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Termolecular Ion–Molecule Reactions in Titan's Atmosphere. II: The Structure of the Association Adducts of HCNH$^+$ With C$_2$H$_2$ and C$_2$H$_4$

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The ion–molecule reactivity of the products formed in the association reactions of HCNH$^+$ with C$_2$H$_2$ (C$_3$H$_4$N$^+$) and C$_2$H$_4$ (C$_3$H$_6$N$^+$) has been investigated to provide information on the structures of the adducts thus formed. The C$_3$H$_4$N$^+$ and C$_3$H$_6$N$^+$ adducts were formed in the reaction flow tube of a flowing afterglow sourced-selected ion flow tube (FA-SIFT) and their reactivity with a neutral molecular "probe" examined. The reactivity of possible known structural isomers for the C$_3$H$_4$N$^+$ and C$_3$H$_6$N$^+$ ions was investigated in both the FA-SIFT and an ion cyclotron resonance spectrometer (ICR). Ab initio investigations of the potential energy surfaces for both structures at the G2(MP2) level have also been performed and structures corresponding to local minima on both surfaces have been identified and evaluated. The results of these experimental and theoretical studies show that at room temperature, the C$_3$H$_4$N$^+$ adduct ion contains two isomers; a less reactive one that is likely to be a four-membered cyclic covalent isomer (~70%) and a faster reacting component that is probably an electrostatic complex (~30%). The C$_3$H$_6$N$^+$ adduct ion formed from HCNH$^+$ + C$_2$H$_4$ at room temperature is a single isomer that is likely to be the four-membered covalently bound cyclic CH$_2$CH$_2$CHNH$^+$ species.   (J Am Soc Mass Spectrom 2001, 12, 557–564)   © 2001 American Society for Mass Spectrometry

Saturn's largest moon, Titan, is known to have a substantial nitrogen-based atmosphere containing a lesser amount (~6%) of the hydrocarbons methane, acetylene, ethylene, and ethane [1, 2]. Models of Titan's ion chemistry using mostly laboratory tested reaction chemistry have suggested that HCNH$^+$ is the most abundant ion species at high altitudes [3, 4] although some workers have argued for hydrocarbon ions being dominant [5]. The abundance of HCNH$^+$ is a result of its apparent unreactivity. The most abundant species in Titan's atmosphere that are known to react with HCNH$^+$ are H$_2$O, HC$_3$N, and C$_4$H$_2$. Of these, HC$_3$N is predicted to be the most abundant with a maximum mole fraction of 0.0001. Because acetylene and ethylene are both an order of magnitude more abundant, it is important to investigate their chemistry. Usually only bimolecular ion–molecule reactions are considered in ionospheric models but Anicich et al. [6, 7] have shown, that under some conditions, termolecular association reactions can have a significant role. Association reactions are interesting in that in the majority of cases, the structure of the adduct formed in the association is unknown. In some cases it is a relatively loosely bound electrostatic adduct; in others it is a covalently bound molecular ion. Evidence for both types of association ions has been provided in studies of several associating systems in the past [8, 9]. The presence of both HCNH$^+$ and the hydrocarbons acetylene and ethylene in Titan's atmosphere, provides some of the motivation for this investigation as it is interesting to discover what the structures of the products of the association of HCNH$^+$ with acetylene and ethylene are.

Termolecular association reactions also have some relevance to the chemistry occurring in dense interstellar clouds but not because they are important processes

in the interstellar medium. Instead, they provide useful indicators of the analogous process of bimolecular association in which the association complex is stabilized under low pressure conditions by photon emission. In this context, Herbst et al. [10] reported a laboratory and theoretical study of the rate coefficients for the termolecular association reactions

$$HCNH^+ + C_2H_2 + M \Rightarrow C_3H_4N^+ + M \qquad (1)$$

$$HCNH^+ + C_2H_4 + M \Rightarrow C_3H_6N^+ + M \qquad (2)$$
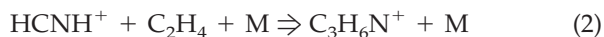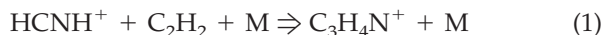
They determined theoretical values for the rate coefficients of reactions 1 and 2 using the modified thermal theory of Bates [11, 12] and found that there was poor agreement between theory and experiment if the lowest energy structures for $C_3H_4N^+$ and $C_3H_6N^+$ were assumed. The rate coefficient estimated for reaction 1, assuming the $C_3H_4N^+$ ion had the structure of protonated acrylonitrile, was calculated to be an order of magnitude faster than the observed rate coefficient. Similarly, the calculated rate coefficient for reaction 2, assuming a structure of protonated ethyl cyanide, was approximately 50 times larger than the observed rate coefficient. The inference is that the structures of the adducts are not protonated acrylonitrile for $C_3H_4N^+$ and not protonated ethyl cyanide for $C_3H_6N^+$.

The thermochemistry of the $C_3H_4N^+$ association adduct has also been examined recently by Vacher et al. who measured equilibrium ion densities of the cluster ions from a $N_2/CH_4/C_2H_2$ mixture in a high pressure mass spectrometer [13]. They estimated an enthalpy change for the formation of $C_3H_4N^+$ from $HCNH^+$ and C_2H_2 of -50.6 kJ mol^{-1}. This value is much smaller than the -244.2 kJ mol^{-1} required if the $C_3H_4N^+$ ion is to be formed with the protonated acrylonitrile structure.

We report here the results of a theoretical and experimental investigation into the association adduct ion structure, $C_3H_4N^+$, formed in reaction 1 and the association adduct ion structure, $C_3H_6N^+$, formed in reaction 2.

Experimental

The ion–molecule reaction chemistry of the two association products, $C_3H_4N^+$ and $C_3H_6N^+$, was examined using the University of Canterbury flowing afterglow source-selected ion flow/drift tube (FA-SIFDT). This instrument has recently been described elsewhere [14] so only those aspects directly relevant to this work will be discussed here. Rate coefficients for both $C_3H_4N^+$ (reaction 1) and $C_3H_6N^+$ (reaction 2) have previously been determined using both helium (purity >99.99%) and nitrogen (purity >99.998%) as bulk carrier gases in the reaction flow tube [7]. The accuracy is ±15% for reaction rate coefficients and ±10% for branching ratios. All reactions were studied at room temperature, 300 K.

Because of the relatively low formation rate coeffi-

cients for these association products, it was not practical to generate them in the ion source. Instead the $HCNH^+$ ion was made from HCN in the ion source and injected into the reaction flow tube where it was reacted either with acetylene to form $C_3H_4N^+$, or with ethylene to form $C_3H_6N^+$. Helium (0.48 torr) was used as the carrier gas in these specific studies. This process generated a mixture of $HCNH^+$ and $C_3H_xN^+$ ($x = 4$ or 6) ions which could react with other neutral species added downstream in the flow tube. The rate coefficients for reaction and the product channels observed were used to provide information on the structure of these association products. Rate coefficients for the reactions of these adducts represent a lower limit as a small amount of the adduct may be generated within the reaction region by the reaction of $HCNH^+$ with residual hydrocarbon. However the flows of C_2H_2 and C_2H_4 were sufficiently large to have most of the $C_3H_xN^+$ formation occurring prior to the reaction region. This conclusion is borne out by the relatively straight lines found for the semilogarithmic decays of the adduct ion signal in the slow reaction of $C_3H_6N^+$ with C_2H_5ONO. Further confirmation that little of the $C_3H_4N^+$ ion is formed in the reaction region was found in the reactions of this ion with HCN and is discussed later.

The ion chemistry of the most stable of the possible structural candidates for the ions viz. protonated acrylonitrile (CH_2CHCNH^+) and protonated ethyl cyanide (propanenitrile, $C_2H_5CNH^+$); was examined in both the Canterbury FA-SIFT (0.48 torr He carrier gas) and the Jet Propulsion Laboratory ion cyclotron resonance (ICR) instrument operating between 10^{-6} and 10^{-4} torr [15].

HCN was prepared by the action of phosphoric acid on sodium cyanide and the resultant gas dried over phosphorus pentoxide. Ethyl nitrite was prepared by the reaction of ethanol and sulfuric acid on sodium nitrite. Ethyl isocyanide was prepared from ethyl formamide according to the method of Casanova et al [16]. All reactants were further purified by multiple freeze–pump–thaw cycles.

Results and Discussion

Theoretical

Computational details.   All calculations were performed using the Gaussian 98 program [17]. The calculations follow the prescription detailed in the original description of the G2(MP2) procedure [18].

Calculations.   The structures of the reactants, possible products, and where possible, transition states, for the reaction of $HCNH^+$ with C_2H_2 and C_2H_4 were calculated at the MP2 = FU/6-31G* level of theory. The calculated G2(MP2) energies of the reactants, possible products, and transition states are listed in Table 1. The relative energies and structures for the $C_3H_4N^+$ species involved in the reaction of $HCNH^+ + C_2H_2$ are shown in Figure 1. The relative energies and structures for the

Table 1. Energies of structures designated in Figures 1 and 2 at the G2(MP2) level of theory

		E[G2(MP2)]/hartree	Theory[a] $\Delta_f H$/kJ mol^{-1}	Literature[b] $\Delta_f H$/kJ mol^{-1}
	HCNH$^+$	−93.55216		
	HCN	−93.28249		
	HNC	−93.26052		
	C$_2$H$_2$	−77.18407		
	C$_2$H$_4$	−78.41429		
	C$_2$H$_3^+$	−77.42181		
	HCNH$^+$ + C$_2$H$_2$	−170.73623	1178.9	1179.0
I	CH$_2$CHCNH$^+$	−170.82728	934.8	925.1
II	c-CHCHCHNH$^+$	−170.76180	1105.2	
III	c-CHCH$_2$CNH$^+$	−170.72350	1205.6	
IV	T shaped C$_2$H$_2$·HCNH$^+$	−170.75241	1135.6	
	C$_2$H$_3^+$ + HNC	−170.68232		
	HCN + C$_2$H$_2$	−170.46655	362.8	361.9
	CH$_2$CHCN	−170.42308	190.3	179.7
	T-shaped C$_2$H$_2$·HCN	−170.46962	355.3	
	HCNH$^+$ + C$_2$H$_4$	−171.96646	1004.7	1004.8
V	CH$_3$CH$_2$CNH$^+$	−172.04371	797.2	787.4
VI	c-CH$_2$CH$_2$CHNH$^+$	−172.03552	815.7	
VII	c-CH$_2$CHCH$_2$NH$^+$	−171.94273	1060.4	
VIII	TS VI to VII	−171.87778		
IX	T-shaped C$_2$H$_4$·HCNH$^+$	−171.98235	962.4	
	HCN + C$_2$H$_4$	−171.69678	188.6	187.6
	CH$_3$CH$_2$CN	−171.74320	61.7	51.5
	c-CH$_2$CH$_2$CHN	−171.69014	198.5	211 (est.)
	c-CH$_2$CHCH$_2$N	−171.65842	281.3	314 (est.)

[a]This work, calculated using as a reference the experimental values for HCNH$^+$ and C$_2$H$_2$.
[b][19].

C$_3$H$_6$N$^+$ species involved in the reaction of HCNH$^+$ + C$_2$H$_4$ are shown in Figure 2. Two possible products can be formed initially in the reaction of $HCNH^+ + C_2H_2$. The more stable product is a cyclic structure: c-CHCH-CHNH$^+$ (II). Some geometric parameters calculated at the MP2 = FU/6-31G* level of theory for this structure are: $R(C_1–C_2)$ = 1.338 Å, $R(C_3–N_4)$ = 1.287 Å, $R(C_1–C_3)$ = 1.522 Å, $R(C_2–N_4)$ = 1.573 Å, $\angle C_2–C_1–C_3$ =

88.7°, $\angle C_1–C_2–N_4$ = 89.4°, $\angle C_1–C_3–N_4$ = 93.6°, and $\angle C_3–N_4–C_2$ = 88.3°. An alternative cyclic structure: c-CHCH$_2$CNH$^+$ (III) (not shown in Figure 1) lies 100.4 kJ mol^{-1} in energy above the c-CHCHCHNH$^+$ structure and above the reactant energies. The calculated
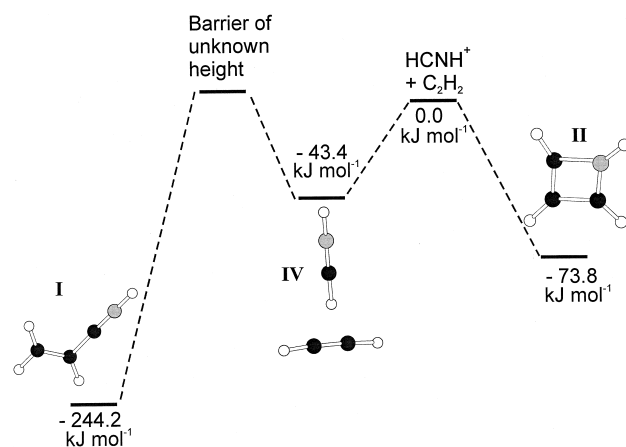
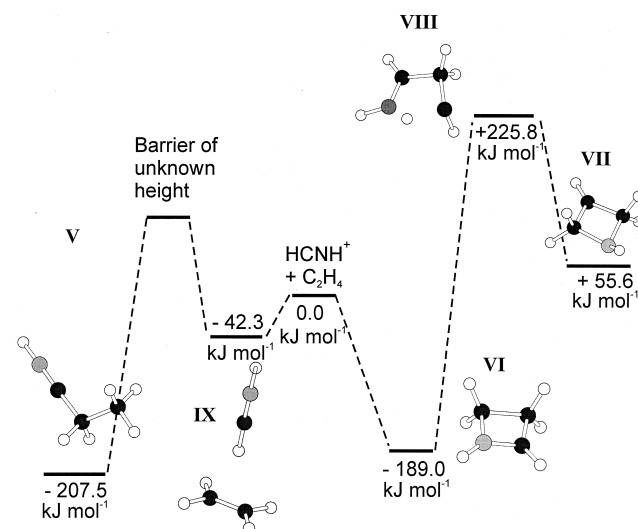

Figure 1. Energy profile of the C$_3$H$_4$N$^+$ potential energy surface calculated at the G2(MP2) level of theory.

Figure 2. Energy profile of the C$_3$H$_6$N$^+$ potential energy surface calculated at the G2(MP2) level of theory.

Table 2. Measured term molecular rate coefficients for the association of $HCNH^+$ with C_2H_2 and C_2H_4. Rate coefficients are expressed in units of cm^6 s^{-1}

Reactant	Reference A[a] M = He (300 K)	Reference B[b]	
		M = He	M = N_2
C_2H_2	5×10^{-29}	6×10^{-29}	4×10^{-28}
C_2H_4	7×10^{-27}	5×10^{-27}	1×10^{-26}

[a] See [10]. Rate coefficients were also measured at 80, 210, and 480 K.
[b] See [7].

proton affinity of c-CHCHCHN is 861.7 kJ mol^{-1}. The alternative initial product is the T-shaped adduct C_2H_2.$HCNH^+$ (IV). The H atom of the $HCNH^+$ lies 3.226 Å above the C_2H_2 entity. For this structure the calculated geometric parameters are $R(C_1–C_2) = 1.220$ Å and $R(C_3–N_4) = 1.154$ Å. The proton affinity for the T-shaped structure C_2H_2.HCN is 749.6 kJ mol^{-1}. The lowest energy $C_3H_4N^+$ structure is protonated acrylonitrile, CH_2CHCNH^+ (I). Formation of CH_2CHCNH^+ (I) from the cyclic structure (II) occurs via the cyclic structure (III) that has an energy higher than the reactants and is clearly not accessible in the current experiments. There does not appear to be a low energy pathway from the T-shaped adduct to protonated acrylonitrile (I). Optimized geometric parameters for structure (I) are: $R(C_2–C_2) = 1.345$ Å, $R(C_2–C_3) = 1.417$ Å, $R(C_3–N_4) = 1.162$ Å, and $\angle C_1–C_2–C_3 = 119.5°$. The proton affinity of CH_2CHCN was calculated to be 785.6 kJ mol^{-1}. At the HF/6-31G* level of theory a stable T-shaped $C_2H_3^+ \cdot CNH$ adduct was found with a transition state structure linking it to the $C_2H_2 \cdot HCNH^+$ structure. However the TS has a higher energy than the $C_2H_3^+ \cdot CNH$ structure when zero point vibrational energies are included. Optimization of the $C_2H_3^+ \cdot CNH$ structure at the MP2 level of theory gave the $C_2H_2 \cdot HCNH^+$ adduct structure.

For the $HCNH^+ + C_2H_4$ reaction there are two possible structures that can be formed initially. Again the more stable structure accessible from the reactants is a cyclic structure, c-$CH_2CH_2CHNH^+$ (VI). Optimized MP2 = FU/6-31G* geometric parameters for (VI) are $R(C_1–C_2) = 1.557$ Å, $R(C_3–N_4) = 1.294$ Å, $R(C_1–C_3) = 1.494$ Å, $R(C_2–N_4) = 1.492$ Å, $\angle C_2–C_1–C_3 = 84.8°$, $\angle C_1–C_2–N_4 = 85.1°$, $\angle C_1–C_3–N_4 = 84.8°$, $\angle C_3–N_4–C_2 = 95.0°$. There is a cyclic structure, c-$CH_2CHCH_2NH^+$ (VII), that has an energy 244 kJ mol^{-1} above the c-$CH_2CH_2CHNH^+$ (VI) structure and is also above the energy of the reactants. A transition state structure (VIII) linking structures (VI) and (VII) lies 170.1 kJ mol^{-1} above (VII). Optimization of a $CH_2CH_2CH_2N^+$ structure at the MP2 = FU/6-31G* level of theory yielded the structure (V). The proton affinity of c-CH_2CH_2CHN [leading to (VI)] was calculated to be 912.7 kJ mol^{-1}. The proton affinity of c-CH_2CHCH_2N [leading to (VII)] was calculated to be 751.0 kJ mol^{-1}. As with the $HCNH^+ + C_2H_2$ system, there is a T-shaped adduct (IX). The H atom lies 2.133 Å above the C_2H_4 entity. The other optimized geometric

parameters for this structure are: $R(C_1–C_2) = 1.343$ Å and $R(C_3–N_4) = 1.154$ Å. The proton affinity of the $C_2H_4 \cdot HCN$ adduct [leading to (IX)] is calculated to be 749.8 kJ mol^{-1}. The lowest energy isomer for $C_3H_6N^+$ is protonated ethyl cyanide, $CH_3CH_2CNH^+$ (V). The optimized geometric parameters for (V) are: $R(C_1–C_2) = 1.540$ Å, $R(C_2–C_3) = 1.453$ Å, $R(C_3–N_4) = 1.159$ Å, and $\angle C_1–C_2–C_3 = 111.7°$. The proton affinity of CH_3CH_2CN [leading to (V)] is calculated to be 794.4 kJ mol^{-1}. As with the $HCNH^+ + C_2H_2$ reaction, there does not appear to be an energetically allowed route for the formation of (V) via either the c-$CH_2CH_2CHNH^+$ (VI) or the T-shaped $C_2H_4 \cdot HCNH^+$ (IX) intermediates.

Experimental

Rate coefficients reported from different laboratories for the association of $HCNH^+$ with C_2H_2 and $HCNH^+$ with C_2H_4 are summarized in Table 2. The current results obtained on the University of Canterbury SIFT were previously published as part of a general study of termolecular reactions pertinent to Titan ion chemistry [7].

Herbst et al. [10] have shown that association reactions 1 and 2 have a negative temperature dependence with the rate coefficients increasing to 1.5×10^{-28} cm^6 s^{-1} ($C_3H_4N^+$) and 1.8×10^{-26} cm^6 s^{-1} ($C_3H_6N^+$) for M = He at 210 K. The low temperature of the largely nitrogen atmosphere present on Titan should make these reactions competitive with bimolecular reactions in the region of Titan's lower ionosphere. If a temperature dependent form of the rate coefficient is taken as

$$k = 5 \times 10^{-29}(300/T)^x \qquad (3)$$

then both the rate coefficients measured by Herbst et al. [10] can be fitted by a value of $x = 2.9$. It is interesting to compare the loss of $HCNH^+$ in Titan's ionosphere from electron recombination with reactions 1 and 2 to form adducts using the rate coefficients of eq 3. This comparison is shown in Figure 3 and demonstrates that the loss rates of $HCNH^+$ by association outstrip loss by electron recombination at altitudes below about 650 km. Figure 3 was produced from the temperature and pressure profiles calculated in the model of Yelle et al. [20]. In this model the temperature varies from 93 K at the surface with a tropopause of 70 K at 40 km altitude, a mesopause of 135 K at 955 km, and an exospheric temperature of 175 K. The atmospheric composition is
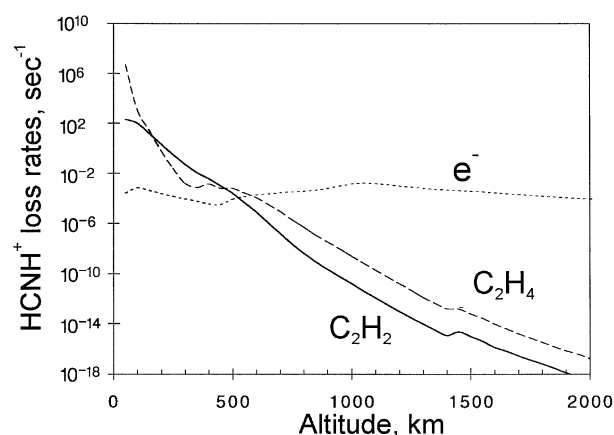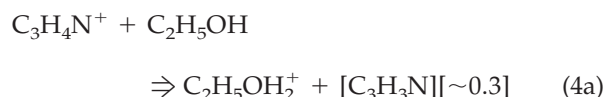
Figure 3. Comparison of loss of $HCNH^+$ in Titan's ionosphere by electron recombination and association with C_2H_2 and C_2H_4 as a function of the altitude. The fine dashed line is the loss of $HCNH^+$ from electron recombination, the regular dashed line is the loss of $HCNH^+$ with ethylene, and the solid line is the loss of $HCNH^+$ with acetylene.

98% nitrogen, 2% methane, and 1% hydrogen. Profiles of the abundances of C_2H_2 and C_2H_4 were taken from the work of Molina-Cuberos et al. [21]. In their model, altitude profiles of C_2H_2 and C_2H_4 are presented between the surface and 700 km. The temperature dependence of the termolecular reactions was taken from Herbst et al. [10]. No temperature dependence was assumed for the electron recombination process.

The structure of the two adducts formed in these systems has been probed in this work by comparing the ion–molecule reactivity of the adducts with the reactivity of a selection of "authentic" samples of possible covalently bound structural isomers. The monitor gases chosen to probe the reactivity were selected in such a way as to have different reactivity with $HCNH^+$ and the protonated covalently bound species. In most cases this was achieved by using a probe gas that had a proton affinity intermediate between HCN and either ethyl cyanide or acrylonitrile.

$C_3H_4N^+$ adduct ion. Ethanol was selected as the most useful probe molecule for the $HCNH^+/C_2H_2$ ($C_3H_4N^+$) adduction. When C_2H_5OH was added to the flow tube containing the $C_3H_4N^+$ adduct, a curved semilogarithmic decay of the $C_3H_4N^+$ ion signal with C_2H_5OH flow was observed and two product channels were identified:

$$C_3H_4N^+ + C_2H_5OH$$

$$\Rightarrow C_2H_5OH_2^+ + [C_3H_3N][\sim 0.3] \qquad (4a)$$

$$\Rightarrow C_3H_3NH^+ \cdot C_2H_5OH \; [\sim 0.7] \qquad (4b)$$

This curved decay is indicative of a $C_3H_4N^+$ ion signal at 54 u that is composed of two species that react differently with ethanol [22]. Approximately one third of the ion signal reacts rapidly (at approximately 1 to 2×10^{-9} cm^3 s^{-1}) while the remaining signal reacts

with a rate coefficient approximately an order of magnitude lower ($\sim 2 \times 10^{-10}$ cm^3 s^{-1}). At the *lower* neutral flows (where the faster reacting component will form the majority of the observed product ions) the products are mainly proton transfer (channel 3a). However at *higher* flows of ethanol, the formation of an association product (channel 3b) becomes much more important and eventually contributes up to 75% of the observed product ions.

In this work it was only possible to produce one authentic sample of a structural isomer of $C_3H_4N^+$: that of protonated acrylonitrile (CH_2CHCNH^+) (Structure I in Figure 1), which exhibited the following reactions with C_2H_5OH:

$$CH_2CHCNH^+ + C_2H_5OH$$

$$\Rightarrow C_2H_5OH_2^+ + CH_2CHCN \; [0.15] \qquad (5a)$$

$$\Rightarrow CH_2CHCNH^+ \cdot C_2H_5OH \; [0.85] \qquad (5b)$$

$$k = 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}.$$

One possible form of the $C_3H_4N^+$ adduct ion could be the electrostatically bound adduct of $HCNH^+$ and C_2H_2: viz. $HCNH^+ \cdot C_2H_2$. This structure would be expected to react similarly to the $HCNH^+$ ion. Some $HCNH^+$ ions were also present in the reaction tube when the adduct was made and its reaction with C_2H_5OH was investigated:

$$HCNH^+ + C_2H_5OH \Rightarrow C_2H_5OH_2^+ + HCN \qquad (6)$$
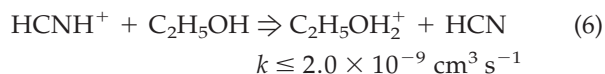
$$k \leq 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$
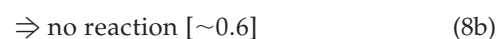
This simple proton transfer reaction proceeds at a rate that is essentially the gas collision rate ($k_{coll} = 1.3 \times 10^{-9}$ cm^3 s^{-1}).

In addition, the reactions of the $C_3H_4N^+$ ion with an HCN neutral were also investigated. $HCNH^+$ reacts with HCN via a slow termolecular reaction at the pressures encountered in the SIFT to give the proton bound dimer $HCNH^+ \cdot HCN$:

$$HCNH^+ + HCN + He \Rightarrow HCNH^+ \cdot HCN + He \qquad (7)$$
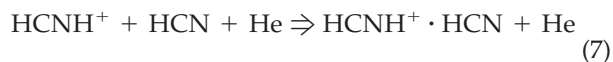
$k = 1.2 \times 10^{-11}$ cm^3 s^{-1} @ 0.48 torr He corresponding to $k_3 = 8 \times 10^{-28}$ cm^6 s^{-1}

When HCN is reacted with the $C_3H_4N^+$ ion, a very similar behavior to that observed for C_2H_5OH is found. A curved semilogarithmic decay of $C_3H_4N^+$ ion signal with HCN flow is apparent. Approximately 40% of the ion count at 54 u reacts rapidly ($k > 5 \times 10^{-10}$ cm^3 s^{-1}) giving a product at 55 u, while the remainder is essentially unreactive:

$$C_3H_4N^+ + HCN$$

$$\Rightarrow HCNH^+ \cdot HCN + C_2H_4 \; [\sim 0.4] \qquad (8a)$$

$$\Rightarrow \text{no reaction} \; [\sim 0.6] \qquad (8b)$$
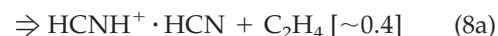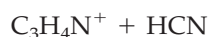
$$k_{8a} > 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

This curvature confirms the results with ethanol (reaction 4) and again demonstrates the presence of two $C_3H_4N^+$ structures in the association adduct. The observed product of the faster reacting component is a 55 u ion and its observation is strongly suggestive of a switching reaction occurring from an electrostatic cluster ion containing the $HCNH^+$ moiety. In this reaction the weakly bound acetylene moiety of the adduct will be replaced by the more strongly bound HCN (binding energy = 109 kJ mol^{-1}, [23]). This switching reaction should be relatively fast and that conclusion is consistent with the observations.

$C_3H_6N^+$ adduct ion. The probe gas chosen for the $HCNH^+/C_2H_4$ ($C_3H_6N^+$) adduct system was ethyl nitrite (C_2H_5ONO). The reaction of ethyl nitrite with the $C_3H_6N^+$ adduct gave a range of products (reaction 9).
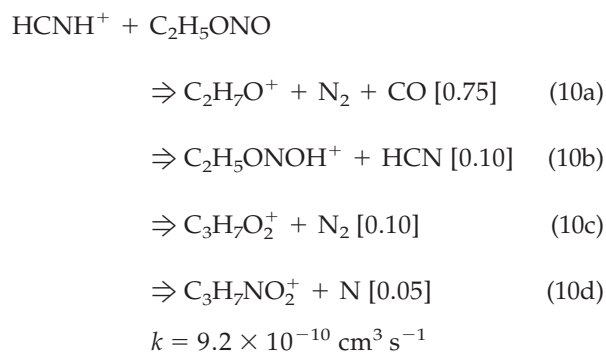
$$C_3H_6N^+ + C_2H_5ONO$$

$$\Rightarrow C_3H_6N^+ \cdot C_2H_5ONO \ [0.45] \qquad (9a)$$

$$\Rightarrow C_4H_8NO_2^+ + CH_2NH \ [0.35] \qquad (9b)$$

$$\Rightarrow m/z = 105 + \text{neutral (26 u)} \ [0.10]$$
$$\qquad (9c)$$

$$\Rightarrow C_4H_6NO_2^+ + CH_3NH_2 \ [0.10] \qquad (9d)$$

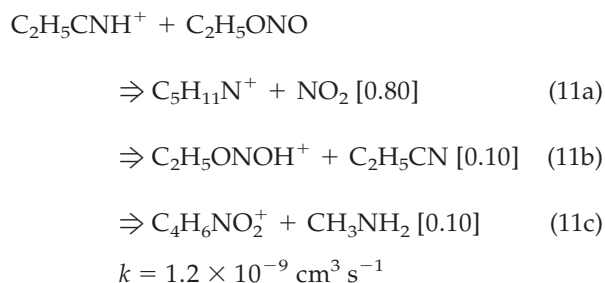$$k = 2.0 \times 10^{-11} \ cm^3 \ s^{-1}$$
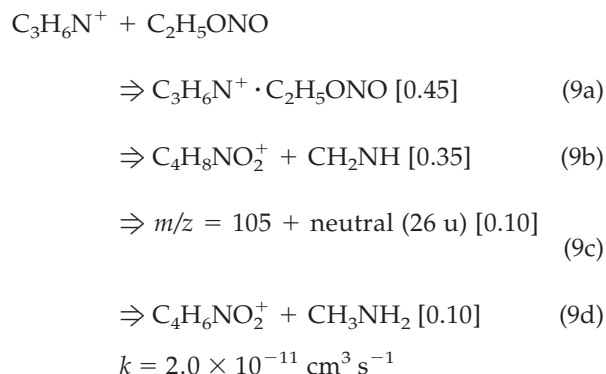
The observed reactivity is consistent with formation of an initial collision complex that survives sufficiently long for some stabilization by collision with the bath gas to occur. The product at $m/z = 105$ could not be identified although the neutral leaving group is almost certainly C_2H_2 and/or CN. The elimination of acetylene could give protonated N,N-dimethyl-1-nitromethanamine as the ionic product but the $\Delta_f H$ data for this species is unknown. The rate coefficient is well below the value expected of a collision rate reaction, suggesting that many complexes have reverted back to reactants before stabilization or fragmentation occurs.

The reaction of ethyl nitrite with protonated hydrogen cyanide is also complex, but significantly different from reaction 9. This is shown in reaction 10 below:

$$HCNH^+ + C_2H_5ONO$$

$$\Rightarrow C_2H_7O^+ + N_2 + CO \ [0.75] \qquad (10a)$$

$$\Rightarrow C_2H_5ONOH^+ + HCN \ [0.10] \qquad (10b)$$

$$\Rightarrow C_3H_7O_2^+ + N_2 \ [0.10] \qquad (10c)$$

$$\Rightarrow C_3H_7NO_2^+ + N \ [0.05] \qquad (10d)$$

$$k = 9.2 \times 10^{-10} \ cm^3 \ s^{-1}$$

Again there is apparently a large amount of scrambling within the collision complex before elimination of the stable neutral species.

Protonated ethyl cyanide (structure V in Figure 2) is the most likely acyclic covalent candidate structure for the $C_3H_6N^+$ isomer. Its reactions with ethyl nitrite showed that a collision rate reaction takes place with some bimolecular scrambling reactions and some proton transfer reactions occurring. The observation of proton transfer is consistent with the known proton affinities of C_2H_5CN (PA = 794.1 kJ mol^{-1}) and C_2H_5ONO (PA = 818.9 kJ mol^{-1}) [19]. This reaction proceeds with a rate coefficient that is close to the gas collision rate:

$$C_2H_5CNH^+ + C_2H_5ONO$$

$$\Rightarrow C_5H_{11}N^+ + NO_2 \ [0.80] \qquad (11a)$$

$$\Rightarrow C_2H_5ONOH^+ + C_2H_5CN \ [0.10] \quad (11b)$$

$$\Rightarrow C_4H_6NO_2^+ + CH_3NH_2 \ [0.10] \qquad (11c)$$

$$k = 1.2 \times 10^{-9} \ cm^3 \ s^{-1}$$

This again is much different than the reactivity of the $HCNH^+/C_2H_4$ ($C_3H_6N^+$) adduct.

Another possible covalent structure of $C_3H_6N^+$ is ethyl isocyanide. The observed rate coefficient for $C_2H_5NCH^+$ with C_2H_5ONO was found to be approximately two orders of magnitude less than the gas collision rate ($k_{coll} = 2.8 \times 10^{-9}$ cm^3 s^{-1}). The major product in the reaction appears to be association (to give a 131 u ion): a result that is consistent with the low rate coefficient:

$$C_2H_5NCH^+ + C_2H_5ONO$$

$$\Rightarrow C_2H_5NCH^+ \cdot C_2H_5ONO \ [\sim 1.0] \quad (12)$$

$$k \sim 9 \times 10^{-12} \ cm^3 \ s^{-1}$$
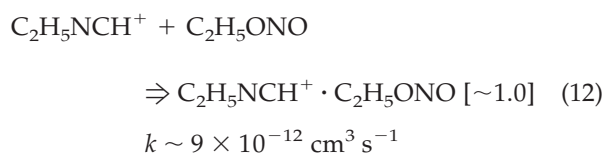
Furthermore, the proton transfer channel available in the protonated ethyl cyanide reaction 11 is not available in protonated ethyl isocyanide as the proton affinity of C_2H_5NC is 851.3 kJ mol^{-1} [19].

Conclusions

The theoretical and experimental data presented in the preceding section allow some conclusions to be drawn as to the identity of the $C_3H_4N^+$ and $C_3H_6N^+$ adducts of reactions 1 and 2.

$HCNH^+/C_2H_2$ ($C_3H_4N^+$)

From the curved decay in the reaction between $C_3H_4N^+$ and C_2H_5OH it is apparent that there are at least two

separate structures present in the adduct signal. The faster reacting ion represents approximately one third of the signal and gives mainly proton transfer ($C_2H_5OH_2^+$) as its product. This ion cannot thus be protonated acrylonitrile as CH_2CHCNH^+ gives mainly an association product (85% $CH_2CHCNH^+ \cdot C_2H_5OH$, channel 5b). The initial reactivity of the adduct is however similar to that of $HCNH^+$ and thus it seems likely that approximately *one third* of the ions formed in the reaction of $HCNH^+$ with acetylene are electrostatically bound. These ions are likely to have the configuration shown by structure (IV) in Figure 1. The fraction of $C_3H_4N^+$ ions formed with this structure will presumably depend on the pressure, temperature, and bath gas.

The remaining *two thirds* of the adduct ion signal does not react like either $HCNH^+$ or CH_2CHCNH^+. The products of reaction of the $C_3H_4N^+$ adduct with ethanol are similar to those observed with protonated acrylonitrile (i.e., adduct formation) but the rate coefficient is an order of magnitude slower. The observation of an adduct type product for the reaction between slow-reacting $C_3H_4N^+$ and ethanol is strongly suggestive of a covalently bound species in the $C_3H_4N^+$ adduct. Electrostatically bound ions are unlikely to be sufficiently strongly bound to undergo an association reaction without dissociation and are more likely to either react via a switching reaction or in a manner similar to the bimolecular reaction of one of its constituent fragments. This suggests that the cyclic structure observed in the theoretical results is being formed [structure (II) in Figure 1]. From this, one can infer that the unknown barrier height between reactants and the energy minimum [CH_2CHCNH^+, structure (I)] is greater than the energy of the reactants.

The reactions of $C_3H_4N^+$ with HCN (reaction 8) also confirm these conclusions. The faster reacting component 8a that exhibits cluster switching is the reaction of the T-shaped electrostatic isomer (IV). The ~60% nonreactive channel 8b represents the presence of the covalent c-CHCHCHNH$^+$ (II).

The experiments of Vacher et al. [13] in which they report an exothermicity of 50.6 kJ mol^{-1} for the reaction when $C_3H_4N^+$ is formed from $HCNH^+$ and C_2H_2 almost certainly represent a compromise between two structures. Their value for the exothermicity is consistent with the values we calculated for a mixture of the electrostatic complex [structure (IV) Figure 1] of 43 kJ mol^{-1} and the covalent structure (II) of 73.8 kJ mol^{-1}.

$HCNH^+/C_2H_4$ ($C_3H_6N^+$)

The reactivity of the $C_3H_6N^+$ formed as a result of the association of $HCNH^+$ with C_2H_4 shows that these ions apparently have a single isomeric form. The reactivity of these ions is not consistent with either an electrostatic adduct or protonated ethyl cyanide. Neither the rate coefficients nor the products observed are consistent with these structures. The rate coefficient for the reaction of $C_3H_6N^+$ with ethyl nitrite is also too great for the

adduct ion to be protonated ethyl isocyanide. These ions probably have the cyclic structure identified in the theoretical study and shown in Figure 2 as structure (VI). This conclusion is consistent with the calculations which show a significant barrier between the cyclic structure and the global minimum on the $C_3H_6N^+$ surface, protonated ethyl cyanide. It is also consistent with the conclusions of Herbst et al. [10] who predicted a structure with a potential minimum less than that of protonated ethyl cyanide.

One question that could be asked here is why are there two structures present in the adduct, $C_3H_4N^+$, but only one in $C_3H_6N^+$ when theory predicts two structures are accessible from the reactants in both reactions 1 and 2. In particular, the electrostatic T-shaped structure (IX) was not found in the $C_3H_6N^+$ adduct in this work. The probable reason is that theory calculates a much lower well depth on the $C_3H_6N^+$ potential surface for the cyclic structure (VI) (189 kJ mol^{-1}) than the equivalent depth for structure (II) on the $C_3H_4N^+$ surface (73.8 kJ mol^{-1}). The lower well strongly favors the formation of the cyclic covalently bound isomer in the $C_3H_6N^+$ case as the density of states at the reactant energies is so much higher above the deeper well. At lower temperatures we would expect to see the onset of formation of the T-shaped electrostatic adduct in the $C_3H_6N^+$ adduct ion also.

Titan's Atmosphere

Finally, we note that termolecular ion–molecule association reactions can play a role in planetary ionospheres as demonstrated in Figure 3 where association is shown to present a greater loss for $HCNH^+$ ions in Titan than electron recombination in the lower ionosphere. In the model of Molina-Cuberos et al. that is based largely on bimolecular chemistry [21], the $HCNH^+$ ion is a terminal ion down to 600 km. Once the current association reactions are included, a new termolecular loss channel for $HCNH^+$ from 600 km down to about 80 km is present. Below 80 km, the chemistry of the ions becomes even more complicated by clustering reactions with nitrogen in the atmosphere and this aspect of the ion chemistry will be presented in a subsequent paper in this series.

In the atmosphere of Titan, bimolecular ion chemistry is adequate for modeling the ionospheric reactions above 1000 km. Recently, Molina-Cuberos et al. [21] looked at the ion chemistry below 400 km and concluded that clustering would play an important role. One of the reactions that they used in their model was reaction 2 but they did not have access to the structural information we have found in this work. We have shown that the association product is mostly a new cyclic covalent ion. This ion is stable in the presence of many of the hydrocarbons known to be present on Titan but it will certainly cluster with nitrogen via termolecular association reactions at the temperature of Titan's middle atmosphere. It is also worth noting that ion

chemistry, can in some cases, influence the neutral number densities. In a recent paper by Banaszkiewicz et al. [24], it was shown that between 800 and 1400 km, neutral abundances can be markedly influenced by the ion–molecule chemistry. Particularly noteworthy is the abundance of the propyne neutral of which 90% is made through ion chemistry. Banaszkiewicz et al. concluded that "the role of termolecular reactions grows rapidly with decreasing height."

Continued study of termolecular processes is very important. This is not only true for Titan ion chemistry, but generally for the complete understanding of ion–molecule interactions in planetary atmospheres. What is particularly significant for Titan however, in contrast with Earth, is the role that carbon in the hydrocarbons on Titan has compared with oxygen on Earth. So many hydrocarbons are present in Titan's atmosphere that termolecular association reactions will play a more significant role on Titan than on Earth. Many of these association reactions lead to covalent products and some new exotic cyclic product molecules will be formed.

Acknowledgments

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