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Reactions of the Carbene Ions C_nN^+ with Labeled Methane: Mechanistic Interpretation

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Abstract: The rate constants and branching ratios for the reactions of C_nN^+ ions (n = 4–8) with methane were determined by using Fourier transform mass spectrometry (FTMS). The C_nN^+ reactant ions are formed by the reaction of C_{n-1}^+ ions (produced by direct laser vaporization of graphite) with HCN. A variety of products are formed in the title reactions, many related to the cyanopolyynes ($HC_{2x+1}N$) and polyynes ($C_{2x}H_2$), species of interest for interstellar chemistry. Carbene attack on the C–H bond in methane, followed by hydrogen migration and C–C bond cleavage, can explain the formation of many of the observed products. However, studies with labeled $^{13}CH_4$ revealed that more complex mechanisms are involved in the formation of some of the observed products. The results of MNDO calculations of the structures and heats of formation of the reactants, various intermediates, and products were used to explore possible mechanisms. It is suggested that a rearrangement mechanism involving a cyclopropenyl intermediate and formation of a cyano–carbene ion is responsible for these products. Reaction at the nitrogen end of the ion does not appear to be important. Electronic state effects are manifested in the reactions of the odd n reactant ions by the formation of radical products.

The reactant ions C_nN^+ belong to the class of carbene compounds, which possess a divalent carbon with two nonbonding electrons. The characteristic reactions of these electrophilic reagents, deduced from work on neutral carbenes, are coordination with a lone pair, insertion into σ bonds, and addition to multiple bonds.[1] Bohme and co-workers have carried out extensive research on the reactions of carbene cations such as C_3H^+, C_2N^+, and C_4N^+.[2-4] They have observed coordination and σ bond insertion reactions which are consistent with the carbene character of the ions. In addition to their carbene site, the C_nN^+ ions also possess some nitrene character. The nitrene is a univalent nitrogen with four nonbonding electrons. Nitrenes undergo reactions similar to those of carbenes but have not been as thoroughly studied.[1] The carbene and nitrene resonance forms of C_4N^+ are shown below:

$:C{=}C{=}C{=}C{=}\overset{+}{N}:$

Carbene

$\overset{+}{C}{\equiv}C{-}C{\equiv}C{-}\ddot{N}:$

Nitrene

If the nonbonding electrons on the carbon and nitrogen in the carbene resonance form are in the σ sp orbitals the carbene is a singlet. Excitation of an electron into an empty p orbital forms the triplet. Both states are known.[1] The nonbonding electrons on the nitrogen in the nitrene are in the sp and the two p orbitals. Singlet states (with an empty p orbital) and triplet states are possible, though the ground state is typically a triplet.[5] The energy separation between the lowest triplet and singlet states for both carbenes and nitrenes is usually small.[5a]

The motivation for this study of the reactions of C_nN^+ with methane was the observation of cyanopolyynes, $HC_{2x+1}N$, in interstellar clouds. Though many reaction schemes have been proposed,[6] none has been shown capable of forming the larger cyanopolyynes (up to 11 carbon atoms) that are observed. One proposed mechanism postulates that the carbon chain in C_nN^+ is lengthened by reaction with methane.[7] Previous work by Bohme and co-workers on this reaction has been limited to ions with four carbon atoms or less,[3,4] due to the difficulty of forming these ions. To test the proposed mechanism the reactions of larger ions need to be investigated, which requires a method of producing reactant ions with longer carbon chains. Our work on the reactions of bare carbon cluster ions, C_{n-1}^+, with HCN[8] showed that one of the major products is C_nN^+. This provides the needed synthetic route.

In this work, the reactions of C_nN^+ (n = 4–8) with methane, deuterated methane, and carbon-13 labeled methane were studied. The reactions with CD_4 were for the purpose of identifying the elemental composition of the products. The kinetic parameters (products, branching ratios, and total reaction rate constants) as well as a discussion of the implications of this work for interstellar chemistry have been previously reported.[9] The focus of this article is on the mechanism of the reactions. In particular, are products due to reaction at the nitrogen end of the molecule observed? What is the effect of the nitrogen on the reactivity of C_nN^+ when compared to that of the bare carbon cluster ion? The experiments with $^{13}CH_4$ provided valuable information by giving some indication of the site of methane carbon incorporation. Further information was obtained from semiempirical MNDO calculations of the structures and heats of formation of the reactants, possible intermediates, and products. The results of these calculations served as a guide in the formulation of reaction mechanisms and the interpretation of the experimental data.

The rest of this article is organized as follows: an experimental section followed by a description of the theoretical method; presentation of the experimental and theoretical results; a discussion of the energetics and mechanisms of the C_nN^+ reactions with methane; conclusions; and tabulation of the calculated heats of formation in an appendix.

Experimental Section

The experiments were performed on a Fourier transform ion cyclotron resonance (ICR) mass spectrometer (FTMS) equipped with a Nicolet 3 tesla superconducting magnet and a Nicolet FTMS/1000 data system. In this apparatus, the formation, reaction chemistry, and detection of ions occur in the same spatial region but are separated in time. Ions of a particular mass-to-charge ratio can be isolated in the ICR cell through

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(1) For an introduction to carbenes and nitrenes, see: Gilchrist, T. L.; Rees, C. W. *Carbenes, Nitrenes, and Arynes*; Appleton-Century-Crofts: New York, 1969.

(2) (a) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Proc.* **1983/84**, *55*, 69–82. (b) Bohme, D. K.; Raksit, A. B.; Fox, A. *J. Am. Chem. Soc.* **1983**, *105*, 5481–3.

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(6) For a recent review, see: Bohme, D. K.; Włodek, S.; Raksit, A. B. *Can. J. Chem.* **1987**, *65*, 2057–61.

(7) Woods, R. C. In *Molecular Ions*; Berkowitz, J., Groeneveld, K. O., Eds.; Plenum Publishing Corporation: New York, 1983; pp 511–5.

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application of an rf pulse whose frequencies correspond to the cyclotron resonance frequencies of the unwanted ions. Power absorption by the ions results in their ejection from the ICR cell. Reactions of the mass-selected ions are followed as a function of reaction time at a constant reagent gas pressure. Sequential reactions can be studied by isolating an ion after its formation in a previous reaction. The apparatus and its operation have been described previously,[8] thus only details pertinent to the present work will be given.

The reactions of C_nN^+ (n = 4–8) with methane were studied by using the experimental sequence

$$C_{\text{graphite}} + h\nu \rightarrow C_{n-1}^+ \tag{1}$$

$$C_{n-1}^+ + HCN \rightarrow C_nN^+ + H \tag{2}$$

$$C_nN^+ + CH_4 \rightarrow \text{products} \tag{3}$$

The solid graphite sample was vaporized by using a frequency-doubled Nd:YAG laser (with an output at 532 nm of 0.1–0.5 mJ/pulse operating at 10 Hz) focussed on the graphite pellet.[10] The positive carbon cluster ions thus formed were trapped in the ICR cell. The cluster ions of the desired carbon number were mass-selected as described above and allowed to react with the neutral reagent gases, HCN and CH_4. Both were admitted into the vacuum chamber by variable leak valves and were at constant pressure in the ICR cell. The reactions of bare carbon cluster ions with HCN and CH_4 have been previously studied in our laboratory.[8,11] After a fixed reaction time, the C_nN^+ product ions were isolated and allowed to react with the HCN/CH_4 gas mixture. Rate constants were determined by following the extent of reaction as a function of reaction time. Reactions were generally followed to 90% disappearance of the reactant ions. The observed rate constants and branching ratios, due to reaction with both CH_4 and HCN, were corrected for the known HCN reaction parameters[8] to give values for the methane reactions. Some of the product ions (CH_3^+ and $C_2H_3^+$) undergo secondary reactions with the neutral gases, leading ultimately to the formation of H_2CN^+. The branching ratios for these three ions were extrapolated to zero reaction time and thus are less accurate than those of the other products. The pressures of HCN used were in the range of $0.8–3.4 \times 10^{-7}$ Torr ($1.1–4.5 \times 10^{-5}$ Pa), and those of methane were $0.6–2.4 \times 10^{-7}$ Torr ($0.8–3.2 \times 10^{-5}$ Pa). The methane pressure was calibrated by measuring the rate constants for the known reactions of CH_3^+ and CH_4^+ with methane at several pressures. To determine the elemental composition of the product ions (since the nominal mass of CH_2 is the same as that of N) the reactions were also studied under the same conditions by using CD_4. Information about the incorporation of the methane carbon was obtained from the reactions with carbon-13 labeled methane, as indicated in the introduction.

The C_nN^+ reactant ions (n = 4, 6, and 8), formed by reaction 2, appeared to be internally excited. This was manifested by nonexponential reactant ion decay curves and a branching ratio for the HCN association product which varied with reaction time. In order to correct the observed rate constants for the contribution from the HCN reaction, the branching ratio of the HCN products must remain constant. To relax the C_nN^+ ions some experimental sequences included a variable relaxation time, which allowed for several collisions with the reactant neutral gases and added Ar buffer gas ($\simeq 1 \times 10^{-6}$ Torr = 1.3×10^{-4} Pa). After the relaxation time all product ions formed by reactions with both HCN and CH_4 were ejected, and the zero time for the reaction was set. By using this procedure, the branching ratio for the HCN association product remained constant with reaction time, and single exponential decay curves were obtained. These results indicate that the HCN association reaction has a strong dependence on the reactant ion internal energy, as expected. In contrast, the methane reaction shows little dependence on the reactant ion internal energy. Analysis of data taken both with and without relaxation of the reactant ions gave the *same* rate constants and product branching ratios for the reaction of C_nN^+ with methane.

Theory

The structures and heats of formation, ΔH_f, used in the interpretation of the reaction data were calculated on the NRL Cray XMP by using MNDO computer code.[12] MNDO is a semiempirical quantum chemical method and has been used in several previous studies of pure carbon clusters.[11,13,14]

In this work, MNDO calculations were performed for the following species in both the neutral and cation form: C_n, C_nH, the HC_nH and H_2C_n isomers, the H_2C_nH and H_3C_n isomers, and H_3C_nH neutral only (all with n = 1–9); also C_nN, the HC_nN and C_nNH isomers, the H_2C_nN and HC_nNH isomers (all with n = 1–9); and C_nNH_2 cation only (for n = 4–8). Calculations on $H_3CC(H)C_{n-1}N^+$ and $C_nN(H)NH_3^+$ (intermediates **1** and **2** below) were also performed for n = 4–8. In the MNDO calculation the spin multiplicity is a fixed parameter. Singlet and doublet electronic states were assumed for the present work. The possible role of triplet states in the reactions is addressed in the Discussion.

In each calculation, all bond lengths were optimized. The geometry defined by the bond and twist angles was held fixed. The C–C and C–N backbone and single terminal H atoms were fixed in a linear configuration, and only multiple H atoms bonded to the same atom (e.g., H_2C–) were allowed to vary from linearity. Allowing all angles to vary produced very little change in the optimized structures and the calculated heats of formation. Holding the angles fixed resulted in a much shorter computation time, with virtually no change in the final results. For the C_nNH and HC_nNH species, a set of calculations in which the C–N–H angle was optimized were also performed. The bent configuration was found to be more stable for some molecules; however, the most stable isomers were the linear HC_nN and H_2C_nN configurations. Mirror symmetry along and perpendicular to the backbone was imposed where appropriate (e.g., H_2C– and C_n).

The optimized bond lengths computed in this fashion agree quite well with the available experimental values. For acetylene, HC_3N, and HC_5N, root mean square deviations of the bond lengths from experimental values[15] were 0.01 Å or less. For HCN, CNH, $HCNH^+$, and H_2CN^+ the agreement with other ab initio calculation[16] was also quite good. The calculated ΔH_f are less accurate. Of the 43 molecules for which comparison with experimental ΔH_f was possible,[17] half agreed to within 5%, another quarter to within 10%, and most of the others to within 20%. Large deviations are due to a number of factors: (1) the calculated ΔH_f is not that of the ground electronic state or of the most stable isomer; (2) the absolute error is small but large as a percentage of ΔH_f; and (3) uncertainties in the experimental ΔH_f for unstable or unusual species. In the tables and figures, the ΔH_f for the most stable isomer is generally used.

Results

Experimental. The experimentally determined products, branching ratios, and total rate constants for the reactions of C_nN^+ with methane are presented in Tables I and II. The product with the carbon-13 label is so indicated. Products related by proton or charge transfer are grouped together. Also included in the tables are the heats of reaction, ΔH_{rxn}, to form the most stable isomers in each product channel. (The ΔH_{rxn} are calculated from the ΔH_f listed in Tables V and VI in the Appendix.) The ΔH_{rxn} are for reactions occurring on a singlet potential energy surface. A few products which are doublets are also observed and will be discussed in more detail below. The last column gives the code letter(s) for the mechanism(s) that can lead to each particular set of products. The different mechanisms will be presented in the Discussion section.

The general trends in these results have been reported and discussed previously.[9] Only a few points will be made here before turning our attention to the mechanism of these reactions. In most of the reactions we observe the following channels: addition of

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Table I. Products, Branching Ratios,[a] Mechanisms, and Rate Constants for the Reactions of the Even n Carbene Ions C_nN^+ with Methane

			reactant ion size (n)			
	products[b]	ΔH_{rxn}[c]	4	6	8	mechanism[d]
i.	$H_2{}^{13}C_{n+1}N^+ + H_2$	−81, −70, −63	7	2		C, N
ii.	$^{13}CH_3{}^+ + HC_nN$	+14, +20, +25	10	3		C, N
	$HC_nN^+ + {}^{13}CH_3$	−16, −19, −20	1			
iii.	$^{13}C_2H_3{}^+ + HC_{n-1}N$	−40, −27, −19	8	7		C
	$H_2C_{n-1}N^+ + {}^{13}C_2H_2$	−64, −55, −49	9	14	9	
iv.	$C_2H_3{}^+ + H^{13}C_{n-1}N$	−40, −27, −19	10			P, S
	$H_2{}^{13}C_{n-1}N^+ + C_2H_2$	−64, −55, −49	8	20	26	
v.	$^{13}C_4H_2{}^+ + H_2C_{n-3}N$	−5, −9, −2	2			C, P, S
	$^{13}C_4H_3{}^+ + HC_{n-3}N$	−64, −48, −40	34	11	7	
	$H_2C_{n-3}N^+ + {}^{13}C_4H_2$	−59, −50, −47	11	2	5	
vi.	$C_4H_3{}^+ + H^{13}C_{n-3}N$	−64, −48, −40		6	5	P, S
vii.	$^{13}C_6H_3{}^+ + HC_{n-5}N$	−, −60, −49		33	11	C, P, S
	$H_2C_{n-5}N^+ + {}^{13}C_6H_2$	−, −46, −42		2		
viii.	$^{13}C_8H_3{}^+ + HC_{n-7}N$	−, −, −57			20	C, P, S
	$H_2C_{n-7}N^+ + {}^{13}C_8H_2$	−, −, −39			17	
direct mechanism only			35	26	9	
direct and/or rearrangement			47	48	60	
rearrangement mechanism only			18	26	31	
rate constant (10^{-10} cm^3/s)			7.0	3.2	0.4	
1 σ error limit			1.5	0.2	0.05	

[a] Total branching ratios for a given product, ignoring carbon-13 labeling, were obtained from the reaction with CH_4. These were multiplied by the fraction of labeled/unlabeled product, obtained from the reaction with $^{13}CH_4$ and rounded to the nearest percent, to give the branching ratios in the table. [b] Only one of the carbons is labeled, i.e., $H_2{}^{13}C_{n+1}N^+$ is actually $H_2{}^{13}C^{12}C_nN^+$. [c] The heats of reaction (in kcal/mol) to form the most stable isomers of the indicated products from the n = 4, 6, 8 reactant ions, assuming singlet or doublet electronic ground states for reactants and products. [d] This code indicates the possible mechanisms responsible for the formation of the products. The codes for the mechanisms presented in the text are as follows: C, carbene attack and fragmentation, N, nitrene attack and fragmentation, P, methylene π bond addition, and S, cyano–carbene σ bond insertion. The direct mechanisms are C and N; the rearrangement mechanisms are P and S.

Table II. Products, Branching Ratios,[a] Mechanisms, and Rate Constants for the Reactions of the Odd n Carbene Ions C_nN^+ with Methane

			reactant ion size (n)		
	products[b]	ΔH_{rxn}[c]	5	7	mechanism[d]
i.	$H_2{}^{13}C_{n+1}N^+ + H_2$	−107, −97	4		C, N
ii.	$^{13}CH_3{}^+ + HC_nN$	−71, −54	23	23	C, N
	$HC_nN^+ + {}^{13}CH_3$	−58, −54	37	33	
iii.	$^{13}C_2H_3{}^+ + HC_{n-1}N$	−18, −9	7	8	C
	$H_2C_{n-1}N^+ + {}^{13}C_2H_2$	−84, −78	4	10	
iv.	$H_2{}^{13}C_{n-1}N^+ + C_2H_2$	−84, −78	5	4	P, S
v.	$^{13}C_3H_3{}^+ + HC_{n-2}N$	−95, −78	5	10	C, S
vi.	$C_3H_3{}^+ + H^{13}C_{n-2}N$	−95, −78	2		N, P, S
vii.	$^{13}C_5H_3{}^+ + HC_{n-4}N$	−107, −88	5		C, P, S
	$H_2C_{n-4}N^+ + {}^{13}C_5H_2$	−42, −30	8		
viii.	$C_5H_2{}^+ + H_2{}^{13}C_{n-4}N$	−42, −43		4	N, P, S
ix.	$H_2C_{n-6}N^+ + {}^{13}C_7H_2$	−, −30		8	C, P, S
direct mechanism only			75	74	
direct and/or rearrangement			20	22	
rearrangement mechanism only			5	4	
rate constant (10^{-10} cm^3/s)			7.5	4.6	
1 σ error limit			1.5	0.5	

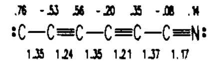
[a] Total branching ratios for a given product, ignoring carbon-13 labeling, were obtained from the reaction with CH_4. These were multiplied by the fraction of labeled/unlabeled product, obtained from the reaction with $^{13}CH_4$ and rounded to the nearest percent, to give the branching ratios in the table. [b] Only one of the carbons is labeled, i.e., $H_2{}^{13}C_{n+1}N^+$ is actually $H_2{}^{13}C^{12}C_nN^+$. [c] The heats of reaction (in kcal/mol) to form the most stable isomers of the indicated products from the n = 5, 7 reactant ions, assuming singlet or doublet electronic ground states for reactants and products. [d] This code indicates the possible mechanisms responsible for the formation of the products. The codes for the mechanisms presented in the text are as follows: C, carbene attack and fragmentation, N, nitrene attack and fragmentation, P, methylene π bond addition, and S, cyano–carbene σ bond insertion. The direct mechanisms are C and N; the rearrangement mechanisms are P and S.

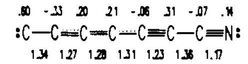
methylene (loss of H_2 from the adduct); CH_3 and $CH_3{}^+$ products; and C_2 hydrocarbon products. The remaining products are predominantly the proton-transfer pairs $C_xH_3{}^+/HC_{n+1-x}N$ and $C_xH_2/H_2C_{n+1-x}N^+$ with the cyano species always having an odd number of carbons. This finding was noted in previous work[9] as being consistent with observations of odd-carbon cyanopolyynes in interstellar clouds. (The even carbon analogues have not been seen.)

No association products were detected in these experiments at room temperature. This agrees with the previous work on the reactions of bare carbon cluster ions; little association occurs when the neutral reactant is nonpolar,[11,13] while significant association is observed when the neutral reactant is polar.[8]

The rate constant decreases with increasing n, with a superposed odd/even size alternation. The large decrease in reactivity between n = 7 and 8 is similar to that observed in the reactions of bare carbon cluster ions with nonpolar neutrals.[11,13]

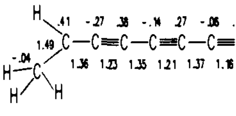
MNDO Calculations. Some relevant examples of calculated structures are given in this section. Species with even and odd values of n differ markedly; thus n = 6 and 7 are used to represent each set. The structures for two of the reactant ions, C_6N^+ and C_7N^+, are shown below:

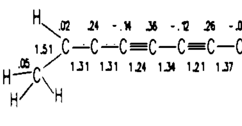




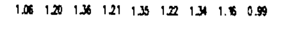
Bond lengths in angstroms and charge in units of e are noted. Bond orders indicate *relative* bond strengths only. Both ions have large oscillations in bond length at the nitrogen end of the molecule. In even n ions this alternation in bond lengths (acetylene structure) persists as one moves toward the carbene end but is damped to give more nearly equal bond lengths (cumulene structure) in the odd n ions. The carbene end of these ions thus resembles the corresponding $C_n{}^+$ ion structures.[13] The charge in both cluster ions is delocalized over the entire molecule and is largest on the terminal carbon atom. The even n ions can be nicely represented by the sum of several resonance structures which all satisfy the octet rule. However the odd n ions are not classical in this sense, as there is no possible resonance structure with the charge on the carbene carbon. For the odd n ions a triplet state which lies less than 10 kcal/mol below the singlet state was found. (No triplet states for the even n ions were found.) The structure of the triplet state ion is the same as that of the singlet state ion shown above. The very short C–N bond in both the even and odd n ions indicates that the C_nN^+ ions have little nitrene character. Rather they are predominantly carbene-like, with a nitrile (—C≡N:) functional group. The two nonbonding electrons on the nitrogen are in an sp orbital.

Carbene insertion into one of the methane C–H bonds forms intermediate **1**:





For even n reactant ions, the methane addition does not change the bond lengths in the C–N backbone. In contrast, methane addition to odd n reactant ions shifts the cumulene portion of the molecule toward an acetylenic structure, enhancing the stability of the odd n intermediates. The methane carbon to carbene bond is always long, and the charge is not delocalized onto the methane carbon. The charge oscillations remain but are attenuated. Loss of methylene from these intemediates will initially form the $H_2C_nN^+$ ions. The substitution of an H for the methyl group in the intermediate has virtually no effect on the bond lengths and charges, which remain very similar to what they were in the intermediate. For odd n ions, hydrogen atom migration to form the more stable HC_nNH^+ isomer



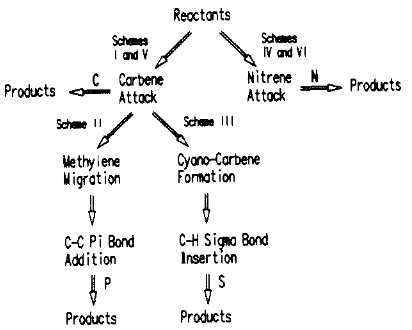
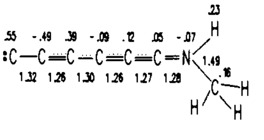
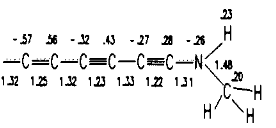


Figure 1. Schematic outline of possible mechanisms for the reactions of C_nN^+ ions with methane.

reconfigures the ion to an acetylenic structure throughout the molecule. The charge distribution is also strongly affected; the charge oscillations now increase toward the nitrogen end of the molecule and the nitrogen itself is negatively charged.

Nitrene attack on the methane forms intermediate **2**:





Surprisingly, we see that compared to the reactant ions the even n ion shifts toward a cumulene structure, while the odd n ion becomes more acetylenic. Also, the odd n ion has a longer C–N bond, which would be expected for nitrene attack. From this, we expect that nitrene attack will be more favorable for odd n ions relative to even n ions. The charge distribution remains skewed toward the carbene end of the molecule. Replacement of the methyl group by hydrogen has no effect on the bond lengths and charge distribution.

The calculated heats of formation are presented in the Appendix.

Discussion

Energetics. Figure 1 is a flow chart of the various mechanisms to be considered and will serve as a "road map" for the discussion. The first step in the reaction is presumably either carbene or nitrene attack on the methane, with insertion into a carbon–hydrogen bond. The ΔH_f for the two reaction intermediates thus formed were calculated (Table VII in the Appendix). As shown in Figure 2, carbene attack to form intermediate **1** is a strongly exothermic process for all the reactant ions, while nitrene attack to form intermediate **2** is exothermic only for the odd n reactant ions and is about thermoneutral for the even n reactant ions. Cleavage of bonds in the reaction intermediates **1** and **2** to form products, without rearrangement of the carbon–nitrogen skeleton, is considered to be a "direct" reaction and is labeled **C**(arbene) or **N**(itrene) in Figure 1. All observed products require transfer of one or more hydrogens from the methane to the reactant ion as none of the products retains all four hydrogens. This indicates that the hydrogens in the intermediate are mobile over the entire carbon–nitrogen chain. Wincel et al.[18] have presented an energy diagram for the various $C_2H_4N^+$ isomers, showing that linear isomers related by 1,2-H shifts have energy differences of 40–85 kcal/mol. In Figure 2 we see that these hydrogen shifts are indeed energetically possible for carbene attack but are likely to be endothermic for nitrene attack.

The products observed in the reactions with $^{13}CH_4$ indicate that some rearrangement of the carbon–nitrogen skeleton occurs. Two possible mechanisms, starting from the carbene attack intermediate **1**, are indicated in Figure 1. The first mechanism, labeled **P**(i addition), involves the formation of methylene (H_2C:) which then migrates along the C–N backbone to a C–C π bond where it can add. The second mechanism, labeled **S**(igma insertion), proceeds via the formation of a cyano–carbene ion (:C_mN^+) which then inserts into a C–H σ bond. Bond cleavage to form products is the last step in each mechanism. It is obvious that these mechanisms require a long-lived complex.

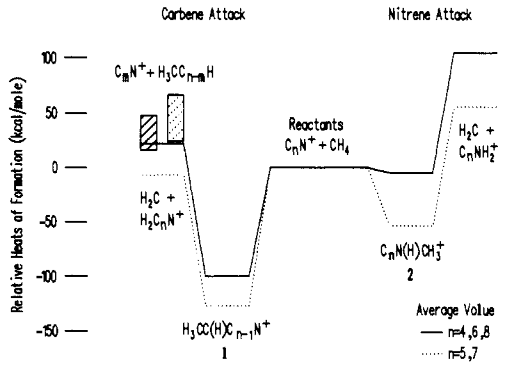
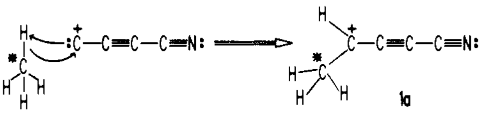


Figure 2. Energy diagram of different pathways for the reactions of C_nN^+ with methane. All energies are relative to that of the separated reactants. Carbene attack pathways are shown on the left side of the figure; nitrene attack is on the right side. Energies of ion/neutral pairs formed from intermediates **1** and **2** are for the separated species. The energy of the reaction complex is lower, due to the attractive ion/neutral interaction (see discussion in text). The hatched rectangles indicate the range in the heats of formation for the cyano–carbene ion/hydrocarbon pairs with different values of m. The energy values represented along the two curves are averages for the species indicated (n = 4, 6, and 8 for the solid curve and n = 5 and 7 for the dashed curve). Actual energies for a particular reactant vary by up to 9 kcal/mol from these average values.

Scheme I



The energetics for both pathways are shown in Figure 2. The lines are for the formation of $H_2C + H_2C_nN^+$ by mechanism **P**. The hatched boxes are for the formation of $C_mN^+ + H_3CC_{n-m}H$ (with different values of m) by mechanism **S**. The ΔH_f shown for these ion-neutral pairs are those of the *separated* species. The ΔH_f for the rearrangement complexes will be lower, due to the attractive ion-induced dipole interaction (equal to $q^2\alpha/2r^4$ where q is the charge, α the neutral polarizability, and r the separation of the ion and neutral), which lowers the energy of the complex. The $C_mN^+ + H_3CC_{n-m}H$ pair at infinite separation is higher in energy than the $H_2C + H_2C_nN^+$ pair. At small separations (≈2–3 Å), the $C_mN^+/H_3CC_{n-m}H$ complex becomes more stable than the $H_2C/H_2C_nN^+$ complex, due to the larger polarizability of the hydrocarbon compared to the methylene. The ΔH_f of the $H_2C/H_2C_nN^+$ complex is lowered by approximately 20 kcal/mol, and that of the $C_mN^+/H_3CC_{n-m}H$ complex by 50–100 kcal/mol, at a 2 Å separation.

Mechanisms. Reactions of even and odd n reactant ions will be discussed separately as the structures, thermodynamics, and products are different for these two sets of reactions. One reaction from each set will be discussed in detail, with brief comments on the remaining reactions.

Even n Reactants: C_4N^+. Carbene attack on methane leads to intermediate **Ia** as shown in Scheme I. (Most of the structures to be presented in the mechanisms were calculated. The bond orders are intended to indicate *relative* bond strengths only. The charge is shown localized onto one atom, though the calculations indicate it is delocalized.) Loss of H_2 from this intermediate yields the products marked i. Cleavage of the three weakest C–C bonds, with H migration, gives the products marked ii, iii, and v in Table

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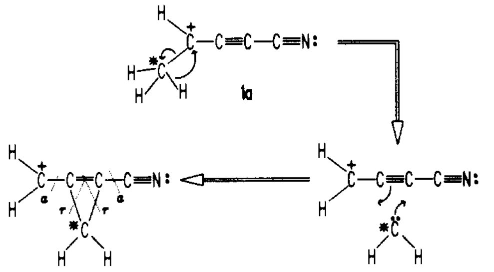
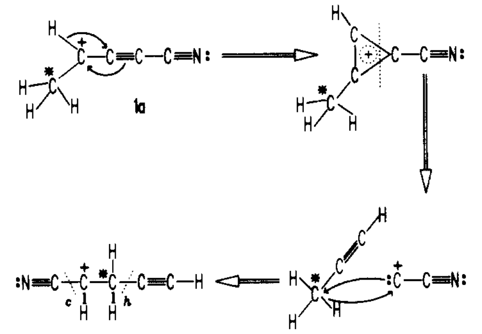
[18] Wincel, H.; Fokkens, R. H.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *88*, 241–56.

Scheme II



Scheme III

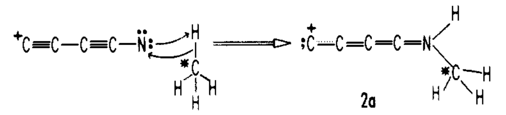


I. These products are formed by the direct mechanism.

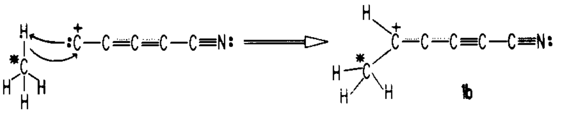
The remaining pair of products, labeled iv, is the same as the pair of products iii with the carbon-13 label switched. To form these products, rearrangement of the C–N chain must occur. Two possible mechanisms were described above. In mechanism **P** the formation of the methylene proceeds via a simple 1,2-H shift, as indicated in the first step of Scheme II. The methylene can add to a C–C π bond (second step in Scheme II), a common process for carbenes.[1,19] Cleaving the ring at sites *r*(*ing*) yields $[C_2/^{13}C_3N]^+$ and $[^{13}C_3/C_2N]^+$ products (in this notation the hydrogens have been omitted for simplicity, and the charge can be on either product, as indicated by the square brackets). Cleaving at sites *a*(djacent) to the ring forms $[C/^{13}C_4N]^+$ and $[^{13}C_4/CN]^+$ products. Of these four sets of products arising from *r* and *a* site cleavages, only the most exothermic from each set of like sites, $[C_2/^{13}C_3N]^+$ and $[^{13}C_4/CN]^+$, respectively, are observed. Cleavage at the *r* site forms the rearrangement products (set iv). The *a* site cleavage products (set v) can also be formed by the direct mechanism.

Rearrangement mechanism **S** involves the formation of a cyano–carbene ion by cyclization, as shown in Scheme III. This is analogous to a mechanism proposed by Bohme et al.[4] The cyclopropenyl cation formed in the first step of Scheme III is more stable than its precursor, the propargyl ion.[2b] The height of the barrier to this rearrangement is unknown though we can obtain an estimate from the $C_2H_4N^+$ system in which the linear-to-cyclic isomerizations have barriers of 80–100 kcal/mol.[18] A barrier of this magnitude is surmountable in these reactions. Cleavage of the cyclopropenyl ring is a well-known synthetic route to carbenes.[21] Insertion of the carbene ion into a C–H σ bond is followed by bond cleavage at the *h*(*ydrocarbon*) and *c*(*yano*) sites to form products. Cleavage at the *h* site gives the $[C_2/^{13}C_3N]^+$ rearrangement products while cleavage at the *c* site forms $[^{13}C_4/CN]^+$, which can also be produced by the direct mechanism.

Scheme IV



Scheme V



One of the questions posed in the introduction asked whether any of the products were formed by nitrene attack. Nitrene attack by C_4N^+ is weakly exothermic and forms intermediate **2a**, as shown in Scheme IV. By cleaving the weakest bonds, the $[C/^{13}C_4N]^+$ and $[^{13}C/C_4N]^+$ products are formed. Only the $[^{13}C/C_4N]^+$ products are observed.

C_6N^+ and C_8N^+. These reactions are very similar to the C_4N^+ reaction discussed above. Most of the products can be formed by carbene attack and bond cleavage (the direct mechanism of Scheme I), except for product sets iv and vi in Table I. For these labeled cyano products, a rearrangement-type mechanism is required. As was found for C_4N^+, either methylene π bond addition (mechanism **P**) or cyano–carbene σ bond insertion (mechanism **S**) can account for the products. Nitrene attack by C_6N^+ and C_8N^+ leads to the same products as for C_4N^+, namely the product sets i and ii.

Summary. We now review the formation of the rearrangement products from all three even *n* reactant ions to obtain further information on the mechanism involved. In methylene π bond addition, the rearrangement products arise from cleavage at *r* sites (see Scheme II). Products due to cleavage at *a* sites can also be formed by the direct mechanism. Cyano–carbene σ bond insertion forms the rearrangement products by cleavage at the *h* site (see Scheme III). Cleavage at the *c* sites forms products which can also arise from the direct mechanism. *Rearrangement products are thus produced by r or h site cleavage only.*

We cannot unambiguously determine which mechanism, methylene π bond addition or cyano–carbene σ bond insertion, is responsible for the rearrangement products iv and vi. Both mechanisms require a long-lived complex with formation of a second carbene and involve a cyclic intermediate. This implies the existence of a barrier in the reaction coordinate. Also, both mechanisms are composed of reactions that have analogues in neutral carbene chemistry. There are two points that favor the cyano–carbene σ bond insertion mechanism. As noted above, the energetics favor the formation of the $C_mN^+/H_3CC_{n-m}H$ complex. Secondly, addition of a carbene to a triple bond is more difficult than addition to a double bond[1] and is certainly less favorable than insertion into a C–H σ bond.

The role played by nitrene attack appears to be negligible for these reactant ions. All of the expected products from the direct fragmentation of the nitrene attack intermediate (Scheme IV) were *not* observed. In contrast, all of the direct fragmentation products from carbene attack (Scheme I) *were* observed. The explanation is most likely one of energetics. The ΔH_f of the nitrene resonance form could not be calculated, but it probably is significantly above that of the carbene resonance form. As noted earlier, carbene attack is also much more exothermic than nitrene attack.

Odd *n* Reactants: C_5N^+. Carbene attack of C_5N^+ on methane is shown in Scheme V. Loss of H_2 gives the i products. Fragmentation at the weakest C–C bonds forms labeled hydrocarbon products with one, two, three, and five carbon atoms (marked ii, iii, v, and vii in Table II). To form the hydrocarbons with two or three carbons, somewhat stronger bonds must be broken, compared to the other products of these reaction and to the reactions of the even *n* reactant ions.

The remaining products are the unlabeled two- and three-carbon hydrocarbons (iv and vi in Table II) which can come from re-

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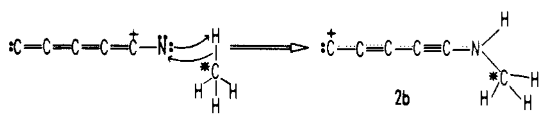
(19) Insertion of the methylene into a C–C σ bond was considered for all reactions, but it was concluded that this pathway is probably negligible. Reactions of carbenes with C–C single bonds are rarely observed. The few reported examples involve either intramolecular reactions of cyclic molecules or intermolecular reactions of ring systems in which a pair of C–C single bonds acts in concert.[20] Also σ bond insertion does not generally lead to the observed rearrangement products but rather to the products that are formed by the direct mechanism.

(20) Jackson, J. E.; Mock, G. B.; Tetef, M. L.; Zheng, G.-X.; Jones, M. Jr. *Tetrahedron* **1985**, *41*, 1453–64.

(21) Griffin, G. W.; Bertoniere, N. R. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley & Sons, Inc.: New York, 1973; Vol. 1, pp 305–49.

Scheme VI



arrangement reactions. The energetics for methylene formation from intermediate **1b** (analogous to Scheme II) are indicated in Figure 2. The ΔH_f of the intermediates in the carbene attack reaction pathway are approximately 30 kcal/mol lower for the odd n reactants compared to the even n reactants. This is due to the rearrangement from a cumulene to acetylenic bond structure in the odd n ions. In addition, when n is odd, the $H_2C_nN^+$ ion has a more stable isomer,[22] the HC_nNH^+ ion, which lies ~13 kcal/mol lower in energy. Both isomers give the same products however. π bond addition, after a 1,3-methylene shift, forms $[C_3/^{13}C_3N]^+$ and $[^{13}C_4/C_2N]^+$ by cleaving at the r sites and $[C_2/^{13}C_4N]^+$ and $[^{13}C_5/CN]^+$ through a site cleavage. All of these products, except for the $[^{13}C_4/C_2N]^+$, are observed. In particular, note that the rearrangement products $[C_2/^{13}C_4N]^+$ (set iv) arise from an a site cleavage. This is in contrast to what is observed for the even n reactants, in which the rearrangement products are all formed by r site cleavage.

Rearrangement via cyano–carbene formation, analogous to Scheme III, can proceed by two pathways. One pathway, via the formation of C_3N^+, produces $[C_2/^{13}C_4N]^+$ and $[^{13}C_5/CN]^+$ products by cleavage at the h and c sites, respectively. The second pathway, via formation of C_2N^+, leads to $[C_3/^{13}C_3N]^+$ and $[^{13}C_5/CN]^+$ products from h and c site cleavage, respectively. All of these products are seen. The unlabeled C_2 and C_3 rearrangement products are both formed by h site cleavage, though on two different pathways.

Nitrene attack to form intermediate **2b** is shown in Scheme VI and is about 50 kcal/mol exothermic, in contrast to the even n reactants. This intermediate appears to have more amine character, corresponding to reaction of a nitrene, than was seen for intermediate **2a** (Scheme III) from the even n reactants. Possible products from nitrene attack and direct bond cleavage are $[C/^{13}C_5N]^+$, $[C_3/^{13}C_3N]^+$, $[C_5/^{13}CN]^+$, and $[^{13}C/C_5N]^+$. Only two of these products (the labeled C and unlabeled C_3 hydrocarbons) are observed, even though the other two products are seen with the carbon-13 label switched.

C_7N^+ and Summary. The direct carbene attack and bond fragmentation mechanism yields the labeled C_1, C_2, C_3, and C_7 hydrocarbon products marked ii, iii, v, and ix in Table II. The unlabeled C_2 and C_5 hydrocarbon products (iv and viii) can be formed by either of the rearrangement mechanisms discussed above. With the methylene π bond addition mechanism, both 1,3- and 1,5-methylene shifts are required, and it is again necessary (see C_5N^+ above) to invoke an a site cleavage for the $[C_2/^{13}C_6N]^+$ products. The cyano–carbene σ bond insertion mechanism will produce both sets of rearrangement products through h site cleavage, by two different pathways, as was also seen for C_5N^+. This mechanism is more plausible for the reasons given for the even n reactant ions. Fragmentation of the nitrene attack intermediate **2** yields unlabeled C_1, C_3, C_5, and C_7 hydrocarbons as well as labeled C_1 hydrocarbon. Only two of these products are observed. In contrast, all the possible carbene attack fragmentation products are observed for the C_5N^+ and C_7N^+ reactants.

Triplet States. As indicated above, C_5N^+ and C_7N^+ have triplet ground states, lying respectively 8 and 4 kcal/mol below the singlet state considered thus far. To investigate the importance of the triplet state, the energetics of the C_5N^+ reaction on the triplet potential energy surface were examined. The general results are the same, irrespective of electronic state. Most of the product channels are *less* exothermic on a triplet surface (i.e., the product ground states are typically singlets). A difference is observed in the nitrene attack scheme. The calculations indicate that the only expected products are $[C/^{13}C_5N]^+$ and $[^{13}C/C_5N]^+$, which are both observed. The strongest indication of triplet state involvement is the HC_nN^+/CH_3 channel (ii in Table II). These products are radicals and can only come from a triplet reactant abstracting an H atom from the methane. This triplet reactant can be either the nitrene or carbene. The calculations suggest that the triplet is in fact the carbene and not the nitrene. The structure of triplet C_5N^+ (and C_7N^+) is similar to that of the singlet which is carbene-like with a nitrile group. The reaction on the triplet surface is exothermic to form HC_nN^+ (carbene attack) but endothermic to form C_nNH^+ (nitrene attack).

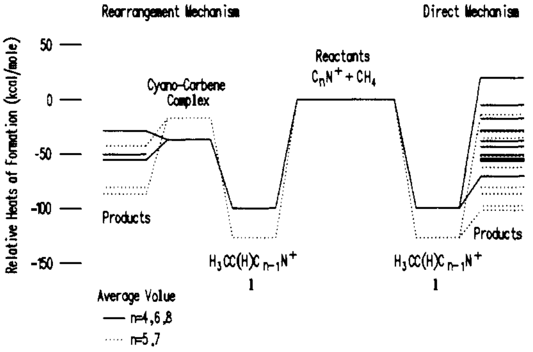


Figure 3. Energy diagram for the direct carbene attack vs cyano–carbene rearrangement pathways for the reactions of C_nN^+ with methane. All energies are relative to those of the separated reactants. The energies of the rearrangement complex include the attractive ion-induced dipole interaction at a separation of 2 Å. The energy values represented along the two curves are averages for the species indicated (n = 4, 6, and 8 for the solid curve and n = 5 and 7 for the dashed curve).

Comparison of Reactions of Even and Odd n Reactants. Many of the possible exothermic products of the rearrangement mechanism are not observed for the odd n reactants. Some of these products are seen with the ^{13}C label switched, formed by the direct mechanism. Such behavior is contrary to what was observed for the reactions of even n ions. This suggests that the rearrangement reactions of the odd n ions are less facile (see below) and that competition between various channels is governed by the details of the potential energy surface, especially the presence of barriers.

Tables I and II indicate the percentage of products which are formed by the direct mechanism only, by a rearrangement mechanism only, or which can be formed by either the direct or rearrangement mechanisms. Comparing the percentages in the two tables, we see that the rearrangement products account for 18–31% of the products when n is even but less than 10% when n is odd. Conversely, the amount of products formed by the direct reaction only is very high (75%) for odd n reactant ions and much lower (9–35%) for even n reactants. These results can be explained by either a preference on the part of the odd n ions for direct reaction or an impediment to the rearrangement reaction for these same ions, when compared to the even n ions. The fragmentation pathway from intermediate **1** is expected to be without significant barriers, and most of the products formed by this route are fairly exothermic. Thus this would not account for the difference in the behavior of even and odd n reactant ions. Returning to Figure 2, we note that the even n and odd n reaction pathways for the rearrangement of intermediate **1** via the methylene carbene are parallel. Considering also that the barrier is likely to be similar for these two pathways, this does not favor rearrangement of some intermediates over others. The parallelism of the energetics between the two sets of reactant ions breaks down when the rearrangement proceeds via the formation of a cyano–carbene. Figure 3 compares the energetics for the formation of products from direct carbene attack and fragmentation (right side) and from cyano–carbene σ insertion (left side) for even and odd n reactant ions. The ΔH_f for the rearrangement complexes include the ion-induced dipole term at a separation of 2 Å. We see that the curves for formation of the rearrangement complex for even and odd n ions cross, resulting in a deeper well in this pathway for the odd n ions. Comparing the two sides of the figure, it is clear that in the competition between the direct and rearrangement pathways, odd n ions will favor the direct mechanism to a greater extent than

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[22] For H_2CN^+, Conrad and Schaefer[16a] found an isomerization barrier of 30 kcal/mol.

Table III. Comparison of the Reactions of C_n^+ and C_nN^+ with Methane

	$n =$				
	4	5	6	7	8
$k(C_n^+)^a/k(C_nN^+)$	1.1	1.2	1.8	1.8	3.8

[a] Rate constants from ref 11.

Table IV. Comparison of Results for the C_4N^+ Reaction with Methane

products	FTMS[a]	SIFT[b]
$H_2C_5N^+ + H_2$	7	5
$H_2C_3N^+ + C_2H_2$	17	35
$H_2CN^+ + C_4H_2$	11[c]	5
$HC_4N^+ + CH_3$	1	
$C_4H_3^+ + HCN$	34	30
$C_2H_3^+ + HC_3N$	18[c]	25
$CH_3^+ + HC_4N$	10[c]	
$C_4H_2^+ + H_2CN$	2	
rate constant (10^{-10} cm^3/s)	7.0 ± 1.5	5.7 ± 1.7

[a] This work. [b] Reference 4. Branching ratios rounded to nearest 5% are accurate to ±30%. [c] The branching ratios of these products are affected by secondary reactions (see text).

the even n ions, in agreement with observation.

Comparison to Previous Work. Comparison of the results from this study with previous work[11] on the reactions of bare carbon cluster ions with methane may give some insight into the role of the nitrogen in the substituted clusters. The variety of products obtained in the present work is greater, which is not unexpected given that the possibilities are increased with the addition of nitrogen. Bare carbon cluster ions react with methane to lose H, H_2, CH_3, C_2H_2, and C_4H_2. All of these pathways, with the exception of H loss, are also observed in the C_nN^+ reactions. Instead of H loss, HCN and cyanopolyyne loss occurs in the C_nN^+ reactions. This is due to the high stability of the cyano species when compared to the analogous hydrocarbons. Relative abundances of the different products and trends in branching ratio with size do not appear to be related for the two sets of reactants. A more detailed comparison of the mechanisms involved is not possible, as it is not known if carbon skeleton rearrangements are also occurring in the reactions of the C_n^+ ions.

The rate constants for the reactions of C_n^+ and C_nN^+ with methane are compared in Table III. If the nitrogen end is nonreactive, the bare carbon cluster ions with two carbene sites should be more reactive than the cyano–carbon cluster ions which possess only one carbene site. The difference in reactivity should increase with the size of the cluster as it becomes less likely that the carbene end of the C_nN^+ ions will be able to orient itself to attack the methane. This is precisely what is seen. However the increase in the ratio $k(C_n^+)/k(C_nN^+)$ is not smooth. It plateaus from $n = 4$ to $n = 5$ and again from $n = 6$ to $n = 7$. This enhanced reactivity of C_5N^+ and C_7N^+ can be due to a reactive nitrogen, but as discussed above this is unlikely. It seems probable that the enhancement comes from the participation of the triplet state, and the accessibility of the associated product channels, for these reactant ions.

Table IV compares the present results for the reaction of C_4N^+ with those of Bohme et al.[4] obtained by using a high-pressure flow tube. Overall the results are in good agreement. The most serious discrepancies are in the branching ratios for $H_2C_3N^+$, H_2CN^+, and CH_3^+. The last two products undergo secondary reactions, resulting in a greater uncertainty in the branching ratios. Observation of CH_3^+ is surprising, as this channel is endothermic, suggesting some degree of excitation of the reactant ions in this work. However, as discussed in the Experimental Section and borne out by the comparison in Table IV, the reaction does not appear to be very sensitive to excess energy.

Conclusions

In conjunction with the labeling studies, the use of structural and thermodynamic information from the MNDO calculations provides a fairly detailed picture of the reactions of C_nN^+ ions with methane. Most of the products are formed by fragmentation of intermediate **1** arising from carbene attack on the methane (Schemes I and V). In these products, the carbon-13 label is incorporated into the hydrocarbon product and not the cyano product. A few products have the carbon-13 label in the cyano product. To produce these species, two rearrangement mechanisms were considered. These are methylene π bond addition (Scheme II) and cyano–carbene σ bond insertion (Scheme III). Though it is not possible to conclusively determine which mechanism is operative, consideration of several factors suggests that the most feasible alternative is the cyano–carbene σ bond insertion mechanism. Intermediate **1** rearranges to form a cyano–carbene ion, which inserts into a C–H bond, followed by fragmentation of the adjacent C–C σ bond on the hydrocarbon end of the molecule. All of the rearrangement products can be produced by this mechanism. This rearrangement is less important for the odd n reactant ions, accounting for less than 10% of the products, versus 20–30% for the even n reactant ions. The explanation for

Table V. Calculated Heats of Formation for Hydrocarbon Species[a]

n	C_n	C_nH	HC_nH	H_2C_n	H_2C_nH	H_3C_n	H_3C_nH
				Neutrals			
1[b]	171[c]	144	107	107	26	26	−12
2	235	163	57	122	64	123	97
3	220	179	139	142	74	144	41
4	284	201	102	168	105	162	120
5	275	222	173	193	120	184	86
6	327	245	147	220	150	205	155
7	330	267	213	246	166	228	130
8	374	290	191	272	195	250	195
9	385	312	255	298	211	274	174
				Cations			
1[b]	431[c]	359	300	300	244	244	
2	493	449	303	351	266	322	
3	474	363	311	361	265	386	
4	487	421	324	370	289	341	
5	502	396	340	392	300	398	
6	517	448	356	408	324	377	
7	539	434	376	432	339	428	
8	555	483	393	451	364	416	
9	581	476	416	476	381	464	

[a] For the singlet or doublet electronic state in kcal/mol. [b] For these one carbon species, the differentiation between isomers is meaningless. [c] From ref 17.

Table VI. Calculated Heats of Formation for Cyano Species[a]

n	C_nN	HC_nN	C_nNH	H_2C_nN	HC_nNH	C_nNH_2
			Neutrals			
1	129	35	68	60	61[b]	
2	164	130	160[b]	53	91[b]	
3	186	82	161[b]	87	106[b]	
4	206	158	206[b]	100	134[b]	
5	228	127	218[b]	130	151[b]	
6	249	196	256[b]	147	179[b]	
7	272	172	273[b]	176	197[b]	
8	294	237	*c*	192	*c*	
9	317	216	*c*	221	*c*	
			Cations			
1	441	331	345	297	227	
2	382	331	363	277	306[b]	
3	440	336	378	299	267	
4	400	346	395	301	329[b]	377
5	454	358	415	324	308	388
6	431	375	433	334	364[b]	418
7	482	390	456	359	350	427
8	468	411	475	373	403[b]	463
9	517	427	499	397	393	

[a] For the singlet or doublet electronic state in kcal/mol. [b] The ΔH_f for the nonlinear configuration, which is lowest in energy for this structural isomer. [c] The ΔH_f for the nonlinear configuration was not calculated. The other structural isomer is lower in energy.

Table VII. Calculated Heats of Formation of Adduct Intermediates[a]

n	$H_3CC(H)C_{n-1}N^+$	$C_nN(H)CH_3^+$
4	285	373
5	312	380
6	320	415
7	347	424
8	359	460

[a] For the singlet electronic state in kcal/mol.

this observation can be found in the energetics (see Figure 3). The rearrangement from intermediate **1** has a higher barrier for odd n reactant ions, leading to a preference for the direct mechanism. Though nitrene attack (Schemes IV and VI) is energetically allowed, it does not appear to play a role in these reactions. The MNDO calculations suggest that the reactant ions in fact have little nitrene character. Electronic state effects are important for the odd n reactant ions. These ions have closely spaced triplet and singlet states. The even n reactant ions have singlet ground states with no nearby triplet states. Hydrogen abstraction to form radical products occurs on a triplet surface and is an important product channel in the reactions of the odd n ions.

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Appendix

The heats of formation obtained from the MNDO calculations described in the Theory section are tabulated in Table V (hydrocarbon compounds), Table VI (cyano compounds), and Table VII (intermediates).

Stereochemistry of the Thermal Acetylenic Cope Rearrangement. Experimental Test for a 1,4-Cyclohexenediyl as a Mechanistic Intermediate

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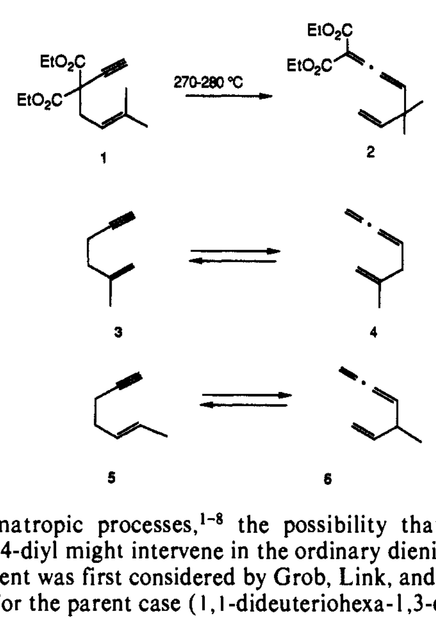
Abstract: The reversible [3,3]-sigmatropic rearrangement that interconverts optically active 4-methyl-5-hepten-1-yne and 4-methyl-1,2,5-heptatriene (an acetylenic Cope rearrangement) occurs with a stereochemistry corresponding to an orbital symmetry allowed suprafacial pathway with essentially complete preservation of enantiomeric purity. Computational simulation of the time-composition profile shows that 1% or less of the rearrangement goes by the stereochemical equivalent of a forbidden antarafacial pathway. Combined with a recent experimental determination of the rate constant for ring conformational inversion of the model 4-cyclohexenyl radical, the results suggest that for the biradical 3,5-dimethyl-1-cyclohexene-1,4-diyl to occur on the energy surface of the rearrangement its rate of decomposition would have to be in the range 1.6–3.8 × 10^{13} s^{-1}. This rate exceeds the upper limit imposed by transition-state theory for the decomposition of an intermediate, which is the rate of decomposition of the transition state itself, about 1 × 10^{13} s^{-1} at the reaction temperature of 471 K. The results strongly suggest that the stepwise mechanism involving the biradical intermediate does not occur to a significant extent in this rearrangement. An allowed concerted mechanism best accounts for the experimental observations.

The acetylenic Cope rearrangement,[1-4] of which the first examples were provided by Black and Landor[1] (**1** → **2**) and by Huntsman, DeBoer, and Woosley (**3** → **4**,[2a] **5** → **6**[2b]), has attracted our attention as the basis of a mechanistic test for a true intermediate on the energy surface of a thermal [3,3]-sigmatropic process. Reasons for the choice of this reaction rather than the more familiar Cope rearrangement of 1,5-hexadienes emerge from a detailed analysis of the interpretive limitations inherent in the latter systems.



Although Cope's proposal[5] of a concerted pathway has provided the framework of most mechanistic discussions of thermal [3,3]-sigmatropic processes,[1-8] the possibility that a cyclohexane-1,4-diyl might intervene in the ordinary dienic Cope rearrangement was first considered by Grob, Link, and Schiess in 1963.[9] For the parent case (1,1-dideuteriohexa-1,3-diene, **7** →

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