Selected-ion flow tube studies of reactions of the carbene cation $:C_4N^+$ and their implications for interstellar gas cloud chemistry

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The carbene cation $:C_4N^+$ was generated in a Selected-Ion Flow Tube (SIFT) apparatus from allyl cyanide by electron impact and reacted at room temperature in helium buffer gas at ca. 0.33 mm Hg with the molecules H_2, CO, HCN, CH_4, CD_4, H_2O, HC_3N, C_2H_2, CH_3CN, CD_3CN, H_2S, NH_3, ND_3, and C_4H_2. The reactions were observed to exhibit a range in reactivity and a variety of reaction products. The observed products are consistent with expectations based on the carbene character of $:C_4N^+$. The results have implications for the role of $:C_4N^+$ as a reaction intermediate in the chemistry of interstellar gas clouds. Possible synthetic routes initiated by $:C_4N^+$ are proposed for the formation of dicyanoacetylene, cyanodiacetylene, and several acyclic as well as cyclic neutral carbenes.

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Opérant à la température ambiante, dans de l'hélium à environ 0,33 Torr comme gaz tampon et utilisant du cyanure d'allyle soumis à un impact électronique que l'on fait réagir avec des molécules de H_2, CO, HCN, CH_4, CD_4, H_2O, HC_3N, C_2H_2, CH_3CN, CD_3CN, H_2S, NH_3, ND_3 et C_4H_2, on a produit le cation carbènique $:C_4N^+$ dans un tube à écoulement à sélectif pour les ions (SIFT). On a observé que les réactivités varient beaucoup et que les réactions conduisent à un grand nombre de produits. Les produits obtenus correspondent à ceux que l'on peut espérer en se basant sur le caractère carbènique du $:C_4N^+$. Les résultats ont des implications concernant le rôle du $:C_4N^+$ comme intermédiare dans la chimie des nuages gazeux interstellaires. On propose diverses voies de synthèse, initiées par le $:C_4N^+$, pour la formation du dicyanoacétylène, du cyanodiacétylène et de plusieurs carbènes neutres tant acycliques que cycliques.

[Traduit par la revue]

Introduction

A recent experimental study in our laboratory of ion/molecule reactions with cyanoacetylene has suggested a pivotal role for this molecule in the chemical evolution of interstellar gas clouds (1, 2). The presence of cyanoacetylene in a number of these clouds has been firmly established by radioastronomers (3). Gas phase cyanoacetylene is destroyed in these clouds predominantly by reaction with carbon ions (4, 5). This destruction reaction has been shown in our laboratory to proceed with an extremely high specific rate, $k = 6.1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K, and to establish both C_3H^+ and C_4N^+ as product ions in the relative amounts indicated by reaction [1].

$$[1] \quad C^+ + HC_3N \xrightarrow{0.8} C_3H^+ + CN$$

$$\xrightarrow{0.2} C_4N^+ + H$$

This result in turn points towards a pivotal role for C_3H^+ and C_4N^+ as intermediate reactant ions in the further chemical evolution of these environments by ion/molecule reactions. We have explored the interesting chemistry of C_3H^+ in a separate study (6–8). Here we report the results of measurement directed towards the characterization of the chemistry of C_4N^+.

The C_4N^+ was produced from allyl cyanide by electron impact and is likely to have the resonance structure indicated in [2]. The ion has carbene character and a charge which is delocalized. There is one report of an ionization energy for C_4N (9) and it indicates a moderate recombination energy for C_4N^+ of 11.9 ± 0.5 eV. The high value reported for the heat of formation of C_4N^+, 449 kcal mol^{-1} (9), is suggestive of a high chemical reactivity. We are not aware of any previous laboratory measurements of this reactivity.

$$[2] \quad :C^+{-}C{\equiv}C{-}C{\equiv}N: \leftrightarrow :C{=}C{=}C^+{-}C{\equiv}N:$$

$$\leftrightarrow :C{=}C{=}C{=}C{=}N^+:$$

The reactivity of C_4N^+ is of interest in interstellar cloud chemistry because of its possible role in the synthesis of cyanopolyacetylenes, cyanoacetylene itself, cumulated and disubstituted carbenes (10), and other molecules not yet identified in the interstellar medium.

Experimental

The measurements were performed with the Selected-Ion Flow Tube (SIFT) apparatus in the Ion Chemistry Laboratory (8, 11). The C_4N^+ was generated in an axial electron impact ionizer (Extranuclear Model 0413) from allyl cyanide, CH_2CHCH_2CN, either pure or diluted with helium, at electron energies in the range from 50 to 55 eV. The ion spectrum recorded downstream when C_4N^+ is selected upstream is shown in Fig. 1. The major impurity ion was C_3^+ which is thought to arise from the collisional dissociation of C_4N^+. The CHO^+ and $C_3H_2N^+$ ions may arise from reactions of C_4N^+ with water impurities in the helium buffer gas, while H_3O^+ will be formed by the further reaction of CHO^+ with water. The ions were injected into helium buffer gas at ca. 12 to 50 V. The total pressure was in the range from 0.32 to 0.35 mm Hg and the ambient temperature was 296 ± 2 K. The reagent gases and vapours as well as the helium buffer gas were generally of high purity with a minimum purity of 99.5 mol%. Hydrogen cyanide was prepared according to the procedure described by Glemser (12).

Results

Table 1 summarizes the rate constants and product distributions obtained in this study. It includes all the primary product ions which were observed to contribute 5% or more to the total products. The reactions are listed in order of decreasing ionization energy of the neutral substrate. Rate constants and product distributions were derived in the usual manner (6, 13). In the derivation of minor product distributions complications were introduced by reactions of the C_3^+ initially present in the flow tube which in some instances gave products in common with the products of the C_4N^+ reactions. These reactions of C_3^+

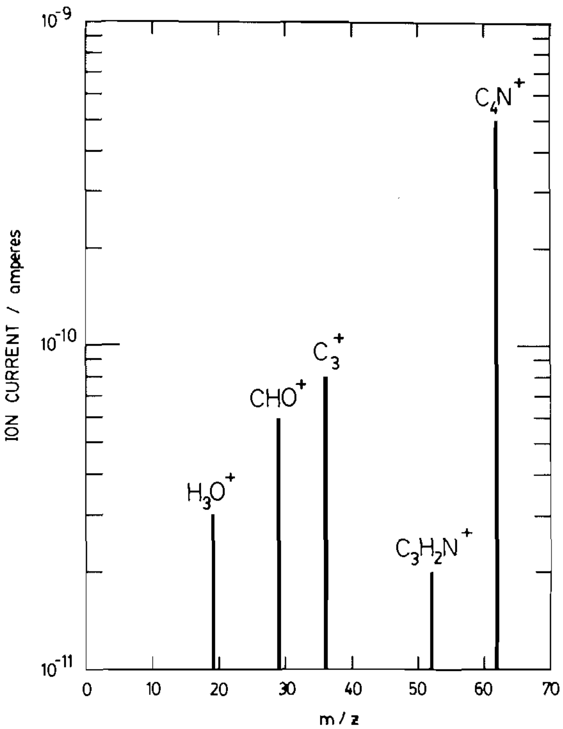


FIG. 1. SIFT spectrum for C_4N^+ derived from pure allyl cyanide by electron ionization at 50 eV. The buffer gas is helium at 0.35 mm Hg and the ion injection energy is ca. 50 V. The background "chemical noise" arises from the collisional dissociation of C_4N^+ and from reactions with water impurity in the buffer gas.

were measured separately and their contributions to the C_4N^+ product spectrum were subtracted where required.

H_2

Molecular hydrogen was observed to react with C_4N^+ only slowly with a specific rate of 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The only product which was apparent is indicated in reaction [3]. There was no evidence for hydrogen atom transfer or the

$$[3] \quad C_4N^+ + H_2 \rightarrow C_3H^+ + HCN$$

addition of molecular hydrogen to C_4N^+. The C_3H^+ product ion reacted further to add molecular hydrogen in a manner reported elsewhere (8).

CO

Only addition was observed with carbon monoxide as shown in reaction [4]. The effective bimolecular rate constant obtained

$$[4] \quad C_4N^+ + CO \rightarrow C_5NO^+$$

from the decay of C_4N^+ at a total pressure of 0.323 mm Hg and a helium density of 1.05×10^{16} atoms cm^{-3} was 9.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The reaction can be presumed to proceed in a termolecular fashion under these operating conditions but no measurements were made as a function of pressure. The C_5NO^+ ion did not appear to add a second molecule of CO.

HCN, HC_3N

Hydrogen cyanide and cyanoacetylene were observed to react with C_4N^+ in a similar fashion. Adduct formation was the predominant channel observed with both molecules at the moderate helium pressures employed. For the addition reaction [5] with HCN an effective bimolecular rate constant of

$$[5] \quad C_4N^+ + HCN \rightarrow C_5HN_2^+$$

8.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1} was measured at a total pressure of 0.33 mm Hg and a helium density of 1.1×10^{16} atoms cm^{-3}. A second molecule of HCN was observed to add, but more than 10 times slower. A third molecule was also observed to add slowly at higher additions of HCN. Previous experiments reported from our laboratory have shown that one molecule of cyanoacetylene also adds rapidly to C_4N^+ according to reaction [6] when the C_4N^+ is generated from the

$$[6] \quad C_4N^+ + HC_3N \rightarrow C_7HN_2^+$$

reaction of C^+ with HC_3N at a total pressure of 0.31 mm Hg and a helium density of 1.0×10^{16} atoms cm^{-3} (2).

TABLE 1. Summary of rate constants (in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}) and product distributions measured for reactions of $:C_4N^+$ with the SIFT technique at 296 ± 2 K

Neutral reactant	Products	Branching[a] ratio	k_{exp}[b]	k_c[c]
H_2	$C_3H^+ + CHN$	1.0	0.022	1.5
CO	C_5NO^+	1.0	0.093[d]	0.78
HCN	$C_5HN_2^+$	1.0	0.84[d]	3.2
CH_4	$C_3H_2N^+ + C_2H_2$	0.35	0.57	1.05
	$C_4H_3^+ + CHN$	0.30		
	$C_2H_3^+ + C_3HN$	0.25		
	$CH_2N^+ + C_4H_2$	0.05		
	$C_5H_2N^+ + H_2$	0.05		
H_2O	$C_3H_2N^+ + CO$	0.5	1.5[d]	2.4
	$CHO^+ + C_3HN$	0.4		
	$C_4H_2NO^+$	0.1		
HC_3N	$C_7HN_2^+$	1.0	1[d]	3.3
C_2H_2	$C_5H^+ + CHN$	≥ 0.7	0.80[d]	1.0
	$C_6H_2N^+$	≤ 0.3		
CH_3CN	$C_2H_3^+ + C_4N_2$	0.6	3.1	3.7
	$C_4HN_2^+ + C_2H_2$	0.4		
H_2S	$CHS^+ + C_3HN$	0.60	0.89[d]	1.4
	$C_2NS^+ + C_2H_2$	0.25		
	$C_3HS^+ + CHN$	0.10		
	$C_4H_2NS^+$	0.15		
ND_3	$ND_3^+ + C_4N$	0.65	1.2	
	$C_3D_2N^+ + CDN$	0.20		
	$CD_2N^+ + C_3DN$	0.15		
C_4H_2	$C_7H^+ + CHN$	0.4	1.6[d]	1.1
	$C_8H_2N^+$	0.6		

[a] Primary product ions which contribute more than 5%. The branching ratio has been rounded off to the nearest 5% and is estimated to be accurate to ±30%.

[b] The accuracy of the rate constants is estimated to be better than ±30%.

[c] Collision rate constants derived from the combined variational transition state theory — classical trajectory study of Su and Chesnavich (14).

[d] In helium buffer gas at a total pressure of ca. 0.3 mm Hg and concentration of ca. 1×10^{16} atoms cm^{-3}.

CH_4, CD_4

The product ions observed for the reaction of C_4N^+ with methane are indicated in reaction [7] along with their relative

$$[7] \quad C_4N^+ + CH_4 \xrightarrow{0.35} C_3H_2N^+ + C_2H_2$$

$$\xrightarrow{0.30} C_4H_3^+ + CHN$$

$$\xrightarrow{0.25} C_2H_3^+ + C_3HN$$

$$\xrightarrow{0.05} CH_2N^+ + C_4H_2$$

$$\xrightarrow{0.05} C_5H_2N^+ + H_2$$

yields. The overall rate constant determined from the decay of C_4N^+ was 5.7×10^{-10} cm^3 molecule^{-1} s^{-1}. Measurements with CD_4 excluded $C_4H_4^+$, CHN^+, and $C_2H_4^+$ as possible product ions. C_3HN^+, which has the same mass as $C_4H_3^+$, could not be completely excluded. Some $m/z = 52$ ions were observed with CD_4. The source for this ion was uncertain. For example, it may be produced from the C_3^+ impurity ions. In any case, the observed ion signals for this ion correspond to a maximum contribution to the products of 5%. The reaction with CD_4 has a measured rate constant of 5.0×10^{-10} cm^3 molecule^{-1} s^{-1}.

The reaction with CH_4 was also investigated using the reaction of C^+ with cyanoacetylene as a source for C_4N^+. Sufficient cyanoacetylene was added into the flow tube to quench most of the C^+ and methane was then added further downstream. The major ion in the flow tube under these conditions was C_3H^+ but the addition of methane did allow an assessment of the products of the C_4N^+ reaction since the products of the reaction of C_3H^+ with methane were known from previous measurements in our laboratory (8). The experiment was carried out at low resolution and products were observed at $m/z = 51 + 52$, $27 + 28$, and 76, in approximately the same proportions as those observed when C_4N^+ was derived directly from allyl cyanide. Also the rate constant determined under these conditions for the decay of C_4N^+, $k = 5.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, is consistent with the rate constant determined when C_4N^+ was derived by electron impact on allyl cyanide. Finally, both the adduct ions $C_3H^+.HC_3N$ and $C_4N^+.HC_3N$ present under these operating conditions were observed not to react with CH_4, $k \leq 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

H_2O

Two major bimolecular channels were observed for the reaction with H_2O. Adduct formation was observed as a minor channel. The reaction was rapid overall, $k = 1.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. The product distribution is indicated in reaction [8]. There was no evidence for the occurrence of

$$[8] \quad C_4N^+ + H_2O \xrightarrow{0.5} C_3H_2N^+ + CO$$
$$\xrightarrow{0.4} CHO^+ + C_3HN$$
$$\xrightarrow{0.1} C_4H_2NO^+$$

hydrogen atom or oxygen atom abstraction. The CHO^+ reacted further with H_2O to establish H_3O^+.

C_2H_2

C_4N^+ appeared to react with acetylene to produce predominantly C_5H^+ as shown in reaction [9]. The reaction was rapid,

$$[9] \quad C_4N^+ + C_2H_2 \rightarrow C_5H^+ + CHN$$

$k = 8.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The C_5H^+ rapidly reacted further by adding acetylene to produce $C_7H_3^+$. Because of insufficient resolution at the signal intensities of these experiments it was not possible to exclude the possibility of some (less than about 30%) formation of the $C_6H_2N^+$ adduct from the reaction of C_4N^+. There was no evidence for the occurrence of charge transfer or the formation of C_3H^+.

CH_3CN, CD_3CN

A rapid reaction was observed between C_4N^+ and acetonitrile, $k = 3.1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Two products were formed in about equal amounts according to reaction [10].

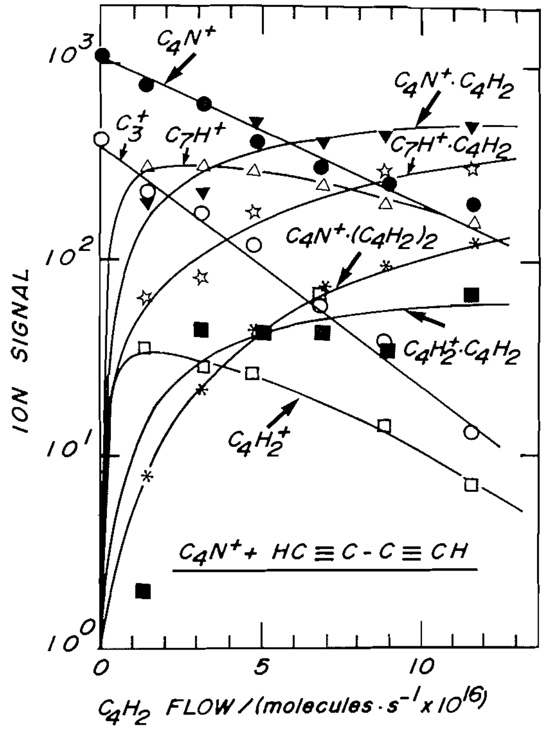


FIG. 2. The variations in ion signals observed for the addition of diacetylene into the reaction region of the SIFT apparatus in which the C_4N^+ cation is initially established in helium buffer gas. $P = 0.348$ mm Hg, $\bar{v} = 6.5 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 295$ K. The C_4N^+ is derived from allyl cyanide at an electron energy of 55 eV.

$$[10] \quad C_4N^+ + CH_3CN \xrightarrow{0.6} C_2H_3^+ + C_4N_2$$
$$\xrightarrow{0.4} C_4HN_2^+ + C_2H_2$$

Experiments with CD_3CN excluded CHN^+ and $C_5H_3N^+$ as possible reaction products. Trace amounts (about 1%) of an ion corresponding to the adduct $C_4N^+.CH_3CN$ were also observed to be formed as a primary product. The predominant primary products $C_2H_3^+$ and $C_4HN_2^+$ both were observed to react further by proton transfer to form CH_3CNH^+ which in turn rapidly added a molecule of acetonitrile to form the protonated dimer $(CH_3CN)_2H^+$.

H_2S

The reaction with hydrogen sulphide was observed to be rapid, $k = 8.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and to lead to a variety of products in the yields indicated in reaction [11].

$$[11] \quad C_4N^+ + H_2S \xrightarrow{0.60} CHS^+ + C_3HN$$
$$\xrightarrow{0.25} C_2NS^+ + C_2H_2$$
$$\xrightarrow{0.10} C_3HS^+ + HCN$$
$$\xrightarrow{0.05} C_4H_2NS^+$$

The occurrence of some charge transfer ($\lesssim 5\%$) could not be ruled out.

NH_3, ND_3

Charge transfer was the predominant reaction channel observed with ammonia. Other products observed were $C_3H_2N^+$ and CH_2N^+ and trace amounts ($\lesssim 1\%$) of the adduct $C_4H_3N_2^+$. The specific rate for the total reaction with ammonia was

1.5×10^{-9} cm^3 molecule^{-1} s^{-1}. Experiments with deuterated ammonia excluded $C_2N_2^+$, N_2^+, and $C_2H_4^+$ as possible reaction products. The branching ratios were determined with ND_3 to be as indicated in reaction [12]. The total rate constant with ND_3

$$[12]\quad \begin{aligned} C_4N^+ + ND_3 &\xrightarrow{0.65} ND_3^+ + C_4N \\ &\xrightarrow{0.20} C_3D_2N^+ + CDN \\ &\xrightarrow{0.15} CD_2N^+ + C_3DN \end{aligned}$$

was measured to be 1.2×10^{-9} cm^3 molecule^{-1} s^{-1}.

C_4H_2

The reaction of C_4N^+ with diacetylene was observed to be rapid, $k = 1.6 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. The predominant channels were as indicated in reaction [13]. Figure 2 shows representative data. In determining the branching ratio for C_7H^+ account had to be taken of the production of some of the C_7H^+ ion from the C_3^+ ion which is initially present. The $C_4H_2^+$ observed in Fig. 2 could be attributed entirely to charge transfer with C_3^+. The adduct ion $C_4N^+.C_4H_2$ ($C_8H_2N^+$) was seen to add a second molecule of diacetylene.

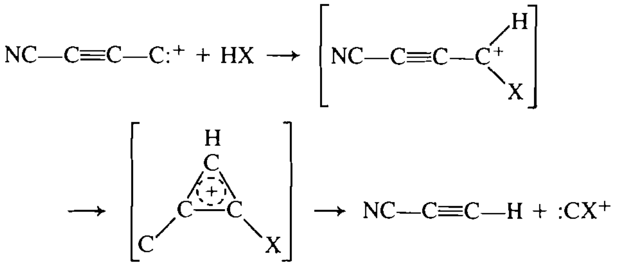
$$[13]\quad \begin{aligned} C_4N^+ + C_4H_2 &\xrightarrow{0.4} C_7H^+ + CHN \\ &\xrightarrow{0.6} C_8H_2N^+ \end{aligned}$$

Discussion and conclusions

The observed reactions of $:C_4N^+$ exhibit an interesting variety of products. Many of these products are consistent with the carbene character of this ion and may be rationalized in terms of σ bond insertion or in terms of coordination with an unbonded electron pair. The structure of the $:C_4N^+$ generated from allyl cyanide by electron impact is taken to be that in which the atom sequence is CCCCN as given in [2]. The heavy atom backbone of allyl cyanide is assumed to be maintained in the dissociative ionization and not to rearrange to a different atom sequence such as CCCNC, for example.

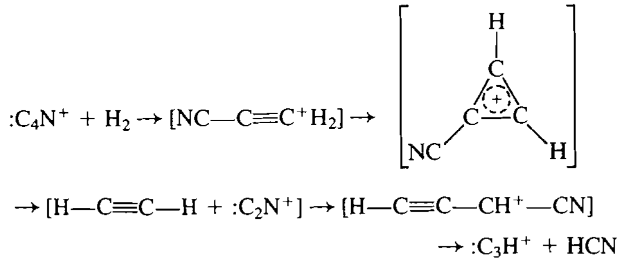
Possible coordination with an unbonded electron pair is evident from the high specific rate of the association reaction with carbon monoxide for which the product ion may be $O{=}C{=}C{=}C{=}C{=}C{=}N{:}^+$. The C_4N^+ also has nitrene character so that formation of $:C{=}C{=}C{=}C{=}N^+{=}C{=}O$ is also plausible.

The reactions between $:C_4N^+$ and molecules of type HX are likely to proceed by carbene insertion into the H—X bond to give the substituted propargyl-like ion NC—C≡C—C$^+$(H)X which may then rearrange, dissociate or be collisionally stabilized. The collisionally stabilized adduct was observed as a partial product in the reactions with HX = H_2O, H_2S, C_2H_2, and C_4H_2, and as the exclusive product in the reactions with HX = HCN and HC_3N. Rearrangement to a substituted cyclopropenyl-like ion with subsequent decomposition or collisional stabilization has been advanced earlier as a possible reaction mechanism for the analogous reactions with the carbene cation $:C_3H^+$ (7, 8, 15). For reactions with $:C_4N^+$ the rearrangement with subsequent decomposition may be expressed in the following manner:

[14]


A more direct mechanism involving 1,2 hydrogen migration in which the cyclopropenyl-like ion does not participate as an intermediate is also feasible and indeed may be preferred. The reaction products observed with CH_3CN are more consistent with a mechanism involving C—C bond insertion.

An inspection of the observed products suggests that the intermediate reaction complex is sufficiently long-lived in these reactions to allow proton transfer to occur before the products separate. This appears to be the case in the formation of $C_3H_2N^+$ and CHO^+ from H_2O and in the formation of $C_3D_2N^+$ and CD_2N^+ from ND_3. Also, two sets of ionic products in the reaction with methane may be connected in this manner, viz. $C_3H_2N^+/C_2H_3^+$ and $C_4H_3^+/CH_2N^+$. A long life-time for the intermediate complex may also have the consequence of allowing secondary carbene insertion steps before the products separate. Such steps would provide ready explanations for the observation of the bimolecular product ions other than $:CX^+$ (and ions derived from $:CX^+$ by proton transfer). For example, the products observed with H_2 may be accounted for by the following reaction sequence:

[15]


The reaction of C_2N^+ with acetylene has been measured separately in our laboratory and has been observed to produce C_3H^+ and HCN with high efficiency. A similar mechanism may apply to the formation of C_5H^+ from C_2H_2, C_7H^+ from C_4H_2, C_3HS^+ from H_2S, and $C_4H_3^+$ from CH_4.

Several of the reactions which have been identified in this study have implications for the chemistry of interstellar gas clouds where C_4N^+ is expected to be a likely reaction intermediate due to reaction [1]. First, the observed low reactivity of C_4N^+ towards molecular hydrogen suggests that this ion may be available for reaction with other, less abundant, constituents in interstellar gas clouds which are rich in molecular hydrogen. The degree to which this is the case will depend on the magnitude of the rate constant of reaction [3] at cloud temperatures which may be much less than the small rate constant of 2.2×10^{-11} cm^3 molecule^{-1} s^{-1} measured at 296 K if the reaction has a small activation energy. The availability of C_4N^+ in interstellar gas clouds may be much more sensitive to the presence of atomic hydrogen. Known heats of formation (16) indicate that the channels in reaction [16] are about

$$[16]\quad \begin{aligned} C_4N^+ + H &\rightarrow C_4H^+ + N \\ &\rightarrow C_3H^+ + CN \end{aligned}$$

70 kcal mol^{-1} and 4 ± 8 kcal mol^{-1} exothermic, respectively, and so may be important loss processes in cloud regions richer in atomic hydrogen.

The measurements reported here indicate that the reaction with the second most abundant molecular gas CO can lead to loss of C_4N^+ in dense interstellar gas clouds only by radiative association as indicated in reaction [17]. The efficiency of this

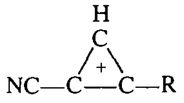
$$[17]\quad C_4N^+ + CO \rightarrow C_5NO^+ + h\nu$$

radiative association is uncertain but it may be noted that the specific rate of association observed at the higher pressures of our SIFT experiments is moderately large, viz. within a factor of ten of the collision rate. This result implies the formation of a moderately strong bond (17–19) and consequently a moderately high efficiency for radiative association (20).

The specific rates of association of C_4N^+ with HCN and HC_3N are within a factor of four of the collision rate. We have argued elsewhere that such high rates may be indicative of covalent bond formation in the adduct ion by C—H bond insertion (21). The much lower specific rates observed for the addition of a second molecule of HCN or HC_3N (which is more likely to lead to weaker electrostatic bonding) are consistent with such an interpretation. Covalent bonding with one molecule of HCN or HC_3N may result in acyclic or cyclic structures as indicated by ions **I** and **II** where R = CN or C_3N.

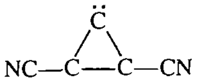
$$NC{-}C{\equiv}C{-}CH\overset{+}{-}R$$

I

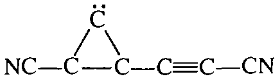


II

Neutralization of these structures may lead to the acyclic disubstituted carbenes :C(CN)C_3N and :$C(C_3N)_2$ or the cyclic carbenes **III** and **IV** (10).



III



IV

Interestingly, the reaction observed in the SIFT experiments with CH_3CN has quite different implications for molecular synthesis. The reaction between C_4N^+ and CH_3CN appears to be a suitable source for dicyanoacetylene. Sixty percent of this reaction leads directly to the neutral molecule C_4N_2 which is likely to be dicyanoacetylene. The remainder of the reaction leads to the protonated form of C_4N_2 which may subsequently neutralize to yield C_4N_2. One such neutralization event was observed in the proton transfer reaction between $C_4HN_2^+$ and CH_3CN. The proton affinity of dicyanoacetylene is not known but the latter observation establishes that PA (C_4N_2) < PA (CH_3CN) = 188.4 kcal mol^{+1} (22).

The rapid charge transfer reaction observed between C_4N^+ and ammonia provides a direct neutralization route for this ion in interstellar clouds which contain ammonia and is therefore a source for neutral C_4N.

The reaction with methane also has implications for molecular growth. In particular it appears to provide a source for diacetylene and cyanodiacetylene: 35% of the reaction either leads to C_4H_2 directly or to its protonated form, 5% of the reaction leads to $C_5H_2N^+$ which is likely to be protonated cyanodiacetylene, the remaining 60% appears to generate neutral or protonated cyanoacetylene. In the interstellar chemistry these latter products lead to chemical feedback in the sense that the cyanoacetylene will become available for reaction with C^+ which regenerates the C_4N^+.

The reactions of C_4N^+ with acetylene and diacetylene have the potential to lead to unsaturated or slightly saturated carbon chains and so represent contributing pathways to interstellar carbon and hydrocarbon molecules. Neutralization of the product ions C_5H^+ and C_7H^+ by proton transfer or electron/ion recombination may lead to C_5 and C_7, respectively, while neutralization by charge transfer will lead to the C_5H and C_7H radicals. Neutralization reactions of this type with interstellar molecules have been observed with C_3H^+, for example (8). The observation of the pentynylidyne radical C_5H has recently been reported for the circumstellar envelope of IRC + 10216 (23).

Acknowledgements

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