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Experimental Studies of the Kinetics of Association Reactions between Neutral Molecules and Carbene Cations

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Laboratory measurements are reported for the reactions of C_3H^+, C_5H^+, C_2N^+, and C_4N^+ with several neutral molecules chosen to allow a response to the carbene character of these cations, viz. CO, H_2, HCN, CH_3CN, HC_3N, and C_2H_2. The measurements were performed with the selected-ion flow tube (SIFT) technique at 296 ± 2 K in helium buffer gas at a total pressure of a few tenths of a Torr. Adduct formation was the predominant but not exclusive feature of the observed chemistry. High rates of association were observed for the addition of one molecule, with further additions being much slower. This behavior was interpreted to be consistent with the formation of strongly bound adduct ions which would be expected if the cations have carbene character. Structures of the observed adduct ions are proposed on the basis of their formation by σ bond insertion or coordination of unbonded electron pairs which may occur as a result of the carbene character in the cations. The possible role of these adduct ions in the synthesis of interesting and novel neutral molecules is briefly indicated.

Introduction

A recent experimental study in our laboratory of the reactivity of the alkynylcarbene ion $:C_3H^+$ has demonstrated that carbene cations may exhibit carbene character in chemical reactions with neutral molecules in the gas phase.[1,2] Bimolecular reaction paths were observed with $:C_3H^+$ which correspond to those characteristic of neutral carbene chemistry, including coordination with a nonbonded electron pair and σ bond insertion. Also of note was the observation of several association reactions with $:C_3H^+$ with relatively large rate constants. Large rate constants in association reactions are indicative of the formation of strongly bound adducts in which strong new chemical bonds are formed, rather than the formation of weakly bound adducts in which bonding is by much weaker electrostatic interaction.[3-5] With $:C_3H^+$, and carbene cations in general, the new chemical bonds in the adduct ions may be double bonds formed directly by coordination with a nonbonded electron pair or single bonds formed by σ bond insertion.

The formation of ionic adducts with strong chemical bonds is of general interest in chemical synthesis by ion/molecule reactions. Association reactions with carbene cations provide an opportunity to generate neutral carbenes.[6] Neutral carbenes may form if the ionic adduct subsequently neutralizes by chemical reaction or electron/ion recombination. For example, the adduct formed by the association reaction 1, which may involve coordination with

$$:C_3H^+ + :CO \rightarrow HC_4O^+ \tag{1}$$

the electron pair on the carbon in carbon monoxide, may neutralize by recombination with electrons or proton transfer as indicated in reactions 2 and 3 to form tetracarbon monoxide. The adduct

$$HC_4O^+ + e\ (M) \rightarrow :C_4O + H\ (MH^+) \tag{2, 3}$$

formed by the association reaction 4, which may involve H-H

$$:C_3H^+ + H_2 \rightarrow C_3H_3^+ \tag{4}$$

bond insertion, may neutralize by reactions 5 and 6 to form cyclopropenylidene or the vinylidene carbene, $:C{=}C{=}CH_2$.

$$C_3H_3^+ + e\ (M) \rightarrow :C_3H_2 + H\ (MH^+) \tag{5, 6}$$

TABLE I: **Effective Bimolecular Rate Constants for Reactions of Selected Ions with Carbon Monoxide and Hydrogen at 296 ± 2 K in Helium at a Total Pressure of 0.34 Torr and Helium Concentration of 1.1×10^{16} atoms cm^{-3}**[a]

ion[b]	CO[c]	H_2[c]
C_3H^+ (propylene)	3.2 (−11)	2.1 (−11)
C_5H^+ (1,4-pentadiyne)	1.0 (−10)	≤1.0 (−13)
C_2N^+ (cyanogen)	7.3 (−13)	≤1.2 (−13)
C_4N^+ (allyl cyanide)	9.3 (−11)	2.2 (−11)[d]

[a] The reactions observed were addition reactions unless indicated otherwise. [b] The source gas from which the ion was derived by electron impact is given in parentheses. [c] a $(-b)$ denotes the rate constant $a \times 10^{-b}$ in cm^3 $molecule^{-1}$ s^{-1}. The accuracy of the rate constants is estimated to be better than ±30%. [d] Rate constant for the reaction to produce C_3H^+ and HCN.

Here we report results of studies of the reactivities of other carbene cations such as $:C_2N^+$, $:C_4N^+$, and $:C_5H^+$ in association reactions with neutral molecules. Two types of neutral substrates were chosen as reactants. Carbon monoxide was chosen since it allows coordination of the unbonded electron pair on carbon with the unbonded electron pair of the carbene cation and so permits the direct formation of a double bond in the association product. Also we have chosen H_2, HCN, CH_3CN, HC_3N, and C_2H_2 as neutral reagents to allow H-H and C-H insertion to occur in the association reactions.

Experimental Section

The measurements were performed with the selected-ion flow tube/flowing afterglow apparatus in the Ion Chemistry Laboratory at York University.[2,7] The reactant ions were generated by electron impact at low pressures at approximately 50 eV. An axial electron impact ionizer (Extranuclear, Model 041-3) was used as the ion source. The C_3H^+ was produced from propylene by electron impact or from the reaction of C^+ with cyanoacetylene. The C_2N^+ ion was generated from cyanogen by electron impact. The C_4N^+ ion was produced from allyl cyanide by electron impact or from cyanoacetylene by reaction with C^+ ions. The C_5H^+ ion was produced by electron impact on 1,4-pentadiyne. Helium was used as the carrier gas. To remove traces of water vapor the buffer gas was passed through zeolite traps (a 50:50 mixture of Union Carbide molecule sieves 4A and 13X) cooled to liquid nitrogen temperatures. The cyanoacetylene was prepared in the laboratory from methyl propriolate[8] and the hydrogen cyanide was prepared according to the procedure described by Glemser.[9] Experiments

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(1) Bohme, D. K.; Raksit, A. B.; Fox, A. *J. Am. Chem. Soc.* **1983**, *105*, 5481.

(2) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1984**, *55*, 69.

(3) Good, A. *Trans. Faraday Soc.* **1971**, *67*, 3495.

(4) Herbst, E. *J. Chem. Phys.* **1979**, *70*, 2201.

(5) Ferguson, E. E.; Adams, N. G.; Smith, D. *Chem. Phys. Lett.* **1986**, *128*, 84.

(6) Bohme, D. K. *Nature (London)* **1986**, *319*, 473.

(7) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259.

(8) Moureu, C.; Bondgrand, J. C. *Ann. Chim. (Rome)* **1920**, *14*, 47.

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TABLE II: Effective Bimolecular Rate Constants for Reactions of Selected Ions with HCN, CH_3CN, HC_3N, and C_2H_2 at 296 ± 2 K at a Total Pressure of 0.34 Torr and Helium Concentration of 1.1×10^{16} atoms cm^{-3} [a]

ion[b]	HCN	CH_3CN	HC_3N	C_2H_2
C_3H^+ (propylene)	$C_4H_2N^+$ 1.1 (−9)	$C_5H_4N^+$ 1.0 (−9)[c]	$C_6H_2N^+$ 1.3 (−9)	$C_5H_3^+$ 7.0 (−10)[c]
C_5H^+ (1,4-pentadiyne)				$C_7H_3^+$ 5.8 (−10)
C_2N^+ (cyanogen)	$C_3HN_2^+$ 3.6 (−10)	$C_2H_3^+/C_2N_2$ $C_3H_2N^+/HCN$ 2.2 (−9)	C_3H^+/C_2N_2 3.1 (−9)	C_3H^+/HCN 7.3 (−10)
C_4N^+ (allyl cyanide)	$C_5HN_2^+$ 8.4 (−10)	$C_2H_3^+/C_4N_2$ $C_4HN_2^+/C_2H_2$ 3.1 (−9)	$C_7HN_2^+$ 1 (−9)	C_5H^+/HCN ($C_6H_2N^+$) 8.0 (−10)

[a] Rate constants are given for the formation of the products indicated. *a* (−*b*) denotes the rate constant $a \times 10^{-b}$ in cm^{-3} $molecule^{-1}$ s^{-1}. The accuracy of the rate constants is estimated to be better than ±30%. [b] The source gas from which the ion is derived is given in parentheses. [c] Competing channels are omitted.

with H_3^+ as the "chemical ionization" reagent indicated a purity of greater than 99% for both compounds. All measurements were taken at a room temperature of 296 ± 2 K.

Results

Most of the measurements were taken in helium carrier gas at a total pressure of 0.34 Torr and a helium concentration of 1.1×10^{16} atoms cm^{-3}. This may be assumed to be the case in the following discussion unless indicated otherwise. Tables I and II provide a summary of the results. Rate constants and product distributions were determined in the usual manner.[10] The accuracy of the rate constants is estimated to be ±30%.

Reactions of C_3H^+. Details of the chemistry of C_3H^+ have been reported previously.[2] Rapid association reactions were observed with H_2, D_2, CO, HCN, CH_3CN, CD_3CN, C_2H_2, C_2D_2, and HC_3N.

Termolecular kinetics was established for the reactions with H_2, D_2, and CO in helium carrier gas. For these reactions this implies stabilization of the adduct ions by collision with the helium atoms. Also a small isotope effect of 1.8 was observed for the relative rates of addition of H_2 and D_2 (after correction for the difference in the collision rates). The adduct ions did not react further. In a separate experiment C_3H^+ was injected into hydrogen carrier gas to form $C_3H_3^+$ and this ion was observed not to react with acetylene, $k \leq 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

The reaction of C_3H^+ with H_2 has also been investigated by Herbst, Adams, and Smith who originally reported $C_3H_2^+$ as the only product ion at 80 and 298 K.[11] These results have since been revised.[12] Herbst et al. now report that only the $C_3H_3^+$ adduct ion is observed at 80 K and that $C_3H_2^+$ formation begins to compete at 295 and 550 K, although the extent of this competition was not specified.[12] Interestingly, the data at 80 K in helium buffer gas indicate an effective bimolecular rate constant of 1.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1} which is pressure independent while the data at 296[2] and 550 K[12] indicate termolecular kinetics with $k = 1.9 \times 10^{-27}$ and 4×10^{-28} cm^6 $molecule^{-2}$ s^{-1}, respectively.[2,12]

C_3H^+ was observed to react with HCN and HC_3N at close to the collision rate to give exclusively the corresponding adduct ions. With CH_3CN and C_2H_2 other channels were observed to compete with adduct formation but the latter channel still proceeded at a substantial rate. With all four molecules addition of a second molecule to the adduct ion was observed to proceed, but with a rate at least 10 times lower than the rate of addition of the first molecule to C_3H^+.

Reactions of C_5H^+. The C_5H^+ derived from 1,4-pentadiyne was observed not to react with H_2. The upper limit to the measured effective bimolecular rate constant was 1×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

An addition reaction was observed with CO to form the HC_6O^+ cation. The profile for the C_5H^+ decay indicated a minor (1–5%) contribution due to an unreactive component. Analysis of the decay attributed to the reactive component yielded a rather high effective bimolecular rate constant of 1.0×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the addition of one molecule of CO. There was no evidence for the addition of a second molecule of CO which was at least 10 times slower. The two components to the C_5H^+ decay probably reflect the presence of at least two isomers of C_5H^+.

A similar situation prevailed with acetylene which was observed to react rapidly with the major reactive component of C_5H^+ and not with the minor unreactive component (<1%). The addition of acetylene to form a $C_7H_3^+$ ion was observed to be the predominant reaction channel. The addition reaction was observed to proceed rapidly with an effective bimolecular rate constant of 5.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Addition of a second molecule of acetylene was more than 50 times slower; some $C_9H_5^+$ was observed to be formed at large additions of acetylene into the reaction region.

Reactions of C_2N^+. No reaction was observed between C_2N^+ and H_2, $k \leq 1.2 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, and $C_2H_2N^+$ was observed not to be formed even at the highest additions of hydrogen.

Addition of one molecule of CO was observed to proceed with the relatively small effective bimolecular rate constant of 7.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. The C_3NO^+ adduct ion did not appear to add a second molecule of CO. No reaction was observed between C_2N^+ and CO in a recent ICR study, $k \leq 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[13]

A molecule of HCN was observed to add rapidly to C_2N^+ with an effective bimolecular rate constant of 3.6×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Additions of a second and third molecule of HCN were also observed but these proceeded at much lower rates. A previous ICR study at low pressures indicated no reaction with HCN, $k \leq 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[13] Thus we can conclude that the addition of HCN to C_2N^+ is termolecular under our experimental conditions and that stabilization of the adduct ion occurs by collisions with helium atoms.

A rapid bimolecular reaction was observed to proceed between C_2N^+ and CH_3CN to form two products according to reaction 7. The bimolecular rate constant for the loss of C_2N^+ was

$$C_2N^+ + CH_3CN \rightarrow C_2H_3^+ + C_2N_2 \quad (7a)$$

$$\rightarrow C_3H_2N^+ + HCN \quad (7b)$$

measured to be 2.2×10^{-9} cm^3 $molecule^{-1}$ s^{-1} and the branching ratio was about 4:1. Experiments with CD_3CN excluded HCN^+ and $C_2N_2^+$ as possible reaction products.

For the reaction between C_2N^+ and HC_3N we have previously reported a bimolecular rate constant of 3.1×10^{-9} cm^3 $molecule^{-1}$ s^{-1} with exclusive formation of C_3H^+ and C_2N_2.[14]

C_2N^+ also reacts rapidly with acetylene in a bimolecular fashion to produce predominantly C_3H^+ and HCN. The data did not exclude possible minor products at *m/e* 28 and 63. The mass 28 ion could be protonated HCN which may form from proton transfer before the C_3H^+ and HCN separate. The mass 63 ion appears primarily as a secondary product due to the secondary reaction of C_3H^+ with C_2H_2 but may also in part be due to HC_4N^+ produced directly from C_2N^+ and C_2H_2. Previous ICR studies have established some primary production of HC_4N^+ through the use of C_2D_2.[13]

Reactions with C_4N^+. Hydrogen was observed to react with C_4N^+ in a slow bimolecular fashion according to reaction 8. The

$$C_4N^+ + H_2 \rightarrow C_3H^+ + HCN \quad (8)$$

rate constant was measured to be 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

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[9] Glemser, O. *Handbook of Preparative Inorganic Chemistry*, Brauer, G., Ed.; Academic: New York, 1963.

[10] Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 275.

[11] Herbst, E.; Adams, N. G.; Smith, D. *Astrophys. J.* **1983**, *269*, 329.

[12] Herbst, E.; Adams, N. G.; Smith, D. *Astrophys. J.* **1984**, *285*, 618.

[13] McEwan, M. J.; Anicich, V. G.; Huntress, W. T.; Kemper, P. R.; Bowers, M. I. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *50*, 179.

[14] Raksit, A. B.; Bohme, D. K. *Can. J. Chem.* **1985**, *63*, 854.

There was no evidence for the formation of an adduct with H_2 even at the highest additions of hydrogen.

A slow reaction was observed with CO to form the adduct ion C_5NO^+. The rate constant was measured to be 9.3×10^{-11} cm^3 molecule^{-1} s^{-1}. No further addition of CO was apparent.

A rapid addition reaction was observed with HCN. The effective bimolecular rate constant was measured to be 8.4×10^{-10} cm^3 molecule^{-1} s^{-1}. A second molecule was observed to add, but more than 10 times slower. A third molecule was also observed to add slowly at higher additions of HCN.

The reaction observed between C_4N^+ and CH_3CN was rapid and bimolecular. Two product ions were formed in about equal amounts according to reaction 9. The rate constant for the loss

$$C_4N^+ + CH_3CN \rightarrow C_2H_3^+ + C_4N_2 \tag{9a}$$

$$\rightarrow C_4N_2H^+ + C_2H_2 \tag{9b}$$

of C_4N^+ was measured to be 3.1×10^{-9} cm^3 molecule^{-1} s^{-1}. It is interesting to note that the two sets of products are related by proton transfer which may occur intramolecularly before the products separate. Experiments with CD_3CN excluded HCN^+ and $C_5H_3N^+$ as possible reaction products.

We have observed adduct formation between C_4N^+ and HC_3N previously in experiments in which C_4N^+ was generated from the reaction of C^+ with cyanoacetylene. The addition reaction proceeded rapidly with an effective bimolecular rate constant of 1×10^{-9} cm^3 molecule^{-1} s^{-1}.[14]

The reaction with acetylene was also observed to proceed analogous to the C_2N^+ reaction to produce predominantly C_5H^+ and HCN. The bimolecular rate constant was 8.0×10^{-10} cm^3 molecule^{-1} s^{-1}. The C_5H^+ reacted further by adding acetylene to produce an ion with *m/e* 87. Because of insufficient resolution at the signal intensities of these experiments it was not possible to exclude the possibility of some (less than about 30%) formation of the $C_6H_2N^+$ adduct ion at *m/e* 88.

Discussion

Adduct formation was the predominant, but not exclusive, feature of the chemistry observed for the reactions selected in this study. High rates of association were observed for the addition of the first molecule. When multiple additions of molecules were observed to occur in sequential association reactions, the rate of association of the first molecule was characteristically the highest. To the degree that the rate constant for association correlates with the strength of the bond formed in the adduct ion, such behavior implies a formation of strongly bonded adduct ions with the first molecule and less strongly bonded higher order adduct ions.

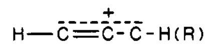
Four cations were selected as reagents: C_3H^+, C_5H^+, C_2N^+, and C_4N^+. We presume these ions to have carbene character as indicated by the following resonance forms: $H{-}C{\equiv}C{-}C{:}^+$, $H{-}C{\equiv}C{-}C{\equiv}C{-}C{:}^+$, $N{\equiv}C{-}C{:}^+$, and $N{\equiv}C{-}C{\equiv}C{-}C{:}^+$. Other resonance forms are possible for each of these ions and the charge can be expected to be delocalized in each case. The carbene character of these cations would allow the formation of double or single bonds with a chosen neutral molecule through coordination or insertion, respectively. The bonding with additional molecules would then be of a different nature, less "chemical", and perhaps even purely electrostatic. The observed chemistry indicates that this appears to be so.

There are a number of indications that the C_3H^+ cation forms strongly bonded adducts with the chosen neutral reagent molecules. For the reactions with H_2 and D_2 the effective bimolecular rate constants observed at 0.34 Torr were at least 10 times larger than that for the reaction with N_2.[2] This observation is significant in that it implies bonding with H_2 and D_2 other than electrostatic. Electrostatic bonding would be weak and depend directly on the polarizability of the bonding molecule. N_2 has a polarizability more than twice that of H_2 or D_2 but was observed not to form an adduct ion.[2] The small isotope effect which was observed is also more consistent with the formation of strongly bonded $C_3H_3^+$ and $C_3HD_2^+$ ions from σ bond insertion reactions involving the breaking of H–H and D–D bonds. It is likely therefore that either propargyl or cyclopropenium cations are formed in the reactions of C_3H^+ with H_2 and D_2. Both are exothermic by more than 100 kcal mol^{-1}.[9,15] Both ions would also be less likely to bond strongly to an additional H_2 or D_2 molecule than the parent carbene cation $C_3H{:}^+$. Indeed no further addition of H_2 or D_2 was observed in the room temperature experiments reported here or even at 80 K in the experiments of Herbst, Adams, and Smith.[11]

More direct insight into the nature of the bonding and the structure of the $C_3H_3^+$ produced from C_3H^+ and H_2 is provided by the observed failure of this ion to react with acetylene. A weakly bound adduct of the type $C_3H^+{\cdot}H_2$ might be expected to undergo a rapid switching reaction with acetylene to form $C_3H^+{\cdot}C_2H_2$, but this did not occur. Also, the propargyl cation is known to react rapidly with C_2H_2,[16] but this did not occur. The observed failure to react with acetylene is therefore consistent with a cyclopropenium structure for the $C_3H_3^+$ ion produced from C_3H^+ and H_2. The cyclopropenium ion is known not to react with C_2H_2.[16]

Carbon monoxide was observed to add to C_3H^+ with a rate higher than that for H_2 or D_2. It has a polarizability about the same as that for N_2 (as well as a small dipole moment). Strong chemical bonding is possible in this case by coordination with the electron pair on :CO to form the cumulated cation $HC^+{=}C{=}C{=}C{=}O$. Similar bonding cannot be reproduced with a second molecule of CO so that a similarly rapid addition of another CO molecule is not expected, nor was it observed.

The very high rates of addition of one molecule of HCN, HC_3N, CH_3CN, and C_2H_2 and the much slower addition in each case of a second molecule can also be taken as indirect evidence for the formation of strongly bound single molecule adduct ions. With these four neutral reagents C–H bond insertion by $C_3H{:}^+$ is possible and likely. Adduct ions formed in this manner are likely to have the acyclic or cyclic structures indicated by **1** and **2**, where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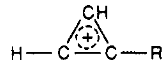
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R = CN, C_2CN, CH_2CN, or C_2H. With these adduct ions there is again likely to be less opportunity for futher chemical bonding with a second molecule.

The response of the other carbene cations toward CO was similar to that for C_3H^+. Rapid addition was observed for the first :CO molecule with $C_5H{:}^+$ and $:C_4N^+$ to form what are likely to be the cumulated cations $HC^+{=}C{=}C{=}C{=}C{=}C{=}O$ and $N{\equiv}C{-}C^+{=}C{=}C{=}C{=}O$, respectively. Curiously, the addition of :CO to $:C_2N^+$ to possibly form $N{\equiv}C{-}C^+{=}C{=}O$ was slower by several orders of magnitude. The failure to observe the addition of a second molecule of CO in all three cases is again consistent with expectations if the bonding with the first molecule of CO proceeds as proposed. The results for all the reactions observed with CO taken together are suggestive of a generic reaction of the type

$$R{-}C{:}^+ + {:}CO \rightarrow R{-}C^+{=}CO \tag{10}$$

The observed response of the carbene cations toward molecular hydrogen exhibits an interesting variation. Curiously, the addition reaction with C_3H^+ is not reproduced with the homologous C_5H^+ cation. With C_3H^+ there is no question about the exothermicity to form either the propargyl or the cyclopropenium cations. There is insufficient thermochemical information to be equally definitive about the formation of $C_5H_3^+$ from C_5H^+ although it is expected to be exothermic. In the case of the failure of C_2N^+ to add H_2 available heats of formation suggest an overall exothermicity for the H–H bond insertion. Formation of a $C_2H_2N^+$ ion of the type derived by electron impact from CH_3CN is about 100 kcal mol^{-1} exothermic.[15] The analogue to the bimolecular reaction observed to proceed slowly with the homologous C_4N^+ ion would produce CH^+ and HCN. Available heats of formation suggest that this

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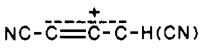
[15] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Ser. Suppl. 1* **1977**, *6*, 106.

channel is endothermic. The observation of C_3H^+ as a product ion with C_4N^+ implies a lower limit to the heat of formation for C_4N^+ of 415 kcal mol^{-1} if HCN is the neutral product.

The high rates of addition of one molecule of HCN to C_2N^+ and C_4N^+ are suggestive of C–H bond insertion as was the case with C_3H^+. The slower additions of a second and third molecule of HCN are more consistent with weaker electrostatic bonding in the higher order adduct ions. C–H bond insertion with C_2N^+ may form the dicyanomethylium cation while addition to C_4N^+ could produce adduct ions with the acyclic or cyclic structures given in **3** and **4**, respectively.



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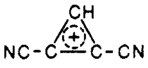

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The results with CH_3CN indicate that the adducts with this molecule are less stable toward decomposition. While some adduct ion formation was observed with C_3H^+, the major products of this reaction were bimolecular. With C_2N^+ and C_4N^+ the reactions observed were exclusively bimolecular. Reasonable mechanisms, in part initiated by C–H or C–C bond insertion, can be ascribed to the observed decompositions of the intermediate adduct ions formed in these three reactions.

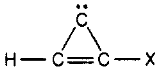
A distinct difference in reactivity was observed for the reactions of C_2N^+ and C_4N^+ with HC_3N. Both reactions proceed near the collision rate with the former leading exclusively to bimolecular products and the latter to adduct formation. C–H bond insertion of C_4N^+ in HC_3N can lead to the symmetric adduct ion N≡C–C≡C–CH$^+$–C≡C–C≡N. Elimination of C_2N_2 from this ion, the analogue of the reaction observed with C_2N^+ which is likely to be exothermic with C_4N^+ as well, may be sterically unfavorable.

HCN is readily eliminated from the intermediate adduct ions of C_2N^+ and C_4N^+ with C_2H_2 although the experiments did not exclude the possibility of some adduct formation with C_4N^+. The rapid addition of C_5H^+ to acetylene is indicative of chemical bond formation in the $C_7H_3^+$ adduct ion, presumably by C–H bond insertion. Possible structures of this ion include those given by **1** and **2** with R = C_4H.

The mechanism of stabilization of the adduct ions observed in this study was not explored in detail. The effective bimolecular rate constant for association was investigated directly as a function of pressure only for the reactions of C_3H^+ with CO, H_2, and D_2 for which the observations were consisitent with termolecular kinetics with helium as the stabilizing third body. Extrapolation to zero pressure indicates that any bimolecular component to these association reactions would have a rate constant of less than approximately 1×10^{-12} cm^3 molecule s^{-1}. Most of the remaining association reactions were observed to proceed with effective bimolecular rate constants close to the collision limit for the addition of the first molecule. The pressure dependence of these reactions was not investigated. In the one case of the reaction of C_2N^+ with CO the independent ICR measurements[13] which showed no addition indicate that collisional stabilization is also predominant for this reaction under our experimental operating conditions. Also the ICR results suggest an upper limit of 3×10^{-11} cm^3 molecule^{-1} s^{-1} to the rate constant for any bimolecular reaction. Bimolecular association may occur under ICR conditions if stabilization proceeds by radiative association.

The theoretical work of Bates suggests that radiative association is favored by high association energies and high numbers of nuclei.[17] The association reactions observed in our experimental study do involve reasonably complex molecular species and apparently strong chemical bonding in the single adduct ions, but it is not clear to what degree radiative association contributes to the observed association reactions for which no information is available at lower pressures. Calculations presented for the model systems chosen by Bates indicate that the room temperature rate constants for radiative association for the systems selected in our study may lie below or near the limit of our experimental technique.

Irrespective of the their mode of formation, the adduct ions which are inferred in this study to be strongly bound provide opportunities for the synthesis of interesting and novel neutral molecules. For example, the adduct ions which formed with CO may neutralize to produce multicarbon monoxides and substituted multicarbon monoxides. HC_4O^+ and HC_6O^+ may neutralize by proton transfer or electron/ion recombination to produce tetracarbon and hexacarbon monoxide, respectively. The adduct ions C_3NO^+ and C_5NO^+ may neutralize by charge transfer to produce the radicals cyanodicarbon and cyanotetracarbon monoxide, respectively. The cyclopropenium $C_3H_3^+$ adduct ion may neutralize to produce the cyclopropenylidene ring carbene.[6] Adduct ions formed by C–H bond insertion with C_3H^+ may neutralize by proton transfer or electron/ion recombination to produce acyclic carbenes of the type :C(C_2H)X or cyclic carbenes of type **5** where



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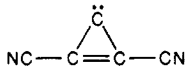
X = CN, C_3N, CH_2CN, and C_2H. Carbenes of this type may also be formed from the neutralization of the adduct between C_5H^+ and C_2H_2 where X = C_4H. Finally, related carbenes also can be expected to be formed from the adduct ions of HCN with C_2N^+ and C_4N^+ and of HC_3N with C_4N^+. Neutralization of these adduct ions can lead to the carbenes :C(CN)$_2$, :C(CN)C_3N, and :C(C_3N)$_2$ and the ring carbenes **6** and **7**. The proposed products



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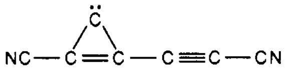

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of all of the neutralization events described here are of course speculative. The relevant charge-transfer, proton-transfer, and electron/ion recombination reactions have not yet been studied in the laboratory. Nevertheless, they are plausible in terms of previous experience with other reactions of this type.

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Registry No. C$^+$, 14067-05-1; C_2H_2, 74-86-2; CO, 630-08-0; H_2, 1333-74-0; HCN, 74-90-8; HC_3N, 1070-71-9; CH_3CN, 75-05-8; propylene, 115-07-1; cyanogen, 2074-87-5; allyl cyanide, 109-75-1; 1,4-pentadiyne, 24442-69-1.

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