

Submitted on
August 28, 1995
to the Journal of Physical Chemistry

The Reactions of CH_3^+ With C_2N_2 , CH_2CHCN and HC_3N : A Low Pressure/High Pressure Study

McEwan, M.J.,^{1,2} Fairley, D.A.,² Scott, G.B.I.² and Anicich, V.G.

Jet Propulsion Laboratory
4800 Oak Grow Dr
Pasadena, CA 91109, USA.
MS183/601

¹ NRC-NASA Research Associate at JPL, 1993-94.

² Department of Chemistry, University of Canterbury, Christchurch,
New Zealand

ABSTRACT

The association of CH_3^+ with the three molecules C_2N_2 , CH_2CHCN and HCCCN has been examined using ion cyclotron resonance (iCR) and selected ion flow tube (SIFT) techniques at room temperature. In each reaction, the mean lifetime of the complex $(\text{CH}_3\cdot\text{N}\equiv\text{C}-\text{R}^+)^*$ formed in the association, has a major influence on the outcome of reaction and the product channels that are observed using ICR and SIFT. Termolecular rate coefficients are reported for the association of $\text{CH}_3^+ + \text{C}_2\text{N}_2$ for the bath gases $\text{M} = \text{He}, \text{Ar}, \text{N}_2$ and C_2N_2 . $k_3 = 8.2 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1}$ ($\text{M} = \text{C}_2\text{N}_2$). In each system the association product channel occurs in competition with other exothermic bimolecular channels. The complex lifetimes in all three systems are expected to be in the range of 30 to 70 μs . Very rapid ion-molecule association reactions have been observed in several systems of hydrocarbons and nitriles and the implications for Titan ion chemistry are discussed briefly.

INTRODUCTION

The unique blend of atmospheric species discovered on Titan during the Voyager 2 fly-by^{1,2} has stimulated interest both in the way in which the observed chemical species are formed and also in the range of molecules and ions that can be anticipated. One of the most efficient ways of synthesizing molecules is via the process of ion-molecule association in which an ion and a neutral molecule combine to form a covalently bound molecular ion of mass equal to the sum of the masses of the reactant ion and neutral molecule.

Ion-molecule association (Reactions (1 a)-(1c)) followed by dissociative recombination has been invoked as a mechanism for synthesizing some of the molecules that have been observed in interstellar clouds. Under the conditions of very low temperatures and pressures that exist in the interstellar medium, stabilization of the association complex is achieved by photon emission (Reaction (1 b)).³ In the laboratory at higher pressures, however, the complex generally undergoes collisional stabilization (Reaction (1 c)) before it can emit a photon.⁴



One ion that is thought to associate with many different neutrals in interstellar clouds is CH_3^+ ⁵ as it is relatively unreactive with H_2 . In earlier studies of CH_3^+ association reactions with the nitriles HCN ,^{6,7} CH_3CN ⁴ and

HC_3N ,⁸ we found the association channel to be remarkably efficient even when it competes with exothermic bimolecular channels. Termolecular rate coefficients as large as $1.9 \times 10^{-22} \text{ cm}^6 \text{ s}^{-1}$ were found for example, in the association between CH_3^+ and CH_3CN .⁴ Termolecular rate coefficients of this magnitude enable three body processes to compete effectively with bimolecular reactions at pressures as low as $2 \times 10^{-5} \text{ Torr}$. Of course such pressures are not relevant to interstellar clouds but they are to planetary ionospheres. This is true for the lower extents of most gas enveloped planets and moons.

We continue in this work, our studies of the factors that influence the rates of ion-molecule association processes. We present here the association behaviour of CH_3^+ with cyanogen (C_2N_2), acrylonitrile (CH_2CHCN) and cyanoacetylene (HC_3N).

EXPERIMENTAL

The pressure dependent measurements ($< 10^{-3} \text{ Torr}$) were all made using the JPL Ion Cyclotron Resonance (ICR) spectrometer operating at a 1.5 T magnetic field.⁹ The ICR instrument was used in two different operational modes. In the trapped mode, ions were trapped for different periods of time in a known pressure of reactant gas before being released to drift through the cell and enter the detection region. In the drift mode of operation the ions drift through the cell immediately after their formation, in a higher pressure of reactant gas than in the trapped mode. The rate of reaction is found from the rate of disappearance of the reactant ion in the trapped mode and from the ratio of the reactant ion to product

ion signals in the drift mode. The branching ratios for CH_3^+ reacting with CH_2CHCN and HC_3N were also obtained with the tandem ICR instrument acquired recently.⁷

The higher pressure measurements (0.3 Torr) were made using the Canterbury Selected Ion Flow Tube (SIFT).¹⁰

Reagent species (except for HC_3N) were obtained from commercial sources and further purified by freeze-pump-thaw cycles. All measurements were made at room temperature 298 ± 5 K. HC_3N was prepared by the action of methyl propiolate and NH_3 followed by dehydration with P_2O_5 as described previously.¹¹

RESULTS

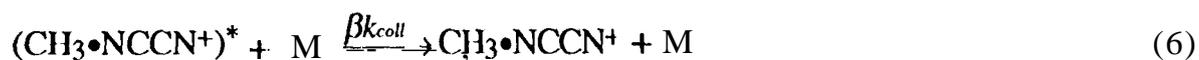
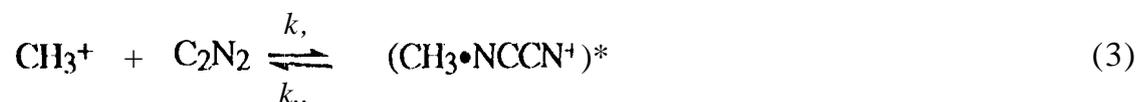
$\text{CH}_3^+ + \text{C}_2\text{N}_2$

The product channels observed by the ICR and SIFT techniques are different in this reaction and this situation often occurs when termolecular association competes with exothermic bimolecular channels. In the ICR, two channels are observed ($\text{CH}_2\text{CN}^+ + \text{HCN}$ production and the association channel product $\text{CH}_3\bullet\text{NCCN}^+$) with a combined rate coefficient $k = 9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at a pressure of 3×10^{-5} Torr of C_2N_2 .



The branching ratio at this pressure was about 4:1 in favour of $\text{CH}_2\text{CN}^+ + \text{HCN}$. In the SIFT instrument, only the association product was observed and the pseudo bimolecular rate coefficient was $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at a helium pressure of 0.3 Torr. The association rate coefficient in the SIFT approximates the collision rate of $k_c = 1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and is expected to be effectively invariant with pressure in the SIFT.

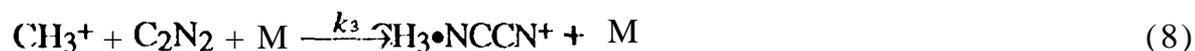
In the ICR however, the branching ratio changes with increasing pressure in favor of the association channel $\text{CH}_3\bullet\text{NCCN}^+$. By measuring the dependence of the rate coefficient with pressure in the ICR instrument, the termolecular rate coefficient for formation of $\text{CH}_3\bullet\text{NCCN}^+$ via collisional stabilization was found. The rate coefficient at each pressure was derived from the relative height of the mass peak at $m/z = 15$ Dalton (CH_3^+) to those of the products at $m/z = 40$ Dalton (CH_2CN^+) and $m/z = 67$ Dalton ($\text{CH}_3\bullet\text{NCCN}^+$) at a measured drift time and C_2N_2 partial pressure. The reactions occurring in this system may be written:



If the observed bimolecular rate coefficient for the reaction is k_2^{obs} , then it has been shown that k_2^{obs} may be expressed in terms of the rate coefficient parameters for reactions (3) through (6) as:⁴

$$k_2^{\text{obs}} = k_f(k_r + k_{-2} + \beta k_s[\text{M}] / (k_{-1} + k_1 + k_{-2} + \beta k_s[\text{M}])) \quad (7)$$

The coefficient β is a number between 0 and 1 that gives a measure of the efficiency of stabilization of the $(\text{CH}_3\cdot\text{NCCN}^+)^*$ complex by the bath gas. A model based on equations (3) through (6) was used to fit the experimental data and the comparison of the model calculations with experiment is shown in Figure 1 for $M = \text{C}_2\text{N}_2$. The value of k_f chosen, $k_f = 1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, was that measured in the SIFT experiment and βk_{coll} was held at the collision-limiting rate coefficient ($\beta k_{\text{coll}} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). The results of this procedure gave the following values for the rate coefficients: $k_f = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $k_{-1} = 276,000 \text{ s}^{-1}$; $k_{-2} = 13,000 \text{ s}^{-1}$ and $k_3 = 8.2 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1}$ for $M = \text{C}_2\text{N}_2$, where k_3 is defined in Reaction (8).



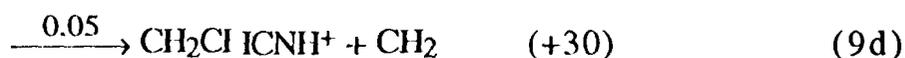
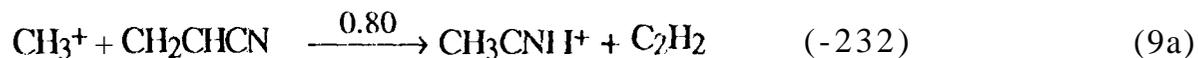
The mean lifetime with respect to unimolecular dissociation of the $(\text{CH}_3\cdot\text{NCCN}^+)^*$ complex is $\tau^* \beta^{-4} \mu\text{s}$.

We also list in Table 1 the relative efficiencies of stabilization and termolecular rate coefficients for the bath gases He, Ar, N_2 and C_2N_2 . The termolecular rate coefficients for the different bath gases were found from a least squares minimization between the model calculation of reactions (3) through (6) and the experimental data. The rate coefficients k_f , k_{-1} , and βk_s for C_2N_2 were fixed at the values obtained for $M = \text{C}_2\text{N}_2$ and the least squares minimization was carried out allowing β and k_f to vary.

$\text{CH}_3^+ + \text{CH}_2\text{CHCN}$

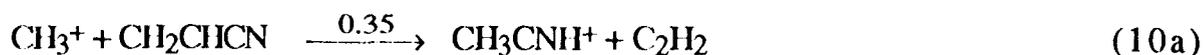
In the ICR instrument, the main product ion of the reaction was at $m/z = 42$ Daltons (CH_3CNH^+) with minor product ions at $m/z = 27, 41$ and 54

Daltons. The product channels assigned to these ions on the basis of their energetic are:



Branching ratios and exothermicities (kJ mol^{-1}) are also listed. In reaction (9a) we have designated CH_3CNH^+ as the ion product but it could equally be an isomer such as CH_3NCH^+ . The channel (9d) appears to be endothermic by 30 kJ mol^{-1} according to the listed heats of formation.¹² There is however, sufficient uncertainty in the listed values to allow the (9d) channel to be only slightly endothermic which is more consistent with our observation of this channel. No association product was observed in the ICR even at bath gas pressures approaching $5 \times 10^{-4} \text{ Torr}$.

A comparison of these results with those of an earlier SIFT study shows a quite different product distribution from the reaction. The SIFT study¹³ found the major product of the reaction to be the association adduct ion $\text{CH}_3\text{NCCH}_2^+$ with two other channels, $\text{c-C}_3\text{H}_3^+ + \text{CH}_2\text{NH}$ and $\text{H}_2\text{C}_3\text{N}^+ + \text{CH}_4$. In view of the apparent discrepancy, we re-examined this reaction in the SIFT, taking special care to eliminate all traces of CH_2^+ contamination from the CH_3^+ reactant ion swarm. We found only two products of reaction in the re-evaluation:



The major channel, as before, was association, but the only other channel of significance was $\text{CH}_3\text{CNH}^+ + \text{C}_2\text{H}_2$. The rate coefficient measured in the SIFT was $k = 5.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This is the same as the collision rate coefficient within the errors of our measurement.

$\text{CH}_3^+ + \text{HC}_3\text{N}$

Two product channels of the reaction were found in the ICR: the major channel was $\text{C}_3\text{H}_3^+ + \text{HCN}$ but small signals corresponding to the association channel $\text{CH}_3\bullet\text{NC}_3\text{H}^+$ were detected at pressures approaching 5×10^{-4} Torr of HC_3N .



An unusual feature of the ICR study of this reaction was the difference in rate coefficient measured using the trapped and drift modes of operation. In the trapped mode, $k = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ where k was found from the rate of disappearance of CH_3^+ . In the drift mode, $k = 7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ where k was derived from the relative ratio of the CH_3^+ ion signal to the product ion signals. We have not identified the process responsible for the decrease in rate coefficient in the drift mode. It is possible that some radiative stabilization of the complex in the trapped mode occurred forming a lower energy complex that subsequently reacted with HC_3N . The

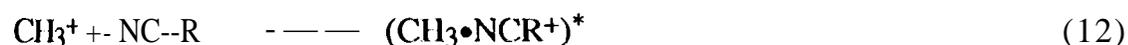
product of the reaction may be a product ion already present in the cell. It is not clear from our analysis why this decrease occurred. Similar behaviour was observed in the $\text{CH}_3^+ + \text{HCN}$ system.⁷

Two studies of this reaction have been reported using the SIFT technique and both investigations reported the same product channels as observed in the ICR; viz. $\text{C}_3\text{H}_3^+ + \text{HCN}$ and association. At 0.3 Torr of helium, channel (11 a) was 40% of the total reaction and channel (11 b) 60% with a rate coefficient $k = 4.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.^{8,14} This is very close to the collision rate coefficient that is calculated to be $5.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

A summary of all the results is given in Table 2.

DISCUSSION

The contrast in results between the low pressure and high pressure techniques is very informative and can be rationalized in terms of how long the $(\text{CH}_3 \bullet \text{NC-R}^+)^*$ complex lives.



In the $\text{CH}_3^+/\text{NCCN}$ system, the low pressure measurements found the $\text{CH}_2\text{CN}^+ + \text{HCN}$ product channel in addition to association whereas the SIFT measurements revealed the association product only, which was produced in the SIFT at a rate close to the collision rate for the reaction. At flow tube pressures (0.3 Torr), there are sufficient collisions of the complex with the helium bath gas to collisionally deactivate $(\text{CH}_3 \bullet \text{NCCN}^+)^*$ before any other exit channel from the $\text{C}_3\text{H}_3\text{N}_2^+$ surface is found. In the ICR

experiment, the much lower ambient pressures allow unimolecular dissociation of $(\text{CH}_3\bullet\text{NCCN}^+)^*$ to take place before collisional stabilization can occur. The smaller rate coefficient in the ICR measurement ($k = 9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 3×10^{-5} Torr) indicates that unimolecular dissociation back to reactants is much faster than dissociation to $\text{CH}_2\text{CN}^+ + \text{HCN}$ ($k_{-1} \gg k_{-2}$). As the bath gas pressure increases, the number of complexes stabilized by collision also increases and this is seen by the increase in k with increasing pressure.

The measured termolecular rate coefficient for complex formation allows an estimate of the mean complex lifetime according to the model presented in reactions (3) through (6) as $\tau^* \beta \sim 4 \mu\text{s}$. An absolute value for τ cannot be deduced from the pressure dependence of k alone, without knowledge of the collision stabilization efficiency, β . One piece of information we learn from the SIFT experiment where all complexes are stabilized at 0.3 Torr of helium, is that the mean complex lifetime is much greater than the time between collisions, viz: $\tau(\text{CH}_3\bullet\text{NCCN}^+)^* \gg 0.25 \mu\text{s}$. This is consistent with the observation that $\tau^* \beta \sim 4 \mu\text{s}$, and since $\beta \leq 1$, then $\tau \geq 4 \mu\text{s}$. From past studies we have found that $\beta \sim 0.08$ (M = HC_3N) and 0.09 (M = CH_3CN) and we expect that it will be about the same for $\text{CH}_3^+/\text{C}_2\text{N}_2$. If so, then $\tau(\text{CH}_3\bullet\text{NCCN}^+)^* \sim 60 \mu\text{s}$.

in the $\text{CH}_3^+/\text{CH}_2\text{CHCN}$ system, no association product was observed in the ICR experiment, even at bath gas pressures as high as 1×10^{-4} Torr. The absence of association and the large rate coefficient in the ICR ($k = 5.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \cong k_{\text{coll}}$) supports the conclusion that the exit channel from the $(\text{CH}_3\bullet\text{NCCHCH}_2^+)^*$ complex is found so quickly after formation, that the complex lifetime is too short for collisional stabilization to be competitive

with **unimolecular** dissociation to products at the pressures in the ICR instrument. While the two collision complexes, $(\text{CH}_3\bullet\text{NCCN}^+)^*$ and $(\text{CH}_3\bullet\text{NCCHCH}_2^+)^*$, have about the same lifetimes, their outcomes are quite different in the ICR cell. In the case of $(\text{CH}_3\bullet\text{NCCN}^+)^*$, the lifetime is determined by the rapid return to reactants ($k_{-1} \gg k_{-2}$). In the $(\text{CH}_3\bullet\text{NCCHCH}_2^+)^*$ case, the lifetime is defined by the rapid rate towards products $\text{CH}_3\text{CNH}^+ + \text{C}_2\text{H}_2$ ($k_{-1} \ll k_{-2}$). However, as collisional stabilization is the major outcome of reaction in the SIFT, then $\tau(\text{CH}_3\bullet\text{NCCHCH}_2^+)^*$ is longer than the time between collisions, i.e. $\tau(\text{CH}_3\bullet\text{NCCHCH}_2^+)^* \gg 0.25 \mu\text{s}$.

The $\text{CH}_3^+/\text{HC}_3\text{N}$ system is in between the behaviour exhibited in the previous two cases. The major product channel in the ICR is $\text{C}_3\text{H}_3^+ + \text{HCN}$, whereas the major channel in the SIFT is association occurring in competition with the $\text{C}_3\text{H}_3^+ + \text{HCN}$ product channel. This system therefore lies somewhere between the previous two cases ($k_{-1} \sim 2k_{-2}$). While the two collision complexes, $(\text{CH}_3\bullet\text{NC}_3\text{H}^+)^*$ and $(\text{CH}_3\bullet\text{NCCHCH}_2^+)^*$, have again about the same lifetimes their outcomes are slightly different. In the case of $(\text{CH}_3\bullet\text{NC}_3\text{H}^+)^*$, the lifetime is defined by a slower return to reactants. Actually the forward and reverse rates are about the same within a factor of two. The mean complex lifetime, $\tau(\text{CH}_3\bullet\text{NCCCCH}^+)^*$ is again clearly larger than the time between collisions in the SIFT ($0.25 \mu\text{s}$).

The latter two systems can be analyzed in a similar manner to the analysis on the $\text{CH}_3^+/\text{NCCN}$ system. Equations similar to Equations (3) through (7) can be defined for the $\text{CH}_3^+/\text{CH}_2\text{CHCN}$ and $\text{CH}_3^+/\text{HC}_3\text{N}$ systems. While we were not able to measure the **termolecular** association directly in the ICR for these two systems, the non-observation sets a lower limit on the overall k_3 . Using the known k_2^{obs} value, the values k_f , k_{-1} , k_{-2} , and $\tau^*\beta$

are estimated from the fit of the kinetics crossover. The formulas used in this calculation are given in the Appendix. The solutions are presented in Table 3 along with the values from the $\text{CH}_3^+/\text{CH}_3\text{CN}$ and CH_3^+/HCN systems. One surprise is that in all three present systems, the $\tau \cdot \beta$ products are very nearly the same in magnitude. The overall estimate for k_3 for $\text{CH}_3^+/\text{HC}_3\text{N}$ is expected to be about $3.8 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ which is very fast for a **termolecular** process.

There is one ambiguous point left, i.e. are the dissociative products observed in the SIFT due to bimolecular processes, or are they due to **termolecular** processes that have a collision-induced dissociative component? The only complexes that are known to dissociate in the flow tube are very **weakly** bound complexes: i.e. bound by less than a few tens of kJ. The collision complexes in the systems that we are discussing here are believed to have relatively deep potential wells of at least 100kJ. Can the model and the values of the **parameters** that we have deduced support the observation of products other than the association **adduct** in the SIFT experiments?

From the experimental data, the SIFT measured rate gives k_f and the **ICR rate** gives the ratio of τ_2/τ_1 . Four decades of pressure are required to span the transition from bimolecular kinetics only, at low pressures, to the region when every complex formed is stabilized by collision. The crossover between **these** two regimes, bimolecular kinetics and **termolecular** kinetics occurs in a specific place in each system (see Figure in Appendix). This crossover defines the total lifetime of the collision complex.

In the $\text{CH}_3^+/\text{CH}_2\text{CHCN}$ system, the reverse rate coefficient, k_{-1} , is much less than the k_{-1} values in the other two systems. Nevertheless it is not

possible to make the k_{-2} value in this system sufficiently large to account for the extent of dissociative product formation that is observed in the SIFT experiment. It would require a larger value of k_{-2} in the SIFT than was found in the ICR experiments. The value of the rate coefficient predicted for k_{-2} can account for about 5% of the SIFT products but no more. Alternatively, if the termolecular rate coefficient is reduced to $k_3 = 3 \times 10^{-25} \text{ cm}^6 \text{ s}^{-1}$, then the reaction has not entered the 'pressure-saturated' regime in the SIFT and larger amounts of dissociative products can be expected.

For the $\text{CH}_3^+/\text{HC}_3\text{N}$ the system, the bimolecular process could contribute up to 40% of the total products observed in the SIFT, but only if the unimolecular life time $\tau \geq 1$ ms. However, a lifetime this large is also inconsistent with the fact that we were unable to make a direct experimental determination of the lifetime in the ICR. With the current parameters deduced for this system we can account for no more than 5% of the observed SIFT dissociative products.

We have assumed in these three systems that $k_f = k_{\text{coll}}$. Under these conditions in the SIFT, all three reactions should have entered the pressure-saturated regime and therefore the extent of dissociative channels should be minimal. It isn't and this raises the question of why?

As mentioned earlier, dissociative product channels might arise from the association adduct through collisional-break up of the adduct ion. This outcome is unexpected because of the assumed stability of the association complex in these systems. Alternatively it is possible that two independent channels with two different types of complexes may occur such that one complex can be stabilized by collision, but the other which has a very

much shorter lifetime, cannot be collisionally stabilized at the SIFT experimental pressures. Other association systems have been described before as having two complex behavior: e.g. $i\text{-C}_3\text{H}_7^+/\text{C}_2\text{H}_5\text{NH}_2$ ¹⁵ and $\text{C}_2\text{N}_2^+/\text{C}_2\text{N}_2$ ¹⁶ with this behavior.

We cannot decide which mechanism is responsible for the occurrence of dissociative channels in the SIFT experiments in the $\text{CH}_3^+/\text{CH}_2\text{CHCN}$ and $\text{CH}_3^+/\text{HC}_3\text{N}$ the systems from these measurements.

Direct measurement of association complex lifetime

We have recently developed a technique for measuring the mean lifetime of ion-molecule association complexes.¹⁷ The technique requires the presence of a bimolecular product channel competing with association. The three association reactions in this study meet that requirement.



The basis of the technique is to monitor the bimolecular product ion (C^+) while employing double resonance ejection of the precursor $(\text{AB}^+)^*$ ion. A distribution of lifetimes is found from the shape of the double resonance ejection curve versus the time of ejection.¹⁷ In our instrument, the shortest ejection times corresponding to the largest V_{rf} amplitudes, are -70 ps. This means complexes with lifetimes shorter than -70 μs will show no double resonance behaviour as they are lost from the cell by

unimolecular decomposition, before they can respond to ejection from their power absorption.

All three systems investigated were examined using this technique. No significant double resonance response was observed in any of the three systems which is consistent with the earlier observation that $\tau^*\beta$ ($\text{CH}_3\bullet\text{NC-R}^+$)* $\geq 4 \mu\text{s}$. In these systems it is expected that $\beta \sim 0.1$, thus we also expect then that the lifetimes are between 30 and 70 μs . If we make this assumption then k_3 ($\text{CH}_3^+/\text{HC}_3\text{N}$) is estimated to be about $3.8 \times 10^{-23} \text{cm}^6 \text{s}^{-1}$, and k_3 ($\text{CH}_3^+/\text{CH}_2\text{CHCN}$) is estimated to be between 1 and $5 \times 10^{-24} \text{cm}^6 \text{s}^{-1}$. These differences in the k_3 values estimated reflect more than just differences in the lifetimes of the collision complexes. They also include the effect of changes in dipole moments of the neutrals and the resultant effect this has on the collision rate (or k_f).

CONCLUSIONS

The question of the relative efficiency of ion-molecule association reactions to competing bimolecular channels is an important one that has application to interstellar synthesis and planetary atmospheres. The crucial parameter controlling the relative efficiency of the association mechanism is the complex lifetime, which is in turn, influenced by the presence of fast exit channels from the energy surface of the complex. In this study, all three ion-molecule systems examined demonstrated association as the major outcome of a reaction event in the SIFT. Thus at a flow tube pressure of 0.3 Torr, the time between collisions is sufficiently short for collisional stabilization to be the principal stabilizing mechanism

and is faster than any of the competing **unimolecular** processes as the rate coefficient approaches the **collision-limiting** value.

What we have not addressed in the **present** study is the more fundamental question of why the lifetimes of the three $(\text{CH}_3 \bullet \text{NC-R}^+)^*$ complexes should or should not differ. The existence of exothermic reactions, the binding energy of the complex and the number of degrees of freedom are the chief factors that influence the lifetime. Some attempts have been made to assess these factors as they influence radiative **association**.^{18,19} None of the structures of the association adducts in this study are known, and therefore the binding energies for the complexes are not known. A comparison of the measured **termolecular** rate for $\text{CH}_3^+ + \text{C}_2\text{N}_2$ with other R-CN systems that **we have studied**^{4,6,7} suggests a binding energy of at least 150 kJ mol^{-1} for the $\text{CH}_3 \bullet \text{NCCN}^+$ complex. Weakly bound complexes do not exhibit fast **termolecular** association in the ICR. The $\text{CH}_3 \bullet \text{NCCN}^+$ is thus a **covalently** bonded molecular ion.

Finally we assess the relevance of association processes to the atmosphere of Titan. A substantial partial pressure of CH_4 has been detected in the atmosphere of Titan.^{1,2} Model calculations predict a peak ion production for CH_3^+ at an altitude of 1100 km ^{20,21} for which the principal loss process is reaction with CH_4 .



It is apparent however from this and other studies that rapid **termolecular** ion-molecule association reactions occur. The directly measured association reaction in this study is $\text{CH}_3^+ + \text{C}_2\text{N}_2$ which requires an ambient neutral density of $6 \times 10^{14} \text{ molecules cm}^{-3}$ before it is competitive with

fast bimolecular reactions. Some association reactions of CH_3^+ are much faster than this. For example the $\text{CH}_3^+ + \text{CH}_3\text{CN}$ association with a termolecular association rate coefficient of $1.9 \times 10^{-22} \text{ cm}^6 \text{ s}^{-1}$,⁴ is competitive with fast bimolecular reactions at a neutral density around $8 \times 10^{12} \text{ molecules cm}^{-3}$. These densities are achieved in the lower ionosphere of Titan. The relatively large mixing ratio of CH_4 in Titan's atmosphere, means that termolecular reactions of CH_3^+ do not constitute significant loss processes for ionospheric CH_3^+ ions. However, the same is not necessarily true of ions which are unreactive with CH_4 such as C_3H_5^+ and H_2CN^+ . What is also not clear is the effect of temperature. The systems studied here are room temperature investigations, yet they show association competing efficiently with fast exothermic channels. For association via collisional stabilization to be competitive with an exothermic bimolecular reaction, there must be a barrier in the exothermic exit channel which lengthens the lifetime of the complex. Few systems have been as closely investigated as the $\text{CH}_3^+/\text{CH}_3\text{CN}$ system.^{4,22} Extensive calculations of the $\text{C}_3\text{H}_6\text{N}^+$ energy surface for the association of CH_3^+ and CH_3CN showed a barrier height to the exothermic channel only about 15 kJ mol^{-1} below the entrance energy to the surface but 85 kJ mol^{-1} above the exothermic products. As the temperature decreases towards the temperature of Titan's atmosphere, the existence of this barrier will favour further the association process over the exothermic channel. We therefore conclude that ion-molecule association processes are an important class of reactions that should be included in models of Titan up to lower ionospheric altitudes. What is needed, however, is a much more extensive data base of such reactions.

ACKNOWLEDGEMENT

The work described in this paper was carried out at the Jet Propulsion laboratory, California institute of Technology, under contract with the National Aeronautics and Space Administration.

REFERENCES

1. Hanel, R. et al. *Science*, 1981, 2.12, 192.
2. Kunde, V. G.; Aikin, A.C.; Hanel, R. A.; Jennings, D.E.; Maguire, W.C.; Samuelson, R.E. *Nature*, 1981, 292, 686.
3. Bates, D.R.; Herbst, E. In "Reaction Rate Coefficients in Astrophysics". Edited by Miller, T.J. and Williams, D.A. 1988 (Reidel, Dordrecht).
4. McEwan, M. J.; Denisen, A. B.; Huntress, W.T. Jr.; Anicich, V. G.; Snodgrass, J.; Bowers, M. J. *J. Phys. Chem.*, 1989, 93, 4064; Smith, S. C.; Wilson, P.F.; Sudkeaw, P.; Maclagan, R.G.A.R.; McEwan, M.J.; Anicich, V. G.; Huntress, W.T. *J. Chem. Phys.*, 1993, 98, 1944; Anicich, V.G.; Sen, A.D.; McEwan, M.J.; and Smith, S.C. *J. Chem. Phys.*, 1994, 100, 5696.
5. Smith, D. *Chem. Rev.*, 1992, 92., 1473.
6. McEwan, M.J.; Anicich, V.G.; Huntress, W.T.; Kemper, P.R.; Bowers, M.T. *Chem. Phys. Lett.*, 1980, 75, 278.
7. Anicich, V. G.; Sen, A. D.; Huntress, W.T. Jr.; McEwan, M.J. *J. Chem. Phys.*, 1995, 102, 3256.
8. Knight, J, S.; Freeman, C.G.; McEwan, M J.; Adams, N.G.; Smith, D. *In? J. Mass Spectrom. Ion Proc.*, 1985, 67, 317.
9. McEwan, M.J.; Denisen, A.B.; Anicich, V. G.; Huntress, W.T. Jr. *Int. J. Mass Spectrom. Ion Proc.*, 1987, 81, 246.
10. McEwan, M.J. In "Advances in Gas Phase Ion Chemistry". Adams, N.G., Babcock, L.M. Eds.; J.A.I. Press: Greenwich, CT, 1992; Vol 1, p1.
11. Sen, A.D.; Huntress, W. T.; Anicich, V. G.; McEwan, M.J. *J. Chem. Phys.*, 1991, 94, 5462 and originally in Miller, F.A. and Mellon, D.H. *Spectrochimica. Acts*, 1967, 23A, 1415.

12. Lias, S. G.; Bartmess, J.E.; Liebman, J.F.; Holmes, J.I.; Levin, R.D.; Mallard, W.G. *J. Phys. Chem. Ref. Data*, **1988**, *17*, Suppl. 1.
13. Petrie, S. A. H.; Freeman, C.G.; McEwan, M.J. *Mon. Not. R. Astron.Soc.*, **1992**, *257*, 438.
14. Bohme, D. K.; Raksit, A.B. *Mon. Not. R. Astron. Soc.*, **1985**, *213*, 717.
15. M. Moet-Ner, *J. Amer. Chem. Soc.*, **1979**, *101*, 2389.
16. McEwan, M.J. and Anicich, V.G. *J. Phys. Chem.*, **1995**, in press.
17. Anicich, V. G.; Sen, A.D.; Huntress, W.T. Jr.; McEwan, M.J. *J. Chem. Phys.*, **1991**, *94*, 4189.
18. Dunbar, R.C. *Int. J. Mass Spectrom. Ion Proc.*, **1990**, *100*, 423.
19. Herbst, E.; Dunbar, R.C. *Mon. Not. R. Astron. Soc.*, **1991**, *253*, 341.
20. Keller, C. N.; Cravens, T. E.; Gan, L. *J. Geophys. Res.*, **1992**, *97*, 12117.
21. Dalgarno, A.; Fox, J.L. In "Unimolecular and Bimolecular Ion-molecule Reaction Dynamics", Eds. C.Y. Ng, T. Baer, I. Powis. John Wiley & Sons, Chichester, England, 1994, p1.
22. Herbst, E.; McEwan, M.J. *Astron. Astrophys.*, **1990**, *229*, 201.

Table 1. Termolecular rate coefficients (k_3^{obs}) measured for the association reaction $\text{CH}_3^+ + \text{C}_2\text{N}_2 + \text{M} \longrightarrow \text{CH}_3^+\bullet\text{NCCN}^+ + \text{M}$ with the bath gas M. Collision efficiencies β_m are relative to $\beta_{\text{C}_2\text{N}_2}$.

M	$k_3^{\text{obs},a}$	$\beta_M/\beta_{\text{C}_2\text{N}_2}$
He	0.8	0.20
Ar	1.3	0.33
N ₂	2.4	0.50
C ₂ N ₂	8.2	1.0

^a In units of $10^{-24} \text{ cm}^6 \text{ s}^{-1}$.

Table 3
Solutions from Crossover Fitting

	k_2^a (ICR)	k_2^a (SIFT)	k_1^a	k_{coll}^a	$\beta * k_1^b$	$\beta * k_2^b$	$\beta * \tau^c$	k_3^d	$k_3^a @$ 1×10^{-4} Torr	% of k_2
CH ₃ CN	1.8	4.0	5.5	5.5	-	23,000	13.	19.0		
C ₂ N ₂	0.09	1.7	2.0	1.94	276,000	13,000	3.5	0.82		
HC ₃ N	1.5	4.4	5.2	5.33	248,000	100,000	2.9	3.8	0.12	11 %
CH ₂ CHCN	5.4	5.5	5.6	5.62	10,000	274,000	3.5	0.1-0.5	0.016	4%
HCN	0.2	2.0	1.68	4.5	532,000	.	1.6	1.1		

^a units are $(\times 10^{-9}) \text{ cm}^3 \text{ s}^{-1}$

^b units are s^{-1}

^c units are μsec

^d units are $(\times 10^{-23}) \text{ cm}^6 \text{ s}^{-1}$

Appendix

The following set of chemical equations can be Represented as a set of partial differential equations. This is a parallel set of equations to Equations (3) through (6) in the text.



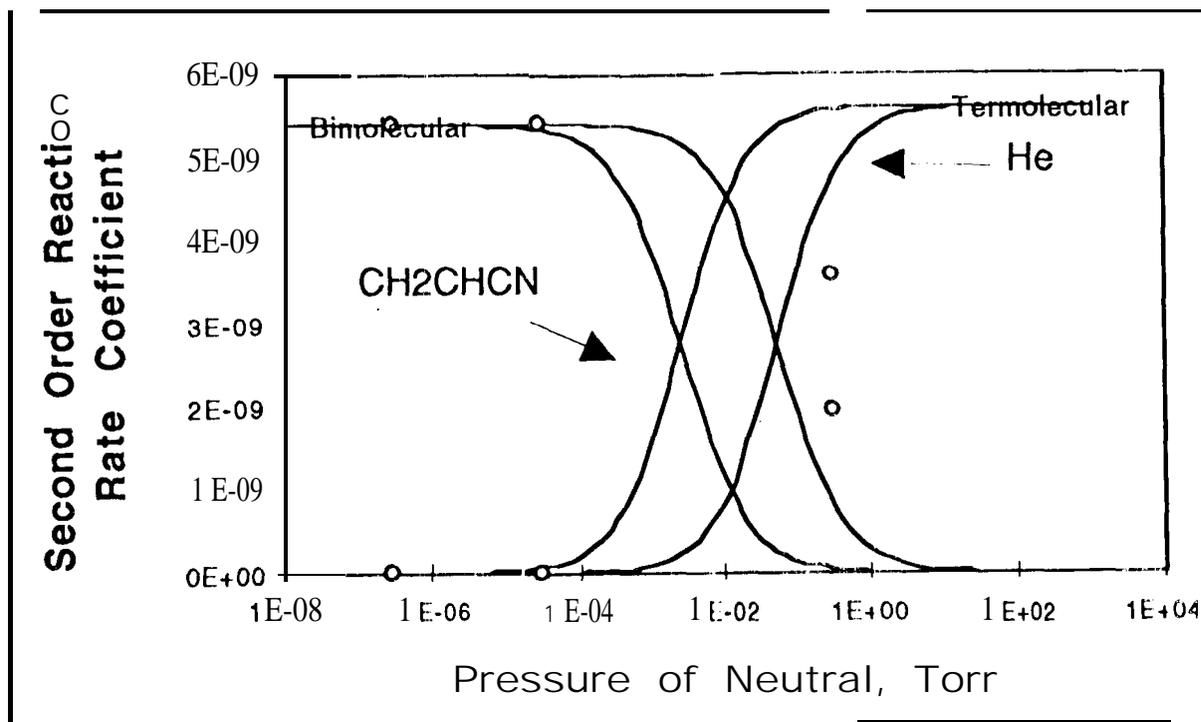
The set of partial differential equations was solved for the concentration of the chemical species in the equations. The reaction rate coefficient for the loss of A^+ is $k_2(A^+)$, the formation reaction rate coefficient for C^+ is given by $k_2(C^+)$, and the formation reaction rate coefficient for AB^+ is given by $k_2(AB^+)$. The equations in k_f , k_{-1} , k_{-2} , and $\beta k_{coll}[M]$ are given below.

$$k_2(A^+) = k_f (k_{-2} + \beta k_{coll}[M]) / (k_{-1} + k_{-2} + \beta k_{coll}[M])$$

$$k_2(C^+) = k_f k_{-2} / (k_{-1} + k_{-2} + \beta k_{coll}[M]) = k_2(ICR)$$

$$k_2(AB^+) = k_f \beta k_{coll}[M] / (k_{-1} + k_{-2} + \beta k_{coll}[M]) = k_2(SIFT) @ 0.3 \text{ Torr of He}$$

This solution is used below to show the estimated crossover position for the system $\text{CH}_3^+/\text{CH}_2\text{CHCN}$.



The expected position of the crossover between bimolecular and termolecular kinetics for the system $\text{CH}_3^+/\text{CH}_2\text{CHCN}$. The effective bimolecular reaction **rate** coefficient is plotted against the pressure of both the parent gas and helium as a buffer. The data point (open circles) are from Table 2. The data points at 0.30 Torr represent the rate coefficients for the two channels observed in the SIFT when $M = \text{He}$.

Fig. 1. The variation in rate coefficient $k_2^{\text{obs}} / (\text{cm}^3 \text{s}^{-1})$ against pressure of $\text{C}_2\text{N}_2 / (\text{Torr})$ for the reaction of CH_3^+ with C_2N_2 . The points are experimental and the curve is the computer-generated line of best fit based on the model presented in equations (3) through (6).



Wayne T. Kasprsak
Goddard Space Flight Center
Code 915.0
Greenbelt, MD 20771

E-mail: kasprsak@paf.gsfc.nasa.gov

 (301) 286-8253



3/21/95



