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AN ION-MOLECULE SCHEME FOR THE SYNTHESIS OF HYDROCARBON-CHAIN AND ORGANONITROGEN MOLECULES IN DENSE INTERSTELLAR CLOUDS

H. I. SCHIFF AND D. K. BOHME
Department of Chemistry, York University, Downsview, Ontario, Canada
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ABSTRACT

A general scheme is proposed for the synthesis of large molecules in dense interstellar clouds based on rates of ion-molecule reactions measured in our laboratory and elsewhere. C–C bond formation is dominated by reactions involving the must abundant ions C^+, CH_3^+, $C_2H_2^+$, and $C_2H_3^+$ and the most abundant neutrals C_2H_2 and CH_x, where $1 < x < 4$. As a particular example, we show that the scheme can account for the observation of methylacetylene, methyl cyanide, and the cyanoacetylenes HC_3N, HC_5N, HC_7N, and HC_9N and is consistent with their observed relative abundance. However, the scheme does require high concentrations of C_2H_2 and $C_2H_2^+$ ions to account for the absolute abundances observed.

Subject headings: interstellar: molecules — molecular processes

I. INTRODUCTION

The recent detection of large, complex molecules in dense interstellar clouds has led to various suggestions for their genesis. Breakdown of even larger molecules formed in stellar atmospheres (Hoyle and Wickramasinghe 1977), recombination on interstellar grains (Watson and Salpeter 1972*a*, *b*; Allen and Robinson 1977), and homogeneous ion-molecule reactions (Herbst and Klemperer 1976; Dalgarno and Black 1976; Dalgarno 1976) have been proposed. The observation of CH^+, HCO^+, DCO^+, N_2H^+, and N_2D^+ provides direct evidence that ions play some role in the chemistry of these clouds. The H/D ratios of a number of molecules are most readily explained on the basis of ion-molecule reactions (Watson 1976). The observation of linear molecules containing long chains of unsaturated carbon atoms and the failure to detect branched or cyclic compounds prompted Fertel and Turner (1975) to suggest that ion-molecule reactions play major roles.

In the present paper we propose a general scheme for the synthesis of large molecules based on measurements of the rates of ion-molecule reactions obtained in our laboratory and elsewhere. It is intended to show plausible, but not necessarily exclusive, routes to the formation of observed molecules. As a particular example we show that the scheme can account for the observation of methylacetylene (H_4C_3) and of the cyanoacetylenes HC_3N, HC_5N, HC_7N (Kroto *et al.* 1978; Churchwell, Winnewisser, and Walmsley 1978), and HC_9N (MacLeod 1978), and is consistent with their observed relative abundances, although high concentrations of C_2H_2 and of $C_2H_2^+$ ions are required to account for the absolute abundances.

II. ION-MOLECULE REACTION SCHEME

In this scheme, synthesis of large molecules by ion-molecule reactions involves successive bond formation in the ion followed by eventual neutralization. A given ion may undergo a number of different reactions, the relative probabilities of which are governed by the rate constants and the concentrations of the neutral reactants. For dense clouds, H_2 is a major neutral molecule and hydrogenation reactions of the type

$$C_nH_x^+ + H_2 \rightarrow C_nH_{x+1}^+ + H \qquad (1)$$

will dominate up to particular values of x beyond which the rate constant becomes small for energetic or kinetic reasons. Formation of bonds between heavier atoms (C–C, C–N, etc.) can then build up the hydrocarbon backbone. But bond formation in the ion is, of course, always in competition with neutralization. The relative abundances of the ions and the neutral products are determined by the outcome of this competition.

Neutralization may occur in a number of different ways and can be conveniently classified according to the degree to which the hydrogen content is altered in the process. Dissociative electron-ion combination, the most familiar of the neutralization processes, will decrease the hydrogen content if a C–H bond is broken, e.g.,

$$C_2H_3^+ + e \rightarrow C_2H_2 + H\,. \qquad (2)$$

Proton transfer from the ion to a neutral having a higher proton affinity, e.g.,

$$C_2H_3^+ + NH_3 \rightarrow C_2H_2 + NH_4^+, \qquad (3)$$

where $PA(NH_3) > PA(C_2H_2)$, produces similar results and generally proceeds at the collision rate (Bohme 1975). Charge transfer to species of low ionization potential, particularly to interstellar metal atoms as discussed in some detail by Oppenheimer and Dalgarno (1974),

$$C_2H_2^+ + Fe \rightarrow Fe^+ + C_2H_2\,, \qquad (4)$$

leaves the hydrogen content unchanged, as does radiative recombination. Finally, the ion may hydrogenate

on neutralization through hydride ion transfer of the type

$$C_2H_2^+ + AH \rightarrow C_2H_3 + A^+. \quad (5)$$

In principle larger negative ion fragments (e.g., CH_3^-) could also be transferred, but in practice such processes are seldom observed when other, energetically allowed, neutralization channels are available.

The general scheme is summarized in Figure 1. It starts with C and C^+, which are abundant species in dense clouds. C^+ can form CH_2^+ ions by radiative association with H_2:

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu. \quad (6)$$

The rate constant for this reaction has been calculated to be $10^{-(14\pm1.5)}$ at 90 K (Herbst, Schubert, and Certain 1977).[1] Other processes may be operative in producing CH^+ (Dalgarno 1976), such as proton transfer to C atoms from some protonated species (H_3^+, H_2^+, OH^+, N_2H^+, HCO^+) whose proton affinity is less than that of carbon, e.g.,

$$C + H_3^+ \rightarrow CH^+ + H_2. \quad (7)$$

Hydrogenation by reaction (1) is exothermic for CH^+ and CH_2^+ but is endothermic for CH_3^+. Further hydrogenation of CH_3^+ may occur by radiative association:

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu. \quad (8)$$

Smith and Adams (1978) have estimated that the rate constant for reaction (8) may be as high as 4×10^{-13} at 50 K on the basis of their measurements of the rate of the three-body association of CH_3^+ with H_2. However, the dominant ions containing one carbon atom are expected to be C^+ and CH_3^+. Neutralization of CH_x^+ ions will lead to neutral species containing one carbon atom. CH has been observed in interstellar clouds (Rydbeck, Elldér, and Irvine 1973; Turner and Zuckerman 1974; Robinson *et al.* 1974), as has CH_4 (Fox and Jennings 1978). There may be other routes to the formation of CH_4, such as the reaction

$$H_3^+ + C_2H_2O \rightarrow CH_4 + HCO^+, \quad (9)$$

which we have observed to have a rate constant of 4.7×10^{-9}.

a) C–C *Bond Formation*

The dominant single-carbon ions C^+ and CH_3^+ can react with single-carbon neutrals to produce double-carbon ions

$$C^+ + CH_x \rightarrow C_2H_{x-1}^+ + H \quad (10a)$$

$$\rightarrow C_2H_{x-2}^+ + H_2 \quad (10b)$$

and

$$CH_3^+ + CH_x \rightarrow C_2H_{x+1}^+ + H_2. \quad (11)$$

[1] Throughout this paper, rate constants will be given in units of cm^3 $molecule^{-1}$ s^{-1} for second-order reactions.

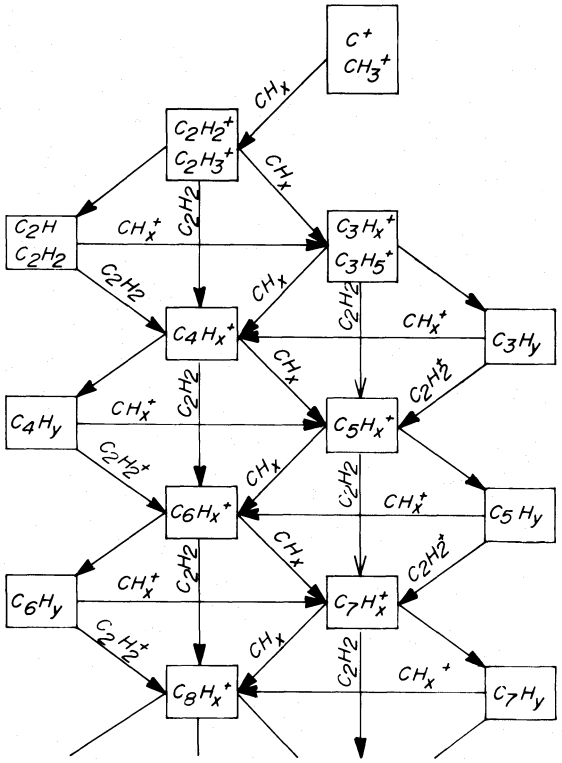

FIG. 1.—Limited scheme for the buildup of the hydrocarbon frame.

The rate constants for these reactions have been measured only with CH_4 and are found to be fast (cf. Table 1). It is likely that the rate constants will also be large for reactions with the free radicals.

Hydrogenation by reaction (1) for C_2^+ and C_2H^+ is fast and leads to $C_2H_2^+$ but is slow for $C_2H_2^+$ and endothermic for $C_2H_3^+$. The major double-carbon ions will then be $C_2H_2^+$ and $C_2H_3^+$ along with $C_2H_4^+$ and $C_2H_5^+$ formed by reaction (11) and for which reaction (1) is also endothermic. The C_2^+ ions can continue to condense with CH_x neutrals by reactions analogous to (11), e.g.,

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 \quad (12)$$

and

$$C_2H_2^+ + CH_4 \rightarrow C_3H_5^+ + H \quad (13a)$$

$$\rightarrow C_3H_4^+ + H_2. \quad (13b)$$

The $C_3H_3^+$ ion is stable toward further hydrogenation. Neutralization of $C_3H_5^+$ by recombination with electrons or charge transfer with $C_3H_4^+$ may produce the observed interstellar molecule, methyl acetylene, H_4C_3.

The hydrocarbon skeleton can continue to build one carbon atom at a time by analogous reactions between $C_nH_x^+$ ions and CH_x neutrals. Alternatively, condensation reactions can occur between C_nH_x neutrals and C^+ and CH_3^+ ions. Radiative recombination of CH_3^+ ions with neutrals may also be important (Smith and

TABLE 1

RATE CONSTANTS

Reaction	Product Distribution			Rate Constant $\times 10^9$ cm^{-3} s
$C^+ + CH_4 \rightarrow C_2H_3^+ + H$	0.71[a]	0.67[b]		1.45,[a] 1.2,[b] 1.6[c]
$\rightarrow C_2H_2^+ + H_2$	0.29[a]	0.33[b]		
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$		...		0.96,[a] 1.2[b]
$C_2^+ + H_2 \rightarrow C_2H^+ + H$		...		1.12,[a] 1.4[b]
$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H$		...		0.78,[a] 1.7[b]
$C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$		...		No reaction,[a] 0.01[b]
$C_2H_2^+ + CH_4 \rightarrow C_3H_5^+ + H$	0.79[a]	0.78[b]	0.80[c]	0.84,[a] 1.0,[b] 0.80[c]
$\rightarrow C_3H_4^+ + H_2$	0.21[a]	0.22[b]	0.2[c]	
$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2$		...		0.22,[a] 0.17,[b] 0.2[c]
$C^+ + C_2H_2 \rightarrow C_3H^+ + H$		...		2.7[c]
$CH_3^+ + C_2H_2 \rightarrow C_3H_3^+ + H_2$		...		1.2,[a] 1[c]
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H$	0.63[a]			1.41[a]
$\rightarrow C_4H_2^+ + H_2$	0.37[a]			
$C_2H_3^+ + C_2H_2 \rightarrow C_4H_3^+ + H_2$		...		0.25,[a] 0.72[c]
$C_3H^+ + C_2H_2 \rightarrow C_5H_2^+ + H$		...		1.3[c]
$C^+ + NH_3 \rightarrow H_2CN^+ + H$	0.47[a]	0.75[b]	0.5 ± 0.2[c]	2.3,[a] 2.3,[b] 2.3[c]
$\rightarrow NH_3^+ + C$	0.50[a]	0.22[b]		
$\rightarrow HCN^+ + H_2$	0.03[a]	0.03[b]		
$CH_3^+ + NH_3 \rightarrow H_4CN^+ + H_2$	0.80[a]	0.70[b]		0.83,[a] 2.2[b]
$\rightarrow NH_4^+ + CH_2$	0.20[a]	0.10[b]		
$\rightarrow CH_3^+ \cdot NH_3$		0.20[b]		...
$CH_3^+ + N \rightarrow H_2CN^+ + H$		...		0.067[d]
$\rightarrow HCN^+ + H_2$		...		
$C^+ + HCN \rightarrow C_2N^+ + H$		...		3.2,[a] 3.5[c]
$CH_3^+ + HCN \rightarrow$ products		...		No reaction[a]
$\xrightarrow{M} CH_3^+ \cdot HCN$	1.0[e]			2.0[e]
$C_2^+ + HCN \rightarrow C_3N^+ + H$		...		2.5[e]
$C_2H^+ + HCN \rightarrow H_2CN^+ + C_2$	0.5[e]			2.5[e]
$\rightarrow C_2H_2^+ + CN$	0.5[e]			
$C_2H_2^+ + HCN \rightarrow H_2C_3N^+ + H$	0.59[a]	~0.05[e]	0.15[f]	0.053,[a] 0.39,[e] 0.71[f]
$\rightarrow H_2CN^+ + C_2H$	0.41[a]	0.05[e]	0.85[f]	
$\xrightarrow{M} C_2H_2^+ \cdot HCN$		0.90[e]		...
$HCN^+ + CH_4 \rightarrow H_2CN^+ + CH_3$	0.84[e]			1.3[e]
$\rightarrow C_2H_3^+ + NH_2$	0.16[e]			
$C_2N^+ + H_2 \rightarrow$ products		...		< 0.0001[e]
$C_2N^+ + CH_4 \rightarrow C_2H_3^+ + HCN$	~0.6[e]			0.0044[e]
$\rightarrow H_2C_3N^+ + H_2$	~0.3[e]			
$\rightarrow H_2CN^+ + C_2H_2$	~0.1[e]			
$C_2N^+ + C_2H_2 \rightarrow C_3H^+ + HCN$	0.9[e]			0.89[e]
$\rightarrow H_2CN^+ + C_3$	0.1[e]			
$C_2N^+ + NH_3 \rightarrow H_2CN^+ + HCN$		...		1.8[e]

NOTE.—Rate constants at 300 K for the total loss of the reactant ion.

[a] Huntress 1977.

[b] Smith and Adams 1977.

[c] Results in this laboratory using the flowing afterglow technique.

[d] Fehsenfeld 1976.

[e] Results in this laboratory using selected ion flow tube (Vlachos *et al.* 1979).

[f] Freeman *et al.* 1978.

Adams 1978) and, if so, can be considered as part of the general scheme represented in Fig. 1.

The backbone can also be built up two carbon atoms at a time by reactions of $C_2H_2^+$ and $C_2H_3^+$ with neutrals or of $C_nH_x^+$ ions with C_2H_2. As mentioned earlier, $C_2H_2^+$ and $C_2H_3^+$ are relatively stable ions. Acetylene, which can be formed by neutralization of these ions, is relatively inert to attack by free radicals or by O and N atoms and should therefore be a relatively abundant neutral species; it has been observed in circumstellar clouds in absorption (Ridgway *et al.* 1976). A number of ion-molecule reactions involving C_2H_2 have been studied in the laboratory and found to be fast, e.g.,

$$C^+ + C_2H_2 \rightarrow C_3H^+ + H_2\,, \quad (14)$$

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H \quad (15a)$$

$$\rightarrow C_4H_2^+ + H_2\,, \quad (15b)$$

$$C_2H_3^+ + C_2H_2 \rightarrow C_4H_3^+ + H_2\,, \quad (16)$$

$$C_3H^+ + C_2H_2 \rightarrow C_5H_2^+ + H\,, \quad (17)$$

$$C_3H_3^+ + C_2H_2 \xrightarrow{M} C_5H_5^+. \quad (18)$$

In principle, condensation reactions can also occur between ions and neutrals, each containing more than two carbon atoms. However, since ion-molecule reactions are always in competition with neutralization, the steady-state abundances of both ions and neutrals will decrease with the number of carbon atoms. Thus C–C bond formation should be dominated by reactions involving either the most abundant ions, C^+, CH_3^+, $C_2H_2^+$, and $C_2H_3^+$, or the most abundant neutrals, CH_x and C_2H_2. These processes are the ones represented in Figure 1.

b) Formation of Organonitrogen Compounds

We will now consider possible routes to some of the nitrogen-containing compounds recently observed, both as examples of the general synthetic scheme discussed above and as an extension of the scheme to heteronuclear bond formation.

An important channel in the reaction of C^+ with NH_3 has been shown to be (cf. Table 1)

$$C^+ + NH_3 \rightarrow H_2CN^+ + H\,. \qquad (19)$$

The same product ion has been observed in the reaction

$$CH_3^+ + N \rightarrow H_2CN^+ + H\,. \qquad (20)$$

Electron recombination of this ion leads to the observed neutral HCN.

The reaction of CH_3^+ with NH_3 has been shown by Smith and Adams (1977) to have three channels:

$$CH_3^+ + NH_3 \longrightarrow H_4CN^+ + H_2 \qquad (21a)$$

$$\longrightarrow NH_4^+ + CH_2 \qquad (21b)$$

$$\xrightarrow{He} CH_3^+ \cdot NH_3\,, \qquad (21c)$$

which have relative probabilities of 7:1:2 at a pressure of 0.2 torr of He. Dissociative recombination of H_4CN^+ probably leads to HCN formation.

The observation of a large three-body channel (reaction [21c]) in their experiment at a pressure of 0.2 torr and room temperature led Smith and Adams (1978) to suggest that the lifetime of the $CH_3^+ \cdot NH_3$ complex might be quite long and that the rate constant for radiative association,

$$CH_3^+ + NH_3 \rightarrow CH_3NH_3^+ + h\nu$$

at 20 K, might be comparable to k_{21a}. Recombination of this ion might produce HCN.

We have found that C^+ reacts rapidly with HCN,

$$C^+ + HCN \rightarrow C_2N^+ + H\,, \qquad (22)$$

and that the reaction of C_2N^+ with H_2 is immeasurably slow. The reaction of C_2N^+ with CH_4 is also slow and has three channels:

$$C_2N^+ + CH_4 \rightarrow C_2H_3^+ + HCN \qquad (23a)$$

$$\rightarrow H_2C_3N^+ + H_2 \qquad (23b)$$

$$\rightarrow H_2CN^+ + C_2H_2\,. \qquad (23c)$$

The reaction leads to the re-formation of HCN by reaction (23a) and by electron recombination of the H_2CN^+ formed in reaction (23c). It is also a source of $C_2H_3^+$ and C_2H_2. Neutralization of $H_2C_3N^+$ formed in reaction (23b) may be a minor source of the observed cyanoacetylene HC_2CN. The low rate constants for these reactions support the conclusion of Hartquist and Dalgarno (1978) that C_2N^+ may be an abundant interstellar ion.

The reaction of C_2N^+ with C_2H_2, however, has a relatively large rate constant and two channels:

$$C_2N^+ + C_2H_2 \rightarrow C_3H^+ + HCN \qquad (24a)$$

$$\rightarrow H_2CN^+ + C_3\,. \qquad (24b)$$

Again, HCN is re-formed and C–C bond formation occurs.

The reaction of C_2N^+ with NH_3 is fast:

$$C_2N^+ + NH_3 \rightarrow H_2CN^+ + HCN\,. \qquad (25)$$

The net result of reactions (22) and (25) is equivalent to reaction (19). Thus reactions of C_2N^+ lead mainly to HCN formation and are not major sources of larger organonitrogen compounds.

HCN formed by any of the above processes may be used as the raw material for synthesis of organonitrogen compounds. Huntress (1977) did not find any reaction between CH_3^+ and NH_3 at a pressure of $\sim 10^{-6}$ torr. At a pressure of ~ 0.5 torr of He we find, however, that the association reaction

$$CH_3^+ + HCN \xrightarrow{M} CH_3^+ \cdot HCN \qquad (26a)$$

occurs with an effective second-order rate constant of 2.0×10^{-9}, which suggests that the radiative recombination counterpart,

$$CH_3^+ + HCN \rightarrow CH_3^+ \cdot HCN + h\nu\,, \qquad (26b)$$

may also have a large rate constant. Electron recombination of the ion could lead to the observed methyl cyanide (CH_3CN) molecule.

The reaction of HCN with $C_2H_2^+$ was found by Huntress (1977) to have a rate constant of 5.3×10^{-11} and two approximately equally probable channels:

$$C_2H_2^+ + HCN \rightarrow H_2C_3N^+ + H \qquad (27a)$$

$$\rightarrow H_2CN^+ + C_2H\,. \qquad (27b)$$

Freeman, Harland, and McEwan (1978), however, report a rate constant of 7.1×10^{-10} and a ratio $k_{27a}/k_{27b} \approx 0.02$. Our results are in much closer agreement with those of Huntress, but we also find that at a He pressure of 0.3 torr the three-body associative channel

$$C_2H_2^+ + HCN \xrightarrow{M} C_2H_2^+ \cdot HCN \qquad (27c)$$

is some 10 times faster than reactions (27a) and (27b). The effective second-order rate constant for the overall reaction at that pressure was found to be 3.9×10^{-10},

which suggests that the radiative recombination counterpart of reaction (27c) might be effective at interstellar temperatures. Neutralization of the ions formed by reactions (27a) and (27c) could produce cyanoacetylene, HC_3N.

At least two routes can be suggested for the formation of successive members of the cyanopolyacetylene series. One involves the addition of HCN to ions of the type $C_nH_{2,3}^+$, where n is an even number,

$$C_nH_2^+ + HCN \rightarrow H_2C_{n+1}N^+ + H, \quad (28a)$$

$$C_nH_3^+ + HCN \rightarrow H_2C_{n+1}N^+ + H_2, \quad (28b)$$

followed by dissociative recombination of the protonated cyanoacetylene. Radiative recombination of these reactants followed by electron recombination of the product ion is, of course, an alternative but can be considered to be part of the same scheme.

The higher hydrocarbon ions are most readily formed by one-step reactions of the type

$$C_nH_2^+ + C_2H_2 \rightarrow C_{n+2}H_2^+ + H_2 \quad (29a)$$

$$\rightarrow C_{n+2}H_3^+ + H \quad (29b)$$

as opposed to the sequential reactions involving CH_x. Reaction (29) has been observed for $C_2H_2^+$ and found to have a rate constant of 1.41×10^{-9}.

This route is summarized in Figure 2, where the competitive steps are as follows: removal of $C_nH_2^+$ by electron-ion recombination or by exothermic reactions with other neutral molecules, X, which lead to products other than cyanoacetylenes. A similar scheme could be invoked involving $C_nH_3^+$ in place of $C_nH_2^+$.

It is possible to derive an approximate expression for the abundance ratio, R, of successive cyanoacetylenes resulting from this scheme. If the rate constants for neutralization of the protonated cyanoacetylenes are approximately equal, then

$$R = \frac{[HC_{n+1}N]}{[HC_{n+3}N]} \approx \frac{[H_2C_{n+1}N^+]}{[H_2C_{n+3}N^+]} \approx \frac{[C_nH_2^+]}{[C_{n+2}H_2^+]}.$$

Under steady-state conditions

$$[C_{n+2}H_2^+] = \frac{k_{29a}[C_2H_2][C_nH_2^+]}{k_x[X] + k_e[e]}.$$

Substitution then gives

$$R = \frac{k_x[X]}{k_{29a}[C_2H_2]} + \frac{k_e[e]}{k_{29a}[C_2H_2]}. \quad (30)$$

The ratio k_e/k_{29a} is of the order of 100. The abundance of electrons is of the order of $10^{-8}n$ (Guélin *et al.* 1977). The abundance of C_2H_2 in dense clouds has not been determined, but for the reasons given above, it is expected to be relatively stable and could well be present in amounts approaching $10^{-6}n$. Thus the second term on the right-hand side of equation (30) could be close to unity. The most abundant neutrals, H_2 and CO, are not included in X since no exothermic two-body reactions are likely with these molecules and

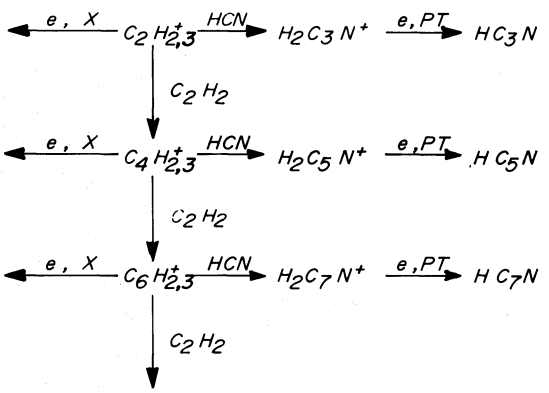

FIG. 2.—Buildup of cyanoacetylenes through C_2H_2

the $C_nH_2^+$ ions. We have found the reaction of $C_2H_2^+$ with H_2O to be immeasurably slow. If reactions with other relatively abundant neutrals such as O and N are also slow, the first term may not make a large contribution. The observed ratios (Churchwell *et al.*; Kroto *et al.* 1978) are estimated to be of the order of 1–4.

The other route for formation of a given cyanoacetylene involves addition of $C_2H_2^+$ or $C_2H_3^+$ to the preceding member of the series:

$$HC_{n+1}N + C_2H_2^+ \rightarrow H_3C_{n+3} + h\nu, \quad (31a)$$

$$HC_{n+1}N + C_2H_2^+ \rightarrow H_2C_{n+3}N^+ + H, \quad (31b)$$

$$HC_{n+1}N + C_2H_3^+ \rightarrow H_2C_{n+3}N^+ + H_2, \quad (31c)$$

as represented in Figure 3. Electron-ion recombination or proton transfer of the product ion leads to formation of the higher cyanoacetylene, while ion-molecule reactions of this ion with other neutrals, Y, which do not proton transfer are the only competitive processes. Reaction (31c) has also been suggested by Churchwell *et al.* Freeman *et al.* report that they did not observe any addition of $C_2H_2^+$ to HC_3N but only rapid proton transfer. This suggests that reactions (31a) and (31b)

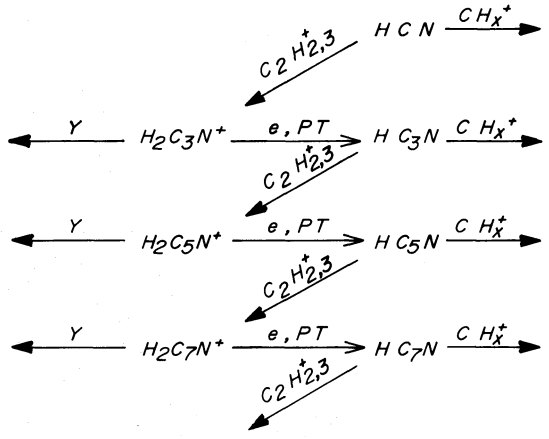

FIG. 3.—Buildup of cyanoacetylenes through $C_2H_2^+$

are unlikely. However, the same authors also find proton transfer to be the major channel for reaction between $C_2H_2^+$ and HCN while we find it to be a minor channel relative to reaction (31a).

Steady-state approximations, similar to those used to derive expression (30), when applied to this scheme give for the abundance ratios of successive cyanoacetylenes

$$R = \left\{1 + \frac{[Y]}{100[e]}\right\}\left\{1 + \frac{[CH_x^+]}{[C_2H_{2,3}^+]}\right\}. \quad (32)$$

The first term in braces should be close to unity. Churchwell *et al.* have estimated that the total number density of the Taurus Molecular Cloud 1, in which they observed HC_3N and HC_5N, is 3×10^4 cm^{-3}. Mitchell *et al.* (1978) have calculated that for these densities $[CH_x^+]/[C_2H_2^+] \approx 1.5$, so that expression (32) would also yield values of R which are consistent with observations. In practice, of course, synthesis of the cyanoacetylenes could involve combinations of both routes. One can also make a crude estimate of the relative abundance of a given cyanoacetylene. For either of the suggested routes, steady-state treatment gives

$$[HC_3N] = \frac{k_e[e][H_{2,3}C_3N^+]}{k_z[Z^+]}$$

and

$$[H_{2,3}C_3N^+] \approx \frac{k_{27}[HCN][C_2H_{2,3}^+]}{k_e[e] + k_y[Y]}.$$

For the reasons given above, $k_e[e] \approx k_y[Y]$. Combination of these equations then gives

$$\frac{[HC_3N]}{[HCN]} = \frac{k_{27}[C_2H_{2,3}^+]}{k_z[Z^+]}.$$

Morris *et al.* (1976) report that in some 17 sources investigated, HC_3N/HCN is within a factor of 10 of unity. Kroto *et al.* (1978) also estimate the ratio to be unity in Sgr B2. Our scheme therefore requires that the abundance of $C_2H_{2,3}^+$ be similar to that of Z^+, i.e., of ions which react with HC_3N at close to classical rates. Although the reactions between HC_3N and the atomic ions He^+, C^+, and S^+ have not yet been studied in the laboratory, there is no *a priori* reason to believe that they will not occur. The model calculations of Mitchell, Ginsburg, and Kuntz (1978) give the ratio of $C_2H_2^+$ to these ions to be about 8×10^{-5} for $n = 10^4$ cm^{-3}. They do not calculate abundances for $C_2H_3^+$. In their model $C_2H_2^+$ is formed only by the reaction of C_2H^+ with H_2. Inspection of Table 1 reveals that reactions of C^+ and CH_3^+ with CH_4 and other CH_x radicals give $C_2H_2^+$ and $C_2H_3^+$ with high efficiency. Mitchell, Huntress, and Prasad (1979) have recently reestimated $CH_4 \approx 3 \times 10^{-6}n$ and $C_2H_2 \approx 1 \times 10^{-6}n$. If electron recombination and reaction with CH_4 and C_2H_2 are the main loss processes for $C_2H_3^+$ and $C_2H_2^+$, then the concentration of these ions can be calculated to be of the order of 10% that of C^+. It should be noted that the cyanoacetylenes are observed in relatively few clouds and even in small regions within a given cloud (Churchwell *et al.*). These regions may well be those in which the densities of $C_2H_2^+$ and $C_2H_3^+$ are particularly high. This in turn implies a high density of C_2H_2, a suggestion also made by Churchwell *et al.*

Undoubtedly there are other routes to the formation of the cyanoacetylenes. Both schemes suggested above could have used CN in place of HCN. Morris *et al.* (1976) have indicated that the CN abundances are similar to those of HCN, so it is doubtful that its inclusion would increase the production of cyanoacetylenes by more than a factor of 2. Mitchell, Huntress, and Prasad (1979) have recently suggested an additional linkage (cf. Fig. 3) between $H_2C_{n+1}N^+$ and $H_2C_{n+3}N^+$ by reaction with acetylene. We are currently attempting to study this reaction in the laboratory.

The above discussion has invoked steady-state assumptions which should be examined in view of the low densities in interstellar clouds. The smaller interstellar molecules (e.g., NH_3, HCN) have concentrations of the order of 10^{-3} cm^{-3}, while large ones such as HC_5N have concentrations of about 10^{-5}. For typical rate constants of 10^{-9} the corresponding reaction times ($1/e$ values) range from 10^4 to 3×10^6 years, which, although large, do not preclude the attainment of steady state within the lifetime of the cloud.

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D. K. BOHME and H. I. SCHIFF: Department of Chemistry, York University, 4700 Keele Street, Downsview, Ontario M3J 1P3, Canada