Ion-molecule reactions with carbon chain molecules: reactions with diacetylene and the diacetylene cation

SEKSAN DHEANDHANOO, LEONARD FORTE, ARNOLD FOX, AND DIETHARD K. BOHME
Department of Chemistry and Centre for Research in Experimental Space Science, York University, Downsview, Ont., Canada M3J 1P3

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Reactions of hydrocarbon and carbon/nitrogen ions with diacetylene and of the diacetylene radical cation with various molecules have been examined with a view to molecular growth by ion–molecule reaction. Measurements were performed with a Selected-Ion Flow Tube (SIFT) apparatus at 296 ± 2 K of the rate constants and product distributions for the reactions of C^+, CH_3^+, $C_2H_2^+$, C_3H^+, CN^+, C_2N^+, and $C_2N_2^+$ with C_4H_2 and of $C_4H_2^+$ with H_2, CO, C_2H_2, C_2N_2, and C_4H_2. Condensation and association reactions which build up the carbon content of the ion were observed to compete with charge transfer. For the reactions of CN^+ and $C_2N_2^+$ with C_4H_2 this growth involved the addition of cyanide to the carbon chain. The kinetics of protonation of diacetylene were also investigated. It was possible to bracket the proton affinity of diacetylene between the known proton affinities of HCN and CH_3OH with a value for $PA(C_4H_2) = 177 \pm 5\,\mathrm{kcal\,mol^{-1}}$, which results in a heat of formation for $C_4H_3^+$ of $305 \pm 5\,\mathrm{kcal\,mol^{-1}}$. Numerous secondary association reactions were observed to form adduct ions in helium buffer gas at total pressures of a few tenths of a Torr with rates near the collision rate. This was the case for $C_6H_4^+$ $(C_4H_2^+.C_2H_2)$, $C_7H_5^+$ $(C_3H_3^+.C_4H_2)$, $C_8H_4^+$ $(C_4H_2^+.C_4H_2)$, $C_8H_5^+$ $(C_4H_3^+.C_4H_2)$, $C_9H_3^+$ $(C_5H^+.C_4H_2)$, $C_9H_4^+$ $(C_5H_2^+.C_4H_2)$, $C_9H_5^+$ $(C_5H_3^+.C_4H_2)$, $C_{10}H_4^+$ $(C_6H_2^+.C_4H_2)$, $C_{10}H_5^+$ $(C_6H_3^+.C_4H_2)$, $C_{11}H_7^+$ $(C_3H_3^+.(C_4H_2)_2)$, $C_{12}H_6^+$ $(C_4H_2^+.(C_4H_2)_2)$, $C_9H_3N^+$ $(HC_5N^+.C_4H_2)$, and $C_{10}H_4N^+$ $(C_2N^+.(C_4H_2)_2)$ where the reactants are indicated in parentheses. The observed high rates of association imply the formation of chemical bonds in the adduct ions but the structures of these ions were not resolved experimentally. In most instances there seems little basis for preferring acyclic over cyclic adduct ions.

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Dans le but d'évaluer la croissance des molécules par des réactions ion–molécule, on a étudié les réactions d'ions hydrocarbonés et d'ions carbone/azote avec le diacétylène ainsi que les réactions du radical cation du diacétylène avec diverses molécules. On a effectué les réactions à 296 ± 2 K et on les a étudiées à l'aide d'un appareil à tube à écoulement à ion choisi; on a mesuré les constantes de vitesse et les distributions de produits pour les réactions du C_4H_2 avec C^+, CH_3^+, $C_2H_2^+$, C_3H^+, CN^+, C_2N^+ et $C_2N_2^+$ et pour les réactions du $C_4H_2^+$ avec H_2, CO, C_2H_2, C_2N_2 et C_4H_2. On a observé que les réactions de condensation et d'association qui provoquent une croissance dans le contenu en carbone de l'ion sont en compétition avec le transfert de charge. Pour les réactions du CN^+ et du $C_2N_2^+$ avec le C_4H_2, cette croissance implique l'addition de cyanure sur la chaîne carbonée. On a aussi étudié la cinétique de la protonation du diacétylène. Il est possible de situer l'affinité protonique du diacétylène entre les affinités protoniques connues du HCN et du CH_3OH et ceci conduit à une valeur de $PA(C_4H_2) = 177 \pm 5\,\mathrm{kcal/mol}$ et à une valeur de la chaleur de formation du $C_4H_3^+$ qui est égale à $305 \pm 5\,\mathrm{kcal/mol}$. On a observé que plusieurs réactions secondaires d'association forment des ions adduits dans un tampon d'hélium à des pressions totales de quelques dixièmes de Torr et avec des vitesses qui sont proches des vitesses de collision. Tel est le cas avec les ions suivants, où l'on a indiqué les réactifs entre parenthèses: $C_6H_4^+$ $(C_4H_2^+.C_2H_2)$, $C_7H_5^+$ $(C_3H_3^+.C_4H_2)$, $C_8H_4^+$ $(C_4H_2^+.C_4H_2)$, $C_8H_5^+$ $(C_4H_3^+.C_4H_2)$, $C_9H_3^+$ $(C_5H^+.C_4H_2)$, $C_9H_4^+$ $(C_5H_2^+.C_4H_2)$, $C_9H_5^+$ $(C_5H_3^+.C_4H_2)$, $C_{10}H_4^+$ $(C_6H_2^+.C_4H_2)$, $C_{10}H_5^+$ $(C_6H_3^+.C_4H_2)$, $C_{11}H_7^+$ $(C_3H_3^+.(C_4H_2)_2)$, $C_{12}H_6^+$ $(C_4H_2^+.(C_4H_2)_2)$, $C_9H_3N^+$ $(HC_5N^+.C_4H_2)$ et $C_{10}H_4N^+$ $(C_2N^+.(C_4H_2)_2)$. Les taux élevés d'association observés impliquent qu'il y a formation de liaisons chimiques dans les ions adduits; toutefois, les structures de ces ions ne sont pas résolues expérimentalement. Dans la plupart des cas, il ne semble pas y avoir de préférence pour des ions adduits linéaires ou cycliques.

[Traduit par la revue]

Introduction

Extended "chain-like" molecules of bonded carbon atoms are formed naturally under a wide range of physical conditions. For example, cyanopolyynes with up to 11 carbon atoms have been identified at the low temperatures and low densities of the interstellar medium (1), while polyacetylenes with at least 12 carbon atoms have been found present at the high temperatures and the high densities of hydrocarbon flames (2). In the presence of ionization the formation and destruction of these chain molecules may involve ions (1, 2) and so it is of interest to establish the rates and products of ion–molecule reactions involving carbon chains. Here we report laboratory studies directed towards the identification and characterization of reactions of ions with diacetylene and reactions of the diacetylene radical cation with various molecules. Neutral and ionized diacetylene can be expected to be early intermediates in the growth of long carbon chain molecules from single carbon units.

Special emphasis is given in this investigation to reactions of diacetylene with the carbonaceous cations C^+, CH_3^+, $C_2H_2^+$, and C_3H^+, which are primal ions in the growth of molecules in the chemistry of interstellar gas clouds (3). Also, several reactions of carbon/nitrogen cations of the type $C_nN_m^+$ with diacetylene and of the diacetylene ion with C_2N_2 have been chosen for study because of their possible role in the chemistry of the ionosphere of Titan (4). Finally, a number of selected proton-transfer reactions have been investigated to estimate the proton affinity of diacetylene, which is useful in the elucidation of the neutralization of protonated diacetylene by proton transfer or electron–ion recombination.

Experimental

All measurements were taken with the Selected-Ion Flow Tube (SIFT) – flowing afterglow apparatus in the Ion Chemistry Laboratory at York University (5, 6). The reagent ions were derived from appropriate 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 ejection energies were in the range 10–20 V. The initial spectrum for the experiments in which $C_4H_2^+$ was the selected ion is

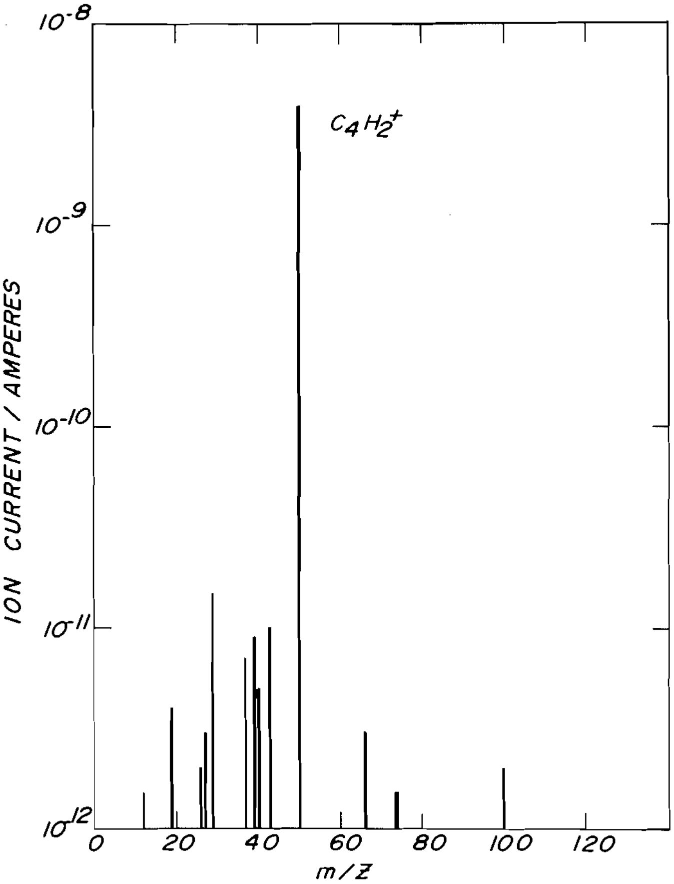

FIG. 1. SIFT spectrum for $C_4H_2^+$ derived from diacetylene (20% in helium) by electron impact at 53 eV. The $C_4H_2^+$ ions are injected at 16 V; the buffer gas is helium at 0.35 Torr. The background spectrum arises in part from collisional dissociation of $C_4H_2^+$ and in part from ion–molecule reactions with water vapour and other impurities in the helium, and with diacetylene leaking through the selection quadrupole.

shown in Fig. 1. Unless otherwise indicated, the individual reagent ions (and impurity ions) were generated in the manner described in a recent study of reactions with cyanoacetylene (7). The carrier gas was either helium or hydrogen. To remove traces of water vapour, the carrier gas was passed through zeolite traps (a 50:50 mixture of Union Carbide molecule sieves 4A and 13X) cooled to liquid nitrogen temperature. The diacetylene was prepared by the alkaline hydrolysis of 1,4-dichlorobut-2-yne (8) and was stored at Dry Ice temperature to avoid polymerization. Experiments with H_3^+ as the "chemical ionization" reagent indicated a purity of greater than 99%. All measurements were taken at an ambient temperature of 296 ± 2 K.

Results

Tables 1 and 2 present summaries of the reaction rate constants and product distributions obtained in this study for reactions of ions with diacetylene. Table 1 gives the results for reactions of carbonaceous ions and nitrogen-containing carbonaceous ions with cyanoacetylene, while Table 2 is restricted to results obtained for the proton-transfer reactions. Table 3 provides a summary for the reactions investigated with the diacetylene cation. Rate constants and product distributions were determined in the usual manner (5, 9). The tables include all of the primary product ions that were observed to contribute more than 5% to the total primary products. The branching ratios have been rounded off to the nearest 5% and are accurate to ±30%. The reaction rate constants are compared with collision rate constants derived with the Langevin theory (10) with an estimated polarizability for diacetylene of 6.0 Å^3 (11). Thermochemical data were taken from the usual sources (12, 13).

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

Reactant ion	Products	Branching ratio	k_{exp}^a	k_c^b
C^+	$C_5H^+ + H$	0.50	2.9	1.84
	$C_4H_2^+ + C$	0.45		
	$C_3H^+ + C_2H$	0.05		
CH_3^+	$C_3H_3^+ + C_2H_2$	0.9	1.3	1.69
	$C_5H_3^+ + H_2$	0.1		
$C_2H_2^+$	$C_4H_2^+ + C_2H_2$	0.9	1.4	1.39
	$C_6H_3^+ + H$	0.1		
C_3H^+	$C_5H_2^+ + C_2H$	0.85	1.2	1.24
	$C_5H^+ + C_2H_2$	0.10		
	$C_4H_2^+ + C_3H$	0.05		
$C_3H_3^+$	$C_3H_3^+.C_4H_2$	1.0	~1	1.23
$C_4H_2^+$	$C_4H_2^+.C_4H_2$	0.9	1.3	1.15
	$C_6H_2^+ + C_2H_2$	0.1		
$C_4H_3^+$	$C_4H_3^+.C_4H_2$	0.9	~1	1.14
	$C_6H_3^+ + C_2H_2$	0.1		
C_5H^+	$C_5H^+.C_4H_2$	1.0	~1	1.09
$C_5H_2^+$	$C_5H_2^+.C_4H_2$	0.4	~1	1.09
	$C_7H_3^+ + C_2H$	0.6		
$C_5H_3^+$	$C_5H_3^+.C_4H_2$	1.0	~1	1.09
$C_6H_2^+$	$C_6H_2^+.C_4H_2$	1.0	~1	1.05
$C_6H_3^+$	$C_6H_3^+.C_4H_2$	1.0	~1	1.05
$C_3H_3^+.C_4H_2$	$C_3H_3^+.(C_4H_2)_2$	1.0	~1	1.01
$C_4H_2^+.C_4H_2$	$C_4H_2^+.(C_4H_2)_2$	1.0	~1	0.99
CN^+	$C_4H_2^+ + CN$	0.75	0.97	1.39
	$HC_5N^+ + H$	0.25		
C_2N^+	$C_5H^+ + HCN$	0.6	1.3	1.23
	$C_4H_2^+ + C_2N$	0.2		
	$C_2N^+.C_4N_2$	0.2		
$C_2N_2^+$	$C_4H_2^+ + C_2N_2$	0.9	1.2	1.14
	$HC_5N^+ + HCN$	0.1		
HC_5N^+	$HC_5N^+.C_4H_2$	1.0	~1	1.05
$C_2N^+.C_4H_2$	$C_2N^+.(C_4H_2)_2$	1.0	~1	1.02

[a] The accuracy of the rate constants is estimated to be better than ±30% unless the rate constant is indicated to be approximate. Only the apparent bimolecular rate constant is given. The measurements were taken at helium pressures in range from 0.27 to 0.37 Torr and helium densities in the range from 9.0 × 10^{15} to 1.2 × 10^{16} atoms cm^{-3}.

[b] Collision rate constants derived from the Langevin theory (10).

He^+/He_2^+

He^+ was derived from helium at 35 eV and injected into helium carrier gas at 0.32 Torr (1 Torr = 133.3 Pa). Approximately 30% conversion of He^+ to He_2^+ was observed downstream. Both ions reacted rapidly with diacetylene to yield a variety of product ions corresponding to charge transfer and dissociative charge transfer. No attempt was made to discern branching ratios for the reactions of the two helium ions. The rate constant for the reaction of He^+ was determined to be 2.7 × 10^{-9} cm^3 molecule^{-1} s^{-1}.

C^+

More than 95% of the C^+ was in the ^2P ground state (7). The C^+ was observed to react rapidly with diacetylene to produce three product ions, as can be seen from Fig. 2. The $C_4H_2^+$ arises from the charge transfer reaction, which is 25 kcal mol^{-1} exothermic. The other major product ion was C_5H^+, which is

TABLE 2. Summary of rate constants (in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}) measured at 296 ± 2 K for proton-transfer reactions with diacetylene

Reactant ion	Product	k_{exp}[a]	k_c[b]
H_3^+	$C_4H_3^+$	2.6	3.4
N_2H^+	$C_4H_3^+$	1.1	1.3
H_3O^+	$C_4H_3^+$	1.1	1.5
H_2CN^+	$C_4H_3^+$	1.4	1.3
$CH_3OH_2^+$	$CH_3OH_2^+.C_4H_2$	0.37[c]	1.3

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

[b] Collision rate constants derived from the Langevin theory (10).

[c] In hydrogen buffer gas at a total pressure of 0.36 Torr and concentration of 1.2×10^{16} molecules cm^{-3}.

TABLE 3. Summary of rate constants and product distributions measured at 296 ± 2 K for reactions with $C_4H_2^+$ derived from diacetylene

Neutral reactant	Products	Product distribution[a]	Rate constant[b]
H_2			≤5 (−13)
CO	$C_4H_2^+.CO$	0.5	1.9(−11)
	$HC_5O^+ + H$	0.5	
C_2H_2	$C_4H_2^+.C_2H_2$	1.0	8.4(−10)
C_4H_2	$C_4H_2^+.C_4H_2$	0.9	1.3(−9)
	$C_6H_2^+ + C_2H_2$	0.1	
C_2N_2	$C_4H_2^+.C_2N_2$	0.98	4.3(−11)
	$HC_5N^+ + HCN$	0.02	

[a] The branching ratio may be in error by as much as ±20%.

[b] Rate constants are expressed as a (−b) to represent $a \times 10^{-b}$. The units are cm^3 $molecule^{-1}$ s^{-1}. The accuracy is estimated to be better than ±30%. All rate constants are effective bimolecular rate constants for the disappearance of $C_4H_2^+$ in helium buffer gas at total pressures in the range from 0.26 to 0.36 Torr and helium concentrations from 8.4×10^{15} to 1.2×10^{16} atoms cm^{-3}.

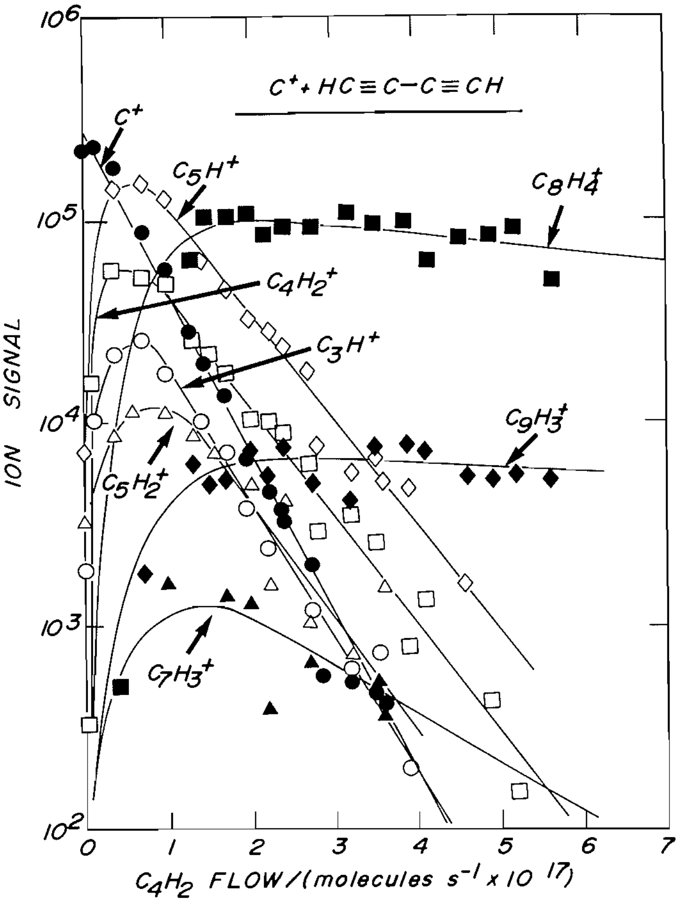

FIG. 2. The varieties in ion signals observed for the addition of diacetylene into the reaction region of the SIFT apparatus in which C^+ is initially established in helium buffer gas. $P = 0.275$ Torr, $\bar{v} = 5.6 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 295$ K. The C^+ is derived from cyanogen (10% in helium) at an electron energy of 60 eV.

probably the carbene cation $HC{\equiv}C\text{-}C{\equiv}C\text{-}C{:}^+$ that may be formed by C—H bond insertion with elimination of a hydrogen atom. Cyclic isomers of C_5H^+ are likely to be less stable. A minor channel of the reaction of C^+ with diacetylene leads to C_3H^+, which is probably the carbene cation $HC{\equiv}C\text{-}C{:}^+$ that may arise by C—C bond insertion with elimination of C_2H. The branching ratios observed for the production of C_3H^+ and C_5H^+ suggest that C—C bond insertion occurs 10 times less frequently than C—H bond insertion. C—H bond insertion can be expected to be more likely since it leads to a secondary carbocation intermediate in which the positive charge can be delocalized, while C—C bond insertion involves a primary carbocation intermediate in which the positive charge is localized.

Figure 2 also shows that secondary reactions were observed for all three primary product ions. The C_5H^+ was observed to rapidly add a molecule of diacetylene according to reaction [1].

[1] $C_5H^+ + C_4H_2 \rightarrow C_9H_3^+$

The structure of the $C_9H_3^+$ product ion is uncertain. However, if the C_5H^+ has carbene character, it can be expected to react with diacetylene by C—H bond insertion to form the acyclic cation $^+CH(C_4H)_2$. The high specific rate of association is consistent with such chemical bond formation in the adduct, as is the failure to observe rapid addition of a second molecule of diacetylene. The secondary reactions of $C_4H_2^+$ and C_3H^+ were similar to those observed in separate experiments, described later in the text, in which these ions were prepared directly in the electron impact source.

CH_3^+

Charge transfer is slightly (7 kcal mol^{-1}) endothermic in this case and was not observed. Figure 3 shows that the major product ion was $C_3H_3^+$ and that $C_5H_3^+$ was a minor product. The secondary reactions [2] to [4]

[2] $C_3H_3^+ + C_4H_2 \rightarrow C_7H_5^+$

[3] $C_7H_5^+ + C_4H_2 \rightarrow C_{11}H_7^+$

[4] $C_5H_3^+ + C_4H_2 \rightarrow C_9H_5^+$

were also observed to occur. They all involve the addition of diacetylene. The fast secondary reaction of $C_3H_3^+$ with diacetylene provides insight into the structure of this ion. Available thermochemical data indicate that the reaction of CH_3^+ with diacetylene may produce either the linear (propargyl) or the cyclic (cyclopropenium) isomer of $C_3H_3^+$. The ICR (ion cyclotron resonance) measurements of Smyth *et al.* (14) at low pressure have shown that only the linear isomer reacts with diacetylene. Our observation of the secondary reaction of $C_3H_3^+$ therefore implies that the reaction of CH_3^+ with diacetylene predominantly forms the linear isomer of $C_3H_3^+$. In the case of the formation of the minor $C_5H_3^+$ product ion, there is no basis for preferring an acyclic isomer (e.g.

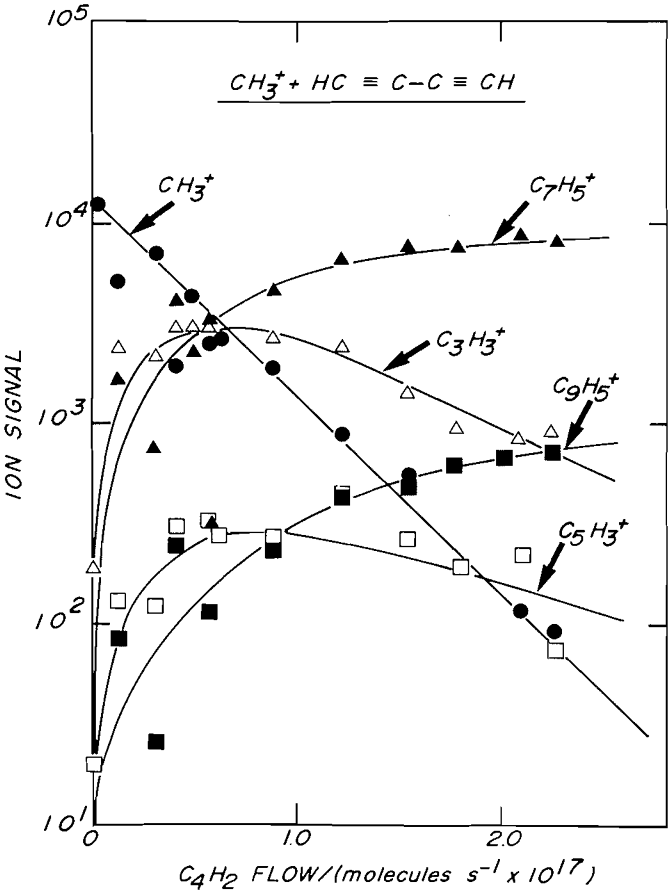

FIG. 3. The variations in ion signals observed for the addition of diacetylene into the reaction region of the SIFT apparatus in which CH_3^+ is initially established in helium buffer gas. $P = 0.335$ Torr, $\bar{v} = 5.3 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 293$ K. The CH_3^+ is derived from pure methane at an electron energy of 23 eV.

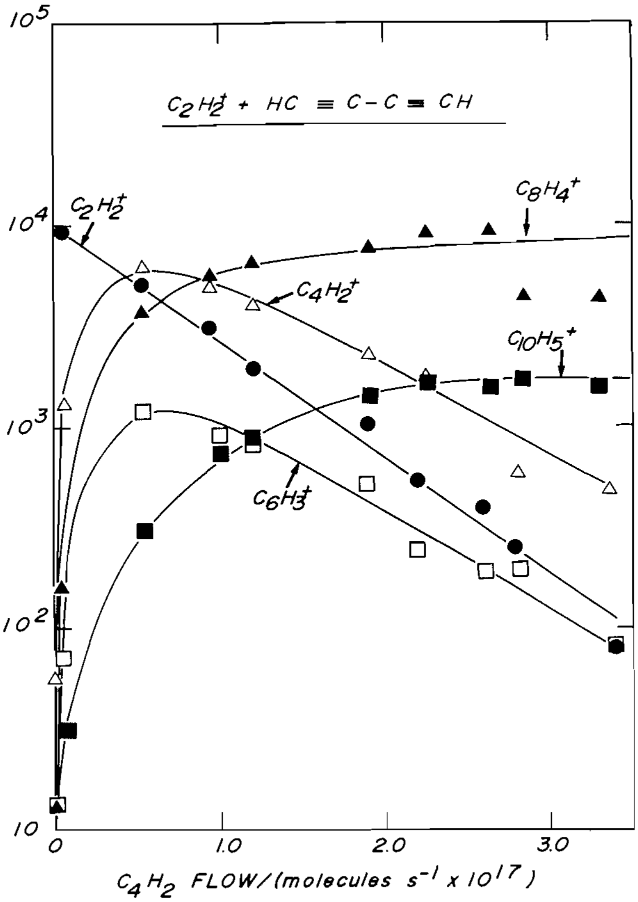

FIG. 4. The variations in ion signals observed for the addition of diacetylene into the reaction region of the SIFT apparatus in which $C_2H_2^+$ is initially established in helium buffer gas. $P = 0.372$ Torr, $\bar{v} = 6.7 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 295$ K. The $C_2H_2^+$ is derived from pure acetylene at an electron energy of 35 eV.

$^+CH_2$-C≡C-C≡CH) over a cyclic isomer (e.g. a C_2H substituted cyclopropenium ion), except perhaps by analogy with the preferred production of the linear propargyl isomer of $C_3H_3^+$.

The structures of the diacetylene adduct ions produced by reactions [2]–[4] are also not known. However, the high specific rates for their formation again imply formation of strong chemical bonds. A possible and interesting cyclic isomer of the $C_7H_5^+$ ion formed in reaction [2] is the phenyl carbene cation, $C_6H_5C{:}^+$. This carbene cation may add a second molecule of diacetylene, as in reaction [3], by C—H bond insertion to yield $^+CHC_4H(C_6H_5)$, a possible cyclic isomer of $C_{11}H_7^+$. Finally, the $C_9H_5^+$ ion formed in reaction [4] may also have a cyclic structure. One possibility is the formation of c-$C_5H_4(C_4H)^+$.

$C_2H_2^+$

Charge transfer was observed to be the main product channel for this reaction but there was a significant (10%) channel leading to carbon-chain lengthening with elimination of H in the formation of $C_6H_3^+$, which presumably is protonated triacetylene. This is evident in Fig. 4. Also, both product ions were seen to rapidly react further with diacetylene. The $C_6H_3^+$ responded to diacetylene with the addition reaction [5]. The

[5] $C_6H_3^+ + C_4H_2 \rightarrow C_{10}H_5^+$

resulting $C_{10}H_5^+$ is likely to be a proton-bound adduct of diacetylene and triacetylene but cyclic isomers again cannot be ruled out. The $C_4H_2^+$ responded to diacetylene in the manner indicated later in the text for the separate study of this reaction.

C_3H^+

The C_3H^+ carbene cation was observed to react with diacetylene primarily by condensation with elimination of C_2H or C_2H_2 leading to carbon-chain lengthening in the ion. Charge transfer appeared as only a minor channel. The predominant $C_5H_2^+$ product ion may result from C—H bond insertion with loss of C_2H and formation of HC≡C—CH=C=C$^{\cdot+}$ or from C—C bond insertion with loss of C_2H and formation of the radical cation $^\cdot C^+(C{\equiv}CH)_2$. The C_5H^+ formed by elimination of C_2H_2 is likely to be the carbene cation HC≡C—C≡C—C:$^+$. All three product ions were observed to react further. The C_5H^+ responded according to reaction [1] and the $C_4H_2^+$ reacted in the manner described later in the text. The $C_5H_2^+$ radical cation appeared to react further by addition and by condensation with elimination of C_2H in the following manner:

[6*a*] $C_5H_2^+ + C_4H_2 \rightarrow C_9H_4^+$

[6*b*] $\rightarrow C_7H_3^+ + C_2H$

In this case C—H insertion could lead to the acyclic radical cation HC≡C—CH=C=CH—C$^\cdot$=C$^+$—C≡CH, which may lose C_2H to form the carbon-chain cation HC≡C—CH=C=CH—C≡C$^+$.

$C_4H_2^+$

Ionized acetylene was reacted with carbon monoxide, acetylene, diacetylene, and cyanogen. No reaction was observed with hydrogen. Charge transfer and hydrogen atom transfer are endothermic with this molecule. Available heats of formation indicate that formation of the adduct ion $C_4H_4^+$ may be exothermic and that several isomers of $C_4H_4^+$ are possible, but it is not clear which one might be preferred. In any case, the very low upper limit to the rate constant for this reaction suggests that formation of the adduct involves a positive activation energy.

A slow reaction was observed with carbon monoxide. Approximately equal amounts were produced of the adduct ion $C_4H_2^+.CO$ and the condensation product HC_5O^+, which involves elimination of H. No further reaction with CO was noticed with either product.

Acetylene was observed to add to $C_4H_2^+$ with a rate constant close to the collision limit but addition of a second molecule of acetylene was not rapid. It is not known whether the failure to add a second molecule of acetylene is indicative of the formation in the initial addition reaction of a cyclic product ion such as ionized benzyne, or an acylic product ion such as ionized 3-hexene-1,5-diyne, but both types of product are possible.

Addition was also the major channel with diacetylene, although in this case about 10% of the reaction led to the elimination of acetylene with formation of what may be ionized triacetylene. Again the measured rate constant for the loss of $C_4H_2^+$ is close to the collision limit. Results are shown in Fig. 5. The $C_6H_2^+$ is seen also to add a molecule of diacetylene but addition of a second molecule of diacetylene appears to be relatively unfavourable for both adduct ions in the product spectrum.

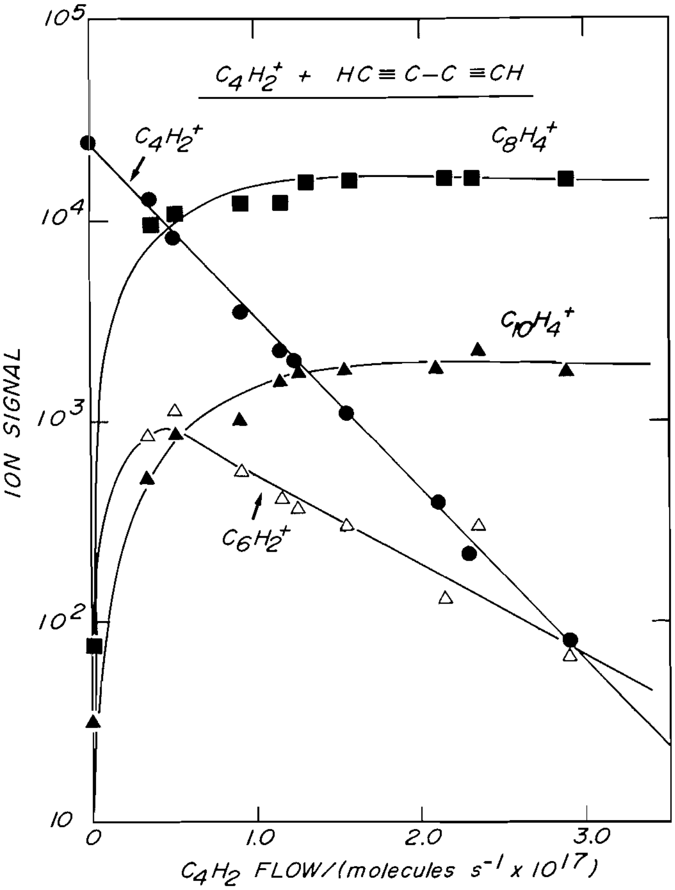

FIG. 5. The variations in ion signals observed for the addition of diacetylene into the reaction region of the SIFT apparatus in which the diacetylene radical cation is initially established in helium buffer gas. $P = 0.259$ Torr, $\bar{v} = 5.3 \times 10^3$ cm s^{-1}, $L = 45$ cm, and $T = 297$ K. The $C_2H_2^+$ is derived from diacetylene (10% in helium) at an electron energy of 35 eV.

The primary product distribution observed for the reaction of $C_4H_2^+$ with C_4H_2 differs from that measured at lower pressures with an ICR (15), which indicates loss of C_2H_2 (83%), H_2 (17%), and H (1%) without any adduct formation. One cause of this difference may be the collisional stabilization of reactant and adduct ions, which proceeds at the moderate pressures of the SIFT experiments and which will be essentially absent in the ICR experiments. Observations that are consistent with such an interpretation have been made very recently in an ICR – high pressure mass spectrometer study (16). Loss from the adduct ion of both acetylene and hydrogen was noted in ICR experiments at ~5 × 10^{-6} Torr, but the loss of H_2 was observed to be entirely quenched in mass spectrometer experiments at pressures above ~0.01 Torr. Furthermore, the $C_6H_2^+$ produced by the reaction of $C_5H_2^+$ with C_4H_2 was seen to react further with C_4H_2, under ICR conditions, to produce $C_8H_2^+$ and $C_{10}H_2^+$ by elimination from the adduct ion of C_2H_2 and H_2, respectively. In contrast, all the adduct ions were observed to be stabilized in the high pressure mass spectrometer.

There is good agreement between the SIFT and ICR results on the rate constants for the loss of $C_4H_2^+$ and $C_6H_2^+$ in their reactions with C_4H_2. In the case of $C_4H_2^+$ the SIFT rate constant of $(1.3 \pm 0.4) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} is the same, within experimental error, as the ICR rate constants of 1.4×10^{-9} cm^3 $molecule^{-1}$ s^{-1} (15) and $(1.39 \pm 0.5) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} (16). Also, for the reaction of $C_6H_2^+$ with C_4H_2, the ICR rate constant of $(1.06 \pm 0.4) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} is the same as the value of 1×10^{-9} cm^3 $molecule^{-1}$ s^{-1} estimated from the SIFT results.

It is of interest to consider briefly the possible structures of the highly unsaturated hydrocarbon ions $C_8H_4^+$ and $C_{10}H_4^+$ produced in the addition reactions of $C_4H_2^+$ and $C_6H_2^+$ with C_4H_2. Carbon-chain isomers may be achieved by the addition of the C—H bond of one reagent across the triple bond of the other. The $C_8H_4^+$ isomer produced in this way would be $HC\equiv C—C\equiv C—CH=CH—C\equiv CH^+$, while $HC\equiv C—C\equiv C—CH=CH—C\equiv C—C\equiv CH^+$ would be a possible $C_{10}H_{4+}$ chain isomer. Formation of carbon-ring isomers can also be imagined. For example, $C_8H_4^+$ may have a cyclic structure with two alternating triple and double bonds while the analogous cyclic $C_{10}H_4^+$ structure would have an additional triple bond. Possible structures of $C_{2n}H_n^+$ and $C_{2n+2}H_n^+$ ions in general have been considered in more detail by Buckley *et al.* (16), who have observed sequential addition of diacetylene up to the formation of $C_{20}H_{10}^+$ and $C_{18}H_8^+$, respectively. Furthermore, these authors have identified reactivity patterns that suggest that the sequence initiated by $C_4H_2^+$ involves production of both cyclic and acyclic ions, with the latter being unreactive and increasingly preferred as the ion grows.

Adduct formation was also predominant in the SIFT experiments for the reaction of $C_4H_2^+$ with cyanogen, but there was also an indication of a minor channel (2%) leading to elimination of HCN and production of what is likely to be ionized cyano- or isocyanodiacetylene. Both product ions did not appear to rapidly react further with cyanogen. The specific rate for the addition of cyanogen to $C_4H_2^+$ is relatively low, so that the adduct ion may not involve chemical bond formation in this case. The ion HC(CN)=C(CN)—C≡CH$^+$ would be one possible chemically bound adduct.

CN^+

The CN^+ ion was observed to react with diacetylene predominantly by charge transfer and by H atom elimination to form what is likely to be ionized cyanodiacetylene. The nature of these reaction channels and the measured branching ratios is very similar to those we have determined previously for the reaction of CN^+ with acetylene (17). Both product ions were observed to rapidly react further with diacetylene in the manner described earlier in the text in the case of $C_4H_2^+$, and by addition in the case of HC_5N^+ to form $HC_5N^+.C_4H_2$. The possible structures of the latter adduct are likely to be analogous to those discussed earlier for the $C_4H_2^+.C_4H_2$ adduct ion.

C_2N^+

The C_2N^+ was derived by electron impact at 60–80 eV from a 10% mixture of cyanogen in helium and exhibited only a single reactivity towards diacetylene (7). Product channels were observed corresponding to charge transfer, formation of C_5H^+, and adduct formation. Formation of C_5H^+ with elimination of HCN was the preferred channel. Since C_2N^+ may have carbene character, it seems likely that the formation of the adduct involves C—H bond insertion. Thus N≡C—CH$^+$—C≡C—C≡CH is a plausible intermediate, most of which eliminates HCN to form C_5H^+ and some of which is stabilized by collision to produce the $C_6H_2N^+$ product. Figure 6 shows that all three primary product ions add a molecule of diacetylene in rapid secondary reactions. The addition reactions with $C_4H_2^+$ and C_5H^+ have already been discussed, while the addition reaction with $C_6H_2N^+$ may proceed in analogy with the addition reaction of $C_5H_3^+$ noted earlier in the text.

$C_2N_2^+$

The $C_2N_2^+$ derived from cyanogen by electron impact was observed to react primarily by charge transfer. A minor channel was observed to lead to what is presumably ionized cyanodiacetylene. The observed secondary reactions of $C_4H_2^+$ and HC_5N^+ with diacetylene were as those described earlier in the text.

H_3^+, N_2H^+, H_3O^+, H_2CN^+, $CH_3OH_2^+$

Except for $CH_3OH_2^+$, these ions all reacted rapidly with diacetylene by proton transfer with rate constants close to the collision limit. The results are summarized in Table 2. The $CH_3OH_2^+$ was observed to react only by addition but with a high effective bimolecular rate constant. The high efficiency implies that the adduct is strongly bound, presumably by the proton. The secondary ion chemistry in helium buffer gas indicated a further rapid reaction of the $C_4H_3^+$ proton transfer product with diacetylene. The main channel of this secondary reaction was observed to correspond to addition to form $C_8H_5^+$ but a significant competing channel, about 10%, led to the formation of $C_6H_3^+$ as indicated in reaction [7].

[7*a*] $C_4H_3^+ + C_4H_2 \rightarrow C_8H_5^+$

[7*b*] $\rightarrow C_6H_3^+ + C_2H_2$

The $C_8H_5^+$ adduct may be the proton-bound diacetylene dimer but cyclic isomers are also possible, such as, for example, $C_6H_5C_2^+$. Complications arose in the secondary ion chemistry from the presence of hydrogen, which was added in the helium buffer gas experiments to generate the primary ions. Reactions with hydrogen became dominant in hydrogen buffer gas. They led to ions with m/z = 103 and 79 and the reactions are believed to be as indicated in [8] and [9].

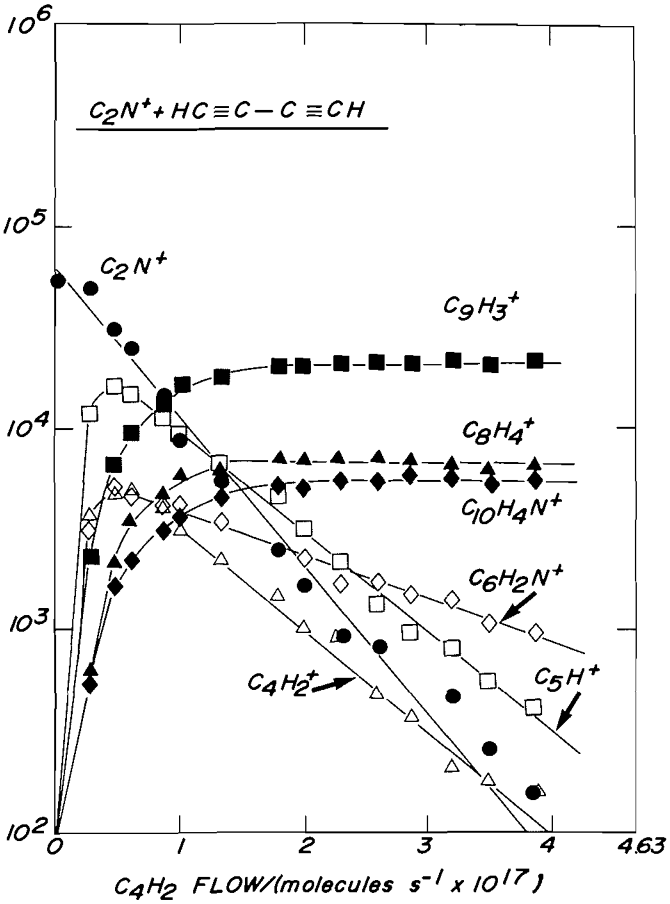

FIG. 6. The variations in ion signals observed for the addition of diacetylene into the reaction region of the SIFT apparatus in which C_2N^+ is initially established in helium buffer gas. P = 0.296 Torr, $\bar{v}$ = 5.8 × 10^3 cm s^{-1}, L = 46 cm, and T = 296 K. The C_2N^+ is derived from pure cyanogen at an electron energy of 80 eV.

[8] $C_8H_5^+ + H_2 \rightarrow C_8H_7^+$

[9] $C_8H_7^+ + H_2 \rightarrow C_6H_7^+ + C_2H_2$

Discussion

Diacetylene was found to be reactive towards all of the carbonaceous and carbon/nitrogen cations chosen for study. Aside from charge transfer, the predominant reaction channels observed correspond to condensation and association, both of which are suited for molecular growth by ion–molecule reactions. Condensation results when the adduct of the reacting ion and molecule dissociates into products before it is stabilized, while association refers to the process in which the adduct is stabilized by collision with a third molecule or by loss of radiation before separation into reactants or products.

Charge transfer was often an exothermic option because the ionization energy of diacetylene, 10.180 ± 0.003 eV, is relatively low in the range of the recombination energies of the selected reagent ions. Indeed, charge transfer was an observed product channel for all the primary ions with a recombination energy known to be larger than the ionization energy of diacetylene, including He^+ (24.6), CN^+ (14.5), $C_2N_2^+$ (13.374),

C_2N^+ (~13), $C_2H_2^+$ (11.41), C^+ (11.260), and C_3H^+ (10.35 ± 0.15) where the recombination energy is given in parentheses in eV (13, 6). The recombination energy of C_2N^+ is not well established. We can improve on the available approximate value by coupling the observation of charge transfer with diacetylene (ionization energy, IE = 10.180 eV) with the failure to observe charge transfer with cyanoacetylene (IE = 11.60 eV). These results imply a recombination energy of 10.9 ± 0.7 eV for the C_2N^+ generated in our experiments from cyanogen by electron impact. CH_3^+ was observed not to charge transfer. It is the only one of the selected ions with a recombination energy (9.842 eV) known to be smaller than ionization energy of diacetylene.

A number of the reaction channels observed to compete with charge transfer are of the condensation type leading to the lengthening of, or the addition of cyanide to the diacetylene carbon chain. Thus C_5H^+, $C_5H_2^+$, and $C_5H_3^+$ were produced from the reactions of C^+, C_3H^+, and CH_3^+ with diacetylene, respectively, and $C_6H_2^+$ and $C_6H_3^+$ were produced from $C_4H_2^+$ and $C_4H_3^+$, respectively. Both CN^+ and $C_2N_2^+$ were observed to produce HC_5N^+, which is presumably ionized cyano- or isocyanodiacetylene. In contrast, C_2N^+ reacted to produce C_5H^+ and thus to effect carbon-chain lengthening without cyanide addition. The most effective chain builders were C_3H^+, C_2N^+, and C^+.

The synthesis of molecules in an ionized environment by means of ion–molecule reactions requires the neutralization of the product ion as a final step. The neutralization may proceed in a number of different ways including electron–ion recombination (EIR), proton transfer (PT), or charge transfer (CT). Thus the carbonaceous neutrals C_5, C_5H, C_5H_2, and C_5H_3 may be derived from C_5H^+, $C_5H_2^+$, and $C_5H_3^+$ as, for example, in reactions [10] and [11]. However, these neutralization steps generally have not been studied in the laboratory and little is known about the relevant recombination energies or proton affinities. The $C_6H_2^+$ and $C_6H_3^+$ ions derived from the reactions of ionized and protonated diacetylene with diacetylene are likely to be ionized and protonated triacetylene, respectively, which may form neutral triacetylene by charge transfer and proton transfer, respectively. The reactions of CN^+ and $C_2N_2^+$ with diacetylene both produce some HC_5N^+ and so are potential sources of cyano- and isocyanodiacetylene, but other isomers are possible. It is interesting to note that under the SIFT conditions the HC_5N^+ was observed to react with diacetylene primarily to form the adduct, even though charge transfer is also exothermic if HC_5N^+ is ionized cyanodiacetylene.

$$[10] \quad C^+ \xrightarrow{C_4H_2} C_5H^+ \xrightarrow[\text{EIR}]{\text{PT}} :C{=}C{=}C{=}C{=}C:$$

$$[11] \quad CH_3^+ \xrightarrow{C_4H_2} C_5H_3^+ \xrightarrow{\text{CT}} H_2C{=}C{=}C{=}C{=}\dot{C}H$$

Addition reactions were observed to be quite common, especially as secondary reactions, and several were observed to compete effectively with exothermic dissociation channels. Thus $C_3H_3^+$, C_5H^+, $C_5H_3^+$, $C_6H_2^+$, $C_6H_3^+$, and HC_5N^+ appeared to react with diacetylene to form stabilized adduct ions exclusively. In contrast, the addition of diacetylene to $C_4H_2^+$, $C_4H_3^+$, $C_5H_2^+$, and C_2N^+ was observed to occur in competition with dissociation channels. Also, the adduct ions $C_3H_3^+.C_4H_2$, $C_4H_2^+.C_4H_2$, and $C_2N^+.C_4H_2$ were observed to add a second molecule of diacetylene. The nature of the mechanism of stabilization of these adduct ions was not discerned and none of these reactions were studied systematically as a function of pressure. Also, no attempts were made to obtain structural information on the adduct ions, most of which may be cyclic or acyclic. In principle such information is available from comparative studies of ion reactivities. However, an elaborate experimental campaign would be required in practice to provide unequivocal results in this fashion.

In a few instances some insight into pressure dependence and stabilization mechanism is available from comparisons with results of photoionization mass spectrometer and ICR measurements performed at much lower pressures. The observation of dissociation products instead of adduct formation for the fast reaction of $C_4H_2^+$ with C_4H_2 in the ICR spectrometer (15, 16) implies collisional stabilization of the adduct at the moderate pressures of the SIFT apparatus. A similar situation appears to apply for the fast reaction of $C_6H_2^+$ with C_4H_2, which has been shown to lead to dissociation in ICR experiments (16) and to adduct formation in photoionization mass spectrometer experiments at ca. 0.01 Torr (16). Adduct formation is the reaction also observed in the SIFT experiments. The situation for the fast reaction of $C_3H_3^+$ with C_4H_2, which proceeds by adduct formation in the SIFT apparatus, is less clear. A similarly fast reaction has been observed with an ICR spectrometer for the linear isomer of $C_3H_3^+$, but products were not elucidated (14).

The diacetylene radical cation was observed to react primarily by addition to the molecules chosen for study, with the exception of hydrogen. The latter molecule failed to react with a measurable rate and this has implications for the lifetime of $C_4H_2^+$ in environments rich in H_2, such as dense interstellar clouds. With CO and C_2N_2, dissociative channels were observed, which lead to ions that, upon neutralization, allow for the growth of the carbon chain and the incorporation of a heteroatom. This is illustrated in the reaction sequences [12] and [13].

$$[12] \quad C_4H_2^+ \xrightarrow{CO} HC_5O^+ \xrightarrow[\text{EIR}]{\text{PT}} :C{=}C{=}C{=}C{=}C{=}O$$

$$[13] \quad C_4H_2^+ \xrightarrow{C_2N_2} HC_5N^+ \xrightarrow[\text{EIR}]{\text{PT}} {}^{\bullet}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$$

The reaction of $C_4H_2^+$ with C_4H_2, only slightly dissociative at the moderate pressures of the SIFT apparatus, becomes completely dissociative at low pressures (15) without changing its overall reaction efficiency and allows for growth of molecules with up to eight carbon atoms. The reaction with C_2H_2 appears to have quite a different behaviour. Only adduct formation is observed, even at low pressures (18, 19). Also, there is some disparity of an unknown origin in the rate constants measured at moderate and low pressures. The SIFT rate constant is 2 to 3 times as large as those determined from measurements at low pressures. Recent ICR experiments have found the disappearance rate constant to be (3.3 × 0.8) × 10^{-10} cm^3 molecule^{-1} s^{-1} and independent of pressure in the range from 2 × 10^{-6} to 3 × 10^{-5} Torr (18). Earlier trapped-ion measurements led to a rate constant of (2.3 ± 0.3) × 10^{-10} cm^3 molecule^{-1} s^{-1} at ca. 10^{-4} Torr, which was also reported to be pressure independent (19). The pressure independence of the rate constant at low pressures has been rationalized both in terms of bimolecular radiative association (19) and in terms of saturated termolecular collisional association (18). The latter interpretation requires a lifetime for the $C_6H_4^+$ collision complex in the millisecond regime. The actual mechanism of stabilization remains unresolved.

There appears to be no previous information on the kinetics of protonation of diacetylene. We have found that protonation occurs with considerable ease under our experimental conditions. The proton-transfer reactions that were observed all proceed essentially at the collision rate at room temperature. The occurrence of proton transfer with H_2CN^+ and the failure of proton transfer with $CH_3OH_2{}^+$ allow the proton affinity of diacetylene to be bracketed between the known proton affinities of HCN and CH_3OH. The proton affinities available for these two molecules (20) yield a proton affinity for diacetylene of 177 ± 5 kcal mol^{-1}. This value corresponds to a heat of formation for $C_4H_3{}^+$ of 305 ± 5 kcal mol^{-1}, which agrees well with the value of 307 kcal mol^{-1} that may be derived from the appearance potential for $C_4H_3{}^+$ from vinylacetylene (12). The bracketed value for the proton affinity agrees with the results of bracketing measurements performed recently with the techniques of ICR and high pressure mass spectrometry (20).

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