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New results for ion–molecule reactions of HC_3N in dense interstellar clouds

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Summary. A selected-ion flow tube (SIFT) apparatus has been employed in the measurement of rate constants and product distributions at 296±2 K for the reactions of C^+, CH_3^+ and $C_2H_2^+$ with cyanoacetylene. The results are in disaccord with those obtained previously with the flowing afterglow technique by Freeman *et al.* and, in contrast to the conclusions drawn by these authors, establish a pivotal role for cyanoacetylene in the chemical evolution of interstellar clouds by ion–molecule reactions.

1 Introduction

The identification of cyanoacetylene and many related and larger molecules in several interstellar sources has initiated a quest for chemical paths which lead to their formation. The likelihood that ion chemistry contributes to this molecular synthesis prompted Freeman, Harland & McEwan (1979) to execute a detailed laboratory study of ion–molecule reactions of HC_3N, the results of which were reported in these Notices. Their investigations appeared to show that the positive ion chemistry of this molecule is dominated by charge-transfer or proton-transfer reactions and is thus, by implication, of minor importance to the chemical synthesis of large molecules. We report here a contrary view based on the results of a new investigation of three of the key reactions reported by Freeman *et al.* (1979). Our measurements were made under operating conditions which allowed individual ion–molecule reactions to proceed essentially in isolation and prevented the complications which can arise when these proceed in a plasma mixture of ions as was the case in the work of Freeman *et al.* (1979). The new results point towards an active rather than a passive role for cyanoacetylene in molecular growth by ion–molecule reactions.

2 Experimental

The measurements were done with the Selected-Ion Flow Tube (SIFT) apparatus in the Ion Chemistry Laboratory at York University. With the SIFT technique ions may be generated in a separate source, selected with a quadrupole mass spectrometer, and then injected into a helium or hydrogen carrier gas to which the neutral reactant gas is added downstream. The apparatus and

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technique have been described in detail (Mackay *et al.* 1980; Raksit & Bohme 1983). The technique has the important advantage over the flowing afterglow technique employed by Freeman *et al.* (1979) in that the selected reactions proceed in the flow tube without significant interference from competing ion–molecule reactions involving extraneous ions or the parent gas of the ion of interest. For the measurement reported here C^+ was produced from C_2N_2, CH_3^+ from CH_4, $C_2H_2^+$ from C_2H_2, and C_3H^+ from propylene. The cyanoacetylene was prepared from methyl propiolate (Moureu & Bongrand 1920). Measurements with H_3^+ as the 'chemical ionization' reagent indicated a purity of greater than 99 per cent. All experiments were performed at 296±2 K in helium buffer gas.

3 Results and discussion

The ions C^+, CH_3^+ and $C_2H_2^+$ are all important precursors in interstellar ion chemistry as they react with H_2 only slowly by association (Schiff & Bohme 1976). For the reactions of these ions with cyanoacetylene Freeman *et al.* (1979) reported charge transfer and proton transfer as the only pathways. Our results for these three ions are summarized in Table 1. They indicate that charge transfer and proton transfer do not occur and that the reactions proceed by condensation and association instead. In so doing they provide opportunities for further chemical evolution.

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 should therefore *not* proceed rapidly at room temperature. This was borne out by our measurements. C^+ was seen to react only to build up the carbon chain as indicated in reactions (1a) and (1b).

$$C^+ + HC_3N \rightarrow C_3H^+ + CN \tag{1a}$$

$$\rightarrow C_4N^+ + H \tag{1b}$$

The C_3H^+ product is predominant and is likely to be the carbene cation $:C^+{-}C{\equiv}CH$ whose chemistry we have investigated in detail in a separate study (Raksit & Bohme 1983). The structure of the C_4N^+ product is uncertain as either $CCCCN^+$ or $CCCNC^+$ may be formed depending on the end of the molecule which is attacked but carbene character is also likely to be associated with this ion as in $:C^+{-}C{\equiv}C{-}CN$, for example. Our measurements indicated

Table 1. 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[a]	Observed rate constant[b]
C^+	$C_3H^+ + CN$	0.8	6.1
	$C_4N^+ + H$	0.2	
CH_3^+	$C_3H_3^+ + HCN$	0.6	4.2[c]
	$CH_3^+ \cdot HC_3N$	0.4	
$C_2H_2^+$	$C_4H_2^+ + HCN$	0.5	3.2[c]
	$C_2H_2^+ \cdot HC_3N$	0.5	
C_3H^+	$C_3H^+ \cdot HC_3N$	1.0	1.3[d]
C_4N^+	$C_4N^+ \cdot HC_3N$	1.0	1[c]

[a] The absolute branching ratio may be in error by ±30 per cent.
[b] The accuracy of the rate constant is estimated to be ±30 per cent.
[c] P=0.31 Torr, He concentration=1.0×10^{16} molecules cm^{-3}.
[d] P=0.35 Torr, He concentration=1.1×10^{16} molecules cm^{-3}.

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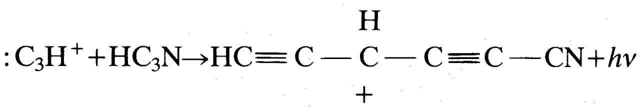
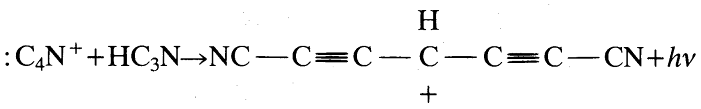
that both C_3H^+ and C_4N^+ react further with HC_3N by rapid association to form the adducts $C_3H^+ \cdot HC_3N$ and $C_4N^+ \cdot HC_3N$. The high rate constants of these association reactions and our previous experience with other C_3H^+ reactions (Bohme, Raksit & Fox 1983) suggest that formation of these adducts involves C—H sigma bond insertion which leads to covalently bonded ions rather than cluster ions which are bound electrostatically. In the interstellar medium additions of this type may proceed by radiative association (Herbst 1976; Smith & Adams 1978: Bates 1983) which is favoured by high association energies and high numbers of nuclei in the complex (Bates 1983). Reactions (2) and (3) can therefore be expected to proceed with relatively high efficiencies.



$$:C_3H^+ + HC_3N \rightarrow HC{\equiv}C-\overset{H}{\underset{+}{C}}-C{\equiv}C-CN + h\nu \tag{2}$$



$$:C_4N^+ + HC_3N \rightarrow NC-C{\equiv}C-\overset{H}{\underset{+}{C}}-C{\equiv}C-CN + h\nu \tag{3}$$

Neutralization of the product ions by proton transfer or electron-ion recombination would then provide a direct route for the synthesis in the interstellar medium of large neutral carbenes such as $:C(C_2H)C_2CN$ and $:C(C_2CN)_2$. Of course $:C_3H^+$ itself may also neutralize by proton transfer or electron/ion recombination to yield the C_3 molecule, presumably the dicarbene $:C{=}C{=}C:$. Our separate investigations of proton transfer reactions of C_3H^+ have established a proton affinity for C_3 of $770 \pm 17\,kJ\,mol^{-1}$ (Raksit & Bohme 1983). C_3H^+ is also a possible progenitor of HC_3O^+ which may yield tricarbon monoxide, $:C{=}C{=}C{=}O$, upon neutralization (Raksit & Bohme 1983). The latter is the newest interstellar molecule which has now been identified (Mathews *et al.* 1984, private communication).

An apparent proton-transfer reaction between CH_3^+ and HC_3N was used by Freeman *et al.* (1979) to set a lower limit to the proton affinity for HC_3N of $824\,kJ\,mol^{-1}$. We have reported elsewhere (Raksit & Bohme 1984) a SIFT investigation of the proton affinity of this molecule in a study of proton-transfer reactions of H_3^+, N_2H^+, HCO^+, $C_2H_3^+$, H_3O^+ and $CH_3NO_2H^+$ with HC_3N and of HC_3NH^+ with CH_3CN and $(CH_3)_2CO$. This study led to a proton affinity for HC_3N of $770 \pm 17\,kJ\,mol^{-1}$ which makes the proton transfer between CH_3^+ and HC_3N endothermic. Proton transfer is therefore not expected to occur at room temperature. Indeed our SIFT experiments indicated that CH_3^+ reacts instead in two other ways as indicated in reactions (4a) and (4b).

$$CH_3^+ + HC_3N \rightarrow C_3H_3^+ + HCN \tag{4a}$$

$$\rightarrow CH_3^+ \cdot HC_3N. \tag{4b}$$

The two product channels may reflect the position of attack on the $H-C{\equiv}C-CN$ molecule. Attack at the carbon alpha to the cyanogen group can lead to HCN elimination with formation of the propargyl cation while attack at the beta carbon is likely to make HCN elimination less favourable and lead preferentially to an adduct which could be the cyanopropenylium ion, $CH_3-CH{=}C^+-CN$. Neutralization of the propargyl cation by proton transfer should yield the carbene $H_2C{=}C{=}C:$ while neutralization of the cyanopropenylium ion may yield methylcyanoacetylene which has also recently been observed in the interstellar medium (Broten *et al.* 1984).

The energetics of the proton-transfer reaction between $C_2H_2^+$ and HC_3N is not known accurately as the known heat of formation of C_2H is quite uncertain (Wyatt & Stafford 1972). Within the uncertainties of $PA(C_2H)$ and $PA(HC_3N)$ the change in enthalpy is -17 ± 37

kJ mol^{-1} so that proton transfer may be exothermic, thermoneutral, or even endothermic. Our SIFT measurements did not indicate occurrence of proton transfer which was identified as the only channel by the earlier flowing afterglow results (Freeman *et al.* 1979). The products observed with the SIFT apparatus indicated carbon-chain lengthening and association instead, in approximately equal amounts, as indicated by reactions (5a) and (5b).

$$C_2H_2^+ + HC_3N \rightarrow C_4H_2^+ + HCN \tag{5a}$$

$$\rightarrow C_2H_2^+ \cdot HC_3N. \tag{5b}$$

The $C_4H_2^+$ product is likely to be ionized diacetylene. In the interstellar medium this ion could lead to diacetylene by charge transfer or the C_4H radical by proton transfer. The latter species has recently been identified in the TMC-1 molecular cloud with an abundance about the same as that of HC_3N (Irvine *et al.* 1981). The nature of the adduct $C_2H_2^+ \cdot HC_3N$ as well as the adduct $C_4H_2^+ \cdot HC_3N$ which was also observed to be formed in a secondary reaction is uncertain, as is the nature of the neutral molecules which may be formed by their neutralization by charge or proton transfer, but there are some intriguing possibilities for formation of long hydrocarbon chain molecules.

4 Conclusions

Cyanoacetylene was observed to be active rather than passive in molecular growth by ion–molecule reactions in contrast to conclusions drawn on the basis of flowing afterglow measurements by Freeman *et al.* (1979). The products identified with the SIFT technique for each of the reactant ions C^+, CH_3^+ and $C_2H_2^+$ are indicative of carbon-chain lengthening reactions with cyanoacetylene. The secondary reactions which were observed indicate that they are also suited for further growth by ion–molecule reactions. A number of the reaction paths which have been tracked appear to be favourable for formation of neutral carbenes and of long-carbon-chain radicals, some of which have recently been identified in the interstellar medium.

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