answer difficult. Mass overlap causes difficulties in making unambiguous species assignments in these systems. Two discriminators have been used in this study to resolve the mass overlap problem. They are deuterium labeling and also the differences in reactivities of each isobar with various neutral reactants. Several differences have been found from the products in previous work. The HCN $^+$ ion is important in both Titan's atmosphere and in the laboratory. (J Am Soc Mass Spectrom 2004, 15, 1148–1155) © 2004 American Society for Mass Spectrometry

This is the fifth in a series of articles on the ion-molecule chemistry that is expected to occur • in the atmosphere of Saturn's satellite Titan. The first four articles described the reactions of the principal ions with the principal neutrals [1]; the structure of the association adducts of $HCNH^+$ with C_2H_2 and C_2H_4 [2]; the clustering of HCNH⁺ with nitrogen [3]; and the reactions of hydrocarbon ions in their pure systems at up to 20 microns of pressure [4]. In the present paper we relate experimental results of the ion-molecule reactions of N⁺, N₂⁺, and HCN⁺ with the hydrocarbons CH₄, C₂H₂, and C₂H₄. These results introduce several new channels to the established ion chemistry and have a significant influence on the ion abundances. To achieve the current results it was necessary to use deuterium labeling and to study the secondary reactions of the primary ion products to determine the branching ratios occurring in the SIFT flow tube.

In our first two studies, the chemistry was examined under conditions in which the parent ion was the only ion present and the ensuing ion-neutral reaction was

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the first reaction of a possible sequence of reactions. In the studies we report here, the neutral reagent partial pressure was increased to allow the product ions to undergo further chemistry with the reactant neutral. The reaction rate coefficients were obtained under these conditions through numerical modeling of the data. When the laboratory data is extrapolated to the actual environment of Titan, it is seen that many consecutive reactions take place after the primary ionization of the nitrogen occurs [5]. As the number of atoms in the ions increases, so too does the possibility for forming isomeric structures and the question might then be raised as to which isomer or isomers are actually present. Isomers generally react at different rates and may have different product distributions. Thus, to reduce the number of isomers that are unidentified, the isomeric ionic species were formed in the flow tube in a way that is similar to their method of formation in Titan's ionosphere [6]. It is then expected that the mixture of isomeric ions produced in our studies will be representative of the ions present in Titan's atmosphere. So by studying the chemistry at varying neutral reagent pressures within the flow tube for several consecutive reactions, the results should be more representative of Titan ion chemistry than the lower pressure individual ion studies previously reported.

Current modeling of Titan's atmosphere shows that the ion chemistry is important in determining the abundances of even some neutral trace species [7]. The models also show that up to the altitude where the electron density peaks, very complex chemical structures may be produced. The previously reported laboratory data does not extend to these species or pressures. The following study will help in removing this deficiency.

The reaction chemistry of N^+ and N_2^+ initiates the ion chemistry of Titan and the reactions reported here lay the foundation on which the subsequent ion chemistry is based. While some broad aspects of these reactions have been reported previously, there is sufficient uncertainty in the published results to warrant the present study. An investigation of the previous reports reveals some conflict with each other and also highlights several substantial uncertainties. It was felt that we could remove some of the uncertainties in the previous studies by using deuterium labeling and following the sequential reactions of the product ions. Then, by accurately modeling these reactions over a range of neutral flow conditions, the branching ratios will be more accurately determined. This procedure of matching the model predictions with the experimental data is quite sensitive to the branching ratios chosen.

Experimental

In these studies the flowing afterglow-selected ion flow tube (FA-SIFT) at Canterbury University was used. All experiments were made at room temperature, about 25°C.

The FA-SIFT experiment has been described previously [8]. A summary follows for the understanding of this paper. The reactant ions are formed in a microwave discharge operating on helium in a flowing afterglow tube and after mass selection, a swarm of the selected reactant ions are injected into the SIFT flow tube through a Venturi injection orifice. Mass selection between the FA and the SIFT was accomplished using a quadrupole mass spectrometer operating at a pressure of about 1×10^{-5} torr. The carrier gas in the SIFT was either helium or nitrogen that was scrubbed by passing the gas over liquid nitrogen-cooled molecular sieve material (He) or a dry ice/acetone bath (N_2) . Measured flows of reactant gases were added downstream of the Venturi injector and 50.4 cm upstream of the nose cone sampling aperture. Ions were sampled from the SIFT using a small orifice in the nose cone, behind which was a second quadrupole mass spectrometer. A particle multiplier tube with pulse counting technology was used to measure the relative ion abundances. The pressure was typically 0.48 torr (He) or 0.28 torr (N2) in the reaction flow tube and the ion flow times were about 3.5 ms from the reactant gas entrance to the skimmer-nosecone of the quadrupole detector.

Gases were obtained commercially and purified using freeze-pump-thaw cycles.

Analytical

The reactions in the SIFT were modeled starting with the injected ions and the background ions. It was not possible to cleanly inject a single mass in every case. In many cases the injected mass was accompanied by small flows of the adjacent masses at the 2% level.

In addition, the impurities in the helium flow also reacted with the injected ions and had to be accounted for. Trace amounts of water were always present and the amount depended on the purity of the starting helium. The number density of H_2O^+ and H_3O^+ ions in the reaction region varied from 4 to 14% of the total ion count. The oxygen ion O_2^+ was also present at levels between 2 to 20% when injecting N_2^+ . The protonated nitrogen molecular ion; N₂H⁺, was also present on occasions. The reactions of all these "impurity" ions are known and can be deconvoluted from the reaction results.

The primary reactions for each system were determined and a kinetic model using these reactions was made. This model included the interfering ions from the injection process or impurities arising from the helium bath gas. In addition, the reactions of the primary products were also modeled. The partial differential equations for the reaction kinetics were compiled and solved. The general solutions for bimolecular reactions are shown in the Appendix. The solutions were then put into an Excel spreadsheet and compared with the normalized raw data. The reaction rate coefficients and branching ratios were adjusted using least squares fitting and the "Solver" function of Excel to achieve the best fit with the raw data. It has been assumed that the branching ratios of the deuterated and undeuterated reactions are the same. Both data sets for the deuterated and undeuterated ions were solved simultaneously. The "least squares" fit minimized the sum of the differences (between the model and the experimental data points) divided by the experimental value all squared. In this procedure the percentage difference between the normalized raw and modeled data was minimized.

Results

The new results are summarized in the Discussions section and in Table 1, while Table 2 contains some values taken from the literature for the secondary reactions and the impurity reactions and some values obtained from this study.

The raw data are in the form of ion abundance plots versus the flow rate of the reactant neutral. The N^+ , N_2^+ and HCN⁺ ions were generated in the FA part of the apparatus. The extent of reaction was controlled by the flow rate of the reactant neutral. Figures 1 and 2 show the behavior of the HCN+ ion with varying flows of methane and deuterated methane. The HCN⁺ ions were generated from He 2³S metastable reactions with HCN in the flowing afterglow ion source and these produce a mixture of HCN⁺/HNC⁺ isomers of which the majority are in the HCN+ form. In the reactions

Table 1. Summary of new reactions from text

Reactant	Reactant neutral	Product ion	Product neutral	Branching ratio	Reaction rate coefficient
N ⁺	CH₄	CH ₃ ⁺ CH ₄ ⁺	NH N	0.38 0.03	1.10E-09
		HCN ⁺	$H_2 + H$	0.05	
		HCNH ⁺	H ₂	0.44	
N^+	C_2H_2	$C_2H_2^+$	N	0.65	1.30E-09
		HCNH ⁺	CH ₂	0.07	
		CNC ⁺	H_2	0.06	
		CHNC ⁺	Н	0.22	
N ⁺	C_2H_+	C_2H_4	NH_2	0.13	1.10E-09
		$C_2H_3^+$	NH	0.44	
		$C_2H_4^+$	N	0.30	
		CHNC ⁺	$H_2 + H$	0.04	
		CH ₂ NC ⁺	H_2	0.10	
N_2^+	CH₄	CH ₂ ⁺	NH_2	0.12	1.00E-09
2	·	CH ₂ ⁺	NH	0.88	
N_2^+	$C_2H_2^+$	C_2H_2	N_2	1.0	5.50E-10
N_2^+	C_2H_4	$C_2H_2^+$	$N_2 + H_2$	0.36	7.10E-10
		$C_2^+H_3^+$	$N_2 + H$	0.64	
HCN ⁺	CH₄	HCNH ⁺	CH ₃	0.90	8.80E-10
		CH ₃ ⁺	HCN + H	0.02	
		CH ₄ ⁺	HCN	0.04	
		HCCNH ⁺	$H_2 + H$	0.01	
		CH ₃ CNH ⁺	Н	0.03	
HCN ⁺	C_2H_2	$C_2H_2^+$	HCN	0.19	1.20E-09
		$C_2H_3^+$	CN	0.01	
		C_3N^+	$H_2 + H$	0.06	
		HC ₃ N ⁺	Н	0.09	
		HC ₃ NH ⁺	H_2	0.66	
HCN	C_2H_4	$C_2H_2^+$	HCN	0.73	1.30E-09
		$C_2H_5^+$	CN	0.13	
		HC ₃ NH ⁺	$H_2 + H$	0.01	
		$H_4C_3N^+$	Н	0.13	

studied there was no evidence for any different behavior between these isomers and we present our results here as HCN⁺. These figures are broken down into three parts representing the primary, secondary, and tertiary ion reactions. Only this data derived from HCN⁺ is shown as a representation of the quality and type of data used in this study. Similar reaction profiles were obtained for all the systems studied.

Discussion

Reactions of the N^+ Ion

Methane. The results found in this study for the N⁺ reaction with methane are in general agreement with the product channels reported in 1993 [9] except that the relative amounts proceeding to each channel are changed. The branching ratios reported in the evaluation [9] were 0.50, 0.05, 0.10, and 0.36 for the product

order CH₃⁺, CH₄⁺, HCN⁺, and HCNH⁺. In the current study the subsequent reactions of the CH₃⁺, CH₄⁺, and HCN⁺ ions were modeled and the fit to the data provided by the model showed a reduction in the CH₃⁺ channel and a small enhancement of the HCNH⁺ channel. The reaction parameters used in achieving this fit are listed in Tables 1 and 2. The protonated water ion production was not modeled since it results from a small water impurity in the flow tube and only represents a couple of percentage points of the total ions.

$$N^{+} + CH_{4} \quad k = 1.10 \times 10^{-9} \text{cm}^{3} / \text{s}$$

 $\rightarrow CH_{3}^{+} + NH \qquad 0.38$
 $\rightarrow CH_{4}^{+} + N \qquad 0.03$
 $\rightarrow HCN^{+} + H_{2} + H \quad 0.15$
 $\rightarrow HCNH^{+} + H_{2} \qquad 0.44$

Table 2. Summary of secondary reactions used in text

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Table 2.	Summary	or seconda	ary reaction	ns usea i	n text
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CH ₂ ⁺	CH₄		H ₂	0.70	1.20E-09
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_2H_5^+$	Н	0.30	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_2H_5^+$	H_2	1.0	1.10E-09
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CH ₄ ⁺	CH₄	CH_5^+	CH₃	1.0	1.14E-09
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_2H_2^+$	C_2H_2	$C_4H_2^+$	H_2	0.43	1.20E-09
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_4H_3^+$	Н	0.49	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_4H_4^+$		0.08 ^a	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_2H_2^+$	C_2H_4		C_2H_2	0.30	1.38E-09
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_3H_3^+$	CH₃	0.48	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_4H_5^+$	Н	0.23	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_2H_3^+$		$C_2H_5^+$	C_2H_2	1.0	8.90E-10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_2H_4^+$	C_2H_4	$C_3H_5^+$	CH₃	0.91	7.90E-10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_4H_7^+$	Н	0.09	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_2H_5^+$	C_2H_4	$C_3H_5^+$	CH₄		5.80E-10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$C_4H_9^+$		0.50	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H ₂ O ⁺	CH.	H ₂ O+	CH-	1.0	1 12F-09
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				-		
$\begin{array}{cccc} \text{HCNH}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \text{HCNH}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \\ \text{CNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \\ \text{CHNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \\ \text{CHNC}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \end{array}$	1120	2114	2.14	112	1.0	1.002 00
$\begin{array}{cccc} \text{HCNH}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \text{HCNH}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \\ \text{CNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \\ \text{CHNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \\ \text{CHNC}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \end{array}$	HCNH ⁺	CH₄				No reaction
$\begin{array}{cccc} \text{HCNH}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \\ \text{CNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \\ \text{CHNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \\ \text{CHNC}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \end{array}$	HCNH ⁺					No reaction
$ \begin{array}{ccc} \text{CHNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \text{CHNC}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \end{array} $	HCNH ⁺					No reaction
$ \begin{array}{ccc} \text{CHNC}^+ & \text{C}_2\text{H}_2 & \text{No reaction} \\ \text{CHNC}^+ & \text{C}_2\text{H}_4 & \text{No reaction} \\ \end{array} $						
$CHNC^+$ C_2H_4 No reaction						
£ 7						
CH_2NC C_2H_4 No reaction	CH ₂ NC ⁺	C_2H_4				No reaction

^aChannel seen in SIFT only.

Acetylene. To achieve a satisfactory fit between the data and the model for the N⁺ ion with acetylene, it was necessary to add a protonated hydrogen cyanide channel, which was not reported in our earlier study [10]. The use of both deuterated and normal acetylene along with the modeling of the subsequent reactions has established this channel at 7%.

It is important to note that the secondary reaction chemistry of the $C_2H_2^+$ ion is different in the SIFT and the ICR. In the SIFT at a pressure of 0.45 torr an 8-11% adduct channel is found from the termolecular association reaction.

$$C_2H_2^+ + C_2H_2 + M \rightarrow C_4H_4^+ + M$$

 $k = 8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

The reaction rate coefficient is for the pseudo-bimolecular reaction at 0.48 torr of helium. This leaves an unmeasured termolecular reaction for future studies.

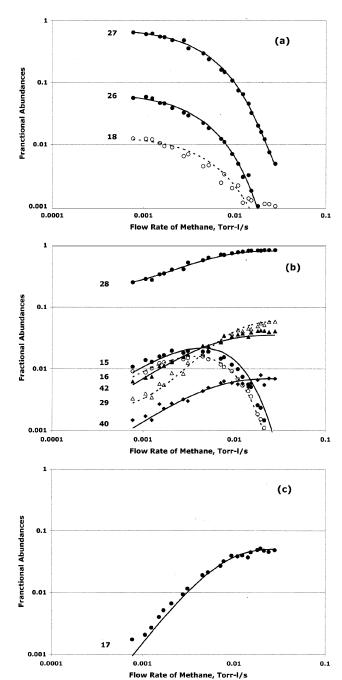
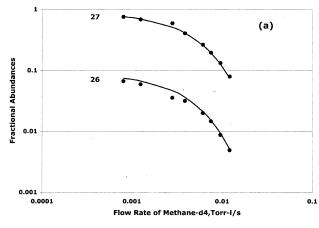
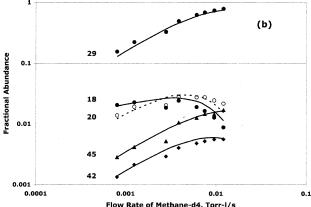


Figure 1. (a) The fraction abundances of the primary ions in the reaction of HCN^+ with methane. (b) The fraction abundances of the secondary ions in the reaction of HCN^+ with methane. (c) The fraction abundances of the tertiary ions in the reaction of HCN^+ with methane. The points are experimental and the lines are the modeled values.

Ethylene. The results found in the study for the reaction of N^+ with ethylene are somewhat different from that reported in the evaluated results of 1993 [9] and the later examination of this reaction [10]. In the present study, both normal ethylene and deuterated ethylene were used. Both reactions were analyzed together to resolve the mass overlap and subsequent reaction and product ion problems. In so doing, the product ions of





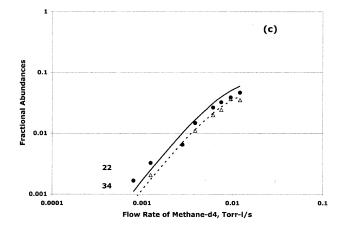


Figure 2. (a) The fraction abundances of the primary ions in the reaction of HCN⁺ with methane-d₄. (b The fraction abundances of the secondary ions in the reaction of HCN⁺ with methane-d₄. (c) The fraction abundances of the tertiary ions in the reaction of HCN⁺ with methane-d₄. The points are experimental and the lines are the modeled values.

 HCN^+ and HCNH^+ reported earlier were found to be absent. Instead, the ions at 27 and 28 u arose solely from $\mathrm{C_2H_3^+}$ and $\mathrm{C_2H_4^+}$. This was deduced from the modeling of the subsequent reactions of these ions. The branching ratios reported here for the $\mathrm{C_2H_3^+}$ and $\mathrm{C_2H_4^+}$ ions are very similar to the evaluated results if the branching ratios previously reported for $\mathrm{HCN^+}$ and $\mathrm{HCNH^+}$ product ions are added to those of the $\mathrm{C_2H_3^+}$ and $\mathrm{C_2H_4^+}$ ions. The best agreement between data and the model

was obtained when both mass 39 (CHCN $^+$) and 40 (CH $_2$ CN $^+$) ions were included as product channels of the reaction.

Reactions of the N_2^+ *Ion*

Methane. The mass 29 channel reported by us in a 1998 paper [10] was not confirmed. The only product mass 29 ions observed were the result of subsequent reactions of the methyl and methylene ions.

$$N_2^+ + CH_4$$
 $k = 1.00 \times 10^{-9} \text{ cm}^3/\text{s}$
 \rightarrow $CH_2^+ + NH_2$ 0.12
 \rightarrow $CH_3^+ + NH$ 0.88

Acetylene. Contrary to our 1998 results [10] for the reaction between N_2^+ and C_2H_2 , the use of acetylene and deuterated acetylene, and modeling the subsequent reactions, we find no evidence for the HCN^+ or N_2H^+ ion products that presumably originated from impurities in the earlier study. The only reaction channel observed was charge transfer.

$$N_2^+ + C_2H_2$$
 $k = 5.50 \times 10^{-10} \text{cm}^3/\text{s}$
 $\rightarrow C_2H_2^+ + N_2$ 1.0

Here again, as in the case of N^+ with acetylene, the secondary reaction of the acetylene ion produced the adduct $C_4H_4^+$ ion.

Ethylene. In the case of the reaction of the N_2^+ ion with ethylene, the major channels are the same as those reported in our 1998 paper [10]. The charge transfer reaction does not seem to be present. The HCN $^+$ ion and HCNH $^+$ ion, while reported in the earlier study are omitted here. Although there is considerable mass overlap with both the normal and deuterated ethylene making the identification of products very difficult, we have been able to carefully model the reactions of the product ions and to follow the reactions over a significant flow range. The results gave good agreement with the model without having to invoke HCN $^+$ and HCNH $^+$ formation.

$$N_2^+ + C_2H_4$$
 $k = 7.10 \times cm^{-10}/s$
 $\rightarrow C_2H_2^+ + N_2 + H_2$ 0.36
 $\rightarrow C_2H_3^+ + N_2 + H$ 0.64

There was one significant and unexpected reaction product. The secondary $C_2H_3^+$ ion reacts to form the $C_2H_5^+$ ion in ethylene.

$$C_2H_3^+ + C_2H_4$$
 $k = 8.9 \times 10^{-10} \text{ cm}^3/\text{s}$
 $\rightarrow C_2H_5^+ + C_2H_2$

This $C_2H_5^+$ ion is known to react with C_2H_4 to form the $C_3H_5^+$ ion. We have determined that it also forms the adduct ion $C_4H_9^+$, in the SIFT. They are produced in equal abundances and with a rate coefficient of 5.80 \times $10^{-10} \text{ cm}^3/\text{s}.$

$$C_2H_5^+ + C_2H_4$$
 $k = 5.80 \times 10^{-10} \text{ cm}^3/\text{s}$
 $\rightarrow C_3H_5^+ + CH_4$ 0.50
 $\rightarrow C_4H_9^+$ 0.50

Reactions of the HCN⁺ Ion

Methane. This reaction has been the subject of several previous studies. All agree that the hydride abstraction reaction is the primary channel for this reaction. There is the suggestion by Schiff et al. [11] that there is also a channel forming a mass 27 ion that was identified as the $C_2H_3^+$ ion. This study shows that $C_2H_3^+$ cannot be formed as a product ion. We have also identified several small channels in the reaction that result from dissociative charge transfer and adduct formation with loss of hydrogen moieties. To determine the branching ratio in this study we used both normal and deuterated methane and also followed the reaction far enough to observe the product ions for confirmation. The uncertainty in the branching ratio of these small channels is of the order of ± 0.02 .

In Figures 1 and 2, the results and modeling are shown for this reaction with methane and methane-d₄ respectively. The three parts of each figure show the primary reactants (H₂O⁺, CN⁺ and HCN⁺), the primary products of their reaction (CH₃⁺, CH₄⁺, HCNH⁺, HCCNH⁺ and CH₃CNH⁺) and the secondary products (CH_5^+) and $C_2H_5^+$). For example, in Figure 1a the three initial components of this reaction, HCN+, CN+, and H₂O⁺ are seen to decay away to zero as the flow of methane is increased. In Figure 1b, the products of the reaction of these three ions with methane are seen to increase and then level off if they are not reactive, or to peak before decreasing in magnitude if they are reactive. The CH₃⁺ and the CH₄⁺ ions react away to form CH_5^+ (for CH_4^+), which is seen in Figure 1c, and $C_2H_5^+$ (for CH_3^+), which is seen as in increase in the amplitude of the mass 29 abundance in Figure 1b. By using this method it is straightforward to distinguish the identity of the product ions and order of the reaction from the shape of the curves. The chemical composition of the abundances at each mass can be determined by comparing the normal and deuterated products seen in Figures 1 and 2. The mass 28 abundance in Figure 1a is seen to correspond to the mass 29 abundance in Figure

2a. Thus the mass 28 and 29 abundances have a single reactive hydrogen (or deuterium) and are therefore HCNH⁺. Another example is the mass 17 abundance in Figure 1c which corresponds to the mass 22 abundance in Figure 2c. Similarly the mass 17 and 22 ion can be deduced to have five reactive hydrogens (or deuteriums) and are therefore CH_5^+ .

$$HCN^{+} + CH_{4} \quad k = 1.27 \times 10^{-9} \text{ cm}^{3}/\text{s}$$

 $\rightarrow HCNH^{+} + CH_{3} \quad 0.90$

 $\rightarrow CH_{3}^{+} + HCN + H \quad 0.02$

 $\rightarrow CH_{4}^{+} + HCN \quad 0.04$

 $\rightarrow HCCNH^{+} + H_{2} + H \quad 0.01$

 $\rightarrow CH_{3}CNH^{+} + H \quad 0.03$

Acetylene. This reaction was observed with both deuterated and undeuterated acetylene in the present study. An earlier investigation of this reaction was reported by Petrie et al. [12] and Schiff et al. [11]. These earlier studies did observe the three main products, but were unable to determine an accurate branching ratio. Also, the previously reported reaction rate coefficients were larger than the calculated collision rate constant. The measured value in this current study is the same as the calculated collision rate constant.

$$HCN^{+} + C_{2}H_{2}$$
 $k = 1.20 \times 10^{-9} \text{ cm}^{3}/\text{s}$
 $\rightarrow C_{2}H_{2}^{+} + HCN$ 0.19
 $\rightarrow C_{2}H_{3}^{+} + CN$ 0.01
 $\rightarrow C_{3}N^{+} + H_{2} + H$ 0.06
 $\rightarrow HC_{3}N^{+} + H_{2}$ 0.09
 $\rightarrow H_{2}C_{3}N^{+} + H$ 0.66

Ethylene. This is the first reported observation of this reaction. It is consistent with the acetylene reaction in that both charge transfer and association with H loss are observed. This has also been confirmed using deuterated ethylene. The measured reaction rate coefficient is consistent with the calculated collision rate constant.

$$HCN^{+} + C_{2}H_{4}$$
 $k = 1.30 \times 10^{-9} \text{ cm}^{3}/\text{s}$
 $\rightarrow C_{2}H_{4}^{+} + HCN$ 0.73
 $\rightarrow C_{2}H_{5}^{+} + CN$ 0.13
 $\rightarrow HC_{3}NH^{+} + H_{2} + H$ 0.01
 $\rightarrow H_{4}C_{3}N^{+} + H$ 0.13

Conclusion

The reactions of N^+ , N_2^+ and HCN^+ with CH_4 , C_2H_2 , and C₂H₄ have been measured. These systems although apparently simple, all have problems with mass overlap of the reactant and product ions. Earlier studies have been made with sometimes conflicting results attributable to these overlap difficulties. The reactions in question are important reactions in the ionosphere of Saturn's satellite Titan as they represent the primary ion chemistry. The nitrogen ion reaction initiates the vast majority of the ion chemistry that occurs there. Understanding the nature of these nitrogen ion reactions is critical to the understanding of the subsequent reactions. In the current work, special care was taken to ensure that the product ions were identified unambiguously. Deuterium labeling has been used on the neutral reactants. The reactions of the reactant ions were also followed to the extent they were completely removed by reaction with the neutral hydrocarbon. Then the reactions of the product ions were used to verify their identification.

This completed study represents the best effort to date on these reactions and the resulting data on the primary reactions can be used with the greatest of confidence. Currently, work is in progress to understand the chemistry occurring in laboratory simulations of the N^+ and N_2^+ reactions in a mixture of the hydrocarbons: CH_4 , C_2H_2 , and C_2H_4 . The reactions measured in this study will greatly help in unraveling the tangle of reactions that proceed in such a mixture. It is a goal of these studies to assist in understanding the observations that will be made of Titan's atmosphere and particularly its ionosphere by the Cassini spacecraft's mass spectrometer.

Acknowledgments

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Appendix

Kinetics

This section presents the solution of the partial differential equations of the following consecutive 2nd order reactions:

The Reactions.

$$A^{+} + B \xrightarrow{k_{1}} C_{i}^{+} + D$$

$$C_{i}^{+} + B \xrightarrow{k_{2i}} E_{ij}^{+} + F$$

$$E_{ij}^{+} + B \xrightarrow{k_{3ij}} G_{ijk}^{+} + H$$

The Solutions—Primary Ion.

$$-\frac{d[A^+]}{dt} = k_1[A^+][B]$$

or

$$\frac{d[A^+]}{[A^+]} = -k_1[B]dt$$

integrating

$$\frac{ln[A^+]}{ln[A^+]_0} = -k_1[B]t$$

or

$$[A^+] = [A^+]_0 e^{-k_1[B]t}$$

The Solutions—Secondary Ions.

$$\frac{d[C_i^+]}{dt} = b_i k_1 [A^+][B] - k_{2i} [C_i^+][B]$$

or

$$\frac{d[C_i^+]}{dt} = b_i k_1 [A^+]_0 [B] e^{-k_1 [B]t} - k_{2i} [C_i^+] [B]$$

$$\frac{d[C_i^+]}{dt} + k_{2i}[C_i^+][B] = b_i k_1 [A^+]_0 [B] e^{-k_1 [B] t}$$

$$[C_i^+] = e^{-k_{2i}[B]t} \int b_i k_1 [A^+]_0 [B] e^{k_{2i}[B]t - k_1[B]t} dt$$
$$+ Ce^{-k_{2i}[B]t}$$

for t=0 and [C⁺] = 0 then
$$C = -[A^+]_0 \left(\frac{b_i k_1}{k_{2i} - k_1}\right)$$

$$[C_i^+] = [A^+]_0 \left(\frac{b_i k_1}{k_{2i} - k_1}\right) (e^{-k_1[B]t} - e^{-k_{2i}[B]t})$$

where b_i in the branching ratio of the i^{th} C_i^+ product.

The Solutions—Tertiary Ions.

$$\frac{d[E_{ij}^+]}{dt} = b_{ij}k_{2i}[C^+][B] - k_{3ij}[E_{ij}^+][B]$$

$$\frac{d[E_{ij}^+]}{dt} + k_{3ij}[E_{ij}^+][B] = [A^+]_0[B] \left(\frac{b_ik_1b_{ij}k_{2i}}{k_{2i} - k_1}\right) (e^{-k_1[B]t} - e^{-k_{2i}[B]t})$$

$$\begin{split} [E_{ij}^{+}] &= e^{-k_{3ij}[E_{ij}^{+}][B]} \int [A^{+}]_{0}[B] \left(\frac{b_{i}k_{1}b_{ij}k_{2i}}{k_{2i}-k_{1}} \right) \\ &\times (e^{k_{3ij}[E_{ij}^{+}][B]-k_{1}[B]t} - e^{k_{3ij}[E_{ij}^{+}][B]-k_{2i}[B]t}) dt \\ &+ Ce^{-k_{3ij}[E_{ij}^{+}][B]} \end{split} \\ &\times \left(\frac{e^{-k_{1}[B]t}}{k_{3ij}-k_{1}} - \frac{e^{-k_{2i}[B]t}}{k_{3ij}-k_{2i}} \right) + Ce^{-k_{3ij}[E_{ij}^{+}][B]} \end{split}$$

for t=0 and [C⁺] = 0 then
$$C = -[A^+]_0 \left(\frac{b_i k_1 b_{ij} k_{2i}}{k_{2i} - k_1} \right) \left(\frac{e^{-k_1 [B]t}}{k_{3ij} - k_1} - \frac{e^{-k_{2i} [B]t}}{k_{3ij} - k_{2i}} \right)$$

$$[E_{ij}^+] = [A^+]_0 \left(\frac{b_i k_1 b_{ij} k_{2i}}{k_{2i} - k_1}\right) \left(\frac{e^{-k_{2i}[B]t} - e^{-k_{3ij}[B]t}}{k_{3ij} - k_1} - \frac{e^{-k_2[B]t} - e^{-k_{3ij}[B]t}}{k_{3ij} - k_{2i}}\right)$$

where b_i is the branching ratio of the i^{th} C_i^+ product and where b_{ij} is the branching ratio of the i^{th} E_{ij}^+ product

$$\sum_{i} \sum_{i} \sum_{k} [G_{ijk}^{+}] = A^{+}]_{0} - [A^{+}] - \sum_{i} [C_{i}^{+}] - \sum_{i} \sum_{i} [E_{ij}^{+}].$$

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