Growing interstellar cyanopolyacetylenes with ion/molecule reactions

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New and recent results of laboratory measurements are presented which allow an assessment of four ion/molecule reaction schemes which have been proposed for the gas-phase synthesis of interstellar cyanopolyacetylenes. The schemes are scrutinized in terms of the manner of growth of the carbon backbone and the manner in which nitrogen is entrained in the formation of ions of the type $H_2C_{2n+1}N^+$ which may neutralize by proton transfer or electron–ion recombination to form cyanopolyacetylenes.

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On rapporte des résultats nouveaux et récents relatifs à des mesures de laboratoires qui permettent d'évaluer quatre schémas réactionnels ions/molécules qui ont été proposés pour la synthèse en phase gazeuse de cyanopolyacétylènes interstellaires. On a examiné les divers schémas en fonction de la croissance de la chaîne carbonée ainsi que de la façon par laquelle l'azote est entraîné dans la formation d'ions du type $H_2C_{2n+1}N^+$ qui peuvent être neutralisés par un transfert de proton ou par une recombinaison ion/électron conduisant à des cyanopolyacétylènes.

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Introduction

Perhaps the most remarkable aspect of the known chemical composition of the interstellar medium is the abundance of the homologous series of cyanopolyacetylene molecules which have been identified by radioastronomers (1). The higher members of this family of chain-like carbon molecules with terminal cyanogen (CN) substituents are not found naturally on earth, but their rotational transitions have been detected at radio frequencies in all types of molecular clouds in interstellar space as well as in circumstellar envelopes. There is now a need to understand the mechanisms of their formation in these environments. Several synthetic pathways have been suggested. These include the fragmentation of grains or very large molecules (2), catalytic surface reactions (3), and homogeneous gas-phase reactions between ions and molecules. Here we examine the various schemes which have been proposed for the latter pathway of gas-phase synthesis by ion chemistry, many elements of which have been included in detailed modelling studies of interstellar clouds. New and recent results of laboratory measurements are presented which advance our understanding of several of these schemes, allow their assessment, and permit some discrimination between them.

Four ion/molecule reaction schemes will be considered. In all of them formation of the cyanopolyacetylene is achieved ultimately by the neutralization of $H_2C_{2n+1}N^+$ through the electron-ion recombination reaction [1].

[1] $H_2C_{2n+1}N^+ + e \rightarrow HC_{2n+1}N + H$

or by a proton-transfer reaction with a molecule having a proton affinity higher than the cyanopolyacetylene. The schemes differ in the manner of growth of the carbon backbone and the manner in which nitrogen is entrained in the formation of $H_2C_{2n+1}N^+$.

The earliest models put forward by Winnewisser and Walmsley (4) and by Schiff and Bohme (5) allow for the buildup of the cyanopolyacetylenes in two ways. In one scheme (Scheme A) the acetylenic chain is conceived to grow two carbon atoms at a time by reactions between acetylene and its ions and then to be substituted by reaction with HCN or CN as indicated in reactions [2] and [3].

[2] $C_{2n}H_{2,3}^+ + HCN \rightarrow H_2C_{2n+1}N^+ + H, H_2$

[3] $C_{2n}H_{2,3}^+ + CN \rightarrow H_2C_{2n+1}N^+ + h\nu, H$

Alternatively (Scheme B), substitution is achieved first, followed by growth of the carbon backbone by reactions with acetylene ions as in reaction [4].

[4] $C_2H_{2,3}^+ + HC_{2n+1}N \rightarrow H_2C_{2n+3}N^+ + H, H_2$

Growth by one carbon atom at a time is the distinguishing feature of the scheme proposed by Woods (6) (Scheme C). The two essential steps in this scheme are given in reactions [5] and [6].

[5] $C^+ + HC_{2n+1}N \rightarrow C_{2n+2}N^+ + H$

[6] $C_{2n+2}N^+ + CH_4 \rightarrow H_2C_{2n+3}N^+ + H_2$

Finally, several authors (7–9) recently have postulated a mechanism (Scheme D) in which build-up of the carbon chain is followed by reactions with N atoms as in reactions [7] and [10]. Depending on the degree of hydrogenation of the carbonaceous reactant ion, secondary hydrogenation reactions may be required as in reactions [8] and [9] before neutralization can yield the cyanopolyacetylene.

[7] $C_{2n+1}H^+ + N \rightarrow C_{2n+1}N^+ + H$

[8] $C_{2n+1}N^+ + H_2 \rightarrow HC_{2n+1}N^+ + H$

[9] $HC_{2n+1}N^+ + H_2 \rightarrow H_2C_{2n+1}N^+ + H$

[10] $C_{2n+1}H_3^+ + N \rightarrow H_2C_{2n+1}N^+ + H$

Reactions with N atoms are attractive in the chemistry of dark interstellar clouds because of the relatively high abundance of these atoms.

Experimental

Several new reactions were measured as part of this more general evaluation of the gas-phase synthesis of cyanopolyacetylenes by ion chemistry. The measurements were performed with the Selected-Ion Flow Tube (SIFT) apparatus in the Ion Chemistry Laboratory (10, 11). Ions were generated in an axial electron impact ionizer (Extranuclear Model 0413) at ca. 50 eV from the pure parent gas or the parent gas diluted with helium: C^+ (cyanogen), C_3^+ (methylacetylene), C_5^+ (*n*-pentane), $C_4H_2^+$ (diacetylene), and C_4N^+ (allyl cyanide). The ions were injected into helium carrier gas at ca. 10 to 50 V. The total pressure was in the range from 0.30 to 0.35 Torr and the ambient temperature was 296 ± 2 K. The reagent gases and helium carrier gas were of high purity (≥99.5 mol%). Hydrogen cyanide was prepared according to the procedure described by Glemser (12). Rate constants and product distributions were derived in the usual manner (13, 14).

Results and discussion

In this section we provide a detailed and comprehensive assessment of the four ion/molecule reaction schemes which have been advanced for cyanopolyacetylene synthesis. Our new results together with recent results are integrated into the discussion as appropriate. An attempt is made throughout to project the chemistry to higher members of the homologous series for which new measurements are not available.

Series A

Scheme A rests on the likelihood of growing polyacetylene cations. Two obvious routes for the growth of polyacetylene cations involve the sequential addition of C_2 units either directly to the ion as follows:

$$[11]\quad C_2H_{2,3}^{+} \xrightarrow{C_2} C_4H_{2,3}^{+} \xrightarrow{C_2} C_6H_{2,3}^{+} \xrightarrow{C_2} C_8H_{2,3}^{+} \xrightarrow{C_2}$$

or indirectly by repeated reaction with the polyacetylene formed through the neutralization of the polyacetylene cations as follows:

[12]
$$\begin{tikzcd}
C_2H_{2,3}^{+} \arrow[d] & C_4H_{2,3}^{+} \arrow[d] & C_6H_{2,3}^{+} \arrow[d] & C_8H_{2,3}^{+} \arrow[d] & {} \\
C_2H_2 \arrow[ur, "C_2^{+}"] & C_4H_2 \arrow[ur, "C_2^{+}"] & C_6H_2 \arrow[ur, "C_2^{+}"] & C_8H_2 \arrow[ur, "C_2^{+}"] &
\end{tikzcd}$$

Both schemes may also operate with polyatomic carbon units containing an even number of carbon atoms, such as neutral or ionized C_4 or C_6 units. At the low pressures of the interstellar medium the addition of the carbon unit in each step may occur either by radiative association or by condensation as indicated in reactions [13] to [16] for diatomic carbon units:

$$[13]\quad C_{2n}H_{2,3}^{+} + C_2 \rightarrow C_{2n+2}H_{2,3}^{+} + h\nu$$

$$[14]\quad C_{2n}H_{2,3}^{+} + C_2H_{1,2} \rightarrow C_{2n+2}H_{2,3}^{+} + \mathrm{H}, \mathrm{H}_2$$

$$[15]\quad C_{2n}H_2 + C_2H_{0,1}^{+} \rightarrow C_{2n+2}H_{2,3}^{+} + h\nu$$

$$[16]\quad C_{2n}H_2 + C_2H_{2,3}^{+} \rightarrow C_{2n+2}H_{2,3}^{+} + \mathrm{H}, \mathrm{H}_2$$

Only a very few of these reactions have actually been explored in the laboratory. The available measurements provide insight primarily into the kinetics of the initiation steps.

There is no information on the reactions of the acetylenic ions with the molecules C_2 and C_2H, but it is well known that the ions $C_2H_2^{+}$ and $C_2H_3^{+}$ react with acetylene to etablish $C_4H_2^{+}$ and $C_4H_3^{+}$ (15). Figure 1 displays results of SIFT measurements which show how the reaction of $C_2H_2^{+}$ with C_2H_2 establishes $C_4H_2^{+}$ and $C_4H_3^{+}$ as well as the adduct ion $C_4H_4^{+}$. The adduct is likely to be collisionally stabilized at the pressures of the SIFT experiments; it is not observed at low pressures in ICR experiments (15). In contrast, the ions $C_4H_2^{+}$ and $C_4H_3^{+}$ form adduct ions with acetylene under SIFT conditions (16) as well as at the low pressures of the ICR technique (15, 17). There has been one report of a minor channel at low pressures which leads to $C_6H_3^{+}$ from $C_4H_2^{+}$ and C_2H_2 (15). The observation of adducts at low pressures implies the occurrence of radiative association, although both collisional and radiative association have been advanced as the mechanism for the association of $C_4H_2^{+}$ and $C_4H_3^{+}$ with C_2H_2 at low pressures (15, 17).

The reactions of acetylene with $C_2H_2^{+}$ and $C_2H_3^{+}$ also initiate the reaction sequence [12] and it is known that C_2H^{+} reacts rapidly with C_2H_2 to produce $C_4H_2^{+}$ exclusively (15). SIFT measurements have shown that the chain-lengthening reaction of diacetylene with $C_2H_2^{+}$ to form $C_6H_3^{+}$ must compete with a predominant charge transfer channel (16). This may also be the case for reactions of $C_2H_2^{+}$ with higher polyacetylenes as the ionization energy decreases with chain length. For the reactions with $C_2H_3^{+}$ proton transfer will be the competitive channel since the proton affinity of C_2H_2 is expected to be lower than that of the polyacetylenes.

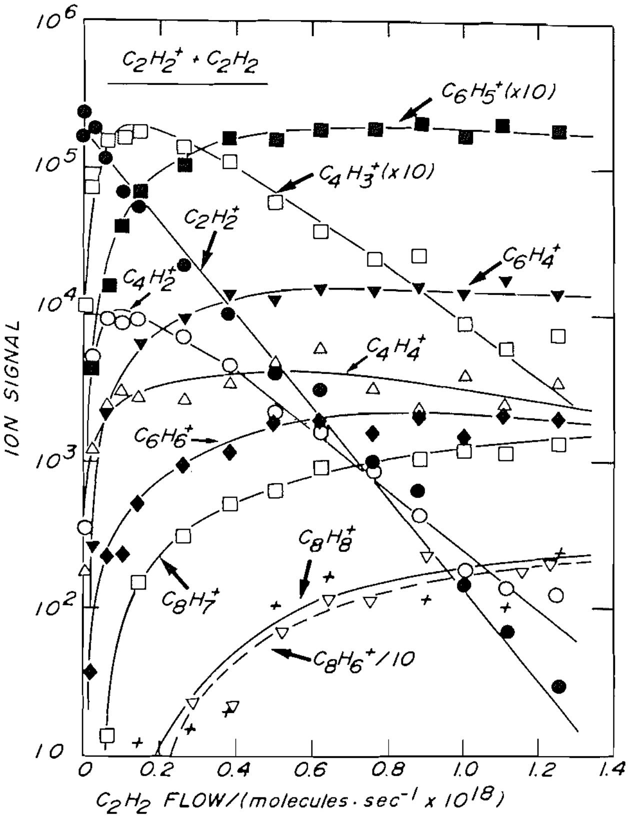

FIG. 1. Observations of the sequential acetylene chemistry initiated by $C_2H_2^{+}$ in the reaction region of a SIFT apparatus. Three steps are seen to lead to the connection of four C_2 units with overall complete retention of acetylenic hydrogen ($C_8H_8^{+}$) and with loss of H ($C_8H_7^{+}$) and H_2 ($C_8H_6^{+}$). The buffer gas is helium. $P = 0.34$ Torr, $\bar{v} = 7.4 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 296$ K. The $C_2H_2^{+}$ is derived from acetylene by electron impact at 20 eV.

Some information is also available for reactions between neutral and ionic C_4 units. Recent SIFT measurements have indicated that the reactions of $C_4H_2^{+}$ and $C_4H_3^{+}$ with diacetylene can establish $C_6H_2^{+}$ and $C_6H_3^{+}$ but that they are dominated by adduct formation, as are the reactions of $C_6H_2^{+}$ and $C_6H_3^{+}$ with diacetylene (16). The situation is different at lower pressures where collisional stabilization is less influential. For the reaction of $C_4H_2^{+}$ with C_4H_2 recent ICR measurements have indicated the formation of the products $C_6H_2^{+}$ (83%), $C_8H_2^{+}$ (17%), and $C_8H_3^{+}$ (1%) (18). Also the reaction of $C_4H_3^{+}$ with acetylene was observed to produce $C_6H_3^{+}$ exclusively (18). Other ICR measurements have shown that the $C_6H_2^{+}$ produced from $C_4H_2^{+}$ and C_4H_2 reacts with diacetylene to produce $C_8H_2^{+}$ and $C_{10}H_2^{+}$ (19). Finally, it has also been shown that C_4H^{+} reacts with diacetylene to produce $C_8H_2^{+}$ exclusively (18).

In summary, the results of laboratory measurements available at this time indicate that polyacetylenic ions are readily generated by sequential reactions involving C_2 or C_4 units. SIFT measurements suggest that collisional association reactions begin to predominate at moderate pressures as the ionic complexity increases, and ICR measurements indicate that ionic growth at the low pressures of interstellar environments may proceed by bimolecular condensation reactions, or possibly radiative association reactions.

For Scheme A to succeed in the ultimate formation of cyanopolyacetylenes, the growth of polyacetylene cations must be followed by the entrainment of CN according to reactions of type [2] and [3]. Experimental observations are unavailable for reactions with CN, but some measurements have been reported for reactions with HCN. ICR measurements (15) indicate a fast reaction of $C_2H_2^+$ with HCN to produce two ions as indicated in reaction [17]:

$$[17]\quad \begin{aligned} C_2H_2^+ + HCN &\xrightarrow{0.65} H_2CN^+ + C_2H \\ &\xrightarrow{0.35} H_2C_3N^+ + H \end{aligned}$$

Both product ions have also been observed in SIFT experiments at a branching ratio of 0.05 each, but the predominant product observed at the higher pressures of the SIFT was the ionic adduct (5). $C_2H_3^+$ was observed with both techniques to react with HCN by proton transfer (11, 15). Recent ICR measurements indicate that both $C_4H_2^+$ and $C_4H_3^+$ do not react rapidly with HCN at low pressures, $k < 2 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ (15). SIFT experiments carried out in this study indicate rapid association in helium at a total pressure of 0.335 Torr and a helium density of 1.1×10^{16} atoms $\mathrm{cm^{-3}}$ at 296 ± 2 K. Reaction [18] was observed to have an effective bimolecular

$$[18]\quad C_4H_2^+ + HCN + He \rightarrow H_3C_5N^+ + He$$

rate constant of $2.2 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ under these conditions. The structure of the adduct ion is uncertain, but it may be a source for neutral cyanodiacetylene if it loses molecular hydrogen upon recombination with electrons. In the interstellar environment the association must proceed radiatively. The upper limit to the rate constant for this reaction determined with the ICR method does not preclude this possibility, and the high rate of collisional association certainly is suggestive of a relatively efficient radiative association.

Scheme B

Scheme B relies on the build-up of the cyanopolyacetylenes by their repeated reaction with the acetylenic ions $C_2H_2^+$ and $C_2H_3^+$ in which the CN substituent is retained. While experiments have shown that this is achieved for one of the first members of the family of reactions, viz. the reaction of HCN with $C_2H_2^+$, it is not for the next higher member. As indicated earlier, ICR and SIFT measurements have shown that HCN reacts with $C_2H_2^+$ to produce some $H_2C_3N^+$ while the $C_2H_3^+$ ion reacts with HCN only by proton transfer. In contrast, recent SIFT experiments in our laboratory indicate that elimination of HCN and association dominate in the reaction of $C_2H_2^+$ with HC_3N for which $k = 3.2 \times 10^{-9}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ (20):

$$[19]\quad \begin{aligned} C_2H_2^+ + HC_3N &\xrightarrow{0.5} C_4H_2^+ + HCN \\ &\xrightarrow{0.5} C_5H_3N^+ \end{aligned}$$

A similar result has been reported recently by Knight *et al.* (21) who suggest that the ionic adduct which must be formed by radiative association at the low pressures of interstellar clouds may yield some HC_5N by electron/ion recombination. $C_2H_3^+$ is known to react with cyanoacetylene only by proton transfer (20, 21).

Scheme C

The scheme proposed by Woods has as its foundation the atomic carbon ion. Growth is achieved by adding single carbon units through sequential reactions with C^+ and methane. No laboratory data were available for the reactions [5] and [6] involving cyanoacetylenes when this scheme was originally conceived by Woods. However, recent SIFT measurements in our laboratory have shown that this scheme is indeed credible. We have shown that C^+ reacts with the first member of the series of cyanopolyacetylenes extremely rapidly, $k = 6.1 \times 10^{-9}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, to produce the C_4N^+ cation 20% of the time as shown in reaction [20] (20):

$$[20]\quad \begin{aligned} C^+ + HC_3N &\xrightarrow{0.8} C_3H^+ + CN \\ &\xrightarrow{0.2} C_4N^+ + H \end{aligned}$$

We report here the results for the subsequent reaction of C_4N^+ with CH_4 which establishes some $H_2C_5N^+$. The latter ion may neutralize to form cyanodiacetylene.

With C^+ as the source ion for C_4N^+, sufficient cyanoacetylene was added into the flow tube of the SIFT apparatus to deplete most of the C^+. The major ion in the flow tube under these conditions was C_3H^+ but addition of methane did provide an assessment of the products of the C_4N^+ reaction since the products of the reaction of C_3H^+ with methane had been characterized previously in our laboratory (10). Experiments performed at low resolution identified product ions at m/z = 51 + 52 ($C_4H_3^+$ or C_3HN^+ and $C_4H_4^+$ or $C_3H_2N^+$), 27 + 28 ($C_2H_3^+$ or CHN^+ and $C_2H_4^+$ or CH_2N^+), and 76 ($C_5H_2N^+$). The rate constant for the decay of C_4N^+ at 296 ± 2 K was determined to be $5.5 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Further experiments were performed to elucidate the product yields by generating C_4N^+ from allyl cyanide by electron impact (22). The observed product ions with their relative yields were as follows:

$$[21]\quad \begin{aligned} C_4N^+ + CH_4 &\xrightarrow{0.35} C_3H_2N^+ + C_2H_2 \\ &\xrightarrow{0.30} C_4H_3^+ + CHN \\ &\xrightarrow{0.25} C_2H_3^+ + C_3HN \\ &\xrightarrow{0.05} CH_2N^+ + C_4H_2 \\ &\xrightarrow{0.05} C_5H_2N^+ + H_2 \end{aligned}$$

The overall rate constant in this case was $5.7 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Experiments with CD_4 excluded $C_4H_4^+$, CHN^+, and $C_2H_4^+$ as possible product ions. C_3HN^+ was shown to contribute less than 5% to the total product ions. The results of one experiment with CD_4 are shown in Fig. 2.

Two pairs of the product ions in reaction [21] are related by intramolecular proton transfer. Thus neutral and protonated cyanoacetylene (or isocyanoacetylene) appear to contribute 60% to the total product ions, while neutral and protonated diacetylene appear to contribute 35%. The remaining 5% of the reaction appears to lead to protonated cyanodiacetylene or an isomer of cyanodiacetylene.

Scheme C presumes similar reactions of C^+ with the higher members of the homologous series of cyanopolyacetylenes and similar reactions of the derivative $C_{2n+2}N^+$ ions with CH_4 as indicated by reactions [5] and [6]. Figure 3 projects the

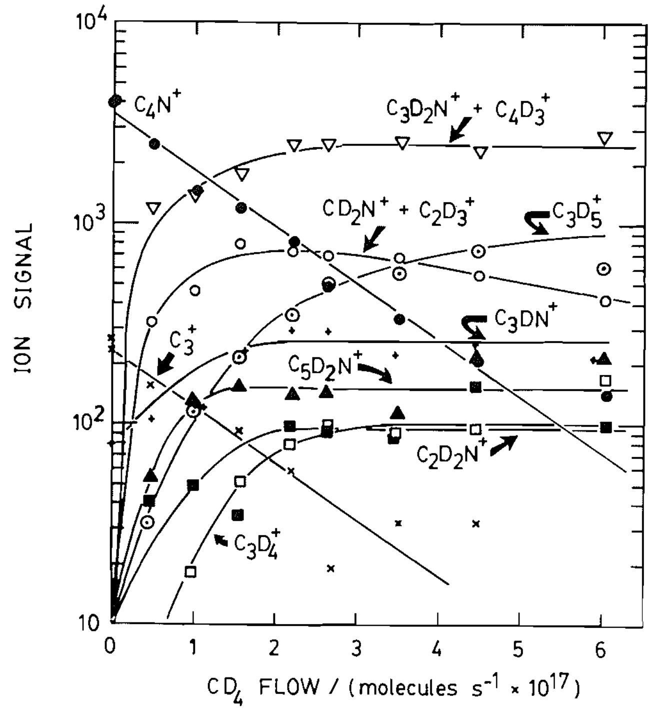

FIG. 2. The variations in ion signals observed for the addition of deuterated methane into the reaction region of the SIFT apparatus in which C_4N^+ is initially established in helium buffer gas. P = 0.35 Torr, $\bar{v} = 6.7 \times 10^3$ cm s^{-1}, L = 46 cm, and T = 294 K. The C_4N^+ is derived from allyl cyanide by electron impact at 55 eV.

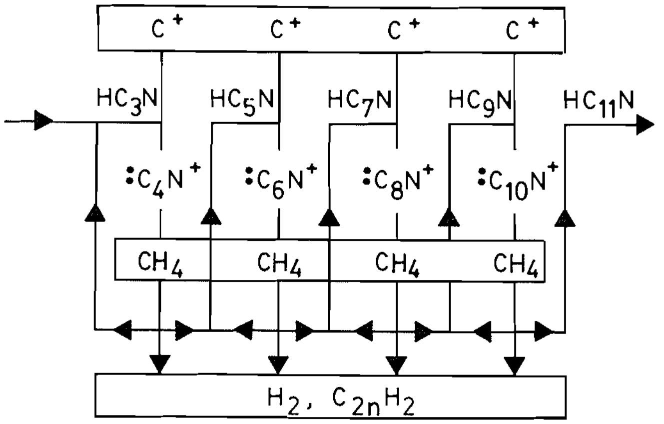

FIG. 3. Hypothetical scheme for the synthesis of cyanopolyacetylenes.

chemistry established in this study for the production of cyanodiacetylene to the production of higher cyanopolyacetylenes. The scheme provides a plausible route to the synthesis of the higher cyanopolyacetylenes. An important feature of this scheme is the chemical feedback of the lower cyanopolyacetylene(s) which may be formed in the reactions of $C_{2n+2}N^+$ with CH_4. In the interstellar chemistry the latter reactions must compete with those involving H_2. In a separate study we have shown that C_4N^+ reacts with H_2 only slowly, $k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K, to produce C_3H^+ (22).

Other reactions of $C_{2n+2}N^+$ which may lead to growth of cyanopolyacetylenes in interstellar chemistry are also possible as is indicated, for example, by reactions [22] and [23]:

[22] $C_{2n+2}N^+ + CH_3 \rightarrow H_2C_{2n+3}N^+ + H$

[23] $C_{2n+2}N^+ + CH_2 \rightarrow H_2C_{2n+3}N^+ + h\nu$

These reactions involve radicals as neutral reactants and would be much more difficult to measure in the laboratory.

Scheme D

The hydrocarbon ions required for reactions [7] and [10] contain an odd number of carbon atoms. There are a number of possible sources for $C_{2n+1}H^+$ ions in the interstellar environment. These include the protonation of odd carbon clusters as illustrated by reaction [24], the hydrogenation of odd carbon ion

[24] $XH^+ + C_{2n+1} \rightarrow C_{2n+1}H^+ + X$

clusters as indicated by reaction [25], or the reactions of C^+

[25] $C_{2n+1}^+ + H_2 \rightarrow C_{2n+1}H^+ + H$

with polyacetylenes as in reaction [26]. Reactions of type [24]

[26] $C^+ + C_{2n}H_2 \rightarrow C_{2n+1}H^+ + H$

have not yet been observed in the laboratory. Also, the proton affinities of neutral carbon clusters are not known. Nevertheless, these reactions are expected to occur in interstellar clouds because of the presence of likely proton donors such as H_3^+, N_2H^+, and CHO^+. Reactions of type [25] have recently been investigated with the SIFT technique. For the reaction of C_3^+ a rate constant of 3.0×10^{-10} cm^{-3} molecule^{-1} s^{-1} has been reported (23). We can report here new results for our observations of the following two deuteration reactions:

[27] $C_3^+ + D_2 \rightarrow C_3D^+ + D$

[28] $C_5^+ + D_2 \rightarrow C_5D^+ + D$

Reactions [27] and [28] were found to have room temperature rate constants of (1.3 ± 0.4) and (5 ± 2) × 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. Reactions of type [26], important in interstellar clouds because of the relatively high abundance of C^+ ions, have been observed with acetylene and diacetylene for which rate constants of 2.2 and 1.5×10^{-9} cm^3 molecule^{-1} s^{-1}, respectively, have been reported (16, 24).

Still another source of C_nH^+ ions has become apparent in a recent study of the chemistry of C_4N^+. This latter ion was observed to react with acetylene and diacetylene to produce C_5H^+ and C_7H^+ respectively through reactions of type [29] (22):

[29] $C_4N^+ + C_{2n+2}H_2 \rightarrow C_{2n+5}H^+ + HCN$

Possible direct sources of $C_{2n+1}H_3^+$ ions which are likely in dense interstellar clouds involve reactions of CH_3^+ with acetylene and polyacetylenes. The kinetics of the reactions with acetylene and diacetylene have now been characterized in the laboratory. The reaction with acetylene produces $C_3H_3^+$ exclusively according to reaction [30] (5):

[30] $CH_3^+ + C_2H_2 \rightarrow C_3H_3^+ + H_2$

while the reaction with diacetylene produces some $C_5H_3^+$ according to reaction [31] (16).

[31] $CH_3^+ + C_4H_2 \xrightarrow{0.9} C_3H_3^+ + C_2H_2$

$\xrightarrow{0.1} C_5H_3^+ + H_2$

There is little experimental information on the reactions of $C_{2n+1}H^+$ and $C_{2n+1}H_3^+$ with N atoms and on the subsequent hydrogenation of the $C_{2n+1}N^+$ ions. Only one member of reactions [7] and [10] has been studied in the laboratory. Recent flow-drift experiments have provided a rate constant of 1.3×10^{-10} cm^{-3} molecule^{-1} s^{-1} for the reaction near thermal energies (0.1 to 0.2 eV) of $C_3H_3^+$ derived by electron impact on C_3H_7Br (25):

$$[32]\quad C_3H_3^+ + N \rightarrow H_2C_3N^+ + H$$

Data for hydrogenation reactions of type [8] is also sparse. SIFT experiments have shown that C_3N^+ rapidly hydrogenates at 300 K according to reaction [33] with a rate constant of 9.1 ×

$$[33]\quad C_3N^+ + H_2 \xrightarrow{0.90} HC_3N^+ + H$$

$$\xrightarrow{0.10} H_2C_3N^+$$

10^{-10} cm^3 $molecule^{-1}$ s^{-1} at ca. 0.3 Torr in helium buffer gas (21). The further hydrogenation of HC_3N^+ is much slower at 300 K and competes with a dissociative channel in the manner expressed by reaction [34] (21, 26):

$$[34]\quad HC_3N^+ + H_2 \xrightarrow{0.5(0.76)} H_2C_3N^+ + H$$

$$\xrightarrow{0.5(0.24)} C_2H_2^+ + HCN$$

Rate constants at 300 K of 1.9 and 7 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} have been reported for this reaction (21, 26). The temperature dependence of this slow reaction is not known but it is conceivable that the rate constant for this reaction increases as the temperature drops in analogy with the reaction of NH_3^+ with H_2 (17).

Conclusions

Some progress has been made in this study and others carried out over the past few years in the characterization of the ion/molecule reactions which constitute the four reaction schemes proposed for the gas-phase synthesis of interstellar cyanopolyacetylenes. Substantial gaps still exist, but there is now sufficient data to allow some discrimination between the four schemes.

The polyacetylenic ions required for Scheme A are readily generated by sequential reactions involving C_2 and C_4 units. But the entrainment of nitrogen through an eventual bimolecular reaction with HCN appears to succeed only with $C_2H_2^+$ and thus only for the formation of cyanoacetylene. The four-carbon ions do not react with HCN in a bimolecular fashion at 300 K; $C_4H_2^+$ was observed to react with HCN in a rapid termolecular association reaction. The success of this scheme must therefore rest on the reactions with CN for which there is no information.

Scheme B relies on the build-up of cyanopolyacetylenes by their repeated reaction with acetylenic ions. However, measurements with cyanoacetylene suggest that this growth may be short-circuited by proton transfer or by elimination of HCN.

Growth by repeated addition of single carbon units to cyanopolyacetylenes through sequential reactions with C^+ ions and CH_n neutrals as described in Scheme C appears to be quite feasible. Results are presented for the critical reaction of C_4N^+ with CH_4 which provides the bridge from cyanoacetylene to cyanodiacetylene. The scheme is projected to higher members of the cyanopolyacetylenes and is attractive especially in view of the chemical feedback that is possible. More information is required for the higher members of the homologous series.

There is still little laboratory evidence for Scheme D in which nitrogen entrainment by slightly hydrogenated hydrocarbon ions occurs through reaction with nitrogen atoms. Nevertheless this route remains an attractive option unless hydrogenation reactions with H_2 are required to build up the hydrogen content before neutralization to form the cyanopolyacetylene. The efficiency of hydrogenation appears variable and unpredictable. New results are presented for the hydrogenation of odd-numbered carbon ions which leads to the slightly hydrogenated hydrocarbon ions which can initiate Scheme D.

Acknowledgment

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