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A Low Pressure Study of C_2N_2 Ion Chemistry

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Abstract

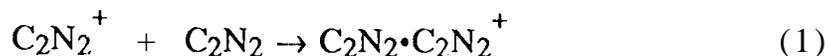
Ion-molecule reactions of C_2N_2^+ and C_2N_2 with several ions and neutrals observed or predicted to be present in the atmosphere of Titan have been examined in an Ion Cyclotron Resonance spectrometer at room temperature and low pressures. Rate coefficients and branching ratios are reported for N^+ , N_2^+ , HCN^+ , C_2H_2^+ , C_2H_4^+ , C_3H_5^+ , C_4H_2^+ and C_4H_3^+ with C_2N_2 and for C_2N_2^+ with N_2 and C_2H_2 . The association reaction between C_2N_2^+ and C_2N_2 forming C_4N_4^+ was examined in some detail. No evidence was found for radiative (bimolecular) association, but rapid collisional stabilization was observed. The termolecular association rate coefficient is $k_3 = 1.7 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ ($M = \text{C}_2\text{N}_2$) and the relative collisional stabilization efficiencies for the bath gases $M = \text{He}$, Ne , Ar and N_2 were also measured. The mean lifetime of the $(\text{C}_4\text{N}_4^+)^*$ complex that exhibited collisional stabilization was $\tau/\beta = 1.04 \mu\text{s}$ where β is the relative efficiency of collisional stabilization. A possible isomeric form of the C_4N_4^+ product of association is the ion NCCNCCN^+ resulting from unrearranged addition. A mechanism is also presented showing how pressure saturation can occur when the rate coefficient for association is much less than the collision rate.

Introduction

The discovery of nitrogen and methane as major atmospheric species in the atmosphere of Titan, Saturn's largest satellite, and the observation of molecules derived from these molecules has focussed attention on atmospheric species containing the -CN group. The unique blend of N₂ and CH₄ in the atmosphere of Titan should result in an interesting array of complex and unusual molecules. Molecular species containing the -CN group that have been identified in Titan's atmosphere include HCN, HC₃N and C₂N₂¹. Although the major synthetic processes involve neutral chemistry^{2,3}, ion chemistry will still play some role in molecular synthesis as the orbit of Titan resides within the magnetosphere of Saturn for much of the time and both magnetospheric electrons and solar UV photons will each contribute to ionization within Titan's upper atmosphere^{4,5}. Ion-molecule association reactions in particular, offer an extremely efficient means of synthesizing large molecules. Some ion-molecule association processes of nitriles have been observed to occur in the laboratory with rate coefficients large enough for these three body association processes to be competitive with bimolecular ion-molecule reactions at pressures as low as 10⁻⁵ Torr⁶. There is thus a need to establish the ion chemistry of nitriles and in this work we devote our attention to the ion chemistry of cyanogen, C₂N₂, at low pressures.

Several earlier studies of different aspects of C₂N₂ ion chemistry have been undertaken. Inoué and Cotton⁷ investigated the reactions of ions derived from C₂N₂ in a mass spectrometer source operating in the pressure range (10⁻⁴ to 10⁻² Torr). Raksit and Bohme⁸ unraveled some of the ion chemistry of C₂N₂ when they examined the reactions of several ions derived from C₂N₂ in a selected ion flow tube (SIFT) operating around 0.35

‘1’err. One of the interesting features observed in those studies was the propensity of C_2N_2 to exhibit reactions yielding polymeric $(CN)_n^+$ ion products. For example, the reaction between $C_2N_2^+$ and C_2N_2 was found to produce $C_2N_2 \cdot C_2N_2^+$ with a rate coefficient $k = 4.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in a helium bath gas



at 0.33 Torr. The product ion, $C_2N_2 \cdot C_2N_2^+$, was also found to associate further with C_2N_2 forming $C_6N_6^+$. Raksit and Bohme suggested some form of electrostatic bonding might account for the observed stability of these polymeric ions⁸. Several reactions of $C_2N_2^+$ with different neutrals were studied with a SIFT by Petrie et al⁹ who also established the proton affinity for C_2N_2 of 674 kJ mol^{-1} .

In the present study, we have undertaken a low pressure investigation of aspects of the ion-molecule chemistry of C_2N_2 of particular relevance to ionospheric processes on Titan. In particular, because of the propensity of $C_2N_2^+$ to associate with itself and form larger ions in the series $C_nN_n^+$, we have directed most of the effort in this paper to an in depth investigation (theoretical and experimental) into the nature of the association reaction between $C_2N_2^+$ and C_2N_2 leading to the production of $C_4N_4^+$.

Experimental Technique

All experiments were made using the JPL Ion Cyclotron Resonance (ICR) spectrometer described previously^{10,11}. In brief, rate coefficients of exothermic bimolecular reactions are obtained in the trapped-mode (1×10^{-7} to 9×10^{-7} Torr) of operation of the ICR cell and the pressure

dependence of the association rate coefficients are found in the drift-mode (1×10^{-5} to 3×10^{-3} Torr) of operation. All rate coefficients and branching ratios are measured in a 1.5 T magnetic field. In the trapped-mode of operation, a Bayard-Alpert ionization gauge, calibrated for each gas against a MKS Baratron capacitance manometer was used to measure pressure. In the drift-mode of operation, the pressure was measured directly using the capacitance manometer. All experiments were conducted at 295 ± 5 K.

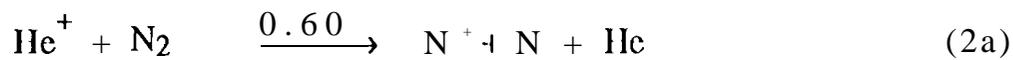
The reagent gases used were obtained from commercial sources and were further purified by trap to trap vacuum distillations.

Results and Discussion

Reactions of ions M^+ with C_2N_2 ($M^+ = N^+, N_2^+, C_2H_2^+, C_2H_4^+, C_3H_5^+, C_4H_2^+, C_4H_3^+, IICN^+$)

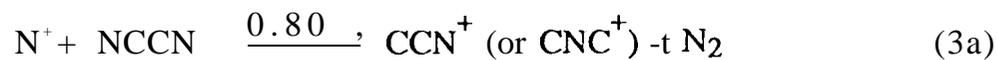
The results of the measurements of the reactions of the listed ions with C_2N_2 are summarized in Table 1.

N^+, N_2^+ reactions: Very similar results were obtained to those reported by Raksit and Bohme⁸. N^+ was produced in the ICR cell by subjecting a mixture of N_2 in a large over pressure of helium to electron impact. The majority of the N^+ was formed in the fast dissociative charge transfer reaction (2a)¹².



Two product channels were observed in the collision rate reaction of N^+ with C_2N_2 as reported earlier. Charge transfer occurs with possible end-on

attack of N^+ to $NCCN$ followed by N transfer to produce N_2 . This mechanism favors CCN^+ over CNC^+ as the ion product of reaction (3a) as



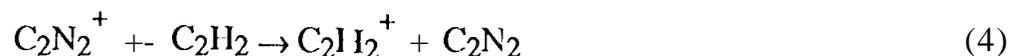
little rearrangement is required. Charge transfer which occurred at the collision rate was the only channel observed in the reaction between N_2^+ and C_2N_2 .

$C_xH_y^+$ reactions: A slow reaction which occurred on about 15% of collisions was found for the reaction of $C_4H_2^+$ and $C_4H_3^+$ with C_2N_2 . The rate coefficients were measured from the rate of removal of $C_4H_2^+$ and $C_4H_3^+$ in the trapped mode of operation at pressures in the 10^{-7} Torr range. What was unusual in these two reactions was that no product of either reaction could be identified using the usual techniques of double resonance in the drift mode of operation of the ICR cell. What may be happening in these two reactions is that an association adduct $(C_4H_n \cdot C_2N_2^+)^*$ is formed which undergoes some radiative stabilization to produce a lower energy longer-lived adduct $(C_4H_n \cdot C_2N_2^+)^{\dagger}$. A subsequent rapid reaction of the radiatively stabilized adduct with C_2H_2 (also present in the cell) would keep the adduct below observable levels in the trapped-mode of cell operation. This behavior has also been observed in other systems¹³ and has been described in detail in the CH_3^+ / HCN system¹⁴.

No reaction was observed between C_2N_2 with $C_2H_2^+$, $C_2H_4^+$ and $C_3H_5^+$.

Reactions of $C_2N_2^+$ ions with C_2H_2 and N_2

Charge transfer was the only significant channel observed with C_2H_2 and it occurred with a rate coefficient $k \geq 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This value is consistent with the rate



coefficient reported by Petrie et al⁹ of $k = 5.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ who used a SIFT technique to study the same reaction. The reason for the lower limit in this study is that some contamination of our reactant ion peak at $m/z = 52$ ($C_2N_2^+$) resulted when a contribution at the same mass arose from the ^{13}C isotope peak of $C_4H_3^+$ ($m/z = 51$) which is a primary product of the simultaneous reaction between $C_2H_2^+$ and C_2H_2 .



No reaction was observed between $C_2N_2^+$ and N_2 ($k \leq 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$).

The Association Reaction Between $C_2N_2^+$ and C_2N_2

A major focus of this work has been directed at understanding the nature of the association reaction between $C_2N_2^+$ and C_2N_2 .

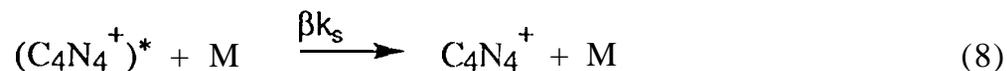
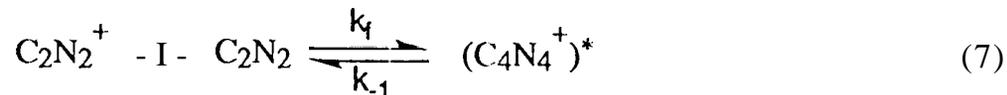


As noted earlier, a SIFT study⁸ using 0.33 Torr of helium as a bath gas reported a pseudo second-order rate coefficient for the reaction of $k = 4.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. An earlier ICR study at much lower pressures reported a smaller rate coefficient $k = 3.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ¹⁵ and these two observations have interesting implications. The fact that the association

adducts seen in the ICR at pressures of 10^{-6} Torr suggests either a rapid bimolecular association (i.e. radiative stabilization) or very efficient collisional stabilization and therefore a large termolecular rate coefficient¹⁶. The low pressure rate reported earlier¹⁵ is consistent with a three body rate coefficient in the $1 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ range at a pressure of 3×10^{-5} Torr. We did not observe any reaction at pressures in the 10^{-7} Torr range in the *trapped-mode* of operation of the ICR, which indicates that any bimolecular association is very slow. A large termolecular rate coefficient implies that at flow tube pressures, the SIFT technique would observe an association reaction as having a rate coefficient which is invariant with pressure, i.e. the reaction has entered the 'pressure saturation' regime. Under these conditions almost all association complexes are collisionally stabilized. The observed association rate was expected to approach the collision rate coefficient of $k_c = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Instead, a rate coefficient of less than half the collision rate was observed⁸. The experiment of Raksit and Bohme⁸ was repeated in the Canterbury SIFT and a similar result found. The pseudo second order rate coefficient of $k = 3.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at a helium pressure of 0.3 Torr¹⁷.

To explore further the association process between C_2N_2^+ and C_2N_2 , we measured the variation of the association rate coefficient with pressure over the range 1×10^{-5} Torr to around 3×10^{-3} Torr. These measurements were all made in the drift mode of operation of the ICR cell and the reactant ion C_2N_2^+ and product ion C_4N_4^+ were each measured at known drift times and reactant pressures. We also compared the efficiency of stabilization of the $(\text{C}_4\text{N}_4^+)^*$ complex by different bath gases ($M = \text{C}_2\text{N}_2, \text{He}, \text{Ne}, \text{Ar}$ and N_2) as we have done for other associating systems exhibiting collisional stabilization^{6, 10, 18}.

The experimental data for each bath gas were modelled according to equations based on the mechanism:



The rate coefficient for the various processes are given by k_f , k_{-1} and k_s ; β is a number between 0 and 1 that gives a measure of the efficiency of collisional stabilization. As shown previously, in an associating system where radiative stabilization and additional bimolecular channels are slow compared with collisional stabilization of the complex, the observed bimolecular rate coefficient, k_2^{obs} and the observed termolecular rate coefficient, k_3^{obs} are given by⁶:

$$k_2^{\text{obs}} = k_f \beta k_s [\text{M}] / (k_{-1} + \beta k_s [\text{M}]) \quad (9)$$

and

$$k_3^{\text{obs}} = k_f \beta k_s / k_{-1} \quad (10)$$

The model represented in Equations (9) and (10) was used to fit the experimental observations and a typical data set is shown in Figure 1. The points are experimental and the solid curve is the iterated computer fit to the data. The results of this procedure yielded the following values for the rate coefficients: $k_f = 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $\beta k_{-1} = 9800 \text{ s}^{-1}$ and $k_3 = 1.7 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ for $\text{M} = \text{C}_2\text{N}_2$. The mean lifetime of the $(\text{C}_4\text{N}_4^+)^*$ complex with respect to unimolecular dissociation is $\tau/\beta = 104 \mu\text{s}$.

The reason for the difference between the k_f obtained from the ICR measurement ($1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and the SIFT experiment ($3.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) is not obvious. The rate coefficient k_f is the rate coefficient for the formation of only those $(\text{C}_4\text{N}_4^+)^*$ complexes that can be stabilized and as such, it is a sensitive function of reactant energy. However, it is not expected that the differences in k_f between the ICR and the SIFT instruments are due to internal energy differences. In the SIFT experiment the ions undergo thousands of collisions with the helium buffer (an inefficient process for deactivation of internal energy) before reaction with C_2N_2 , whereas in the ICR, there are up to 20, collisions with the parent neutral. In addition to association, collisions of C_2N_2^+ with the parent neutrals are also expected to result in charge transfer collisions which should occur at a frequency of at least one half the collision rate, based on comparison with other resonant charge transfer reactions. It is thus expected that over the range of pressures used in the ICR, the parent ions should be quickly deactivated of any internal energy and should approach the same k_f as observed in the SIFT experiment. However no noticeable change in k_f with pressure in the ICR was observed.

We list in Table 2 the efficiencies of stabilization (β) of $(\text{C}_4\text{N}_4^+)^*$ with each bath gas M, relative to the stabilization efficiency of C_2N_2 . For these bath gases, a least squares minimization was undertaken between the model calculation and the experimental data with the constraints $k_f = 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $k_{-1} = 9800 \text{ s}^{-1}$, and $\beta k_s (\text{M} = \text{C}_2\text{N}_2) = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The best fit achieved by varying $\beta_M k_s$ resulted in the k_3^{obs} rate coefficients and β 's shown in Table 2.

A noticeable curvature was found at pressures higher than about 10-4 Torr (see Figure 1). This suggests that a significant fraction of the

complexes formed in the ICR at higher pressures are stabilized by collision and the rate coefficient approaches k_f asymptotically. The termolecular rate coefficient of $k_3^{\text{obs}} = 2.0 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1}$ ($M = \text{He}$) measured for Reaction (6) is also very large and it might be expected at the flow tube pressures in the SIFT, the association rate coefficient will approach the collision limit ($k = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) corresponding to the situation where every complex formed is stabilized by collision with the bath gas. Instead only $\sim 1/3$ of all collision complexes are stabilized. This behavior is quite different from association in the CH_3^+/HCN ¹⁹ and $\text{CH}_3^+/\text{CH}_3\text{CN}$ ¹⁰ systems where much less curvature was seen in the k_2^{obs} versus pressure plots measured in the ICR. Yet in each case, the association rate coefficients measured using the SIFT technique went at, or close to, the collision rate. Clearly there is a very different type of association process occurring in the $\text{C}_2\text{N}_2^+/\text{C}_2\text{N}_2$ system. Another distinctive feature found in the $\text{C}_2\text{N}_2^+/\text{C}_2\text{N}_2$ association is the value of k_f in Equation (7). In most other association reactions of nitriles we have studied, the value of k_f given by the SIFT measurement is at or near the collision rate¹⁶. In the $\text{C}_2\text{N}_2^+/\text{C}_2\text{N}_2$ system our SIFT measurement was only $3.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ¹⁷ and the present ICR results gave a lower value of $k_f = 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

We note that k_f may be distinct from the capture collision coefficient k_c , which estimates the total number of collisions only. k_f is a measure of the formation rate coefficient for only those complexes that can be stabilized by collision. If only one type of complex is formed, then k_f must ultimately approach the collision rate at flow tube pressures providing the complex has a lifetime with respect to unimolecular dissociation longer than several micro-seconds. If, however, two different complexes are formed: one having a longer lifetime (μs) and the other a very short

lifetime, then the behavior exhibited by the $C_2N_2^+/C_2N_2$ system will be observed.

Similar behavior has been found in other ion-molecule association complexes^{10,20-22} but is unexpected in nitriles based on our previous experience with them. Alternative explanations have been offered to account for k_f values that are much less than the collision rate. These explanations include variations in the unimolecular dissociation rate coefficient, k_{-1} with pressure and that a dual complex mechanism can occur in which a 'tight' complex is formed from a much 'looser' complex²². We look next at the structure of possible $(C_4N_4^+)^*$ complexes formed in the association of $C_2N_2^+$ and C_2N_2 .

Isomers and energetics of $C_4N_4^+$: Calculations at the HF/6-31 G* and in some cases, MP2/6-31 G* level of theory were available for the structures: NCCN, $NCCN^+$, NCNC, $NCNC^+$, $NCCNCCN^+$, $NCNCNCNC^+$, $NCNCNCCN^+$, $NC(CNCN)CN^+$, $c-(NCCN)_2^+$ and the aromatic c-2,3,6 and c-2,4,6 triazine cations²³. Calculations at a higher level of theory on NCCN and its isomers have also been undertaken by several groups²⁴⁻²⁸.

The calculations indicate that at least four bound states of $C_4N_4^+$ are possible after entry to the $C_4N_4^+$ potential surface at $NCCN^+ + NCCN$. These structures are $NCCNCCN^+$, $NCNCNCNC^+$, $NCNCNCCN^+$, and the aromatic heterocyclic triazine $(NCCNNC)CN^+$. It is evident that the $C_4N_4^+$ product ion of the association reaction between $C_2N_2^+$ and C_2N_2 is a stable covalently bonded molecular ion and not an electrostatically bound complex as was suggested earlier⁸.

Why is k_f much less than k_{coll} ? Evidence for a mixture of isomeric forms in a reactant ion can be detected through the different

reactivities of the isomers³⁰. No such difference in reactivity was observed in the semi-logarithmic decays of $C_2N_2^+$ with a variety of reactive neutral flows either in the ICR or SIFT. Consequently we believe the principal positive ion at $m/z = 52$ Daltons generated by electron impact on NCCN is $NCCN^+$, this is consistent with the observations of Bickelhaupt et al²⁵. From the very rapid termolecular rate coefficient found for the association reaction between $NCCN^+$ and NCCN, ($k_3 = 1.7 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$, $M = C_2N_2$) the structure of the association product $C_4N_4^+$ must correspond to a well in the potential surface of $C_4N_4^+$ that is at least 200 kJ mol^{-1} below the surface entrance energy (corresponding to $NCCN^+ + NCCN$) of $1903.4 \text{ kJ mol}^{-1}$. A rapid termolecular rate implies that τ , the lifetime of the $(C_4N_4^+)^*$ complex with respect to unimolecular decomposition is sufficiently long for collisions with the bath gas to occur. In all other associating systems containing similar numbers of atoms that we have studied and that exhibit termolecular rate coefficients of this magnitude, the well depth of the complex has been greater than 200 kJ mol^{-1} . The preliminary *ab initio* calculations show the likely $C_4N_4^+$ candidates fulfilling these requirements are the four bound structures previously mentioned. Of these, only $NCCNNCCN^+$ is formed by simple addition without any rearrangement.

The experimental observations of the pressure dependence of the association reaction between $C_2N_2^+$ and C_2N_2 can then be explained by the two different outcomes of the collision process. In the first type of outcome, which accounts for - 67% of all collisions, symmetric charge transfer occurs. In the second type of reaction outcome, (-33% of collisions) a complex is formed that has a lifetime with respect to unimolecular dissociation to reactants of $\tau/\beta \sim 10^4 \mu\text{s}$. Almost all of these second-type complexes are stabilized at flow tube pressures. Indeed, a considerable

fraction of them are even stabilized at the highest pressures achieved in the ICR cell as is evidenced by the curved k_2^{obs} versus C_2N_2 pressure plots (Figure 1). This means that in the SIFT, saturation behavior may be exhibited when the observed reaction rate coefficient is much smaller than the collision rate coefficient.

CONCLUSIONS

Cyanogen, C_2N_2 exhibits mainly charge transfer and proton transfer reactions with the major non-hydrocarbon ions of Titan's ionosphere. Simple hydrocarbon ions are generally unreactive with C_2N_2 , with the one notable exception of CH_3^+ , which will be discussed elsewhere¹. What C_2N_2 does display is a marked propensity to association with its cation. The variation in the observed association rate with bath gas pressure indicates two outcomes of reaction: symmetric charge transfer and complex formation. The association complex has a mean lifetime of $\tau/\beta \sim 10^4 \mu\text{s}$ at its formation energy. It is this complex that is collisionally stabilized and the C_4N_4^+ isomer that is produced in the association may be the unrearranged ion NCCNCCN^+ . The aromatic cyclic triazine cation is also possible on the grounds that it probably occupies a lower minimum on the C_4N_4^+ potential surface and could be formed by a Diels-Alder type 4 + 2 cyclo addition.

Similar associations may well occur with other nitriles and the possibility that quite exotic molecules may be formed in Titan's atmosphere lead to intriguing prospects for what the Cassini mission will find when it begins its orbiting phase around the Saturnian system in 2004.

Finally, the two reaction outcomes of $\text{NCCN}^+ + \text{NCCN}$, charge transfer and association are found to proceed independently of each other.

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References

1. Hanel, R. et al. *Science*, **1981**, 212, 192; Kunde, V. G.; Aikin, A. C.; Hanel, R. A.; Jennings, D.E.; Maguire, W. C.; Samuelson, R.E. *Nature*, 1981, 292, 686.
2. Yung, Y.L.; Allen, M.; Pinto, J.P. *Astrophys. J.*, 1984, 55, 465; Yung, Y.L. *Icarus*, **1987**, 72, 468.
3. Monks, P. S.; Romani, P.N.; Nesbitt, F. L.; Scanlon, M.; Stief, L.J. *J. Geophys. Res. Planets*, 1993, 98, 17115.
4. Keller, C.N.; Cravens, T. E.; Gan, L. *J. Geophys. Res.*, **1992**, 97, 2117.
5. Gan, L.; Keller, C.N.; Cravens, T.E. *J. Geophys. Res.*, 1992, 97, 2137.
6. McEwan, M. J.; Denisen, A. B.; Huntress, W.T.; Anicich, V. G.; Snodgrass, J.; Bowers, M.T. *J. Phys. Chem.*, 1989, 93, 4064.
7. Inoué, M.; Cottin, M. *Adv. Mass Spectrom.*, 1966, 3, 339.
8. Raksit, A. B.; Bohme, D.K. *Int. J. Mass Spectrom. Ion Proc.*, **1985**, 63, 217.
9. Petrie, S. A. H.; Freeman, C.G.; McEwan, M. J.; Mautner, M. In? *J. Mass Spectrom. Ion Proc.*, 1989, 90, 241.
10. McEwan, M.J.; Denisen, A. B.; Anicich, V. G.; Huntress, W.T. Jr.; *Int. J. Mass Spectrom. Ion Proc.*, 1987, 81, 247.
11. Anicich, V. G.; Huntress, W.T. Jr., McEwan, M.J. *J. Phys. Chem.*, 1986, 90, 2446.

12. Dunkin, D. B.; Fehsenfeld, F. C.; Schmeltekopf, A. I.; Ferguson, E. E. *J. Chem. Phys.*, 1968, 49, 1365.
13. McEwan, M. J.; McConnell, C. L.; Freeman, C. G.; Anicich, V. G. *J. Chem. Phys.*, 1994, 98, 5068.
14. Anicich, V. G.; Sen, A. D.; Huntress, W. T. Jr.; McEwan, M. J. *J. Chem. Phys.*, 1995, 102, (in press).
15. Buckley, T. J.; Sieck, L. W.; Metz, R.; Lias, S. G. *Int. J. Mass Spectrom. Ion Proc.*, 1985, 65, 181.
16. Anicich, V. G.; Sen, A. D.; McEwan, M. J.; Smith, S. C. *J. Chem. Phys.*, 1994, 100, 5696.
17. Scott, G. II.; Fairley, D.; McEwan, M. J. Private communication, 1993.
18. Anicich, V. G.; Sen, A. D.; Huntress Jr, W. T.; McEwan, M. J. *J. Chem. Phys.*, 1990, 93, 7163.
19. Kemper, P. R.; Bass, L. M.; Bowers, M. T. *J. Phys. Chem.*, 1985, 89, 1105.
20. Meert-Ner, M.; Field, F. H. *J. Amer. Chem. Soc.*, 1975, 97, 5339.
21. Neilson, P. V.; Bowers, M. T.; Chan, M.; Davidson, W. R.; Aue, D. H. *J. Amer. Chem. Soc.*, 1978, 100, 3649.
22. Meert-Ner, M. in "Gas Phase Ion Chemistry", M. T. Bowers (Ed.), Vol. 1, Academic Press, New York, 1979, p. 197.
- 2,3. Maclagan, R. G. Private communication, 1994.
- 2,4. Sunil, K. K.; Yates, J. H.; Jordan, K. J. *Chem. Phys. Lett.*, 1990, 171, 185.

- 2.5. Bickelhaupt, F. M.; Fokkens, R.H.; De Koning, L.J.; Nibbering, N.N.; Baerends, E.J.; Goede, S.J.; Bickelhaupt, F. *Int. J. Mass Spectrom. Ion Proc.*, 1991, 103, 157.
26. Botschwina, P.; Sebald, P. *Chem. Phys.*, 1990, 141, 311.
27. Botschwina, P. *Chem. Phys. Lett.*, 1994, 225, 480.
28. Sherrill, C. D.; Schaefer, H.F. *J. Chem. Phys.*, 1994, 100, 8920.
29. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R.D.; Mallard, W.G. *J. Phys. Chem. Ref. Data*, 1988, 17 (Suppl. 1).
30. McEwan, M.J. in "Advances in Gas Phase Ion Chemistry" Adams, N. and Babcock, L.M. (eds) 1992, Vol. 1, p. 1, JAI Press Inc., Greenwich, Connecticut.
31. McEwan, M.J.; Fairley, D.; Scott, G.B.I.; Anicich, V.G. To be submitted (1995).

Table 1. Rate Coefficients (in units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$) and product distributions measured for the given ions with C_2N_2 .

Ion	Product	Branching Ratio	k_{obs}	k_{other}	$-\Delta H^\circ/\text{kJ mol}^{-1}$
N^+	$\text{C}_2\text{N}^+ + \text{N}_2$	0.80	2.0	1.4 ^a	562
	$\text{C}_2\text{N}_2^+ + \text{N}$	0.20			112
N_2^+	$\text{C}_2\text{N}_2^+ + \text{N}_2$	1.0	1.0	0.86 ^a	213
C_2H_2	no reaction		< 0.01		
C_2H_4^+	no reaction		< 0.01		
C_3H_5^+	no reaction		< 0.01		
C_4H_2^+	products ^b		0.20		
C_4H_3^+	products ^b		0.19		
HCN^+	$\text{C}_2\text{N}_2\text{H}^+ + \text{CN}$	1.0	1.1		153
C_2N_2^+	no bimolecular reaction		< 0.01		

(a) Reference 8

(b) No products could be identified - see text for discussion

Table 2. Termolecular rate coefficients (k_3^{obs}) measured for the association reaction $\text{C}_2\text{N}_2^+ + \text{C}_2\text{N}_2 + \text{M} \rightarrow \text{C}_4\text{N}_4^+ + \text{M}$ with the listed bath gas, M. Collision efficiencies β_m are relative to $\beta_{\text{C}_2\text{N}_2}$.

M	$k_3^{\text{obs}, \text{ a}}$	$\beta_m/\beta_{\text{C}_2\text{N}_2}$
C_2N_2	17	1.0
He	2.0	0.24
Ne	1.2	0.15
Ar	2.1	0.26
N_2	2.2	0.20

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

Figure Captions

Figure 1 The variation in the rate coefficient k_2^{obs} /($\text{cm}^3 \text{ S}^{-1}$) against pressure of C_2N_2 /(Torr). Tile points are experimental and the curve is the computer-generated line of best fit.

