Flow-tube studies of reactions of selected ions with cyanoacetylene

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Rate constants and product distributions have been determined for ion/molecule reactions of cyanoacetylene (HC_3N) with He^+, $C^+(^2P)$, CH_3^+, C_2^+, C_2H^+, $C_2H_2^+$, CN^+, C_2N^+, $C_2N_2^+$, N_2^+, CO^+, H_3^+, N_2H^+, HCO^+, $C_2H_3^+$, H_3O^+, $CH_3NO_2H^+$, CH_3CNH^+, $(CH_3)_2COH^+$, $i\text{-}C_3H_7OH_2^+$, C_3H^+, and C_4N^+. The measurements were performed with the selected-ion flow-tube (SIFT) technique at 296 ± 2 K. The observed reactions exhibit a variety of pathways including charge transfer, proton transfer, condensation, and association. The condensation and association reactions are suited for molecular growth by ion/molecule reactions. Special consideration is given to the active role of cyanoacetylene in the possible molecular synthesis which occurs in dense interstellar gas clouds by ion/molecule reactions.

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On a déterminé les constantes de vitesse et les distributions des produits des réactions ions/molécules entre le cyanoacétylène (HC_3N) et les ions He^+, $C^+(^2P)$, CH_3^+, C_2^+, C_2H^+, $C_2H_2^+$, CN^+, C_2N^+, $C_2N_2^+$, N_2^+, CO^+, N_3^+, N_2H^+, HCO^+, $C_2H_3^+$, H_3O^+, $CH_3NO_2H^+$, CH_3CNH^+, $(CH_3)_2COH^+$, $i\text{-}C_3H_7OH_2^+$, C_3H^+ et C_4N^+. On a effectué les mesures à 296 ± 2 K en faisant appel à la technique des tubes à écoulement avec ions sélectifs (TEIS). Les réactions observées présentent une variété de voies réactionnelles, y compris des transferts de charges, des transferts de protons, des condensations et des associations. Les réactions de condensations et d'associations se prêtent bien à une croissance moléculaire par des réactions ions/molécules. On a accordé une considération spéciale au rôle actif que pourrait jouer le cyanoacétylène dans les synthèses moléculaires qui peuvent se produire, par des réactions ions/molécules, dans les nuages gazeux interstellaires denses.

[Traduit par le journal]

Introduction

Cyanoacetylene has attracted attention recently in astrochemistry as a consequence of its identification in the radiospectrum of several interstellar sources including cold dark molecular clouds and the circumstellar shells of late type stars (1). The molecular cloud TMC-1 is an example of such a source. This cloud also has been found to contain many related molecules such as the cyanopolyynes, $HC_{2n}CN$, with values of n up to 4, methylcyanoacetylene, CH_3C_2CN, and the radicals C_4H and C_3N (2). The concomitance of these molecules suggests that they have a common chemical lineage and that perhaps cyanoacetylene itself is a key progenitor. Here we report laboratory measurements of gas-phase reactions of various carbonaceous and organonitrogen ions with cyanoacetylene which begin to explore the latter possibility.

Gas-phase ion/molecule reactions have been invoked successfully in astrochemistry to account for the molecular synthesis of many simple molecules in interstellar clouds (3–5). Ion/molecule reactions are also expected to play an important role in the formation and destruction of larger and more complex molecules. The chemical paths to larger molecules become increasingly more difficult to track as the molecules become more complex and so they are not understood nearly as well. The studies reported here represent an attempt to identify such paths which are specific to cyanoacetylene.

A previous laboratory study of ion/molecule reactions with cyanoacetylene has led to the conclusion that the positive ion chemistry of cyanoacetylene is dominated by charge-transfer or proton-transfer reactions and is thus, by implication, of minor importance to the chemical synthesis of larger molecules (6). The observations reported here establish serious discrepancies with the earlier results for a number of key reactions and point towards an active rather than a passive role for cyanoacetylene in molecular growth by ion/molecule reactions.

Experimental

The measurements were performed with the selected-ion flow tube/flowing afterglow apparatus in the Ion Chemistry Laboratory at York University (7, 8). The reagent ions were derived from suitable parent gases by electron impact at low pressures. An axial electron impact ionizer (Extranuclear, Model 041-3) was used as the ion source. Typical ion injection energies were in the range 10 to 15 V. The carrier gas was either helium or hydrogen. To remove traces of water vapour the buffer gases were passed through zeolite traps (a 50:50 mixture of Union Carbide molecule sieves 4A and 13X) cooled to liquid nitrogen temperature. The cyanoacetylene was prepared in the laboratory from methyl propiolate (Aldrich) (9). Experiments with H_3^+ as the "chemical ionization" reagent indicated a purity of greater than 99%. All measurements were made at an ambient temperature of 296 ± 2 K.

Results

The reaction rate constants and product distributions obtained in this study for reactions of ions with cyanoacetylene are summarized in Table 1. Rate constants and product distributions were determined in the manner described previously (7, 10). Table 1 includes all the primary product ions which were observed to contribute more than 5% to the total product spectrum. The branching ratios have been rounded off to the nearest 5% and are accurate to ±30%. The experimental rate constants are compared with collision rate constants, k_c, derived according to a recent combined variational transition state theory/classical trajectory study of thermal energy ion polar molecule capture collisions (11) with an estimated polarizability for HC_3N of 5.29 $Å^3$ (12) and a dipole moment of 3.6 D (13).

He^+

He^+ was derived from helium by electron impact at 26 eV and injected into helium buffer gas. Approximately 30% conversion to He_2^+ was observed at pressures of about 0.3 Torr. The conversion occurs by termolecular association along the length of the flow tube. The added cyanoacetylene was observed to react rapidly with both He^+ and He_2^+ although some of the observed decrease in the He_2^+ signal was due to depletion of the precursor He^+. Figure 1 shows the plethora of product

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

Reactant ion	Products	Branching ratio	k_{exp}[a]	k_c[b]
He^+	C_2^+, C_3^+, C_2H^+, CN^+, C_2N^+, C_3N^+		6.9 (8.2)	9.0
C^+ (^2P)	$C_3H^+ + CN$	0.8	6.1 (8.7)	5.6
	$C_4N^+ + H$	0.2		
CH_3^+	$C_3H_3^+ + HCN$	0.6	4.2[c] (2.7)	5.1
	$CH_3^+ \cdot HC_3N$	0.4		
C_2^+	$C_3N^+ + C_2H$	0.5	4.8	4.3
	$C_5N^+ + H$	0.2		
	$C_3H^+ + C_2N$	0.2		
	$C_2N^+ + C_3H$	0.1		
C_2H^+	$HC_3NH^+ + C_2$	0.5	3.2	4.2
	$C_4H_2^+ + CN$	0.2		
	$HC_5N^+ + H$	0.2		
	$HC_3N^+ + C_2H$	0.1		
$C_2H_2^+$	$C_4H_2^+ + HCN$	0.5	3.2[c] (1.9)	4.2
	$C_2H_2^+ \cdot HC_3N$	0.5		
CN^+	$HC_3N^+ + CN$	0.8	3.9 (5.3)	4.2
	$C_3N^+ + HCN$	0.2		
C_2N^+	$C_3H^+ + C_2N_2$	1.0	3.1	3.7
$C_2N_2^+$	$HC_3N^+ + C_2N_2$	1.0	1.6	3.4
N_2^+	$HC_3N^+ + N_2$	1.0	4.1	4.1
CO^+	$HC_3N^+ + CO$	1.0	3.1 (2.3)	4.1
H_3^+	$HC_3NH^+ + H_2$	1.0	10.5 (9.1)	10.3
N_2H^+	$HC_3NH^+ + N_2$	1.0	4.2 (4.2)	4.0
HCO^+	$HC_3NH^+ + CO$	1.0	4.0 (3.7)	4.0
$C_2H_3^+$	$HC_3NH^+ + C_2H_2$	1.0	3.9 (1.8)	4.1
H_3O^+	$HC_3NH^+ + H_2O$	1.0	3.8 (4.0)	4.7
$CH_3NO_2H^+$	$HC_3NH^+ + CH_3NO_2$	0.5	1.8	3.3
	$(H_4C_4N^+ + HNO_2)$	0.5		
CH_3CNH^+	$CH_3CNH^+ \cdot HC_3N$	1.0	0.5[d]	3.6
$(CH_3)_2COH^+$	$(CH_3)_2COH^+ \cdot HC_3N$	1.0	0.05[e]	3.3
i-$C_3H_7OH_2^+$	i-$C_3H_7OH_2^+ \cdot HC_3N$	1.0	0.6[d]	3.3
C_3H^+	$C_3H^+ \cdot HC_3N$	1.0	1.3[f]	3.7
C_4N^+	$C_4N^+ \cdot HC_3N$	1.0	1[c]	3.3

[a] The accuracy of the rate constants is estimated to be better than ±30%. Values in parentheses are the flowing afterglow results reported by Freeman *et al.* in ref. 6.

[b] Collision rate constants derived from the combined variational transition state theory/classical trajectory study of Su and Chesnavich (11).

[c] In helium buffer gas at a total pressure of 0.31 Torr and concentration of 1.0 × 10^{16} atoms cm^{-3}.

[d] In hydrogen buffer gas at a total pressure of 0.21 Torr and concentration of 6.8 × 10^{15} molecules cm^{-3}.

[e] In hydrogen buffer gas at a total pressure of 0.185 Torr and concentration of 6.0 × 10^{15} molecules cm^{-3}.

[f] In helium buffer gas at a total pressure of 0.347 Torr and concentration of 1.1 × 10^{16} atoms cm^{-3}.

ions which appeared in response to these reactions. All of them can be derived by dissociative charge transfer. C^+, CH^+, and HCN^+ were also observed as primary product ions but they were produced in relatively small amounts and are not shown in Fig. 1. Also it should be noted that formation of HC_3N^+ itself was observed but the data analysis indicated that it could be accounted for entirely by secondary reactions. The secondary product spectrum was complex as would be expected from the high reactivity of all the primary product ions which is evident from the decays shown in Fig. 1. Several of these secondary reactions are elucidated in the following sections.

C^+

The C^+ ions were produced from C_2N_2 at an electron energy of 32 eV and selected with an injection energy of 12.4 V. HCO^+ and C_2N^+ were two other ions observed in the C^+ spectrum downstream but with intensities less than 10% and 1% of the C^+ signal, respectively. Their origin can be attributed to reactions of C^+ with H_2O impurity in the buffer gas and with C_2N_2 which leaks through the selection quadrupole region. Separate experiments in which CO was added into the reaction region indicated that more than 95% of the C^+ generated in this fashion was in the ^2P ground state (14). Charge transfer to form CO^+ which is exothermic only with the excited ^4P state of C^+ was observed to proceed with less than 5% of the initial C^+ population.

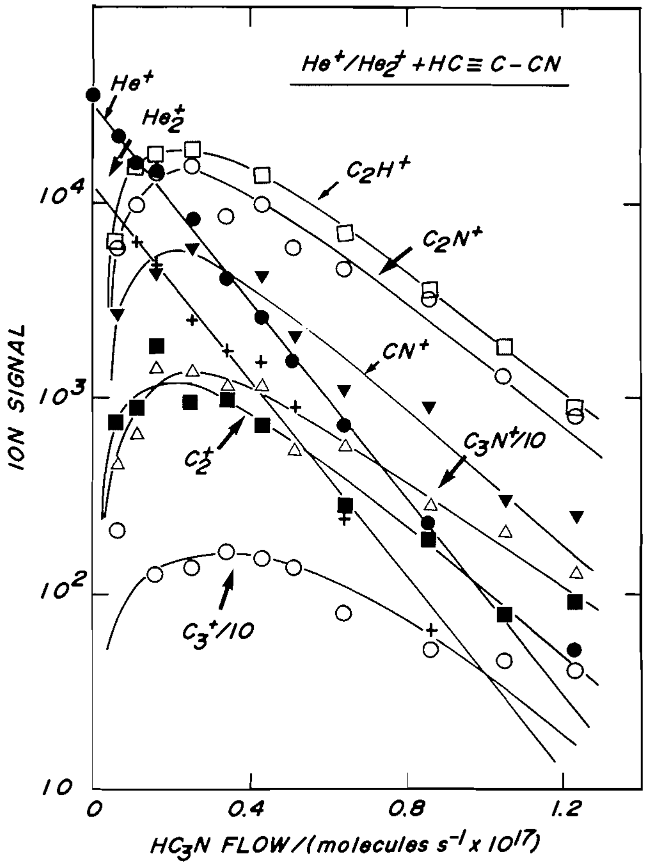

FIG. 1. The observed variations in ion signals recorded for the addition of HC_3N into the reaction region of the SIFT apparatus in which He^+ is initially established in helium buffer gas. P = 0.332 Torr, $\bar{v}$ = 7.4 × 10^3 cm s^{-1}, L = 46 cm, and T = 297 K. He^+ is derived from He at an electron energy of 25.7 eV.

Figure 2 shows data observed for the reaction of C^+ with HC_3N proceeding in our SIFT apparatus. The predominant primary product ion was identified as C_3H^+ and it was accompanied by some production of C_4N^+. The C_3H^+ and C_4N^+ ions may be formed by C—H insertion with elimination of CN and H, respectively. Formation of C_3^+ + HCN was not observed. Available heats of formation for C_3H^+ and C_3^+ (15, 16) indicate that formation of C_3^+ is approximately 30 kcal mol^{-1} less exothermic. The C_3H^+ product is likely to be the carbene cation $:\overset{+}{C}\text{—C}\equiv\text{CH}$ whose chemistry we have investigated in detail in a separate study (8). The structure of the C_4N^+ product is uncertain as either $CCCCN^+$ or $CCCNC^+$ may be formed depending on which end of the molecule is attacked. Carbene character is also likely to be associated with this ion, as for example in $:\overset{+}{C}\text{—C}\equiv\text{C—CN}$. Figure 2 also shows rapid reac-

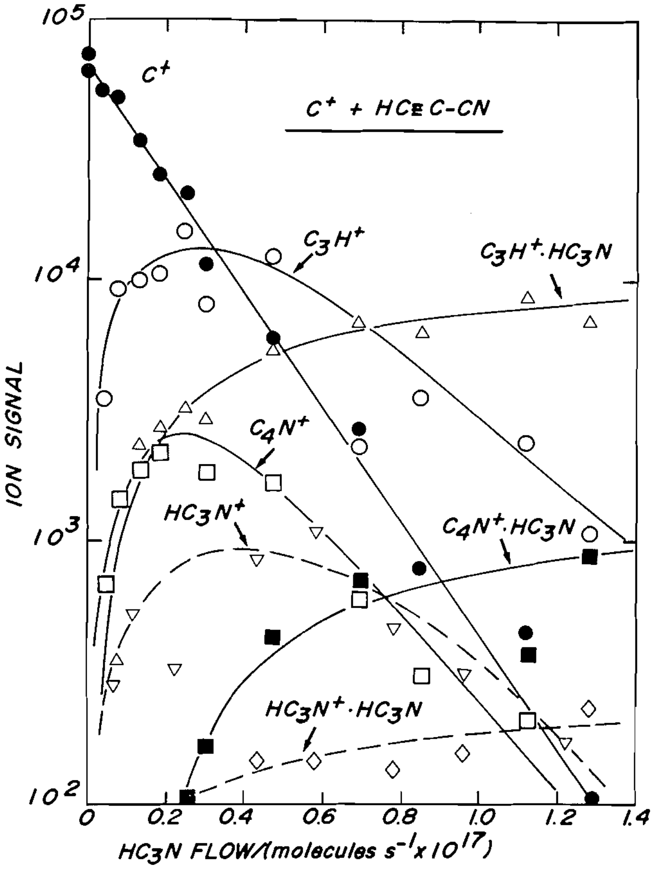

FIG. 2. The observed variations in ion signals recorded for the addition of HC_3N into the reaction region of the SIFT apparatus in which C^+ is initially established in helium carrier gas. $P = 0.314$ Torr, $\bar{v} = 7.2 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 296$ K. C^+ is derived from C_2N_2 at an electron energy of 32 eV.

tions of C_3H^+ and C_4N^+ with HC_3N to form the adducts $C_3H^+ \cdot HC_3N$ and $C_4N^+ \cdot HC_3N$. Also HC_3N^+ was produced as a primary ion and it reacted further to form the adduct $HC_3N^+ \cdot HC_3N$. The production of HC_3N^+, which accounts for about 5% of the initial C^+, may be attributed entirely to the excited ^4P component of C^+ which can react with HC_3N in an exothermic fashion by charge transfer. Not shown in Fig. 2 are the impurity ions at m/z 29 (HCO^+) and 38 (C_2N^+) which were present initially at levels of less than 10% and 1% of the initial C^+ signal, respectively. Separate experiments indicated that HCO^+ reacts by proton transfer to yield $H_2C_3N^+$ and that C_2N^+ produces C_3H^+. Also the observations allowed for some production (5%) of C_2N^+ directly from the reaction of C^+ with HC_3N.

CH_3^+

This ion was derived from CH_4 at 24 eV. Background ions were present at $m/z = 19$, 29, and 33. These were ascribed to H_3O^+, N_2H^+, and $CH_3^+ \cdot H_2O$. Figure 3 shows the appearance of the product ions which were assigned to the reaction of CH_3^+ with cyanoacetylene. Major primary products were observed at $m/z = 39$ and 66. Since formation of HC_2N^+ (m/z 39) + C_2H_3 is endothermic, the m/z 39 product must be $C_3H_3^+$. The ion with m/z 66 must be the adduct $CH_3^+ \cdot HC_3N$. Both product ions reacted further to form the adducts $C_3H_3^+ \cdot HC_3N$ and $CH_3^+ \cdot (HC_3N)_2$. An ion with m/z 52 was also observed in the product spectrum with an intensity up to 5% of the total product ions but its origin could be attributed entirely to proton-transfer reactions with the impurity ions.

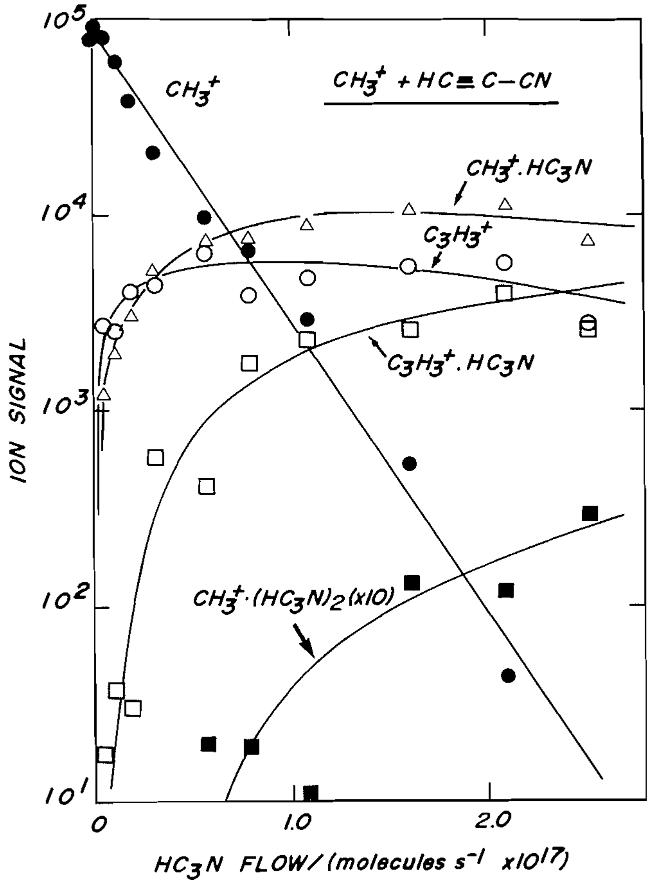

FIG. 3. The observed variations in ion signals recorded for the addition of HC_3N into the reaction region of the SIFT apparatus in which CH_3^+ is initially established in helium carrier gas. $P = 0.311$ Torr, $\bar{v} = 7.4 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 295$ K. CH_3^+ is derived from CH_4 at an electron energy of 24.1 eV.

The two primary product channels appear to reflect the position of attack on the cyanoacetylene molecule. Attack at the carbon α to the cyanogen group can lead to elimination of HCN and formation of the propargyl cation while attack at the β carbon would make HCN elimination less favourable and lead preferentially to an adduct which could be the cyanopropenylium ion, $CH_3\text{—}CH\text{=}\overset{+}{C}\text{—}CN$. However, neither of these structures can be considered to be established by these measurements. Alternatives include formation of the cyclopropenium isomer of $C_3H_3^+$ which is also exothermic and formation of an adduct which is electrostatically bound.

C_2^+

This ion was derived from C_2N_2 by electron impact at 50 eV. Background ions of known identity and origin were present at levels of less than 5% of the initial C_2^+ signal. Primary product ions with a contribution of more than 5% of the total observed included m/z 50 (C_3N^+), 74 (C_5N^+), 37 (C_3H^+), and 38 (C_2N^+). The corresponding reactions dictated by thermochemistry and their product distributions are indicated in Table 1. The predominant channel to produce C_3N^+ corresponds to hydride transfer. H atom elimination to form C_5N^+ leads to carbon chain lengthening. The mechanisms of the two remaining channels is less certain but they may arise from side-on attack by C_2^+. The adducts $C_3N^+ \cdot HC_3N$, $C_5N^+ \cdot HC_3N$, and $C_3H^+ \cdot HC_3N$ appeared to be formed rapidly by secondary reac-

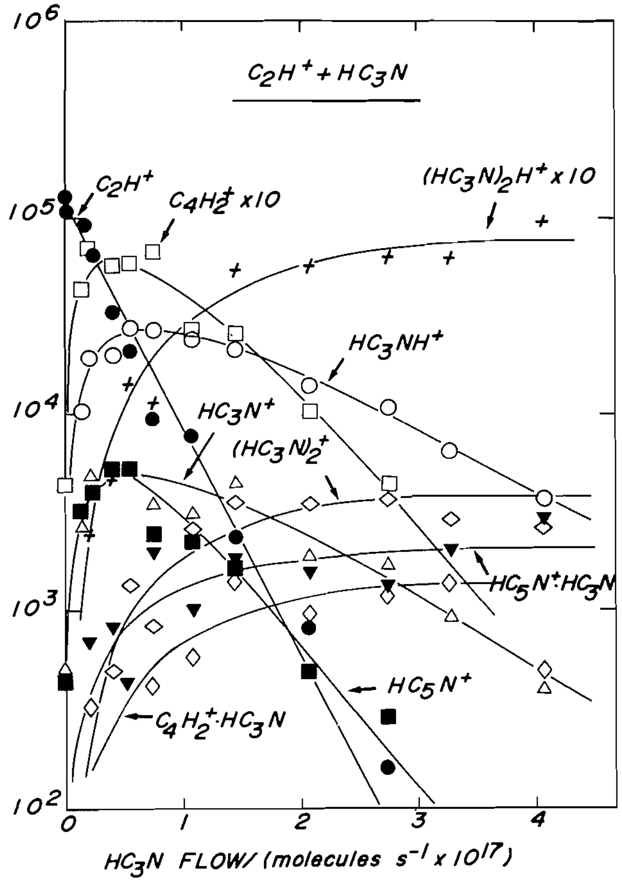

FIG. 4. The observed variations in ion signals recorded for the addition of HC_3N into the reaction region of the SIFT apparatus in which C_2H^+ is initially established in helium carrier gas. $P = 0.339$ Torr, $v = 7.1 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 297$ K. C_2H^+ is derived from cyanoacetylene by electron impact at 31 eV.

tions with cyanoacetylene. Only the adduct of C_2N^+ was not observed. It is shown in a later section that this ion reacts with HC_3N to produce C_3H^+.

C_2H^+

This ion was generated from HC_3N by electron impact at 31 eV. The main impurity ions present initially were *m/z* 19 (H_3O^+), 26 ($C_2H_2^+$), and 42 ($H_2C_2O^+$) at 5%, 2%, and 2%, respectively, of the initial C_2H^+ signal. All three of these impurity ions have been shown in separate experiments to be derivatives of the reaction of C_2H^+ with H_2O impurity. Their presence was taken into account in the product analysis. The evolution of the product ions observed with addition of HC_3N is shown in Fig. 4. The predominant product channel corresponds to proton transfer and the minor channel apparently to charge transfer although CN transfer cannot be excluded. The two other intermediate channels both appear to result in C—C bond formation. The $C_4H_2^+$ product is likely to be ionized diacetylene which may arise by attack at the carbon α to CN while HC_5N^+, presumably ionized cyanodiacetylene, may be the result of attack at the β carbon with elimination of H. All four of the product ions reacted further with HC_3N to rapidly establish the adducts $(HC_3N)_2H^+$, $(HC_3N)_2^+$, $C_4H_2^+ \cdot HC_3N$, and $HC_5N^+ \cdot HC_3N$.

$C_2H_2^+$, $C_4H_2^+$

The $C_2H_2^+$ was derived from acetylene by electron impact at 31 to 51 eV. Major primary products were observed at *m/z* 50 and 77 which were assigned to $C_4H_2^+$ and $C_2H_2^+ \cdot HC_3N$, respectively. Production of *m/z* 50 = C_3N^+ is endothermic according to available heats of formation (16). The *m/z* 77 ion is produced exclusively from $C_2H_2^+$ and not from a secondary reaction of $C_4H_2^+$ with HC_3N which was shown in the C_2H^+ experiments to produce only the adduct $C_4H_2^+ \cdot HC_3N$. There was no indication for the formation of an ion at *m/z* 52 which would be indicative of proton transfer. Evidently carbon chain lengthening and association are the only two primary product channels. Proton transfer was identified as the only channel by earlier flowing afterglow measurements (6). It is possible that proton transfer is in fact endothermic although the energetics for proton transfer are not well known due to the uncertainty in the heat of formation of C_2H (17). Within the uncertainties of PA(C_2H) and PA(HC_3N) the change in enthalpy for the proton transfer is -4 ± 9 kcal mol^{-1}.

CN^+

CN^+ was derived from C_2N_2 by electron impact at ca. 55 eV. CN^+ reacts rapidly with H_2O and a number of ions derived from this reaction were present as impurity ions. The major reaction channel between CN^+ and HC_3N corresponds to charge transfer although C_2H transfer is also a possibility. Some production of an ion with *m/z* 50 was observed and it was ascribed to formation of C_3N^+ + HCN which may result from hydride transfer. Also an ion with *m/z* 52 (HC_3NH^+ or $C_2N_2^+$) was observed to be produced but its origin could be attributed entirely to a proton transfer between H_3O^+ and cyanoacetylene. The C_3N^+, HC_3N^+, and *m/z* 52 ions were all observed to undergo secondary reactions to form adducts with HC_3N.

C_2N^+

This ion was derived from cyanoacetylene at an electron energy of 35 eV. C_3H^+ was the only primary product observed and it reacted further to form the adduct $C_3H^+ \cdot HC_3N$. Separate experiments performed in our laboratory have shown that the C_2N^+ derived from HC_3N (and also from C_2N_2) is a mixture of at least two states. One component has been found to react rapidly with O_2 to form C_2NO^+ and O_2^+ and comprises about 5% of the total mixture. The remaining 95% was observed to be unreactive towards O_2. It is not clear whether the observed difference in reactivity is due to the two structural isomers $C—N—C^+$ and $C—C—N^+$ or whether singlet and triplet forms of this carbene cation are involved. Calculations have shown the $C—N—C^+$ isomer to be more stable than the $C—C—N^+$ isomer by ca. 30 kcal mol^{-1} (18).

H_3^+, N_2H^+, HCO^+, $C_2H_3^+$, H_3O^+

We have investigated proton transfer reactions with cyanoacetylene in a separate study directed towards a determination of the proton affinity of HC_3N by the bracketing technique (19). All five of the protonated species listed above were observed to react rapidly with HC_3N by proton transfer with rate constants in close agreement with predicted collision rate constants. The observations recorded for the fastest of these reactions, viz. the reaction with H_3^+, are shown in Fig. 5 which also includes the reactive behaviour of the impurity ions H_3O^+ and N_2H^+. The protonated cyanoacetylene reacts further to establish the protonated dimer.

$CH_3NO_2H^+$, NO^+

These two ions were generated by injecting $CH_3NO_2^+$ into H_2 buffer gas (19). At the injection energies employed (12.4 V) some NO^+ was present (≈ 10%) which is presumed to arise

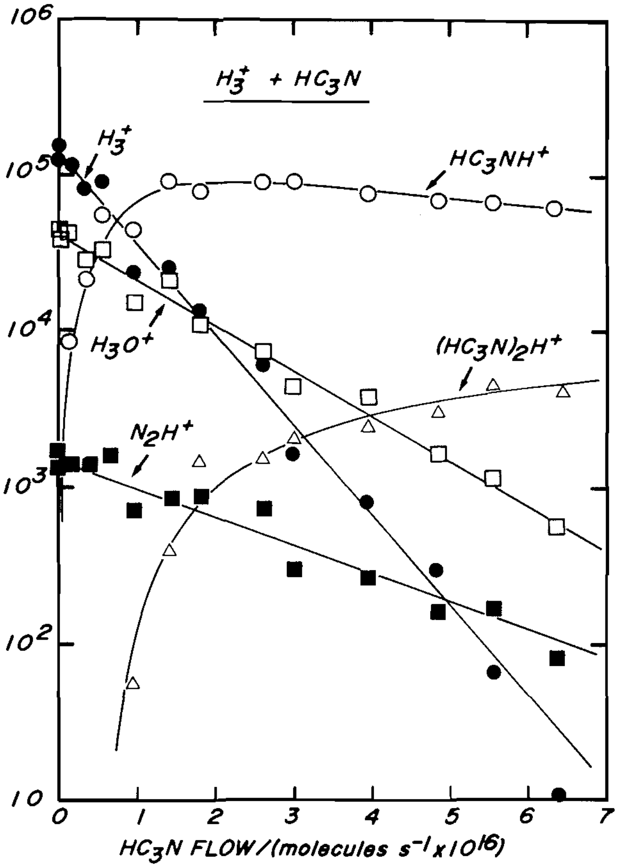

FIG. 5. The observed variations in ion signals recorded for the addition of HC_3N into the reaction region of the SIFT apparatus in which H_3^+ is initially established in hydrogen carrier gas. $P = 0.188$ Torr, $v = 6.5 \times 10^3$ cm s^{-1}, $L = 45$ cm, and $T = 296$ K. The selected ion is H_2^+ derived from H_2 by electron impact at 30 eV. H_3O^+ and N_2H^+ arise from reactions of H_3^+ with impurities in the carrier gas.

from collisional dissociation of $CH_3NO_2^+$. The NO^+ was observed to react only slowly to form the adduct $NO^+ \cdot HC_3N$. The rate constant for this association is estimated to be $< 1 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at a total pressure of 0.18 Torr and a hydrogen density of 5.9×10^{15} molecules cm^{-3}. The $CH_3NO_2H^+$ was observed to react rapidly to form two products in about equal proportions: an ion at m/z 52 which corresponds to protonated HC_3N and an ion at m/z 66 which may be $H_4C_4N^+$, $H_2C_4O^+$, or C_3NO^+. The possible m/z 66 product ions would involve concomitant production of the neutrals HNO_2, H_3N_2O, and H_5CNO, respectively. The first option appears most likely and could produce the cyanopropenylium ion as shown in reaction [1]

$$[1] \quad CH_3NO_2H^+ + HC{\equiv}C{-}CN \rightarrow CH_3{-}CH{=}\overset{+}{C}{-}CN + HNO_2$$

N_2^+, CO^+, $C_2N_2^+$

N_2^+ was derived from N_2 at an electron energy of 45 eV, $C_2N_2^+$ from C_2N_2 at 51 eV, and CO^+ from OCS at 34 eV. All these ions have recombination energies higher than the ionization energy of cyanoacetylene so that charge transfer was observed to be the dominant channel (>95%) for all three ions. Impurity ions were present at m/z 18 (H_2O^+), 19 (H_3O^+), and 29 (N_2H^+ or HCO^+) and these reacted predictably by proton transfer to establish HC_3NH^+. Both the HC_3N^+ produced by charge transfer and the HC_3NH^+ produced by proton transfer reacted further by addition of HC_3N to form $(HC_3N)_2^+$ and $(HC_3N)_2H^+$, respectively.

$(CH_3)_2COH^+$, CH_3CNH^+, i-$C_3H_7OH_2^+$

These three protonated species were observed to form adduct ions with cyanoacetylene. Each was generated in H_2 buffer gas by reaction [2]

$$[2] \quad X^+ + H_2 \rightarrow XH^+ + H$$

where X^+ was derived by electron impact of $X = (CH_3)_2CO$, CH_3CN, and i-C_3H_7OH, respectively (19). Table 1 shows that the association reactions with CH_3CNH^+ and i-$C_3H_7OH_2^+$ are quite rapid and about 10 times faster than the association reaction with $(CH_3)_2COH^+$. The adduct of CH_3CNH^+ was observed to react further with HC_3N in a manner which may be described by the solvated proton transfer reaction [3].

$$[3] \quad CH_3CNH^+ \cdot HC_3N + HC_3N \rightarrow HC_3NH^+ \cdot HC_3N + CH_3CN$$

The reverse of reaction [3] is actually the preferred direction. This was shown in a separate study in which $HC_3NH^+ \cdot HC_3N$ was generated in H_2 buffer gas by the reaction sequence [4] and [5]

$$[4] \quad H_2^+(H_3^+) + HC_3N \rightarrow HC_3NH^+ + H(H_2)$$

$$[5] \quad HC_3NH^+ + HC_3N \rightarrow HC_3NH^+ \cdot HC_3N$$

The $HC_3NH^+ \cdot HC_3N$ adduct was observed to react rapidly with CH_3CN by the reverse of reaction [3] with a rate constant of 1.9×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. The analogue of reaction [3] was not observed for the adduct ions $(CH_3)_2COH^+ \cdot HC_3N$ and i-$C_3H_7OH_2^+ \cdot HC_3N$. The smaller rate constants for these two reactions are consistent with the larger intrinsic basicities of $(CH_3)_2CO$ (PA = 194 kcal mol^{-1}) and i-C_3H_7OH (PA = 190 kcal mol^{-1}). Finally, the observations indicated no measurable tendency of any of the adduct ions to add a second HC_3N molecule. The rate of addition of the second molecule of HC_3N is estimated to be at least 10 times slower than the rate of addition of the first. This difference in rate is likely to reflect a difference in the nature of the bonding in these adduct ions.

C_3H^+, C_4N^+

These two ions are likely to be the carbene cations with the linear structures $:\overset{+}{C}{-}C{\equiv}C{-}H$ and $:\overset{+}{C}{-}C{\equiv}C{-}CN$. When generated from the reaction of C^+ with HC_3N both ions were observed to add one molecule of HC_3N rapidly (see Fig. 2 and Table 1). Representative data for a separate study of the reaction of C_3H^+ with HC_3N where C_3H^+ is derived from electron impact of propylene is shown in Fig. 6. The two reactions were not investigated as a function of pressure. Stabilization of the adduct ions may proceed by collision with the buffer gas atoms but radiative association cannot be ruled out. The further addition of a second molecule of HC_3N was observed to proceed much more slowly.

Discussion and conclusions

The measurements reported here show that cyanoacetylene is very reactive towards ions at room temperature. The reactivity is manifested in a number of different ways. The moderate ionization potential of HC_3N and its moderately high proton affinity ensure that charge transfer and proton transfer can be effective. Cyanoacetylene also exhibits a range of interesting and rapid condensation and association reactions which are suited for molecular growth by ion/molecule reactions.

The ions selected in this study for reaction with cyano-

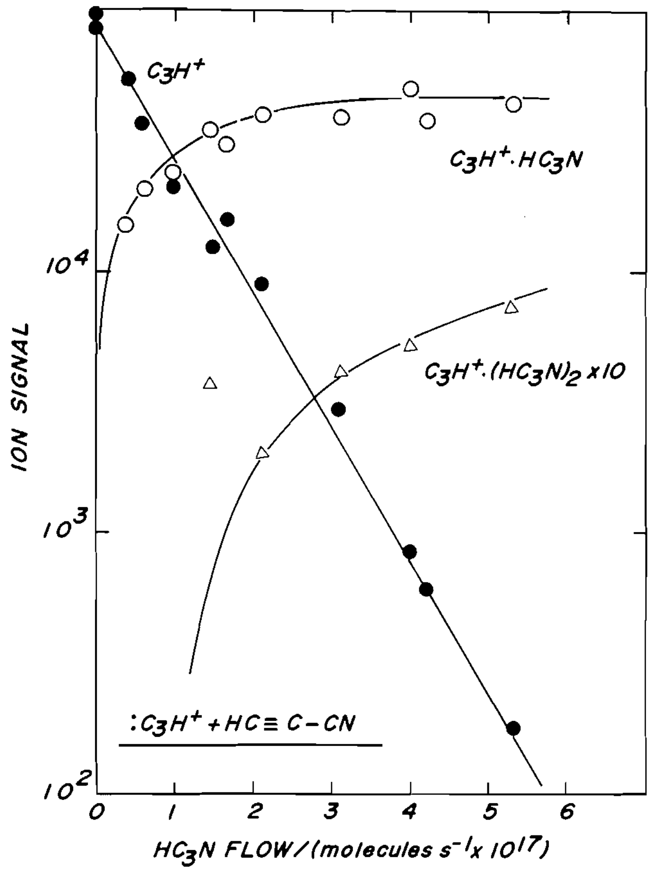

FIG. 6. The observed variations in ion signals recorded for the addition of HC_3N into the reaction region of the SIFT apparatus in which C_3H^+ is initially established in helium carrier gas. $P = 0.347$ Torr, $\bar{v} = 7.3 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 296$ K. C_3H^+ is derived from propylene by electron impact at 55 eV.

acetylene span a large range in recombination energy up to 24.6 eV for He^+. Charge transfer is exothermic for ions with a recombination energy greater than 11.60 ± 0.01 eV which is the ionization energy of HC_3N (20). Indeed charge transfer was an observed product channel with all of the ions which met this criterion, viz. He^+ (24.6), C^+ (^4P) (16.6), N_2^+ (15.6), CN^+ (15.1), CO^+ (14.0), $C_2N_2^+$ (13.4), and C_2H^+ (11.6), where the recombination energy is given in parentheses in eV (21). The charge transfer with He^+ was completely dissociative. For dissociative charge transfer to be exothermic to form any of the product ions indicated for He^+ in Table 1 the recombination energy of the ion must be greater than 17.7 eV and this is the case only for He^+. For the reactions of the other ions dissociative charge transfer is endothermic and was not observed. Charge transfer was observed to be only a minor channel with C_2H^+. The recombination energy of this ion is quite uncertain but appears to be very close to the ionization energy of cyanoacetylene. Values of 11.96 ± 0.05 eV (22), 11.6 ± 0.5 eV (17), 11.51 eV,[1] and 11.31 ± 0.13 eV (24) have been reported in the literature. Given this large uncertainty it is conceivable that charge transfer between C_2H^+ and HC_3N is in fact slightly endothermic at room temperature but this would still be consistent with our observation.

Freeman *et al.* (6) have reported flowing afterglow measurements of the charge transfer reactions of He^+, CN^+, and CO^+. The rate constants agree with those obtained in the SIFT study reported here within the combined error estimates of both experiments. However, Freeman *et al.* (6) did not report any dissociative charge transfer with He^+ and apparently also did not observe the small production of C_3N^+ from CN^+ which proceeds by hydride transfer. Furthermore these authors reported exclusive charge transfer for the reaction of C^+ with HC_3N which is not in agreement with our observations. Charge transfer between HC_3N and the $C^+(^2P)$ ground state is endothermic since the ionization energy of HC_3N (11.60 ± 0.01 eV) is higher than the recombination energy (11.260 eV) of $C^+(^2P)$. Charge transfer with C^+ should therefore not proceed rapidly at room temperature unless it is mostly in the (^4P) excited state. About 5% of the C^+ appeared to be in the (^4P) state in the SIFT experiments reported here and a charge transfer product was observed consistent with this population but the remaining 95% of the C^+ ions was seen to react to build up the carbon chain in the formation of C_3H^+ and C_4N^+.

Proton-transfer reactions with cyanoacetylene have been discussed in detail in a separate study directed towards a determination of the proton affinity of HC_3N (24). A value of 184 ± 4 kcal mol^{-1} was derived from bracketing measurements. Proton transfer was observed to proceed with H_3^+ (101), N_2H^+ (117), HCO^+ (141), $C_2H_3^+$ (153), H_3O^+ (166), and $CH_3NO_2H^+$ (180) but not with the CH_3CNH^+ (187) or $(CH_3)_2COH^+$ (194) where proton affinities are given in parentheses in kcal mol^{-1}. Proton transfer was observed by Freeman *et al.* (6) for H_3^+, N_2H^+, HCO^+, $C_2H_3^+$, and H_3O^+ and the rate constants obtained for these reactions with the two techniques again are in good accord. However, there are serious discrepancies for the reactions of CH_3^+ and $C_2H_2^+$ for which Freeman *et al.* (6) have also reported exclusive proton transfer. For these two ions the SIFT measurements indicate only condensation and association. The proton affinity of CH_2 can be calculated to be 197 kcal mol^{-1} from available thermochemical information (21) and this makes the proton transfer with HC_3N endothermic. The energetics of the proton-transfer reaction between $C_2H_2^+$ and HC_3N is less certain due to the uncertainty in the heat of formation of C_2H (17). Within the uncertainties of PA(C_2H) and PA(HC_3H) the change in enthalpy is -4 ± 9 kcal mol^{-1}. The SIFT measurements did not indicate occurrence of proton transfer which suggests that this channel is in fact endothermic also.

The remaining reactions which were investigated result predominantly in condensation and association and are of interest in chemical synthesis by ion/molecule reactions. Several condensation reactions lead to the buildup of purely carbonaceous ions as in the generation of C_3H^+ from C^+, $C_3H_3^+$ from CH_3^+, and $C_4H_2^+$ from C_2H^+ and $C_2H_2^+$. Others lead to the lengthening of the carbon backbone of the cyanoacetylene as in the formation of C_4N^+ from C^+, C_5N^+ from C_2^+, HC_5N^+ from C_2H^+ and possibly $H_4C_4N^+$ from $CH_3NO_2H^+$. The association reactions which were observed with HC_3N exhibited an interesting range in specific rate. The apparent bimolecular rate constants were generally $\geq 5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} which is close to the collision limit. These are large values and as such are indicative of the formation "tight" adducts in which the bonding is quite strong (25, 26). Strong bonding is not entirely unexpected for the adducts observed. CH_3CNH^+, *i*-$C_3H_7OH_2^+$, and $(CH_3)_2COH^+$ should form proton bound adducts with HC_3N. The proton affinities of CH_3CN, *i*-C_3H_7OH, and $(CH_3)_2CO$ are within 10 kcal mol^{-1} of that for HC_3N. Charge delocalization is possible with $(CH_3)_2COH^+$ as is expressed in the resonance structures [6].

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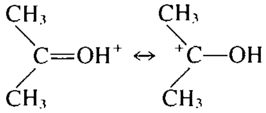
[1] S. I. Miller and J. Berkowitz. Referred to in ref. 22.

[6]


This may result in a weaker proton bond in this case and thus account for the smaller rate constant observed for the formation of $(CH_3)_2COH^+ \cdot HC_3N$.

With C_3H^+ and C_4N^+ and possibly also $C_2H_2^+$ and $C_4H_2^+$ the bonding in the observed adducts is likely to be covalent. The carbene cations C_3H^+ and C_4N^+ should react with HC_3N by C—H σ bond insertion in a manner analogous to the bimolecular insertion reactions already reported for C_3H^+ (8, 27). Sigma bond insertion would lead to the product ions [7] and [8].

$$[7] \quad HC{\equiv}C{-}\overset{+}{C}H{-}C{\equiv}C{-}C{\equiv}N$$

$$[8] \quad N{\equiv}C{-}C{\equiv}C{-}\overset{+}{C}H{-}C{\equiv}C{-}C{\equiv}N$$

Charge delocalization is possible in these two ions and this may account for the observed decrease in the rate of addition of a second molecule of HC_3N. The nature of the bonding in the adducts $C_2H_2^+ \cdot HC_3N$ and $C_4H_2^+ \cdot HC_3N$ is less certain.

In ionized environments such as, for example, dense molecular interstellar clouds, ion/molecule reactions proceed in competition with neutralization reactions. Neutralization may proceed by electron-ion recombination (EIR), charge transfer (CT), or proton transfer (PT) and, when coupled to an ion/molecule reaction leading to bond formation in the ion, may result in the synthesis of a neutral molecule in which the new bond is preserved (23). For example, electron–ion recombination or proton-transfer reactions with the carbonaceous ions C_3H^+, $C_3H_3^+$, and $C_4H_2^+$ may establish the neutral molecules C_3, C_3H_2, and C_4H, and with $H_4C_4N^+$ may establish methylcyanoacetylene. $C_4H_2^+$ may neutralize by charge transfer to form diacetylene while HC_5N^+ may charge transfer to form cyanodiacetylene. The new bond may also be preserved directly in the neutral product of an ion/molecule reaction as in the reaction of C_2N^+ with HC_3N to form C_3H^+ where the neutral product must be C_2N_2.

For the specific case of the molecular cloud TMC-1 the results obtained in this study provide an indication of the possible role of cyanoacetylene in the synthesis of derivative molecules. Efficient routes are available for the synthesis of C_4H and C_4N according to reactions [9] and [10], respectively.

$$[9] \quad C_2H_2^+ \xrightarrow{HC_3N} C_4H_2^+ \xrightarrow[EIR]{PT} C_4H$$

$$[10] \quad C^+ \xrightarrow{HC_3N} C_4N^+ \xrightarrow{CT} C_4N$$

C^+ and $C_2H_2^+$ are attractive ionic precursors in models of interstellar ion chemistry as they react with H_2 only slowly by association (23). CH_3^+ is attractive for the same reason. With cyanoacetylene it yields the propargyl cation which may neutralize to form the carbene $H_2C{=}C{=}C$: as shown in reaction [11].

$$[11] \quad CH_3^+ \xrightarrow{HC_3N} C_3H_3^+ \xrightarrow{PT} C_3H_2$$

The $CH_3^+ \cdot HC_3N$ adduct observed in the laboratory may form in the molecular cloud by radiative association and then neutralize to form methylcyanoacetylene according to reaction [12].

$$[12] \quad CH_3^+ \xrightarrow{HC_3N} CH_3{-}CH{=}\overset{+}{C}{-}CN \xrightarrow[EIR]{PT} CH_3C_2CN$$

Another possible route towards methylcyanoacetylene is reaction [13]

$$[13] \quad CH_3NO_2H^+ \xrightarrow{HC_3N} CH_3{-}CH{=}\overset{+}{C}{-}CN \xrightarrow[EIR]{PT} CH_3C_2CN$$

but this route is less attractive for TMC-1 as CH_3NO_2 has not been identified. Plausible routes are also available for the synthesis of cyanopolyynes. Cyanodiacetylene may be produced directly from C_2H^+ according to reaction [14].

$$[14] \quad C_2H^+ \xrightarrow{HC_3N} HC_5N^+ \xrightarrow{CT} HC_5N$$

Several of the primary product ions allow build up of the cyanopolyynes in secondary reactions. For example, recent measurements of the reaction of C_4N^+ with CH_4 in our laboratory indicate a channel leading the $H_2C_5N^+$ which may neutralize to form cyanodiacethylene. Other intriguing possibilities include the neutralization of the adducts $C_2H_2^+ \cdot HC_3N$ and $C_4H_2^+ \cdot HC_3N$ to form HC_5N and HC_7N, respectively, by elimination of H_2. Also the radiative recombination counterparts of the adduct formation observed in the flow tube for the carbene cations C_3H^+ and C_4N^+ expressed in reactions [15] and [16]

$$[15] \quad C_3H^+ + HC_3N \rightarrow HC{\equiv}C{-}\overset{+}{C}H{-}C{\equiv}C{-}CN + h\nu$$

$$[16] \quad C_4N^+ + HC_3N \rightarrow NC{-}C{\equiv}C{-}\overset{+}{C}H{-}C{\equiv}C{-}CN + h\nu$$

may provide direct routes for the synthesis in the interstellar medium of the large neutral carbenes $:C(C_2H)C_2CN$ and $:C(C_2CN)_2$. These may form on neutralization by proton transfer or electron–ion recombination. They constitute a new class of complex organonitrogen molecules whose presence may provide still further opportunities for molecular growth in the interstellar medium.

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