International Journal of Mass Spectrometry 279 (2009) 82–86

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Some ion chemistry of HC_5N

Samuel J. Edwards, Colin G. Freeman, Murray J. McEwan*

Department of Chemistry, University of Canterbury, PB 4800 Christchurch, New Zealand

ARTICLE INFO

Article history:
Received 15 August 2008
Received in revised form 5 October 2008
Accepted 6 October 2008
Available online 18 October 2008

Keywords:
Cyanopolyynes
SIFT
HC_5N
Titan
Proton affinity

ABSTRACT

The ion–molecule chemistry of 2,4-pentadiynenitrile, HC_5N, a cyanopolyyne, has been investigated in a flowing afterglow-selected ion flow tube (FA-SIFT) operating at room temperature. The ion chemistry of a selection of ions of relevance to the interstellar and Titan environments was examined. The proton affinity of HC_5N was found from both measurement and calculation to be $770 \pm 20\,\mathrm{kJ\,mol^{-1}}$. Rapid proton transfer was observed to occur for many of the ions known to be present in Titan's ionosphere.

1. Introduction

The cyanopolyyne series of molecules designated by the formula $HC_{2n+1}N$ ($n = 1–5$) has been observed in molecular interstellar clouds such as TMC-1 for many years [1–5]. The observation of these molecules in the interstellar medium provides evidence that there are efficient synthetic mechanisms in operation in interstellar clouds providing a source of production for them. There has been considerable speculation on their formation processes including participation by ion–molecule reactions [6–10]. The relative abundance of the various analogues in molecular clouds has even been postulated as a means of determining cloud age [11]. Cyanoacetylene (also known as propiolonitrile or propynenitrile), HC_3N, has been detected on Titan, Saturn's largest satellite, and observers are optimistic that improved sensitivity in the infrared spectrometer on board the Cassini spacecraft may show the presence of the next member of the series, HC_5N [12]. The presence of HC_5N (known as 2,4-pentadiynenitrile and cyanodiacetylene) has however been inferred in Titan's upper atmosphere from the appearance of an ion at m/z 76 in the ion mass spectrum from the ion neutral mass spectrometer on board the Cassini orbiter [13]. In making this deduction, ions containing a single N atom were found to appear at even masses and the ion at m/z 76 was assigned to HC_5NH^+ [13].

The ion chemistry of the smaller analogue, HC_3N, has been addressed in several studies [14–18]. It has not been feasible to investigate the ion chemistry of HC_5N, the next member in the series of cyanopolyynes, because of the difficulties in synthesizing a sample. Recently however, an improved synthesis for HC_5N has become available [19]. We have synthesized a sample using the method of Trolez and Guillemin [19] and report here the first ion–molecule reactions of 2,4-pentadiynenitrile with a series of ions of relevance to the chemistry occurring in interstellar clouds and also in Titan's ionosphere.

2. Experimental

The experiments outlined in this work were carried out using a flowing afterglow-selected ion flow tube (FA-SIFT) which has been described previously [20]. The reactant ions are generated in the FA source using a microwave discharge on helium to which a trace of the molecule used to generate the reactant ion has been added. The ion of choice from the mixture of ions formed in the discharge region is mass-selected by the upstream quadrupole mass filter and is directed into the flow tube where the ion chemistry takes place. Samples of HC_5N in helium are then added to the flow tube in monitored amounts through a neutral reactant inlet located 50.4 cm upstream of the orifice through which the ions are transferred to the downstream quadrupole mass filter. The composition of the helium/2,4-pentadiynenitrile mixture was determined by assuming that proton transfer from H_3O^+ to HC_5N occurred at the capture collision rate which is a good approximation for exothermic proton

---

* Corresponding author. Tel.: +64 3 364 2875; fax: +64 3 364 2110.
E-mail address: murray.mcewan@canterbury.ac.nz (M.J. McEwan).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.10.003

transfer. Although most of the emphasis of this paper was directed at determination of the ion products from reaction, some rate coefficients were also found relative to the H_3O^+/HC_5N reaction rate coefficient. The ions were generated as follows: H_3O^+ from H_2O; CH_3^+ from CH_4; $C_2H_3^+$, $C_2H_5^+$ and $C_3H_5^+$ from C_2H_4; $C_3H_3^+$ from allene; $C_3H_7^+$ from C_3H_7Br; $C_4H_2^+$ and $C_4H_3^+$ from C_4H_2; $HCNH^+$ from HCN; HC_3NH^+ from HC_3N; CH_3CNH^+ from CH_3CN; CH_3CHOH^+ from CH_3CHO; $HCOOH_2^+$ from HCOOH; C^+ and CO^+ from CO, N^+ and N_2^+ from N_2, O_2^+ from O_2 and $C_6H_6^+$ from benzene. Branching ratios were found from the relative peak heights of the product mass scans at very low concentrations of 2,4-pentadiynenitrile.

These reagents with the exception of HCN, HC_3N and C_4H_2 were obtained from commercial suppliers and were further purified by multiple freeze-pump-thaw cycles. HCN was prepared by the action of sulphuric acid on KCN and was dried over P_2O_5 [21]. The synthesis of HC_3N required two steps. Liquid ammonia was first added to methyl propiolate to obtain propiolamide which was then dehydrated with P_2O_5 to produce HC_3N [22,23]. C_4H_2 was prepared by the reaction of KOH and 1,2-dichloro-2-butyne at 70 °C [24]. These were further purified by freeze-pump-thaw cycles.

3. Preparation of HC_5N

The method of Trolez and Guillemin was used with some small modifications [19]. First butadiynal tributyltin (1) was prepared using a two step synthesis. In the first step diacetylene (prepared as previously described) was collected in two cold traps containing dry THF at −78 °C. Next *n*-butyllithium was added dropwise to the combined diacetylene–THF solutions. A molar excess of diacetylene (approximately 2:1) is necessary to reduce the formation of lithium di-substituted diacetylene. Next tributyltin chloride is added to the mixture generating the desired reactant (1), butadiynyl tributyltin. Removal of the solvents under vacuum yields a viscous red–brown oil. The purity of (1) is important to the purity of cyanodiacetylene (3). Cyanodiacetylene (3) is prepared by the reaction of (1)

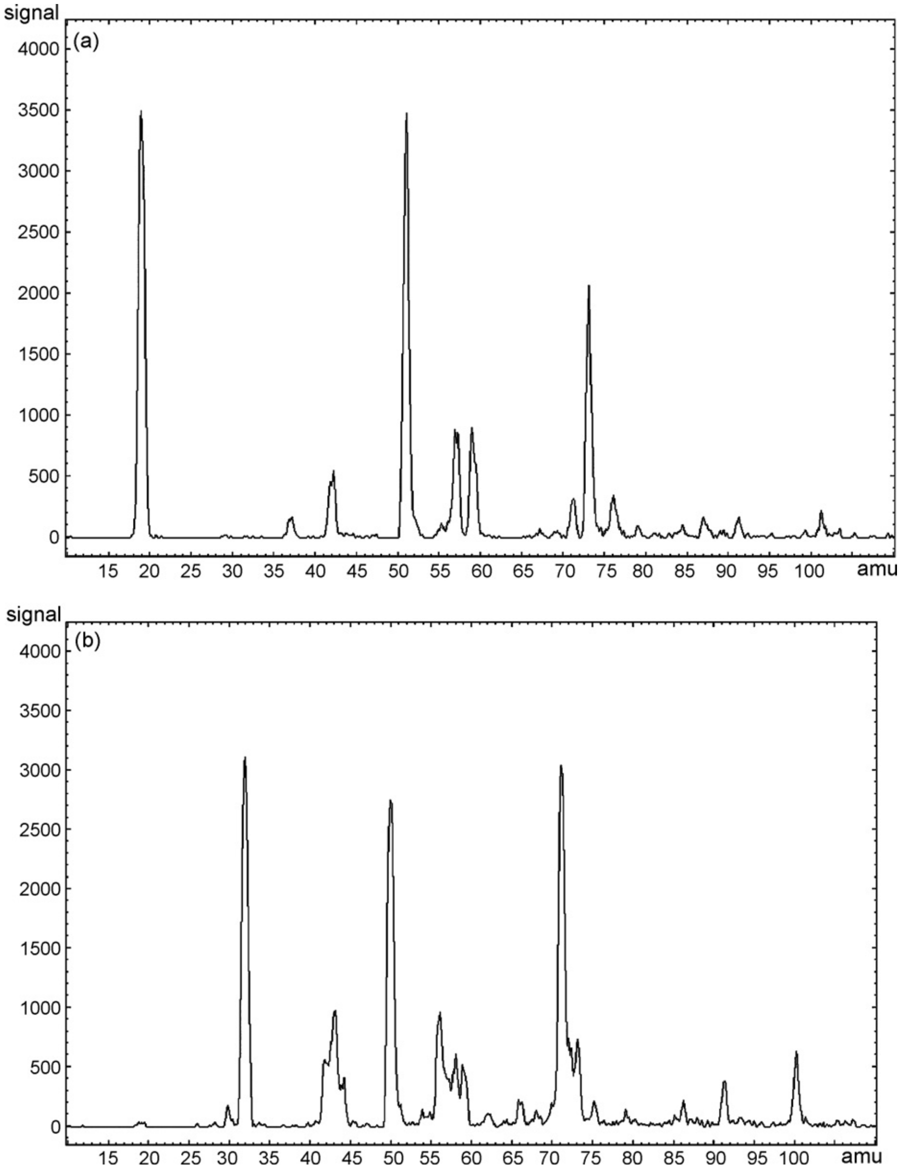


Fig. 1. (a) Chemical ionization spectrum generated from HC_5N out of trap 2 at −78 °C derived from H_3O^+. The parent peak of HC_5N is seen at *m*/*z* 76 (HC_5NH^+) and the dominant impurity is diacetylene at *m*/*z* 51 ($C_4H_3^+$). (b) Chemical ionization spectrum generated from HC_5N out of trap 2 at −78 °C derived from O_2^+. The parent peak of HC_5N is seen at *m*/*z* 75 and the dominant impurities are diacetylene at *m*/*z* 50 ($C_4H_2^+$) and solvent residues at *m*/*z* 72 (either pentane or THF).

Table 1
Observed products for the listed ion with HC_5N.

Reagent ion	PA of neutral (kJ mol^{-1})	Products	Branching ratio[a]	k_c[b] (10^{-9} cm^3 s^{-1})
H_3O^+	691	$HC_5NH^+ + H_2O$	1.0	(5.6)
CH_3^+		$HC_5N{\cdot}CH_3^+$	1.0	(6.1)
$C_2H_3^+$	641.4	$HC_5NH^+ + C_2H_2$	0.90	(4.9)
		$HC_5N{\cdot}C_2H_3^+$	0.10	
$C_2H_5^+$	680.5	$HC_5NH^+ + C_2H_4$	1.0	(4.7)
$C_3H_3^+$	951	$HC_5N{\cdot}C_3H_3^+$	1.0	(4.3) <0.0014
$C_3H_5^+$	775[c]	$HC_5NH^+ + C_3H_2$	0.75[d]	(4.2) <4.2
		$HC_5N{\cdot}C_2H_3^+$	0.20	
		$H_4C_8N^+ + H_2$	0.05	
$C_3H_7^+$	751.6	$HC_5NH^+ + C_3H_6$	0.90	(4.1)
		$HC_5N{\cdot}C_3H_7^+$	0.10	
$C_4H_3^+$	737.2	$HC_5NH^+ + C_4H_2$	0.80	(3.9)
		$HC_5N{\cdot}C_4H_3^+$	0.20	
$HCNH^+$	713	$HC_5NH^+ + HCN$	1.0	(4.8)
HC_3NH^+	751.2	$HC_5NH^+ + HC_3N$	1.0	(3.9)
CH_3CNH^+	779	$HC_5NH^+ + CH_3CN$	0.50[d]	(4.2) <4.2
		$HC_5N{\cdot}CH_3CNH^+$	0.50	
CH_3CHOH^+	768.5	$HC_5NH^+ + CH_3CHO$	0.90[d]	(4.1) <4.1
		$HC_5N{\cdot}CH_3CHOH^+$	0.10	
$HCOOHH^+$	742	$HC_5NH^+ + HCOOH$	1.0	(4.0)
$C_4H_2^+$		$HC_5N{\cdot}C_4H_2^+$ (slow)	(4.0) <0.001	
$C_6H_6^+$	9.24	No reaction		(3.5) <0.001

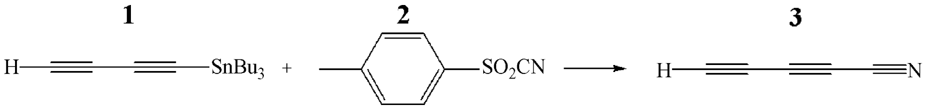
[a] Errors associated with branching ratios are ±30%.

[b] The capture collision rates are in parenthesis. Unless shown by measured values not in parenthesis, all reactions appeared to proceed at the capture collision rate.

[c] For allene

[d] Upper limits due to the presence of H_3O^+ impurities which could have led to HC_5NH^+ (see text)

with para-toluenesulfonyl cyanide (2) obtained commercially from Sigma–Aldrich.



(1)

Reagents (1) and (2) were mixed at 75–80 °C for 2 h under vacuum. Gaseous products from the reaction were collected in two cold traps as described by Trolez and Guillemin [19]. The first cold trap was held at −30 °C for removing impurities and the second at −78 °C for trapping the product. The yield from 2.5 g of (2) with 1.75 g of (1) was ~20 mg of HC_5N which was immediately diluted in 200 Torr of helium.

Analysis of the products collected from the trap at −78 °C showed a mixture of products were present as shown in Fig. 1a and b for the chemical ionization spectrum for H_3O^+ and O_2^+, respectively. The presence of HC_5N is evident from the signal at *m*/*z* 76 (HC_5NH^+) in Fig. 1a and *m*/*z* 75 (HC_5N^+) in Fig. 1b. The major component in the mixture from this trap was diacetylene observed at *m*/*z* 51 ($C_4H_3^+$) in Fig. 1a and *m*/*z* 50 ($C_4H_2^+$) in Fig. 1b. Surprisingly, when the contents of the first cold trap at −30 °C that was designed to trap other impurities was examined it was found to contain essentially pure HC_5N as shown in Fig. 2a and b for H_3O^+ and O_2^+, respectively. The isolation of HC_5N at −30 °C has a minor conflict with the method described by Trolez and Guillemin [19] although it is consistent with the observation of Haas and Winnewisser [25] who found the purest fraction of HC_5N to evaporate between −20 and 0 °C. The diluted sample of HC_5N in helium did not decay appreciably after 2 days at room temperature.

4. Results and discussion

A summary of the reactions of ions containing a potentially transferable proton with HC_5N is presented in Table 1. The relatively small amount of HC_5N we prepared did not allow us to measure absolute reaction rate coefficients for all reactions investigated. It is known however, from experimental observations of many reactions that exothermic proton transfer reactions occur at the capture collision rate. The calculated collision rate values [26] are presented for all the reactions in column 6 of Table 1. These values were determined using the dipole moment of Kroto [5] (4.33 Debye) and the molecular polarizability of HC_5N which we calculated using Gaussian to a relatively high level of theory (RMP2-FC\Aug-CC-pVTZ) to be 10.77×10^{-24} cm^3 [27]. Multiple products where found, are listed in column 5. Those reactions which occurred at substantially less than the listed collision rate coefficient are shown with the upper limit to the rate coefficient in parenthesis.

The reactions of several other ions with HC_5N observed in this study are shown in Table 2. The capture rate coefficients for these ions are also given. All of these reactions were fast and went at the collision rate or within 15% of it. As in the majority of reactions listed in Table 1, the rate coefficients of the reactions in Table 2 were not measured directly (with the exception of CO^+) although all were observed to react at close to their collision capture rate coefficients. The rate coefficient for the reaction of CO^+ and HC_5N was measured

Table 2
Reactions of ions not containing a transferable proton with HC_5N.

Reagent ion	Neutral IE (eV)	Products	Branching ratio[a]	k_c[b] (10^{-9} cm^3 s^{-1})
O_2^+	12.07	$HC_5N^+ + O_2$	1.0	(4.6)
C^+	11.26	$HC_5N^+ + C$	0.65	(6.7)
		$C_6N^+ + H$	0.35	
N^+	14.53	$HC_5N^+ + N$	0.50	(6.3)
		$C_5H^+ + N_2$	0.50	
N_2^+	15.58	$HC_5N^+ + N_2$	1.0	(4.8)
CO^+	14.01	$HC_5N^+ + CO$	1.0	(4.8)

[a] Errors associated with branching ratios are ±30%.

[b] The capture rates are in parenthesis. All these reactions appear to have collision or close to collision rates.

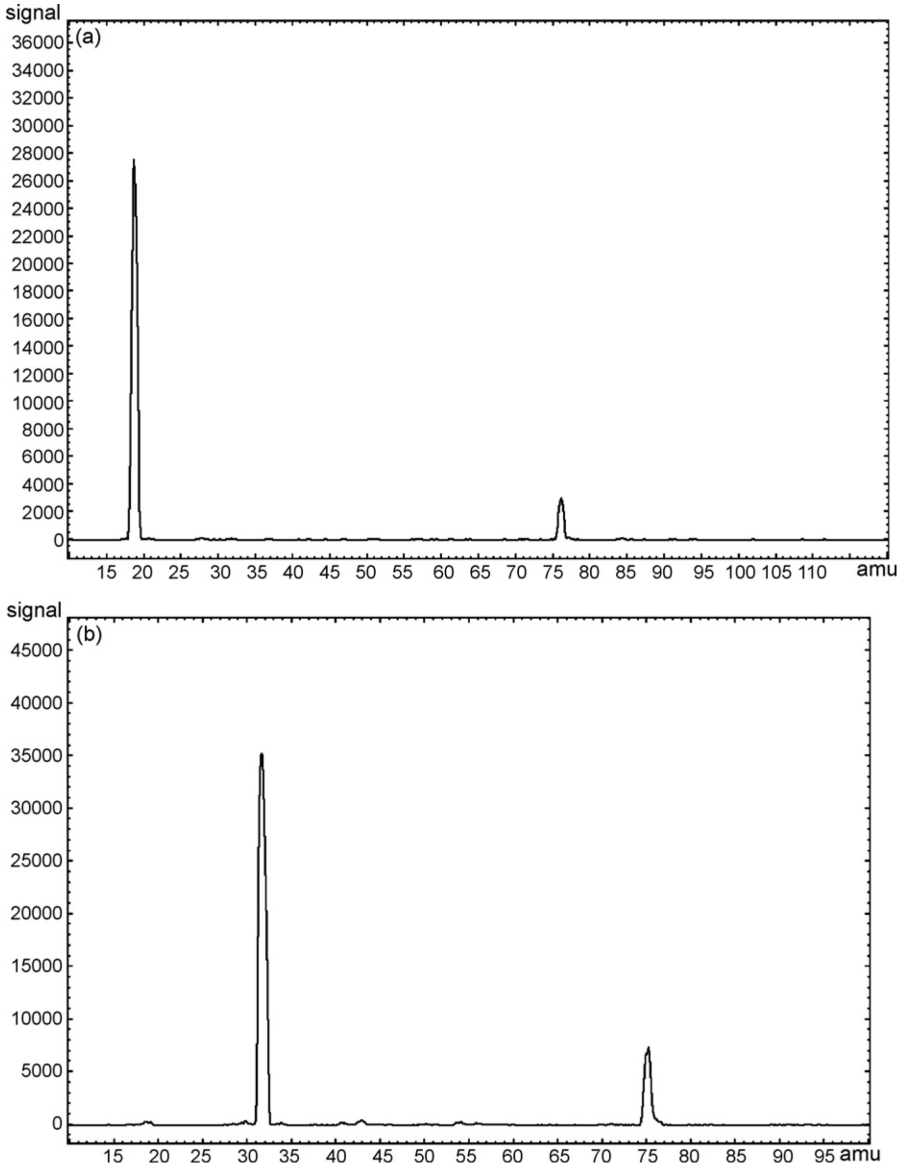


Fig. 2. (a) Chemical ionization spectrum generated from HC_5N out of trap 1 at $-30\,^{\circ}C$ derived from H_3O^+. The parent peak of HC_5N is seen at m/z 76 (HC_5NH^+). (b) Chemical ionization spectrum generated from HC_5N out of trap 1 at $-30\,^{\circ}C$ derived from $O_2{}^+$. The parent peak of HC_5N is seen at m/z 75 (HC_5N^+).

as collision rate. The major reaction channel of the ions in Table 2 was found to be electron transfer although two atomic ions, C^+ and N^+, also exhibited an additional product channel. In the reaction of C^+ and HC_5N, a 35% product channel was apparent from insertion of C^+ into the neutral followed by H loss.

$$C^+ + HC_5N \rightarrow HC_5N^+ + C \quad (0.65) \tag{2a}$$

$$\rightarrow C_6N^+ + H \quad (0.35) \tag{2b}$$

From a comparison with the ion chemistry of C^+ and HC_3N, it appears that these insertion reactions are typical for the cyanopolyynes as with HC_3N an analogous 20% channel leading to C_4N^+ was observed [15,28].

The reaction with N^+ is also interesting and a similar situation exists for the reaction of N^+ and HC_5N where loss of N_2 from the complex takes place in one channel in addition to electron transfer in the other channel.

$$N^+ + HC_5N \rightarrow HC_5N^+ + N \quad (0.50) \tag{3a}$$

$$\rightarrow C_5H^+ + N_2 \quad (0.50) \tag{3b}$$

Presumably the energy required for the formation of C_5H^+ is offset by the energy gain in forming N_2. In the analogous N^+ reaction with HC_3N, a 50% channel leading to C_3H^+ was observed in addition to the electron transfer channel [15,28]. These reactions that we have observed for HC_5N allow us to distinguish trends in the ion chemistry of the cyanopolyynes as already discussed. For the HC_nN class of compounds which have been investigated in the laboratory ($n = 1$, 3, and 5), the following types of reactions are apparent. In reactions with C^+, some C atom insertion occurs and for the N^+ reactions, some loss of N_2 by N atom abstraction occurs. These trends are summarized in Table 3 for C^+ reactions and Table 4 for N^+ reactions.

Proton affinity of HC_5N The ion chemistry of HC_5N is dominated by proton transfer reactions where they can occur and this is particularly relevant to the chemistry on Titan. The proton affinity (PA) of HC_5N is not well established. We employed G3 theory [31] beginning with the geometries of Botschwina et al. [32] and calculated a PA of 775.5 $kJ\,mol^{-1}$. This value is consistent with the observed chemistry summarized in Table 1. Rapid proton transfer was observed from all those compounds in this

Table 3
Reaction trends of C^+ with HCN and cyanopolyynes.

Cyanopolyyne	Products	Rate coefficient[a]	Ref.
HCN	$C_2N^+ + H$	2.95	[b]
HC_3N	$C_4N^+ + H$	1.40[c]	[d]
HC_5N	$C_6N^+ + H$	~2.3[e]	This work

[a] In units of 10^{-9} cm^3 s^{-1}.

[b] Ref. [29].

[c] From the branching ratio. Occurs in competition with the $C_3H^+ + CN$ channel.

[d] Ref. [15].

[e] From the branching ratio. Occurs in competition with an electron transfer channel.

Table 4
Reaction trends of N^+ with HCN and cyanopolyynes.

Reactant	Products	Rate coefficient[a].	Ref.
HCN	$HCN^+ + N$	3.7	[b]
HC_3N	$C_3H^+ + N_2$	2.1[c]	[d]
HC_5N	$C_5H^+ + N_2$	3.1[c]	This work

[a] In units of 10^{-9} cm^3 s^{-1}.

[b] Ref. [30].

[c] From the branching ratio. Occurs in competition with an electron transfer channel.

[d] Ref. [15].

study having a PA between 737.2 (C_4H_2) and 775 kJ mol^{-1} (C_3H_4, allene). An apparent slow proton transfer was observed from CH_3CNH^+ (PA CH_3CN = 779 kJ mol^{-1}) in conjunction with adduct formation. However, the presence of trace amounts of H_3O^+ may also have been responsible for the HC_5NH^+ signal from this reaction and we have therefore listed the observed branching ratio as an upper limit. A similar situation exists for both CH_3CHOH^+ (PA CH_3CHO = 768.5 kJ mol^{-1}) and allene (PA C_3H_4 = 775 kJ mol^{-1}) where adduct formation occurs in both cases in conjunction with proton transfer which may also have resulted from a small amount of H_3O^+ also present in the flow tube. These results indicate a proton affinity for HC_5N of 770 ± 20 kJ mol^{-1}.

5. Conclusions

The proton affinity of 2,4-pentadiynenitrile is sufficiently high for many simple hydrocarbon ions and some nitriles to undergo proton transfer reactions with it. The ion chemistry of HC_5N observed in this study therefore supports the view that proton transfer reactions of 2,4-pentadiynenitrile have a major influence on its chemistry in the upper atmosphere of Titan. Simple hydrocarbon ions such as $C_2H_3{}^+$, $C_2H_5{}^+$, $C_3H_5{}^+$, $C_3H_7{}^+$, $C_4H_3{}^+$ and $HCNH^+$ will all proton transfer to HC_5N at the collision rate. It is therefore a reasonable assumption that the presence of low densities of HC_5N in Titan's atmosphere will result in a peak at *m*/*z* 76 corresponding to HC_5NH^+ as a result of its ion chemistry as suggested by Vuitton et al. [13] Less reactive ions such as $C_3H_3{}^+$ in keeping with their known chemistry with other neutrals, only exhibit slow association. We anticipate that c-$C_3H_3{}^+$ which is unreactive in Titan's atmosphere with most neutrals is also unreactive with HC_5N.

Acknowledgement

SJE thanks the Tertiary Education Commission of New Zealand for the award of a Top Achiever doctoral scholarship.

References

[1] M. Morris, B.E. Turner, P. Palmer, B. Zuckerman, Astrophys. J. 205 (1976) 82.
[2] L.W. Avery, N.W. Broten, J.M. MacLeod, T. Oka, Astrophys. J. 205 (1976) L173.
[3] N.W. Broten, J.M. MacLeod, T. Oka, L.W. Avery, J.W. Brooks, R.X. McGee, L.M. Newton, Astrophys. J. 209 (1976) L143.
[4] F.F. Gardner, J.B. Whiteoak, G. Winnewisser, Astron. Astrophys. 67 (1978) L23.
[5] H.W. Kroto, C. Kirby, D.R.M. Walton, L.W. Avery, N.W. Broten, J.M. MacLeod, T. Oka, Astrophys. J. 219 (1978) L133.
[6] G. Winnewisser, C.M. Walmsley, Astrophys. Space Sci. 65 (1979) 83.
[7] D.K. Bohme, S. Wlodek, A.B. Raksit, Can. J. Chem. 65 (1987) 2057.
[8] E. Herbst, C.M. Leung, Astrophys. J. Suppl. Ser. 69 (1989) 271.
[9] C.M. Walmsley, G. Winnewisser, F. Toelle, Astron. Astrophys. 81 (1980) 245.
[10] V. Wakelam, E. Herbst, F. Selsis, Astron. Astrophys. 451 (2006) 551.
[11] S.W. Stahler, Astrophys. J. 281 (1984) 209.
[12] A. Jolly, Y. Benilan, A. Fayt, Molecules in Space and Laboratory conference, Paris, France, 2007.
[13] V. Vuitton, R.V. Yelle, M.J. McEwan, Icarus 191 (2007) 722.
[14] C.G. Freeman, P.W. Harland, M.J. McEwan, Astrophys. Lett. 19 (1978) 133.
[15] J.S. Knight, C.G. Freeman, M.J. McEwan, N.G. Adams, D. Smith, Int. J. Mass Spectrom. Ion Phys. 67 (1985) 317.
[16] A.B. Raksit, D.K. Bohme, Int. J. Mass Spectrom. Ion Proc. 57 (1984) 211.
[17] A. Fox, A.B. Raksit, S. Dheandhandoo, D.K. Bohme, Can. J. Chem. 64 (1986) 399.
[18] G.B.I. Scott, D.A. Fairley, C.G. Freeman, M.J. McEwan, V.G. Anicich, J. Chem. Phys. 109 (1998) 9010.
[19] Y. Trolez, J.-C. Guillemin, Angew. Chem. Int. Ed. 44 (2005) 7224.
[20] D.B. Milligan, D.A. Fairley, C.G. Freeman, M.J. McEwan, Int. J. Mass Spectrom. 202 (2000) 351.
[21] H. Melville, B.G. Gowenlock, Experimental Methods in Gas Reactions, MacMillan, London, 1964.
[22] F.A. Miller, D.H. Lemmon, Spectrochim. Acta 23A (1967) 1415.
[23] A.D. Sen, W.T. Huntress Jr., V.G. Anicich, M.J. McEwan, A.B. Denison, J. Chem. Phys. 94 (1991) 5462.
[24] L. Brandsma, Preparative Acetylinic Chemistry, Elsevier Science Publishing BV, New York, 1988.
[25] S. Haas, G. Winnewisser, K.M.T. Yamada, Can. J. Phys. 72 (1994) 1165.
[26] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 Revision C. 02, Gaussian Inc., Wallingford, CT, 2004.
[28] D.K. Bohme, A.B. Raksit, Can. J. Chem. 63 (1985) 854.
[29] D. Clary, D. Smith, N.G. Adams, Chem. Phys. Lett. 119 (1985) 320.
[30] D. Clary, C.E. Dateo, D. Smith, Chem. Phys. Lett. 167 (1990) 1.
[31] L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov, J.A. Pople, J. Chem. Phys. (1998) 7764.
[32] P. Botschwina, A.C. Heyl, M. Oswald, T. Hisano, Spectrochim. Acta 53A (1997) 1079.